

LASER SURFACE ALLOYING OF METALLIC SUBSTRATES

WITH CARBON AND SILICON

by

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For CLARE.

ABSTRACT

Laser surface alloying (LSA) is the process of modifying the surface composition of a substrate by adding alloying elements to the substrate while it is being melted with a laser. Self quenching causes microstructural refinement and retention of non equilibrium phases. This thesis examines three LSA processes. A 2kW CO₂ laser was used to process over 500 alloyed tracks using various operating parameters ranging from 1.0 - 5.0mm beam diameter, 2 - 250mm/s scan velocities and 0.8 - 1.9kW laser power. Particular emphasis is placed on microstructural examinations of the alloyed tracks. Optical microscopy was used in conjunction with SEM and TEM. A novel means of utilizing SEM was adopted; samples were fractured and deep etched, illustrating three dimensional proeutectic and eutectic growth. Chemical analysis was used to quantify weight fractions of elements alloyed, while X-ray diffractometry and TEM were used to identify phases and phase relationships. Limited tests were carried out to determine physical properties ie hardness, wear testing.

Laser hardening of grey cast irons by transformation of the pearlitic matrix to martensite is a prime application for commercial laser surface processing. The recent investigation sought to extend this work, surveying the phase and microstructural species attainable in self quenched white irons produced by LSA carbon into ferrous substrates. Rapid cooling refines the eutectic and solid state decomposition of eutectic austenite occurs. The decomposed eutectic consists of ferrite and cementite. Cooling rates are estimated via proeutectic austenite dendrite arm spacing and interlamellar eutectic spacing. The importance of melt pool stirring and pool geometry on the homogeneity of carbon alloying is discussed.

The high reflectivity and high thermal conductivity of aluminium alloys has limited their suitability to laser processing. Surface "peening", surface oxidation and black-body coatings are shown to reduce reflectivity. Laser melting of Al-Si alloys and LSA of silicon to Al alloys has been investigated (Si imparts rigidity and reduces wear). Processing parameters, laser beam diameter, scan velocity and laser power are evaluated. The microstructural features of both hypo and hypereutectic alloys are reported; ie pro^ueutectic Al refinement, proeutectic Si morphology (idiomorphic or dendritic), eutectic

nucleation and growth. Alloy wear is shown to be reduced by Si alloying.

Development of titanium alloys for aerospace applications has expanded enormously over the past 30 years; however, in applications which involve sliding or fretting severe wear occurs. The use of laser processing to reduce surface wear has been investigated. Surface cladding of WC-Co alloys and TiC solid particle injection is reviewed. A method of LSA C to Ti alloys is described whereby TiC dendrites form in the laser track producing a wear resistant layer.

CONTENTS

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE NO</u>
	Abstract	i
	Contents	iii
	Symbols	viii
	Introduction	xi
CHAPTER 1	PRINCIPLES OF LASER TREATMENT	
1.1.	Processing Parameters	1
1.2.	Reflectivity	4
1.3.	Parameters of Solidification Associated with Laser Melting	8
1.4.	Laser Surface Alloying	9
CHAPTER 2	CARBON ALLOYING TO FERROUS SUBSTRATES	
2.1.	Introduction	11
2.2.	Physical Structure of White Irons	13
2.2.1.	Hypoeutectic Solidification	15
2.2.1.1.	Primary Dendrite Arm Spacing	16
2.2.1.2.	Secondary Dendrite Arm Spacing	17
2.2.2.	Hypereutectic Solidification	19
2.2.3.	Eutectic Solidification	19
2.2.3.1.	Modern Concepts of Eutectic Solidification Theory	22
2.2.3.2.	Lamellar-Rod Transition	26
2.2.3.3.	Impurity Elements	28
2.3.	Experimental Procedure	29
2.4.	Results	33
2.4.1.	C Alloying into S135	33
2.4.1.1.	Conduction Limited Melt Zones	33
2.4.2.	C Alloying into Pure Fe	34
2.4.2.1.	Hypoeutectic White Iron	36

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE NO</u>
2.4.2.2.	Hypereutectic White Iron	40
2.4.2.3.	Eutectic White Iron	46
2.5.	Discussion	47
2.5.1.	Hypoeutectic Solidification	47
2.5.1.1.	Conduction Limited Melt Zones	47
2.5.1.2.	Key-holed Melt Zones	50
2.5.2.	Eutectic Solidification and Decomposition	51
2.5.2.1.	Nucleation and Growth	51
2.5.2.2.	Eutectic Spacing	54
2.5.2.3.	Eutectic Decomposition	56
2.5.2.4.	C Diffusion	57
2.5.2.5.	A Decomposition Theory	58
2.5.2.6.	Pearlite Formation	61
2.5.3.	C Diffusion at the HAZ Interface	62
2.5.4.	Melt Zone Geometry and its Effects on Thermal Fluid Flow	63
CHAPTER 3	SURFACE MELTING OF Al-Si ALLOYS AND SURFACE ALLOYING OF Si TO Al ALLOYS	
3.1.	Introduction	67
3.2.	Review	70
3.2.1.	The Al-Si System	70
3.2.2.	Solidification Mechanisms	71
3.2.2.1.	Eutectic Growth	71
3.2.2.2.	Proeutectic Si Growth	73
3.2.3.	Determination of Solidification Conditions	76
3.2.3.1.	The Eutectic	76
3.2.3.1.1.	Undercooling, Thermal Gradients and Growth Velocity	76
3.2.3.1.2.	Thermal Analysis	80
3.2.3.2.	Proeutectic Al Dendrite Spacing	81
3.3.	Experimental Procedure	84
3.4.	Results	88

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE NO</u>
3.4.1.	Operating Parameters	88
3.4.1.1.	Alteration of Scan Velocity	88
3.4.1.1.1.	Surface Melting	88
3.4.1.1.2.	DAG Coating	90
3.4.1.1.3.	Si Alloying	90
3.4.1.2.	Recoating and Reprocessing	97
3.4.1.2.1.	DAG Coating	97
3.4.1.2.2.	Si Alloying	97
3.4.2.	Mictrostructural Analysis	99
3.4.2.1.	Hypoeutectic Al-Si Alloys	99
3.4.2.1.1.	Proeutectic Al	99
3.4.2.1.2.	Eutectic	100
3.4.2.2.	Hypereutectic Al-Si Alloys	101
3.4.2.2.1.	Proeutectic Si	101
3.4.2.2.2.	Proeutectic Al	103
3.4.2.2.3.	The "Al Shell"	103
3.4.2.2.4.	Eutectic	104
3.4.3.	X-Ray Diffract ^o metry [^]	105
3.4.4.	Wear Results	105
3.5.	Discussion	107
3.5.1.	Processing Parameters	107
3.5.1.1.	Substrate Melting	107
3.5.1.1.1.	Substrate Composition	107
3.5.1.1.2.	DAG Coating	109
3.5.1.1.3.	Power Density and Interaction Time	109
3.5.1.2.	Si Alloying	111
3.5.2.	Microstructure	113
3.5.2.1.	Proeutectic Si	113
3.5.2.2.	Eutectic Formation	114
3.5.2.3.	Solidification Conditions	115
3.5.3.	Physical Properties	118

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE NO</u>
CHAPTER 4	SURFACE MELTING AND C ALLOYING OF Ti AND Ti-6Al-4V	
4.1.	Introduction	119
4.2.	Review	120
4.3.	Experimental Procedure	123
4.4.	Results	125
4.4.1.	Surface Melting	125
4.4.2.	C Alloying	126
4.4.2.1.	Processing Parameters	126
4.4.2.2.	Microstructural Analysis	129
4.4.2.2.1.	Solid State TiC Precipitation	129
4.4.2.2.2.	Proeutectic Dendritic TiC	131
4.4.3.	Wear Results	133
4.5.	Discussion	135
4.5.1.	Microstructure	135
4.5.2.	Physical Properties	137
CHAPTER 5	CONCLUSION	
5.1.	Processing Properties	138
5.1.1.	Substrate Parameters	138
5.1.2.	Melt Zone Geometry	139
5.2.	Physical Properties	140
5.2.1.	Ferrous Alloys	140
5.2.2.	Al Alloys	140
5.2.3.	Ti Alloys	141

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE NO</u>
APPENDICES		
APPENDIX I	LASER TRANSFORMATION HARDENING	143
APPENDIX II	LASER CLADDING	145
A.2.1.	Introduction	145
A.2.2.	Review	145
A.2.2.1.	Continuous Pneumatic Powder Cladding	147
A.2.3.	Continuous Cladding Technique	149
A.2.4.	Stellite 31	149
A.2.4.1.	Introduction	149
A.2.4.2.	Experimental Procedure	150
A.2.4.3.	Results	150
A.2.5.	Cladding WC-Co Alloys	151
A.2.5.1.	Introduction	151
A.2.5.2.	Results	152
A.2.5.3.	Discussion	154
APPENDIX III	WEAR RESISTANCE	157
APPENDIX IV	ORIGIN OF LEDEBURITE SOLIDIFICATION AND EUTECTOID GROWTH	159
APPENDIX V	Al ALLOY MODIFICATION BY ELEMENTAL ADDITIONS	163
APPENDIX VI	LASER SURFACE ALLOYING C TO Al ALLOYS	165
A.6.1.	Introduction	165
A.6.2.	Results	166
	REFERENCES	167
	PREVIOUS PUBLICATIONS	185
	ACKNOWLEDGEMENTS	

SYMBOLS

All compositions are in wt% unless otherwise stated.

<u>Symbol</u>	<u>Meaning</u>	
A	surface or cross-sectional area	m ²
	constant	
B	constant	
C	chemical composition	
C _E	eutectic composition	
CSMA	cross sectional melted area	m ²
D	diffusion coefficient	m ² /s
D _B	boundary diffusion coefficient	m ² /s
D ₀	pre-exponential term (diffusion)	
d	beam diameter	mm
	distance	m
e	exponent	
f	volume fraction	
f _E	eutectic volume fraction	
G	Gibbs free energy	J/mol
	interface temperature gradient	K/m
H	enthalpy	J/mol
HV	hardness	Vickers number
I	laser beam intensity	W/cm ²
K	boundary segregation coefficient	
k	distribution coefficient	
	wear coefficient	
L	load	kg
LSA	laser surface alloying	
LSP	laser surface processing	

<u>Symbol</u>	<u>Meaning</u>	
M_s	martensite start temperature	K
M_f	martensite finish temperature	K
m	liquidus slope	K/at.%, K/wt.%
N	number	
n	exponent	
P	laser power	kW
	hardness	kg/m ²
	diffusion parameter	
R	radius	mm,m
	growth rate	mm/s
R_G	gas constant	J/mol.K
RSP	rapid solidification processing	
r	radius	mm,m
S	entropy	J/mol.K
T	temperature	K
T_E	eutectic temperature	K
T_l	liquidus temperature	K
T_s	solidus temperature	K
ΔT	undercooling	K
ΔT_d	undercooling due to solute	K
ΔT_c	undercooling due to curvature of the solid-liquid front	
ΔT_k	undercooling due to kinetics of molecular attachment	K
t	interaction time	s
t_f	local solidification time	s
V	scanning velocity	mm/s
X	volume	m ³
δ	boundary thickness	m
$\varepsilon_\lambda(T)$	emissivity of substrate at temp T	
θ	Gibbs-Thompson coefficient	K mm
λ	spacing	m

<u>Symbol</u>	<u>Meaning</u>	
λ_1	primary dendrite spacing	m
λ_2	secondary dendrite arm spacing	m
λ_3	eutectic inter_lamellar spacing	m, μm
λ_w	radiation wavelength	μm
ρ	density	kg/m^3
σ	interfacial free energy	J/mm^2
Ω	supersaturation (eq 3.7, 3.8)	

INTRODUCTION

The benefits of rapid solidification processing (RSP) of metals as a method of microstructural refinement, retaining non-equilibrium phases and extending solid solubility limits have been widely demonstrated¹⁻⁴. Commercial rapid solidification techniques⁵ can be grouped into two categories: atomized and continuous. Atomization dominates RSP; liquid metal is converted into small droplets, quenched and the powder used in sintering⁶ or plasma spraying. Continuous RSP includes melt spinning and laser surface processing (LSP)⁷⁻¹⁶. As a laser beam traverses a workpiece it transmits energy causing heating; subsequent high cooling rates are a property of self quenching.

Flexible control of the laser 'thermal' cycle widens the processing applications; from welding¹², cutting and drilling using a high intensity at the focal spot, to hardening¹³ (Appendix I), tempering, glazing¹⁴, alloying^{7,15} and cladding¹⁶ (Appendix II) using a lower intensity. The advantages of LSP can be summarised:

- a. Heat input is relatively low, hence thermal distortion is minimised.
- b. The process permits localised treatment.
- c. Inaccessible areas can be readily treated, eg deep slots.
- d. Complex component shapes can be treated, eg camshafts and gears.
- e. High processing speeds with instantaneous stop-start is possible, leading to high production rates.
- f. The process lends itself towards automation.
- g. Usage can be increased by switching the beam between work stations.

The objective of this thesis is to evaluate the technique of laser surface alloying (LSA) when applied to three binary metallic systems:

Fe-C, Al-Si, and Ti-C. The results are assessed with regard to laser process parameters (laser beam coupling, melt pool profile, alloying fraction, etc) and in terms of the effects of rapid cooling (microstructural refinement, phase compositions, phase morphologies etc). Melt pool homogeneity is discussed, the importance of mixing is identified, and the effect of melt pool profile on convection assessed.

Relatively small amounts of C were LSA to Fe (<6 wt% C). The microstructural changes induced by increased C alloying (in associated with rapid cooling) are reported. LSA of C to ferrous substrates to produce alloys in the 'steels' composition range has been previously reported. This study places particular attention on hypoeutectic and hypereutectic white irons. The solidification mechanisms of proeutectic austenite, proeutectic cementite and the eutectic are discussed. Solid state decomposition of the eutectic to a divorced eutectoid is postulated. Larger amounts of Si (up to ~ 70 wt% Si) were LSA to various Al alloy substrates. The equilibrium Al-Si phase system comprises of limited levels of solid solubility of each element in the other and a simple eutectic; however, rapid solidification induces more complex structures. Proeutectic Si assumed either a plate or dendritic morphology depending on composition and the eutectic adopted a fibrous morphology and skewed to higher Si compositions. In many respects, the solidification mechanism and physical structures of rapidly solidified near eutectic Fe-Fe₃C and near eutectic Al-Si alloys can be related; microstructural refinement (hypoeutectic dendrite arm spacing), eutectic nucleation, eutectic growth etc.

The thesis includes a limited study of Stellite laser cladding and WC-Co laser cladding. It was hoped that WC-Co might provide a tough wear resistant layer; however, WC was found to be intrinsically unstable. TiC is less susceptible to dissociation and was thought a suitable substitute. A number of other workers have explored TiC injection in laser melted substrates and demonstrated the superior wear properties of such materials. This thesis demonstrates that C laser surface alloyed to Ti alloys forms TiC. TiC precipitated either from the solid state in small fractions (in low C alloys) or as primary dendrites (in higher C alloys). Substrate hardness and wear resistance were shown to increase significantly with TiC precipitation.

1. PRINCIPLES OF LASER TREATMENT

1.1. PROCESSING PARAMETERS

For most engineering applications, the laser can be regarded simply as a device for producing a finely controllable beam of energy which in contact with a material generates heat. The energy is in the form of an intense beam of coherent, mono-chromatic electromagnetic radiation¹⁷. Heat transfer during laser heating is achieved by photons of the laser beam interacting with free electrons of the substrate, which raises the energy state of the electrons of the conducting band. The subsequent energy transfer mechanism is the same as classical thermal conduction.

Interaction between a laser beam and a specimen is controlled by a number of variables. The principle parameters include: radiation wavelength, laser power, beam diameter, beam shape (gaussian, uniform etc), substrate scanning velocity, thermophysical properties of the substrate, its reflectivity etc. Bergmann et al ¹⁸ have considered the parameters influencing the structural changes that occur in laser surface melting and have sub-divided them into those depending on laser variables and those fixed by the material chosen (see Table 1.1.). Alloying and cladding further increase the variables. When continuously feeding powder these include: powder composition, density, size, shape, rate of delivery, delivery velocity, the angle and spread of delivery and the type of carrier gas.

The laser beam can be focused by optical elements to a specific diameter. The power and diameter of the beam when incident on a surface can be combined to give one laser parameter, the power density. The second parameter is the rate at which this power density is traversed across the surface, expressed as the interaction time. Using these two parameters a plot illustrating the various regimes of operation for the different laser processes can be constructed (Fig.1.1.). For surface processing a more 'reduced' power density than that required for drilling or penetration welding is used. Defocusing reduces power density while increasing contact-beam diameter, treating a wider band of the component. Fig.1.2. illustrates the actual conditions for surface melting DAG coated Fe substrates

described in Chapter 2. Optical beam handling systems for surface treatments can be designed to give deep depths of field. Irregular component shapes can be accommodated without significantly affecting the power density incident on the surface, by using a 150mm focusing beam rather than a 50mm.

TABLE 1.1¹⁸ Parameters influencing hardening mechanisms in laser melting

Determined by laser variables		Determined by composition	
Quenching rate	$\epsilon = \frac{\Delta T}{\Delta t}$	Initial composition	C^*
Solidification rate	$R = \frac{\Delta X}{\Delta t}$	Temperature of equal enthalpies in solid and liquid states	$T_o^j(C^*)$
Temperature gradient	$G = \frac{\Delta T}{\Delta x}$	Ratio of solidus/liquidus temperature	$\frac{T_S}{T_L}(C^*)$
$\epsilon = R \times G$		heat diffusivity	$h^j(C^*, T) =$
			$\frac{\lambda^j(C^*, T)}{C_p^j(C^*, T) \cdot \rho(C^*, T)}$
		thermal conductivity	$\lambda^j(C^*, T)$
		specific heat	$C_p^j(C^*, T)$
		density	$\rho(C^*, T)$
for the same composition and melting depth and steady state conditions		molar heat of fusion	$h_{fm}^j(C^*, T)$
		diffusion coefficient	$D_i^j(C^*, T)$
		absorption coefficient	$A^j(C^*, T, \lambda_w)$
		λ_w	wave length of the light
		i	indicating the i-th element
power density $\frac{P}{A}$ scan speed V beam diameter d beam area A interaction time $\frac{d}{V}$ laser power P		j	indicating the j-th phase

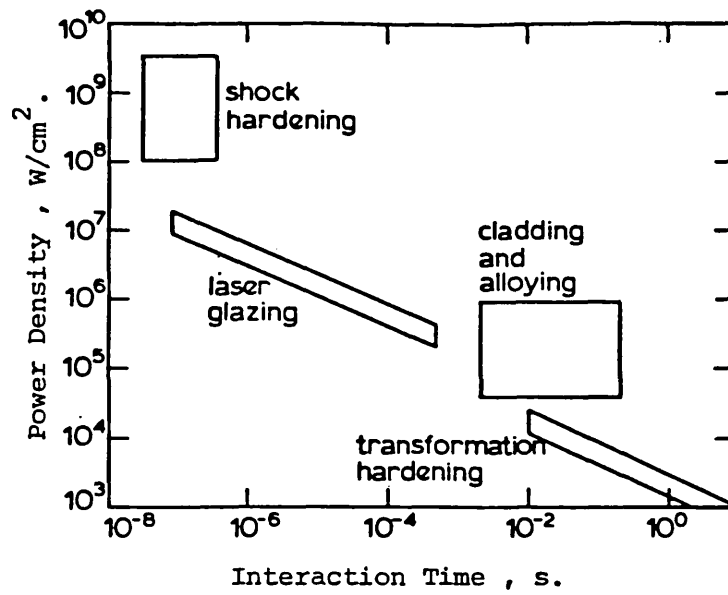


Fig.1.1.⁸ Operational Regimes for Laser Surface Treatment of materials

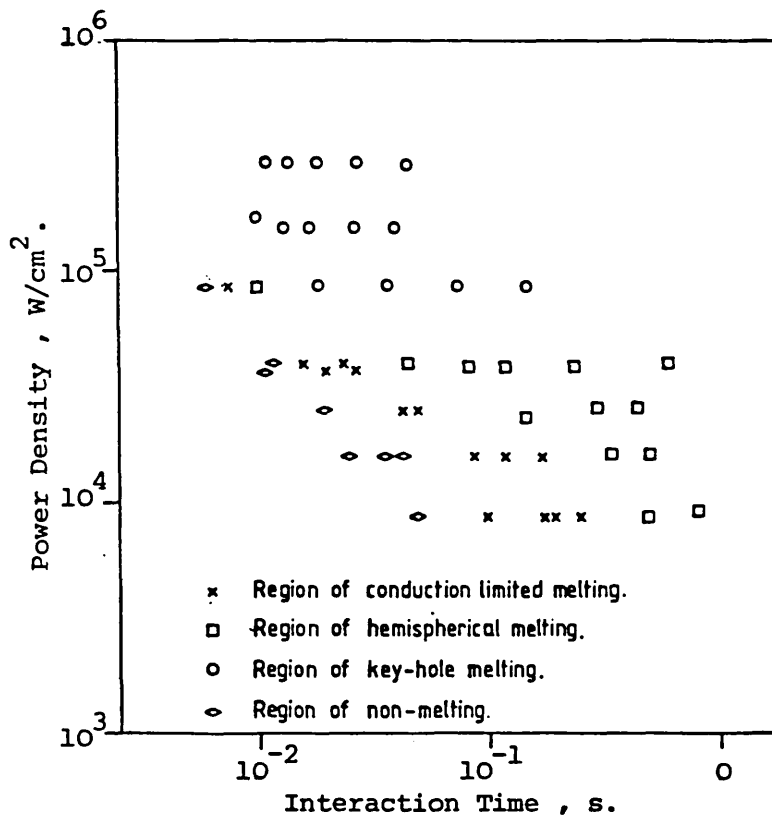


Fig.1.2. Actual coupling conditions for surface melted, grit blasted/graphite, pre-coated, Fe substrates (Ch.2.). These actual processing conditions are compatible with the alloying regime illustrated in Fig.1.1.

1.2. REFLECTIVITY

Laser beam coupling and energy absorption is of dominant importance. At temperatures below the melting point clean metallic surfaces are poor absorbers of infra-red energy and as much as 95%¹⁷ of the incident laser beam can be reflected and lost. However, as the temperature rises, the absorptivity increases, Table 1.2.a. and 1.2.b. and ultimately surface melting and vaporisation occur.

The reflectance behaviour of a substrate during laser irradiation determines the laser energy which is directly absorbed. Absorptivity depends on conductive absorption by free electrons and is, therefore, a function of substrate electrical resistivity. Arata and Miyamoto^{20,21} determined the absorptivity of various polished materials and concluded that absorptivity was proportional to electrical resistivity. At 20°C the resistivity of Al is 2.67 $\mu\Omega$ cm and Fe 10.1 $\mu\Omega$ cm, therefore, Fe has a higher absorptivity¹⁹. Bramson²² derived a temperature dependence relationship between emissivity and electrical resistivity. Since absorptivity equals emissivity the formula is distinctly applicable:

$$\epsilon_{\lambda_w}(T) = 0.365 \left[\frac{\text{Pr}(T)}{\lambda_w} \right]^{\frac{1}{2}} - 0.667 \frac{\text{Pr}(T)}{\lambda_w} + 0.006 \left[\frac{\text{Pr}(T)}{\lambda_w} \right]^{3/2} \quad (1.1)$$

where Pr = electrical resistivity at absolute zero, Ωcm

$\epsilon_{\lambda}(T)$ = emissivity of substrate at T°C

λ_w = radiation wavelength

Metals are generally more absorptive at 1.06 μm , the Nd:YAG laser wavelength, than they are at 10.6 μm , the CO₂ laser wavelength, Table 1.2.c. Ignoring all other considerations, one would choose a Nd:YAG laser to process metals, but the total power output from a CO₂ laser far exceeds that of a Nd:YAG²³.

TABLE 1.2. SUBSTRATE EMISSIVITIES¹⁹

a. Total Normal Emissivity of Metals

Material \ Temp°C	100	500	1000
Al	0.038	0.064	-
Polished Steel	0.13 - 0.21	0.18 - 0.26	0.55 - 0.80
Cleaned Steel	0.21 - 0.38	0.25 - 0.42	0.50 - 0.77

b. Total Normal Emissivity of Oxidised Metals

Material \ Temp°C	200	400	600	800
Al	0.11	0.15	0.19	-
Stainless Steel (buffed and oxidised @ 600°C)	-	0.41	0.44	0.54
Stainless Steel (shot blasted and oxidized @ 600°C)	-	0.65	0.67	-

c. Spectral Normal Emissivity of Metals at Room Temperature

Wavelength μm	10	5	3	1
Al	0.02-0.04	0.03-0.08	0.03-0.12	0.08-0.27

In order to promote more efficient coupling of the beam, it has become common practice to cover a surface which is to be laser treated with a coating which is absorbing at the laser wavelength²⁴⁻²⁶. Christodoulou et al²⁴ concluded that graphite or MnO₂ precoating significantly enhances laser melting of ferrous substrates. Wissenbach et al²⁶ report that work piece absorption increases from 10 - 50% for uncoated, to 77% for phosphate coated and increases to 88% for graphite coated CK-85 steel. With increasing power density the coatings are destroyed and the base material governs the absorption. Surface roughening reduces reflectivity²⁵, Table 1.2.a. and 1.2.b., and grit blasting prior to laser treatment is regularly practiced.

The absorptivities of Al alloys when laser processed are reported as being 2 - 3% that of stainless steels^{20, 21} and because of its high reflectivity Al might normally be considered unsuitable for laser processing, Plate 1. This thesis includes a study of the processing parameters and physical properties of Al alloys. Consequently it became necessary to increase absorptivity by pretreatment, so being able to initiate melting at 'commercially viable' laser powers (1-2kW for CO₂ lasers). All samples were 'roughened' by uniformly grit blasting for 3 minutes and then heated in air at 370 - 450°C for 1 hour, allowing a thick oxide layer to form (surface oxidation enhances absorptivity, Table 1.2.). This pretreatment was both reproducible and initiated surface melting at laser powers of 0.95kW. Some substrates were subsequently graphite coated (Section 3.4.1.1.2.).

Once beam coupling is established a substrate can be heated; however, if like Al (238W/mK @ 0 - 100°C¹⁹), the substrate is a high thermal conductor, heat is readily dissipated. This flattens the melt pool penetration profile and only shallow conduction limited melts are possible. Substrate preheating enhances melt penetration, Table 1.3. Thin substrates, with limited thermal capacity, can be clamped to an insulating furnace plate to promote heat retention. This increases melting and reduces cooling rate. Preheating also reduces both reflectivity and 'premelting' time, hence increasing total energy absorption. Where Al alloy samples were preheated in excess of 400°C and processed using a focused beam, vaporisation occurred.

TABLE 1.3. EFFECT OF PREHEATING TO 300°C ON SURFACE MELTING CP Al

These results are based on a preliminary study of laser melting Al alloys prior to the investigation of Si alloying reported in Ch.3. (The vol% vapourised was determined by measuring CSMA).

Laser Power and Beam Diameter		Scanning Velocity (mm/s)	Sample Pretreatment	Melt Track Width (mm)	Melt Track Depth (mm)	Cross Sectional Melt Area (mm ²) (CSMA)	Vol% Track Vapourized
Processing Parameters	1.65kW, 1.5mm.	10	Not Preheated	1.50	0.45	0.45	0
			Preheated	2.20	0.95	0.98	21
		20	Not Preheated	1.40	0.44	0.42	1
			Preheated	1.95	0.62	0.68	12
	1.65kW, 3.0mm.	10	Not Preheated	1.96	0.54	0.56	2
			Preheated	2.42	1.02	1.05	5
		20	Not Preheated	1.94	0.51	0.48	0
			Preheated	2.24	0.62	0.70	2

1.3. PARAMETERS OF SOLIDIFICATION ASSOCIATED WITH LASER MELTING

The solidification behaviour of laser melted/alloyed substrates is akin to that of arc butt welds ²⁷ and is dependent on heterogeneous nucleation, heat flow, solidifying interface velocity and the thermal gradient immediately ahead of the solidifying interface. The laser melted track is formed by melted regions of substrate and any alloy addition; thus there is always a region of solid in contact with the liquid. Heterogeneous nucleation initiates at the 'solid' substrate interface and growth is usually epitaxial. Such a process generates grains in the melt track having the same crystallographic orientation as those in the substrate. The rapid cooling associated with laser processing is a self quenching property of the processed substrate; hence heat flow is always directional.

Rapid cooling imparts supercooling of the melt and this could, in extreme conditions, lead to partitionless or massive solidification (solute partitioning would be avoided and a single phase structure produced). Cohen⁴ described supercooling to produce segregationless solidification as hypercooling. In laser melting, however, conditions usually favour phase separation and solute segregation. Where compositional equilibrium is maintained at the moving interface the thermal gradient in the melt just ahead of the interface and the interface velocity are important²⁸. Steep thermal gradients would smooth out any protuberances in the advancing interface and induce a planar solidification front (under such circumstances there would be no microsegregation). In reality, high interface velocities cause interface instability. Any protuberances tend to grow preferentially in as much as there will be combinations of temperature and composition ahead of the interface where the melt would be otherwise supercooled with respect to the solid phase. Cellular or dendritic growth morphologies with solute segregation between the cells or dendrite arms will occur; ie hypoeutectic Fe -Fe₃C, hypoeutectic Al-Si.

If the geometry of the molten pool is to retain a constant shape, then certain requirements concerning the rate of grain growth relative to the speed of the pool have to be fulfilled. Assuming grain growth occurs in a direction perpendicular to the isotherms then the growth rate will vary with geometry. The interface at the centre of the pool

must, by the nature of its shape, travel a greater distance than the growing interface at any other position. Hence, the 'bead' centre would be expected to have the "finest" solidification structure. This assumes, however, that crystal growth is isotropic and takes place along the direction of the maximum thermal gradient. In fact, rapid growth takes place along that favoured growth direction nearly aligned with the direction of the maximum thermal gradient. Both bcc and fcc structures have preferred easy-growth direction $\langle 100 \rangle$.

1.4. LASER SURFACE ALLOYING

Laser surface alloying (LSA)^{7, 15, 29} is the process of modifying the surface composition of a substrate by adding quantities of alloying elements to a substrate which has been melted to a controlled depth using a laser. Since alloying elements diffuse in a thin liquid layer at the surface, it is feasible to obtain the required depth of alloying in short time intervals. Thus, a desired alloy composition can be generated in situ on given substrate surfaces. The essential problem in surface alloying is to redistribute the various components from an initially very inhomogeneous distribution and obtain a spatially uniform composition. Ideally, mixing on a macroscopic scale is achieved by the flow of molten material within the melt pool.

LSA enjoys many advantages over conventional coating processes:

- a. Bulk characteristics of the substrate are retained due to the small HAZ.
- b. Scarce alloy materials are conserved.
- c. A high degree of adhesion is obtained between the substrate and coating.
- d. The high cooling rates available open up the possibility of generating novel microstructures.
- e. The depth of alloying can be accurately varied, from μm to mm .

Development of laser alloyed structures is influenced by the nature and relative amounts of the alloyed species, their distribution and the cooling rates that occur during laser processing. Generally, alloy composition governs microstructure, and laser processing conditions (cooling rate) govern the degree of microstructural refinement. Laser surface alloys are typically used in applications that are composition and structure sensitive, such as those related to corrosion or wear (Appendix III). The alloy layer physically separates the substrate from the environment and its refined microstructure reduces chemical attack.

LSA dates back to the early 1960's; Cunningham's work on the surface alloying of steels³⁰ is probably the earliest referenc^eable work in this area. Development over the past 20 years has been sluggish. Draper's survey^{7,15,29} of the state of the art discusses this lack of progress and speculates that interest will intensify as the savings realisable through surface rather than bulk alloying become significant.

Activity has been greatest in the area of surface alloying of ferrous substrates. Much of the early work on ferrous systems was carried out in Russia and, in most part, is not translated. While the Russians opted for pulsed solid state lasers (pulse lengths 1 - 10 milliseconds), most western research has been carried out using multikilowatt CW CO₂ lasers. CO₂ lasers offer a degree of control over dwell time ie greater control over melt depth and time in the liquid phase.

Initial development interests lay in producing hard wear resistant surfaces³². More recently there has been an active effort to produce stainless steel quality surfaces on lesser corrosion resistant ferrous substrates³³⁻³⁶. The method of producing highly alloyed, uniform surface layers on ferrous substrates, via LSA is fairly well established. Cast iron diesel engine valve seats are a typical application suitable for laser alloying³⁷. The operating temperature of the exhaust valve seat may exceed the tempering temperature of a transformation hardened layer, resulting in a softening of the seat. If the seat is alloyed with chromium, hardness is maintained at high temperature.

PLATE 1

a. Plan View of Laser Melted Ni Strip on Al Substrate

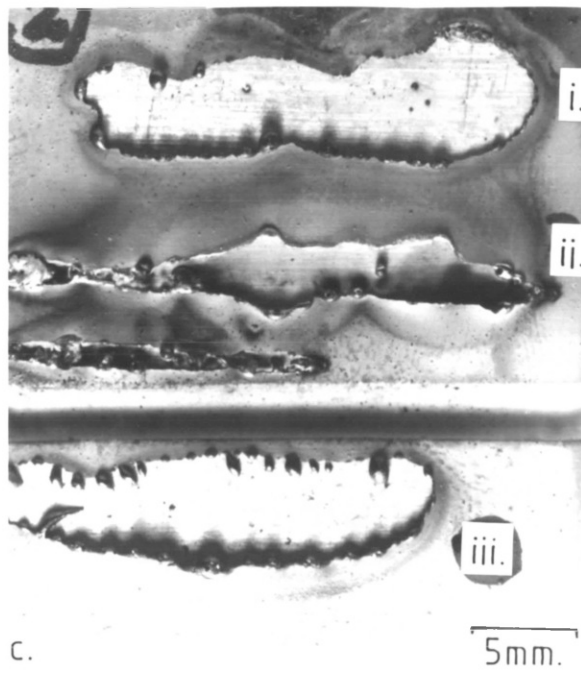
0.25mm thick Ni strip was "rolled" on to a smooth Al substrate. When laser treated with a focused beam (1.8kW, 0.8mm, 7mm/s) the Ni melted (i), while the substrate was unaffected (ii).

b. Plan View of Laser Melted Ni Powder on Al Substrate

Ni powder was laid in a milled slot on a smooth Al substrate and laser treated (1.7kW, 1.0mm, 6mm/s). The powder melted and conglomerated but the substrate was unaffected.

c. Plan View of Laser Melted Electrodepositedⁱ Ni on Al Substrate ^

Ni was electrodeposited on a smooth chemically clean Al substrate and laser treated ((i) 1.6kW, 1.0mm, 7mm/s, (ii) 1.6kW, 0.4mm, 7mm/s, (iii) 1.7kW, 1.0mm, 20mm/s). Ni was melted and vapourised while the substrate remained unaffected.



2. CARBON ALLOYING TO FERROUS SUBSTRATES

2.1. INTRODUCTION

Grey cast irons are extensively used in combustion engines. Bearing surfaces and moving components such as cam-shafts are hardened to reduce wear, typically by induction hardening, transforming the pearlite matrix into martensite. The feasibility of laser processing ferrous metals has been assessed³⁸⁻⁴², and the commercial viability of laser hardening realised (Appendix I). Wear properties of laser hardened specimens are comparable with induction hardened, while laser melting produces a superior wear surface^{18, 38-40}.

Rapid solidification studies of ferrous alloys has led to a partial understanding of metastable phase formation. Authors⁴³ have reported the presence of proeutectic austenite, sometimes partially transformed to martensite, in a ledeburite matrix. Secondary dendrite arm spacing, λ_2 , and eutectic interlamellar spacing have been correlated with cooling rate⁴⁴ ($\lambda_2 = 1\mu\text{m}$ is equivalent to 3.3×10^5 K/s).

It is known that the progress of the austenite-martensite transformation can be influenced by cooling rate. Rapid quenching can considerably depress M_s ⁴⁵⁻⁴⁸. Studies⁴⁸ on splat quenched Fe-X-C alloys show that the phases present in rapidly solidified specimens are composition dependent. Specifically in Fe-10Mo-C alloys the dominant phase was either austenite or martensite depending on whether the C content was greater or less than 1C. Increased C content markedly depresses M_s ⁵⁰:

$$M_s(^{\circ}\text{C}) = 539 - 439 \% \text{C} - 30.4 \% \text{Mn} - 17.7 \% \text{Ni} - 12.1 \% \text{Cr} - 7.5 \% \text{Mo} \quad (2.1)$$

Christodoulou and Steen⁵¹ laser melted a graphite coated 1C, 1.4Cr aerospace steel and produced austenitic melt zones. The retained austenite originally thought to be due to rapid self quenching was later found to be caused, at least in part, by surface alloying of graphite⁵². This result led to a study⁵³ of preplaced surface alloying, and a series of steels of various C contents were produced ranging in structure from predominantly martensitic to totally austenitic. C alloying was thought to be controlled by melt zone geometry, shallow melt zones having a higher surface/volume ratio and consequently greater alloying potential than key-holed melt zones.

Carbucicchio et al⁵⁴ subsequently reported the effects of C 'contamination' when laser melting graphite coated 0.4C steel; the C enriched melt formed as austenite-cementite structure on cooling.

The present investigation seeks to survey the phases and microstructural species attainable in self quenched white irons produced by laser surface alloying C into either S135 steel or pure iron. The rationale for this choice was:

- a. To extend the limits of alloying in Christodoulou et al's⁵³ original steel beyond the γ - α martensitic-austenitic range.
- b. Using pure iron minimises alloy variables, solely illustrating the effect of increasing C alloying on iron under rapidly quenched conditions.

Both hypoeutectic and hypereutectic white irons were produced. Excessive C alloying produced alloys containing near 100 vol% proeutectic cementite. The solidification mode of the proeutectic phases and the interrelation of eutectic nucleation and growth are reported. The eutectic was found to undergo a ('non-pearlitic') solid-state decomposition forming a ferrite-cementite lamellar structure. Cooling rates are estimated from microstructural refinement and the values are compared with the predictions of various laser solidification/cooling models.

2.2. PHYSICAL STRUCTURE OF WHITE IRONS

A cast iron melt may be made to solidify grey by slow cooling and white by rapid cooling⁵⁵. A critical cooling rate determines the solidified morphology of an individual cast iron. Graphite is more easily nucleated than cementite; however, once nucleated, cementite will grow much faster. White solidification initiates with proeutectic precipitation of either fcc dendritic austenite and/or orthorhombic plate-like cementite, and is succeeded by solidification of the matrix to ledeburite at the eutectic. Fig.2.1.⁵⁶ shows the Fe-Fe₃C equilibrium phase diagram. Proeutectic austenite precipitation in hypoeutectic melts will cause the C content in the remaining liquid melt to increase. At a temperature below the eutectic temperature the melt may become hypereutectic. Examples of a mixture of the two proeutectic phases in the same melt are common^{55, 58}. Proeutectic cementite growth is not orientated to the dendritic austenite.

Ruhl and Cohen⁴⁶ splat quenched a series of Fe-C alloys at cooling rates of $10^5 - 10^8 \text{ Ks}^{-1}$. The splat quenched structure of binary Fe-C alloys ranging in composition from 0.39 to 1.96C consisted of martensite and austenite only. Splat cooled medium (above 1.90C) and high C alloys consisted of retained austenite. In Fe-3.7C cementite, austenite and hexagonal (ϵ) precipitated. Higher C alloys, up to 5.2C, contained ϵ . Laser melting does not usually induce sufficient^{ly} rapid cooling to induce ϵ formation.

Bergmann et al¹⁸ laser surface melted various ferrous alloys. For a given processing condition C content was shown to control microstructure. Binary Fe-C steels in the range 0.4 - 1.4C were shown to solidify as austenite and partially transform to martensite upon self quenching to ambient. Microstructural hardnesses varied over HV400 - 700. Cast irons in the range 2 - 4.4C were also laser melted and consisted of epitaxially grown austenite dendrites and interdendritic eutectic. Further increases in C content led to the formation of proeutectic cementite.

Tucker et al⁴¹ laser melted eutectic cast iron (Fe-4.2C). Using a scanning laser, a melted track comprising of cementite, martensite and small amounts of retained austenite was produced. Pulsing the laser induced surface melting which subsequently underwent more rapid

cooling, $\sim 10^8 \text{Ks}^{-1}$. This produced a featureless microstructure though X-ray phase analysis identified cementite, austenite and ϵ .

Blarasin et al³⁸ laser melted grey iron (Fe-3.3C-1.85Si-0.45Mn) and described the solidified microstructure as "dendritic ledeburite and a pattern of cementite, pearlite or residual austenite and martensite". The structure may have been misinterpreted and is better described as consisting of proeutectic dendritic austenite, proeutectic plate cementite in a eutectic matrix. The authors have demonstrated that sample preheating reduces the cooling rate and causes microstructural coarsening. Blarasin et al³⁸ imply that cooling is sufficiently slow to permit pearlitic transformation of austenite.

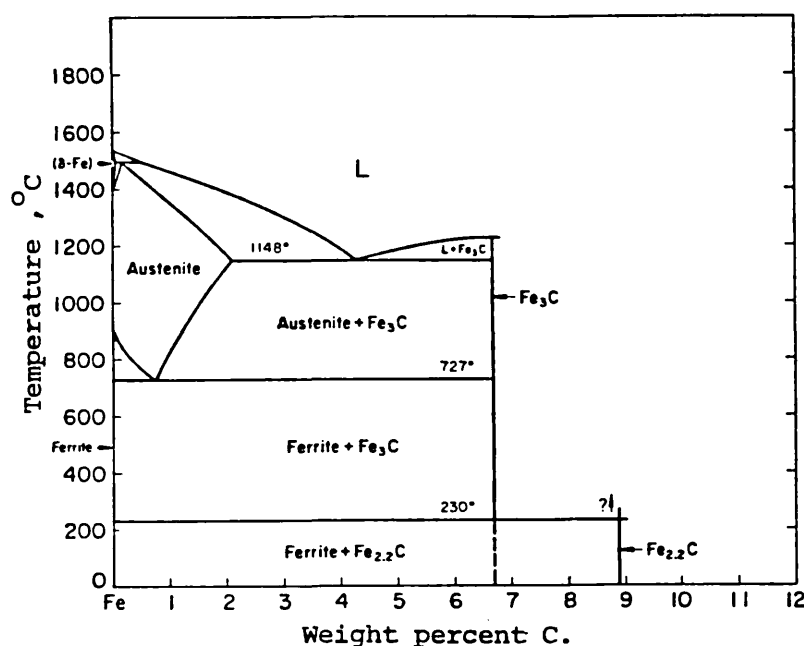


Fig.2.1.⁵⁶ Fe - Fe₃C Equilibrium Phase Diagram

Eiselstein et al⁴³ made a comprehensive study of three rapidly cooled hypoeutectic cast iron powders (2.4C, 3.0C, 3.0C + 1.5Cr). Their findings help explain the microstructural features reported above. Particles were quenched via a forced convective cooling process developed by Pratt and Whitney Aircraft (known as 'Rapid Solidification Rate'). For particles smaller than 100 μm quench rates were estimated as $>10^5 \text{Ks}^{-1}$. After quenching all three alloy powders were found to

consist of retained austenite and small amounts of cementite and martensite. The retained austenite remained stable down to -196°C . Both cellular and dendritic austenite was observed. Cell size and secondary arm spacing decreased with particle size. Lattice parameter measurements indicated that the average C content of the austenite was 1.67C for the 2.4C powder, and 1.43C for the 3.0C + 1.5Cr powder. Using these values the M_s was calculated as -196°C and -102°C respectively. Eiselstein et al³⁹ assumed that any martensite seen at ambient was induced by plastic deformation. Tucker⁴¹ analysed the C content of martensite in his scan melted samples as 1.2C. This corresponds closely to the value reported by Ruhl and Cohen⁴⁶ for splat quenched Fe-4.27C-1.18Cr. A 1.2C composition should induce $M_s \approx 12^{\circ}\text{C}$ (eq 2.1.). While direct comparison between splat quenched and laser melted material is perhaps dubious the similarity between the studies of Ruhl and Cohen⁴⁶, and Tucker⁴¹ is notable. Eiselstein et al's⁴³ results highlight a need to quantify austenite volume fractions and C content of austenite against cooling rate, so permitting better correlation with M_s .

2.2.1. Hypoeutectic Solidification

In hypoeutectic alloys proeutectic austenite nucleates and grows. At a temperature below the equilibrium liquidus, and at a sufficient degree of supersaturation, austenite nucleates and spreads as dendrites, ideally by repeated branching in three perpendicular directions. Thermal gradients through mould walls initiate solidification. Dendrite formation begins with a failure to establish a stable planar solid/liquid interface. Perturbations are amplified and the developing dendrites adopt an orientation which is as close as possible to any heat flux direction, but following a preferred growth axis. Cubic crystals have six[001] growth axes. Secondary arms appear, initially as sinusoidal perturbations of the paraboloid. These perturbations grow, become cell-like, and finally develop into secondary dendrite arms, in the case of a cubic crystal growing perpendicular to the primary trunk⁶⁰.

Cooling rate and alloy content control dendritic refinement. The cooling rate is dominant, increased quench rate refines both primary

and secondary arm spacing. Fritsch and Barton⁵⁹ have illustrated how laser processing conditions control cooling rate and so influence microstructural refinement. X210, a 12Cr Steel was melted with a 1.4kW laser, when beam scanning velocity was increased from 0.5 to 4m/min dendrite arm spacing halved.

2.2.1.1. Primary Dendrite Arm Spacing

A number of workers⁶³⁻⁶⁵ have correlated primary arm spacings with cooling rate (GR) and produced a 'general' equation where primary spacing is presented as a power relation ie:

$$\lambda_1 = A(GR)^{-1/2} \quad (2.2)$$

Suzuki and Nagaoka⁶⁶ using a vertical semi-steady state solidification apparatus attempted to separate the variables. They suggested that the primary arm spacing of two steels Fe-25Cr-20Ni and Fe-1Cr-0.25Mo gave a relationship of the form:

$$\lambda_1 = A G^{-0.4} R^{-0.2} \quad (2.3)$$

Rickinson and Kirkwood⁶⁷ carried out steady state solidification on a 1.5Cr-1C alloy and concluded that primary arm spacing may be represented as:

$$\lambda_1 = A G^{-0.7} R^{-0.48} \quad (2.4)$$

Rickinson and Kirkwoods results are scattered and their exponent values cannot be considered accurate to more than ± 0.1 . In the same publication Hunt⁶⁸ predicted a general equation:

$$\lambda_1 = A G^{-1/2} R^{-1/4} \quad (2.5)$$

Hunt⁶⁸ demonstrated the minimal effect of the exponent on λ_1 . It is for instance difficult to distinguish between (eq 2.2) and (eq 2.5). All these relationships are, therefore, in quantitative agreement. Jones and Kurz⁶⁹ attempted to solve (eq2.5), a likely value for A being 104 ± 13 .

Kishitake et al^{64,70} have considered the effects of C content in ferrous alloys and suggested that λ_1 is inversely proportional to the square root of (GR) and increases with C content ie:

$$\lambda_1 = a \frac{mC(k-1)^{1/6}}{(GR)^{1/2}} \quad (2.6)$$

where $a = 110\mu\text{m K}^{1/3}/\text{s}^{1/2}$ for Fe-C alloys

$mC(k - 1)$ represents the effect of chemical composition.

2.2.1.2. Secondary Dendrite Arm Spacing

The dependence of secondary arm spacing, λ_2 , on cooling rate has been measured for a number of ferrous alloys^{62-66, 70-73}. Observations of continuous coarsening of dendritic structures during isothermal holding within the freezing range, ΔT_o , and of a progressive increase in λ_2 between dendrite tip and dendrite root lead to a relationship of the form:

$$\lambda_2 = A t_f^n \quad (2.7)$$

$$\text{where } t_f = \Delta T_o / GR \quad (2.8)$$

This relation is consistent with control of coarsening by bulk diffusion of solute driven by capillarity. Kurz and Fisher⁶⁰ suggest that, after secondary arm growth, a ripening process analogous to Ostwald ripening of precipitates occurs. Highly branched arms change with time into coarser, less branched and more widely-spaced ones. The driving force for the ripening process is the difference in chemical potential of the two arms with different interfacial energies (ie different curvature). λ_2 is determined by eq.2.7 where t_f is proportional to the ^{inverse} rate of cooling through the freezing range.

$$\text{hence: } B = A T_o^n \quad (2.9)$$

$$\text{and } \lambda_2 = B(GR)^n \quad (2.10)$$

Joly and Mehrabian⁷¹ have determined λ_2 for Maraging 300 steel over a wide cooling range (up to 10^3 K/s) and concluded that:

$$\lambda_2 = 39.8 (GR)^{-0.30} \quad (2.11)$$

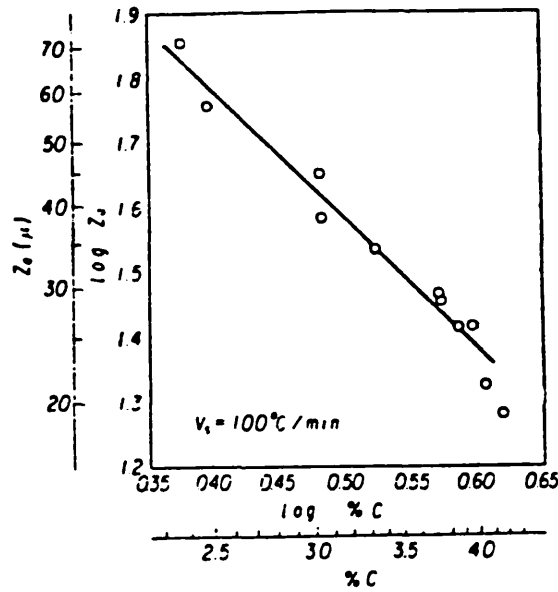


Fig.2.2.⁶⁵ Relationship Between λ_2 (Z_a) at 100°C/min and C Content According to Ibaraki

Ibaraki et al⁶⁵ studied the structure of unidirectionally solidified Fe - C alloys in the range 2.4 - 4.7C and observed that λ_2 decreases with increasing C content (Fig.2.2.) such that:

$$\lambda_2 = \frac{1380}{\text{wt}\%C^2 (\text{GR})^{0.28}} \quad (2.12)$$

Kishitake et al^{64, 70} concurred with Ibaraki⁶¹ and suggested that:

$$\lambda_2 = a \left[\frac{\Delta T}{mC(k-1)(\text{GR})} \right]^{1/3} \quad (2.13)$$

where $a = 35-45\mu\text{m K}^{1/3}/\text{sec}^{1/3}$. For alloys with 1-2C and <7Cr "a" varies little with C content.

Okamoto et al⁷³ considered the partition of C between solid (austenite) and liquid in Fe-C systems. Alloys of 3.81 - 1.79C were equilibrated in the range 1150 - 1400°C and then quenched. Measured diffusion distances varied from 30 - 90 μm

$$\text{GR} = \left[\frac{340 (1/C) - (1/4.3)^{0.35}}{\lambda_2} \right]^{100/37} \quad (2.14)$$

In 'general' equations where λ_1 is presented as a power relation with (GR) the exponent n is usually observed to be larger for λ_1 than λ_2 , thus at high cooling rates λ_1 becomes less than λ_2 ie secondary arms eventually disappear.

2.2.2. Hypereutectic Solidification

In hypereutectic irons proeutectic cementite forms initially. Considerable undercooling is required to nucleate the phase; hence nucleation usually initiates at 'mould walls' rather than homogeneously within the melt. Proeutectic cementite grows as plates, spreading edgewise as two-dimensional 'dendrites', with a number of preferred growth directions. All these directions have a common plane however, and plate formation follows as the spaces between neighbouring branches are filled. Plates of slightly different orientation are formed successively and the reaction spreads in a fan-like fashion. Hillert and Steinhaüser⁵⁷ made a detailed examination of separate plates within individual fans, but neighbouring plates of different lattice orientations were never found to be connected by any curved region with a gradually rotating lattice orientation. Hillert⁵⁷ suggested that cementite, which is known to be brittle at low temperatures, retains its brittleness at high temperatures and that cracks form within proeutectic plates, due either to thermal motion of the melt or thermal stresses within the plates. These broken fragments in turn act as nuclei for new plate growth. While cooling rate will obviously affect the coarseness of cementite plates other factors such as melt stirring will also influence microstructural refinement.

2.2.3. Eutectic Solidification

The white iron eutectic⁷⁴⁻⁷⁷ occurs at 4.27C and solidifies as ledeburite, a quasi-regular composite of austenite and cementite, with a near 1:1 phase ratio. Eutectic solidification proceeds with undercooling over a range of compositions. Elliott^{74,75} has described this region as a coupled zone; it exists where the two phases grow with similar velocities.

In systems where the melting temperatures of the component phases are widely different the eutectic composition is displaced from the centre of the phase diagram, and the coupled zone is displaced from a position of symmetry about the eutectic⁷⁴. Figure 2.3. shows the corresponding plot of limiting growth temperature for Fe-Fe₃C and Fe-C as a function of alloy composition. Graphite has a much higher melting point than iron, hence the grey eutectic exhibits an asymmetric coupled zone. Graphite requires greater supercooling and its temperature dependence of R is much greater. Conversely the Fe-Fe₃C eutectic is more symmetrical⁶⁹.

Hillert and Steinhaüser⁵⁷ have made a detailed study of white iron/eutectic solidification. They have suggested a mode of nucleation and two growth mechanisms, Fig.2.4. Solidification of proeutectic cementite will locally deplete the C content of surrounding liquid. This stimulates eutectic austenite to nucleate at the surface of the cementite and spread across the cementite plate. As the solidifying austenite spreads it rejects C and so flattens the 'liquid' interfacial C concentration. Sideways growth is limited by diffusion rate (though Hillert and Steinhaüser⁵⁷ suggest that the mechanism is not completely diffusion controlled, cementite has a strong tendency to develop flat interfaces characteristic of proeutectic cementite). Co-operative growth leads to more rapid growth. Perturbations at the interface develop into rods. As the sideways growth interface breaks up edgewise growth occurs and spreads parallel to the original proeutectic plate. Lateral concentration gradient_λ^S exist ahead of the edgewise solidification interface controlling interlamellar spacing. Where steps occur in the flat faces of the proeutectic cementite these steps advance edgewise as the regular eutectic grows sideways. Thus, the eutectic grows as a hybrid of the two mechanisms. Where directional solidification is initiated only edgewise growth occurs, growing in the direction of the thermal gradient. Eutectic growth can be compared to the eutectoid transformation ie pearlite forms by co-operation of ferrite and cementite (Appendix IV). Hillert's⁵⁷ concepts are compared with pearlite formation and discussed in terms of edgewise and sideways growth in greater detail elsewhere (Section 2.5.2.).

Newcombe et al⁷⁸ melt spun an Fe-3.5C alloy and made a TEM foil of the ribbon; two phases were identified, ferrite and cementite. There was no evidence of retained austenite and the authors suggest that a

eutectoid rather than a eutectic cooling path has been followed. The eutectoid cooling path suggested by Newcombe et al is not fully understood; it is assumed that the authors⁷⁸ are suggesting that a hypoeutectic alloy solidifies and proeutectic austenite subsequently undergoes a pearlite transformation.

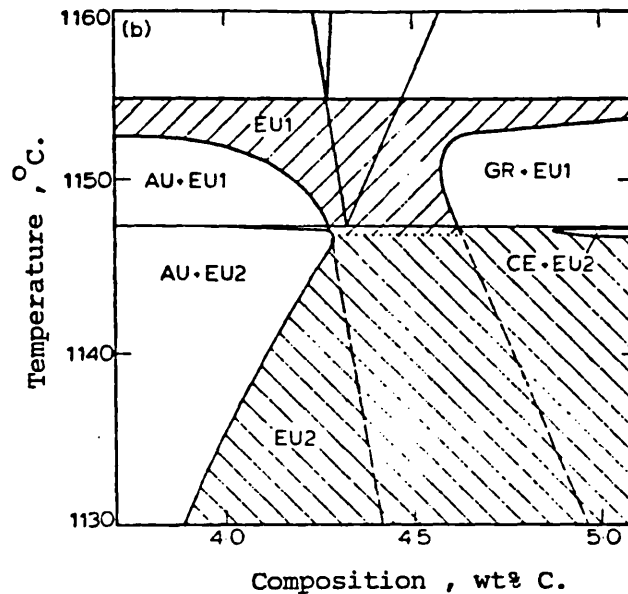


Fig.2.3.⁶⁹ Temperature Composition Diagram with Superimposed Fe-C and Fe-Fe₃C Phase Diagrams
Stable eutectic (EU1), Metastable eutectic (EU2), Austenite dendrites (AU), Graphite plate (GR), Cementite plate (CE).
The white eutectic exhibits a symmetric coupled zone.

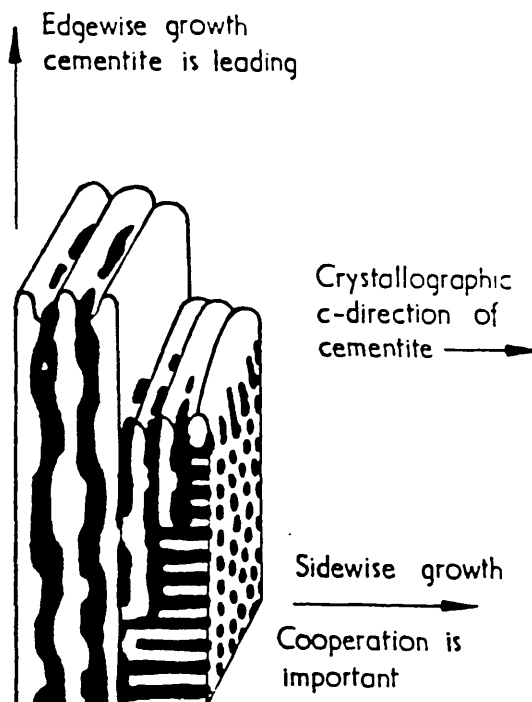


Fig.2.4.⁶⁵ Formation of Eutectic Structure According to Hillert and Steinhauser. White Phase is Cementite, Black Phase is Austenite

2.2.3.1. Modern Concepts of Eutectic Solidification Theory

It can be seen from Fig.2.1. that the solubility of C in austenite ($\sim 2.11\text{C}$) is substantially less than the C content of cementite ($\sim 6.69\text{C}$). There will be considerable redistribution of C, at the solidification front, as ledeburite advances.

Jackson and Hunt⁷⁹ presented a comprehensive analysis of eutectic growth, which is generally accepted as the basis of current theory (the origins of eutectic solidification and eutectoid transformation are outlined in Appendix IV). Jackson and Hunt⁷⁹ derived a steady state solution for the diffusion equation for lamellar and rod growth and obtained expressions for average composition and average curvature at the interface. Tiller's interpretation⁸⁰ of undercooling was developed, the interface undercooling required for transformation being expressed as:

$$\Delta T = \Delta T_D + \Delta T_C + \Delta T_K \quad (2.15)$$

ΔT_D is the undercooling necessary to promote solute redistribution ahead of the solid eutectic and will be, approximately, proportional to the product of the diffusion parameter. This contribution is calculated from:

$$\Delta T_D = m(C_E - C) \quad (2.16)$$

The magnitude of ΔT_D varies across each lamellae and the interface undercooling is maintained constant by curvature of the interface. ΔT_C is the contribution due to interfacial curvature:

$$\Delta T_C = a/r(x) \quad (2.17)$$

a = constant given by the Gibbs-Thomson relationship

$r(x)$ = local curvature of the interface

ΔT_K is the kinetic undercooling, which for a non-faceting/non-faceting system is insignificant.

The Jackson and Hunt analysis gave the following equation for lamellar eutectics:

$$\frac{\Delta T}{m} = R\lambda_3 Q^L + \frac{a^L}{\lambda_3} \quad (2.18)$$

m^L , Q^L and a^L = constants, functions of alloy composition.

A similar relationship can be derived for rod growth of the form

$$\frac{\Delta T}{m} = Rr Q^R + \frac{a^R}{r} \quad (2.19)$$

with r , Q^R , a^R replacing λ_3 , Q^L , a^L respectively

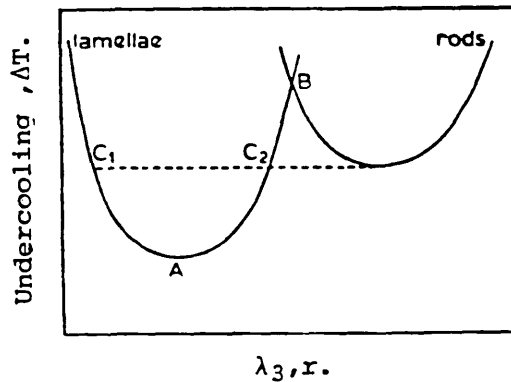


Fig.2.5.⁷⁹ Average undercooling of interface plotted against interlamellar or inter-rod spacing for a given velocity

Fig.2.5. schematically illustrates the relationships between ΔT and λ_3 or r (eqns 2.18 and 2.19). Lower and upper limits of steady state lamellar growth are defined by points C_1 and C_2 . Growth probably occurs close, but to the right of the extremum point A, because spacings smaller than the extremum are inherently unstable and the interface cannot maintain an isothermal interface for spacings larger than the minimum, Fig.2.6. The simplest condition is that proposed by Zener⁸¹ in which it was assumed, that the solid^{which} grows at the extremum has a minimum at constant growth velocity given by:

$$\lambda_3^2 R = \frac{a^L}{Q^L} \quad (2.20)$$

$$\text{or } \frac{\Delta T^2}{R} = 4m^2 a^L Q^L \quad (2.21)$$

$$\text{or } \Delta T \lambda_3 = 2ma^L \quad (2.22)$$

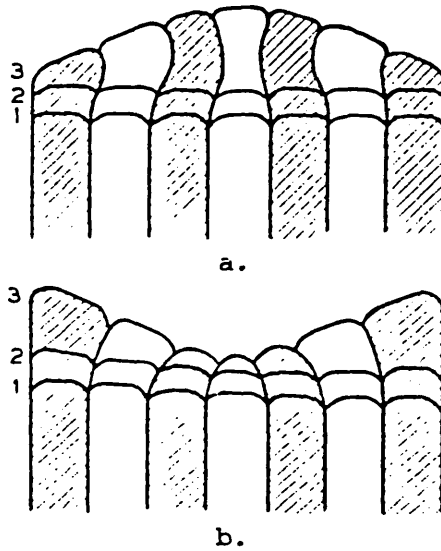


Fig.2.6.⁷⁹ The lamellae in (a) are wider than the extremum spacing, in (b) narrower than the extremum spacing. Interface position 1 shows the original regular lamellae; position 2 the formation of narrower lamellae at centre; position 3 the change in interface shape, due to the change in local undercooling. For (a) the structure is restabilized by the change in interface shape in (b) it is not. In the latter case a lamella will grow out.

Series et al⁸² have used an electrical analogue as an aid to solving the diffusion equation, and have used the results obtained to assess two of the main assumptions made in Jackson and Hunt's analysis⁷⁵. These are that the composition profile along the curved interface is

the same as that for a plane interface and that composition variations in the liquid at the interface are small. Although the interface shapes derived from the analogue study differ from a planar form the analogue composition profiles do not differ appreciably from those calculated using Jackson and Hunt's analysis. At low growth velocities analogue values for Q^L compared favourably to Jackson and Hunt's, however, there is appreciable difference at high growth velocities. Series et al⁸² permitted the mean composition ahead of the lamellae to have different and unrestricted values rather than assuming the composition variation along the interface to be small. This leads to a modified Q^L parameter:

$$Q'^L = Q^L \left[1 - \frac{R\lambda_3 Q^L}{C_o} \left(1 - \frac{m_\alpha}{n_\alpha} \right) \right]^{-1} \quad (2.23)$$

Where m_α is the solidus slope of the α phase.

This modification restores the anomaly (at the extremum condition). The modified theory predicts:

$$\lambda_3^2 R = \frac{a^L}{Q^L} \left[1 - \frac{R\lambda_3 Q^L}{C_o} \left(1 - \frac{m_\alpha}{n_\alpha} \right) \right]^{-2} \quad (2.24)$$

The rapid cooling and high growth rates associated with laser processing imply that extrapolation of the $\lambda_3^2 R = \text{constant}$, relationship to calculate cooling rate is likely to be inaccurate.

Jones and Kurz⁸³ measured growth temperature as a function of G for Fe-C melts, demonstrating the formation of a grey eutectic and dendrites at low R which gives way to a white eutectic at high R . The authors reported that steady state unidirectional growth for a number of regular eutectics can be predicted by Jackson and Hunt's analysis (the relationships implied by eqs. 2.20 - 2.22 are closely obeyed). No comparison can be drawn for irregular eutectics such as Fe-C and Al-Si, Table 2.1.

TABLE 2.1.⁸³ Extremum Predictions for λ_3 as a Function of R for Fe-C and Fe-Fe₃C Eutectics

		$\lambda_3, \sqrt{R}$
		$\mu\text{m}^{3/2}/\text{s}^{1/2}$
Fe-C:	Measured	12 - 120
	Predicted for extremum	4 - 20
Fe-Fe ₃ C:	Measured	11 - 29
	Predicted for extremum	17

2.2.3.2. Lamellar - Rod Transition

In its simplest form eutectic morphology can be explained as a function of interfacial area and interfacial free energy, σ . Rods form when the minimum undercooling is lower than that for lamellae^{79, 84}:

$$\Delta T_L > \Delta T_r \quad (2.25)$$

or
$$\Delta T_{D_L} + \Delta T_{C_L} > \Delta T_{D_r} + \Delta T_{C_r} \quad (2.26)$$

For isotropic solid-liquid and $\alpha - \beta$ interfacial free energies the volume fraction of the two phases should determine its form. For a particular spacing the total solid-solid interfacial area of a rod structure increases rapidly with increasing phase volume fraction, whereas that of a lamellar structure is independent of volume fraction.

Consider two unit cubes of eutectic. If $\Delta T_{C_r} = \Delta T_{C_L}$, the boundary energy for lamellae and rods per unit cube must be equal:

$$2\pi r N_r \sigma_r = 2N_L \sigma_L \quad (2.27)$$

where N_r is the No. of rods and N_L the No. of lamellae.

let $\sigma_r = A\sigma_L \quad (2.28)$

then $\pi r N_r A = N_L \quad (2.29)$

The diffusion parameter for lamellae, P_L , will be half the lamellae spacing.

$$P_L = \frac{1}{2N_L} \quad (2.30)$$

For a rod, diffusion can occur in all directions away from the rod tip.

The diffusion parameter can be approximated by considering a section through each rod to be surrounded by a square, then taking half the length of the square

$$P_r = \frac{1}{2} \sqrt{\frac{1}{N_r}} \quad (2.31)$$

The system will be rod if $P_L > P_R$ or if:

$$\frac{1}{2N_L} > \frac{1}{2} \sqrt{\frac{1}{N_r}} \quad (2.32)$$

substituting N_L from (eq 2.30) gives:

$$\frac{1}{\pi^2 r^2 N_r^2 A^2} > \frac{1}{N_R} \quad (2.33)$$

But $\pi r^2 N_r = V_A$, the volume fraction of rods. Thus, rods will form if:

$$V_A < \frac{1}{A^2 \pi} \quad (2.34)$$

When $A = 1$ a rod structure will be obtained if $V_A < 32\%$. However the interphase boundary energy for rods, σ_R , is probably greater than the interphase energy for lamellae. This is because the lamellar eutectic will tend to grow so that the interphase boundary energy is small, allowing some coherence, whereas it is unlikely that any coherence is possible around the cylindrical rod. If $A = 2$ a rod structure results if $V_A < 8\%$. Pearlite in steels exhibits a lamellar morphology, even though the structure contains about 12vol% Fe_3C . Anisotropic interfacial energy has displaced the Lamellar-Rod transition to $V_A < 12\%$. The ferrite/cementite interface must be coherent or semi-coherent and the establishment of a low energy interface is an important factor in the development of co-operative growth. Ibaraki et al⁶⁵ report that lamellar eutectic colonies of ledeburite undergo a rod transition at the extremities of cell growth, ie where two or more cells interface. Hunt and Chilton⁸⁴ have demonstrated that when a eutectic is forced to grow in a direction other than the preferred lamellar growth direction, a rod structure can be formed. Restricted growth causes σ_L to increase, A to approach unity, and the rod volume fraction of formation to approach 32%. It is not suggested that 32% is a significant figure but it is one that indicates a trend.

2.2.3.3. Impurity Elements

The eutectic microstructure is modified by the presence of impurity elements, which lead to colony formation within eutectic grains.

The colony structure in eutectic alloys is entirely analogous with the impurity cellular structure in single phase alloys, and both depend upon the presence of a zone of constitutionally supercooled liquid at the interface. It was shown by Tiller et al⁸⁵ that the criterion for the onset of constitutional supercooling and interface instability could be expressed as:

$$\frac{G}{R} \leq \frac{mC}{D} \left[\frac{1 - k}{k} \right] \quad (2.35)$$

A formally identical expression can be obtained for the onset of constitutional supercooling in impure eutectic materials:

$$\frac{G}{R} \leq \frac{m_E C}{D} \left[\frac{1 - k_E}{k_E} \right] \quad (2.36)$$

The values of m_E and k_E are not generally known, therefore the criterion cannot be tested for quantitative accuracy. However, it has been shown by Kraft and Albright⁸⁶ that planar to colony transition in impure eutectic alloys changes with G , R and C , and has a dependence on (Eq.2.36). Nash⁸⁷ offers an explanation for velocity induced lamellar-rod transition. He has considered the process as a free boundary problem and presented an analysis that decouples the calculation of the interfacial quantities from the computation of the bulk temperature and solute distributions.

Colony formation could be retarded by increasing G or reducing R . A eutectic transformation from lamellar to fibrous structures is often associated with colony formation (Section 2.2.3.2.). Chadwick⁸⁸ has attributed the change in structure directly to the impurity element by an argument of localized constitutional cooling. Ibaraki et al⁸⁵ suggest that lamellar ledeburite becomes unstable at locally ^{de}uncooled regions causing branching of rod-like austenite. Hunt and Chilton⁸⁴ have argued that microstructural changes are due to the constraints of non-unidirectional growth imposed by the alloy during cellular growth. It seems probable that both impurity effects and anisotropy of interfacial energy are jointly responsible.

2.3. EXPERIMENTAL PROCEDURE

Over 120C alloyed laser tracks were produced. Scan rates of 10-80mm/s used in conjunction with beam diameters of 1.5-5mm produced melt depths of 0.1-2.5mm. Surface layers were built up by overlapping a series of single runs. The substrate was traversed sidewise, usually $\times 0.4$ beam diameter, after each laser processing. The substrates used were commercially available S135 aerospace steel, previously austenitized at 844°C for 1 hour, and nominally pure iron cut from a hot rolled billet. Their analysed compositions are given, Table 2.2. All specimens were grit blasted before processing, giving a uniform surface finish.

TABLE 2.2. Compositions of Ferrous Substrates.

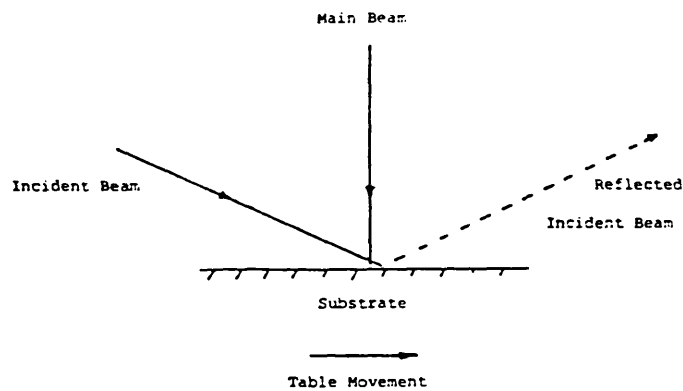
Wt %	C	Si	Mn	P	S	Cr	Mo	Ni
Fe	0.016	<0.02	0.12	0.06	0.007	<0.01	<0.005	0.02
S135	1.0	0.29	0.42	0.005	0.005	1.39	-	0.17

15mm thick specimens were given single and multipass treatments using a 'Control Laser' 2kW CO₂ laser with a gaussian beam, typically operating at 1.7kW. The specimen thickness was sufficient to facilitate rapid self quenching without substantially increasing subsurface temperature. An Ar gas shroud was used to suppress plasma generation while simultaneously shielding the melt from atmospheric contamination. Preplaced surface alloying was carried out. DAG graphite coatings were applied by either of two methods:

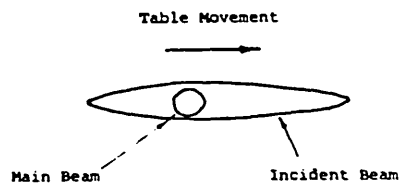
- a. By diluting the DAG with methanol and then 'painting' on. The methanol evaporated, leaving a thin even DAG layer of $0.010 \pm 0.001\text{g/cm}^2$.
- b. By diluting the DAG to a lesser extent, producing a paste or slurry. This was applied as evenly as possible in thicker coats and after drying had a coating of $0.033 \pm 0.004\text{g/cm}^2$. These thicker coats were protected with adhesive masking tape.

In some experiments, successive laser processing treatments (up to 24) were given to the same region, with the reapplication of DAG coating between each treatment.

Two of the problems encountered with high C alloying were gas entrainment in the melt zone and melt zone cracking during cooling. It was thought that post heating using a second glancing laser beam might increase the molten time, allowing more time for entrained gases to escape and, also, reduce the cooling rate, thus, reducing the likelihood of quenching cracks. This procedure involved the use of two 2kW lasers, the beams being fired simultaneously, one vertically and the other at 65° to the vertical⁸⁹, Fig.2.7. Much of the power of this second beam (1.56kW incident) was reflected off the specimen because of the acute angle. The dual beam system did not significantly reduce either porosity or cracking and it was abandoned in favour of a single vertically fired laser.



a. Configuration of laser beams.



b. Burn print of twin beams in a perspex plate.

Fig.2.7. Dual laser beam arrangement for post heating the substrate

In order to determine the stability of retained austenite, refrigeration treatments were carried out on some specimens, by quenching into liquid nitrogen within 1 hour of laser processing, holding for 30 minutes and slowly warming to ambient. Any instability was reflected in the degree of martensite transformation as assessed by hardness changes.

A detailed microstructural study of white iron produced by laser alloying ^{with} C was carried out. Optical microscopy, SEM, TEM and X-ray analysis were the principle techniques used.

An optical microscopical examination was made of all specimens. Most samples were sectioned in three planes (plan , longitudinal and transverse) on a surface grinding machine fitted with a slitting wheel. Continuously fed coolant minimised heating so eliminating tempering. The specimens were polished with successively finer grades of diamond paste and then finish polished using an alumina slurry, containing $0.03\mu\text{m}$ Al_2O_3 particles. All optical micrographs were obtained from samples etched in 2% nital, though picral and alkaline sodium picrate were experimented with. The "quantity" of the melted track is expressed in terms of cross sectional melted area (CSMA). A minimum of three transverse sections were taken from each track, polished and etched. The average area of the track is the CSMA. Polarised filters were used to discern individual eutectic colonies and their relationship to proeutectic phases. Oil immersion extended magnifications up to X1500.

A JEOL T200 scanning electron microscope was used to study both polished and fractured specimens at magnifications of X35 to X10,000. Primary dendrite arm spacings were determined by average measurements of the separation of neighbouring primary arms. Sections cut parallel to primary arms allowed accurate measurement of secondary arm spacing. Scatter of measurements was minimized by averaging over groups of up to 10 secondary arms. Although research has led to a correlation between eutectic interlamellar spacing and transformation temperature, researchers determined either minimum interlamellar spacing or an average apparent interlamellar spacing^{90, 91}. The minimum interlamellar spacing is characteristic only if the interlamellar spacing is constant throughout the whole sample, and this is not always the case. On the other hand, the average apparent interlamellar spacing is also not unambiguously characteristic of lamellar structures. In the recent study average apparent interlamellar spacings together with λ_{min} and λ_{max} are given. The wide depth of focus available with SEM was used to study 3 dimensional sections. Polished samples were fractured along existing solidification cracks and then soaked in a warm solution of 10% nital for ~30 seconds until deep etched. The specimens were

thoroughly rinsed by repeated immersion in alcohol followed by a 30 minute ultrasonic wash in alcohol, changing the washing solution after 1, 2, 5 and 10 minutes. Where possible, specimens were examined within 1 hour of preparation. Specimens were tilted so as the eutectic was perpendicular to the field of view, the view was photographed and the eutectic spacings measured from prints. The spacings of several micrographs were averaged to give a mean value.

A TEM analysis of the eutectic and HAZ melt interface using an EM7 1000kV microscope was made. Sections of laser track were cut parallel to the top surface of the treated layer and at a depth of less than half the depth of the laser melted track. The sections were ground to a thickness of $\sim 60\mu\text{m}$ on silicon carbide wheels. 3mm discs were cut by spark erosion (mechanical punching causes deformation) and subsequently ion beam thinned. The foils were studied at magnifications of up to X100,000 and individual phases identified by their diffraction patterns.

An X-ray diffraction examination of the surfaces of various specimens was carried out using a 'Philips Wide Range Goniometer, model PW-1050', fitted with a Cu radiation source. Where small phase volume fractions were to be identified single tracks proved to be an insufficient X-ray source. The most desirable sample size was typically 10mm x 15mm. Hypereutectic specimens were readily produced by overlapping hypereutectic tracks. However, where hypoeutectic tracks overlapped hypereutectic alloys formed. Surface alloyed layers were analysed after laser processing, after grit blasting and after etching in 10% nital. The latter treatments make phase identification easier. The results indicated the presence of ferrite in the alloyed track. In order to corroborate this, specimens were crushed using a mortice, mounted on a glass slide and analysed using a Guinier camera with a Co radiation source.

Hardness tests were carried out using either an AKASHI microhardness machine fitted with 100 or 500g loads or using a Vickers machine fitted with a 5kg load. Where average track hardness was determined the average value was based on a minimum of 8 impressions. Where microhardness traverses across track sections were determined a minimum of 3 traverses were carried out.

2.4. RESULTS

2.4.1. C Alloying into S135

2.4.1.1. Conduction Limited Melt Zones

To produce white irons a greater amount of C must be alloyed than in earlier work^{52, 53}. Previous work⁵² indicated that the high surface/volume ratio associated with shallow melt zones, produced by using a defocused laser beam would enhance C alloying. The laser processing parameters were adjusted to produce conduction limited melt zones. A systematic series of treatments using a laser power of 1.7kW and a defocused beam, 5mm diameter were carried out. Scanning speeds were varied between 5 and 75mm/s. The width and depth of the laser melted track decreased with increased scanning speed. A scan speed of 25mm/s was found to give consistent repeatable shallow melting.

Samples were reprocessed up to five times in an attempt to induce further C alloying. Plate 2 illustrates sections taken from a melt track (width 4.9mm, depth 0.2mm) produced by 5 successive DAG painted runs, this example is typical of 'conduction limited' C alloyed tracks. Microstructure is not uniform and ranges from hypoeutectic at the melt/substrate interface to hypereutectic near the surface. This heterogeneity is attributed to unhomogeneous mixing of the C. Plates 2b and c 'graphically' illustrate this C gradient, decreasing with penetration. The interfacing HAZ is martensitic (HV 900). A single layer of soft equiaxed grains (HV 350, 20 μ m) extends the full length of the interface; these were interpreted as being austenite partially transformed to martensite. Columnar austenite dendrites grow upwards epitaxially from this interface. The inter-dendritic regions contain a fine broken lamellar eutectic, originating from the liquid $\rightarrow \gamma + \text{Fe}_3\text{C}$ reaction. At approximately one third the melt depth (from the surface) the proeutectic austenite is entirely superceded by the eutectic matrix, eutectic spacing $\sim 0.8\mu\text{m}$. In intermittent but definable regions near the surface a plate shaped proeutectic phase, interpreted as cementite, precipitated. Plate 2.e. illustrates both the broken lamellar nature of the eutectic and a growth interrelationship between proeutectic cementite and eutectic (discussed Section 2.5.2.).

Microstructural anomalies cause wide fluctuations in proeutectic austenite primary and secondary arm spacings; these range from $\lambda_1 = 8.5 \pm 3.1 \mu\text{m}$ and $\lambda_2 = 2.3 \pm 1.2 \mu\text{m}$ near the melt/substrate interface to $\lambda_1 = 7.0 \pm 2.8 \mu\text{m}$ and $\lambda_2 = 0.9 \pm 0.3 \mu\text{m}$ in the melt track 'core'. Eutectic spacing was constant $\lambda_{\text{Eu}} = 0.4 \pm 0.2 \mu\text{m}$. (These spacings are average spacings taken for similar positions in 4 transverse sections of the same track).

On quenching to -196°C , areas of austenite (both the dendritic regions in the melt and the equiaxed interface grains) transformed to martensite. Transformation was sporadic, some grains transformed totally, others were unaffected, possibly due to austenite of varying compositions.

With shallow zones of the type produced by this treatment there is insufficient depth to establish a good mixing cycle.

2.4.2. C Alloying into Pure Fe

In a series of experiments involving C alloying into Fe a more focused (1.5mm dia) beam was used, producing deeper and narrower melt zones. This melt zone geometry induces melt pool mixing creating a more homogeneous track. Fig.2.8 illustrates the effect of successive 'DAG' painted treatments. 1 or 2 treatments alloys sufficient C for martensite to form on quenching. Further C alloying depresses M_s below room temperature, the microstructure consisting of soft, retained austenite. Successively processing 6, 8, 10 and 12 times gradually decreases the volume of retained austenite in favour of harder eutectic, raising the overall track hardness (as illustrated elsewhere^{52, 53}). 18 and 24 successive treatments produces hypereutectic melts of hard proeutectic cementite and eutectic. Quenching in liquid nitrogen (-196°C) transforms lower C austenite to martensite increasing overall track hardness. 'Liquid nitrogen quench' hardness declines between 4 and 12 reprocessings despite an increasing room temperature hardness, presumably^{because} an increasing proportion of the retained austenite has a high C content and an M_s below -196°C . The wide range of hardnesses in the austenite region is caused by localised martensitic transformation; some austenite dendrites preferentially transform while others were unaffected. Low C laser alloying has been previously studied^{52, 53}.

Martensite and retained austenite are reported^{52,53} in terms of morphology and refinement. The effects of increased C alloying, combined with rapid cooling, on M_s have also been discussed.

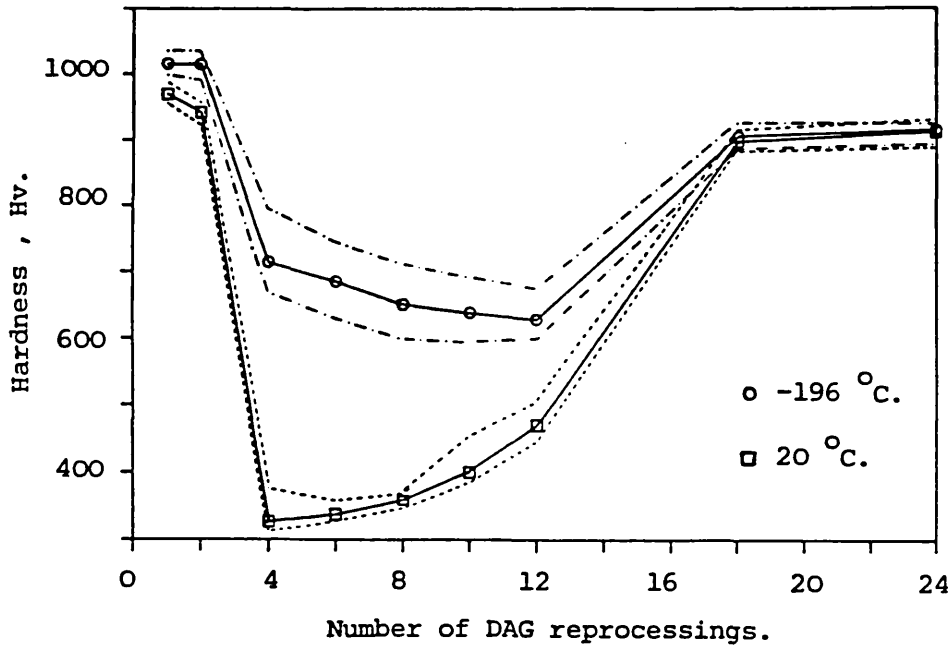


Fig.2.8.Hardness of Fe substrate successively recoated with C and laser melted (1.5kW, 1.5mm, 20mm/s)

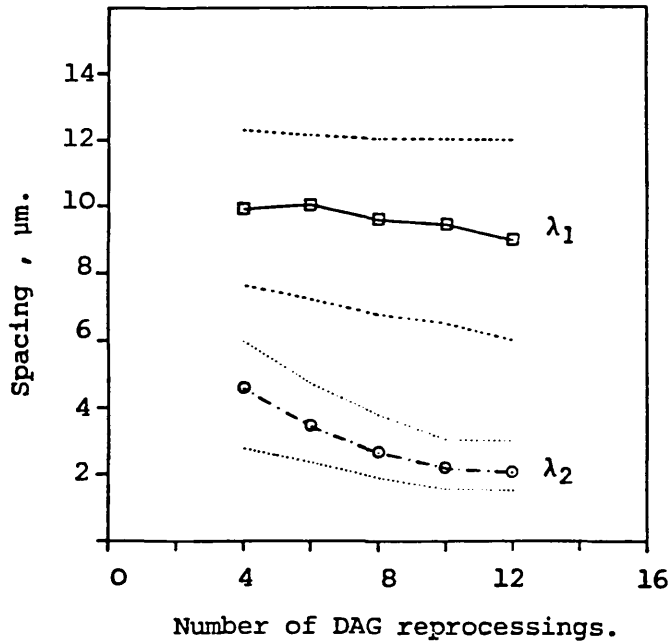


Fig.2.9.Mic rostructural refinement, of proeutectic austenite, of successively C re-alloyed Fe substrate (1.5kW, 1.5mm, 20mm/s). λ_1 and λ_2 varied across individual alloyed tracks hence min, max and mean spacings are given.

2.4.2.1. Hypoeutectic White Iron

The samples DAG processed 4 - 12 times, Fig.2.8., are hypoeutectic white irons (the 12 DAG track is illustrated, Plate 3). Track profile was largely unaffected by the number of reprocessings. All track specimens had 'near key-hole' melt zones and a homogeneous hypoeutectic structure. The only apparent difference between the 4 and 12 run track is the percentage C alloyed. This increasing C content is reflected in a change in microstructure. The average primary arm spacing of each track was unaffected by the number of reprocessings, mean $\lambda_1 \sim 10\mu\text{m}$, Fig.2.9. However, all tracks exhibited similar variations across individual specimens, λ_1 being finer near the keyhole than near the surface. Fig.2.10a illustrates this fluctuation for one individual run. This explains the wide λ_1 range difference shown in Fig.2.9. Secondary arm spacing is directly affected by reprocessing; λ_2 decreases steadily from $\lambda_2 = 4.6\mu\text{m}$ after 4 reprocessings to $\lambda_2 = 2.1\mu\text{m}$ after 12 reprocessings. λ_2 fluctuations across individual tracks do occur ^{and} all specimens are finer near the keyhole than at the surface, Fig.2.10a.

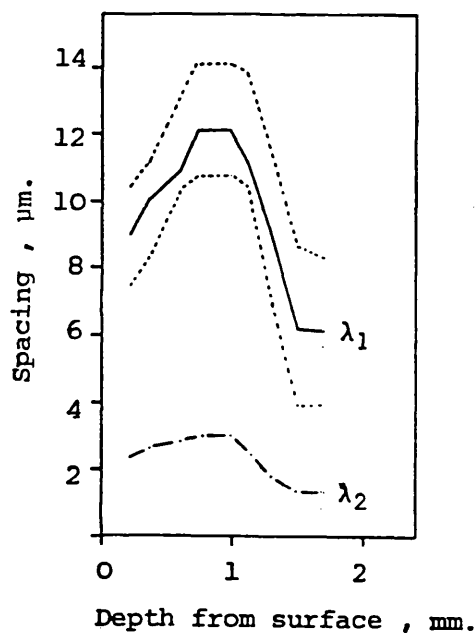


Fig.2.10a. Microstructural Refinement across transverse section of track Plate 3a.

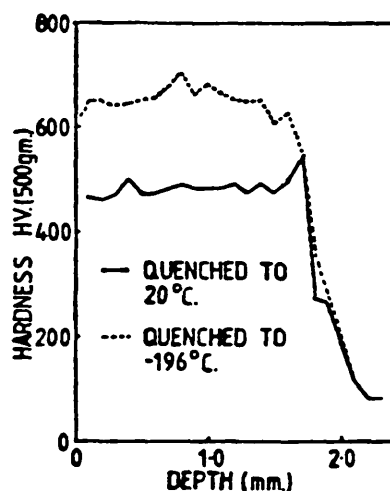


Fig.2.10b Hardness traverse through centre axis of hypoeutectic laser track, Plate 3a.

The hypoeutectic track produced by 12 successive DAG reprocessings Fig.2.8., Plate 3, has been taken as a representative specimen of hypoeutectic cast iron produced by LSA and has been studied in greater detail. The specimen is interpreted as consisting of austenite dendrites in a eutectic matrix. Austenite nucleates epitaxially at the melt/substrate interface and dendrites grow perpendicular to the interface completely filling the melt zone with a lattice like network. This dendritic network ranges from $\lambda_1 = 6 \pm 2 \mu\text{m}$, $\lambda_2 = 1.5\mu\text{m}$ at the keyhole to $\lambda_1 = 12 \pm 3\mu\text{m}$, $\lambda_2 = 3.0\mu\text{m}$ in the track core, Fig.2.10a.

Those dendrites most closely orientated to the cooling direction grow selectively, at the expense of the more poorly orientated dendrites. There is no apparent growth relationship between eutectic and proeutectic phase. The lamellar eutectic is seen to lie at various angles to the main growth direction of the proeutectic. Plate 3c shows the eutectic lying at $\sim 45^\circ$ to the main growth direction of the proeutectic, Plate 3e shows the eutectic lying almost perpendicular to the main growth direction.

As previously observed (Section 2.4.1.1.) a layer of equiaxed austenite grains (25 μ m) completely bounds the substrate interface, Plate 3b. Although the proeutectic austenite had not transformed to martensite, individual martensite laths have formed in the interface layer. Plate 3g illustrates a deep etched section of the interfacial austenite grains. Grain boundaries are clearly outlined as are the martensite plates. A band of martensite ($\sim$ 30 μ m) borders the 'substrate side' of the equiaxed austenite region. A band of grain-refined ferrite ($\sim$ 0.45mm) separates the martensite from unaffected substrate.

The SEM microstructural study revealed that the phase ratios of the eutectic differed from that usually associated with ledeburite; ie carbide-austenite ratio 1:1.⁵⁷. In perfectly lamellar regions the thickness ratios were $1.99 \pm 0.5 : 1$, Table 2.3. A TEM study corroborated this observation⁹². Analysis of diffraction patterns showed that the carbide was Fe₃C, while the metallic phase was exclusively ferrite rather than retained austenite or martensite, Plate 4a-d. In most cases examined, the cementite and ferrite phases exhibited the same orientation relationship, the Bagaryattski relationship⁹³:

$$(100)_c // (0 \bar{1} 1)_\alpha$$

$$(010)_c // (1 \bar{1} \bar{1})_\alpha$$

$$(001)_c // (2 \ 1 \ 1)_\alpha$$

Localised regions of ledeburitic austenite decomposed to extremely fine lamellar pearlite, $\lambda = 55$ nm. Plate 4e shows one such pearlite region; carbon-ferrite ratio $\sim 1 : 7$.

The equiaxed melt/substrate interface grains were identified as consisting of heavily dislocated austenite and martensite needles, Plate 4f. Analysis of diffraction patterns showed that the martensite was related to the austenite by the Kurdjumov-Sachs relationship⁹⁹:

$$(111)_\gamma // (011)_{\alpha'}$$

$$[\bar{1} \ 0 \ 1]_\gamma // [\bar{1} \ \bar{1} \ 1]_{\alpha'}$$

The errors of measurement of the diffraction patterns did not permit exact determination of the c/a ratio of the tetragonal martensite but measurements indicated an approximate value of about 1.04 which using (eq 2.37) is equivalent to 0.9C.

$$\text{Roberts Relationship}^{95} \quad c/a = 1.000 + 0.045 \text{ wt\%C} \quad (2.37)$$

When the sample was quenched in liquid nitrogen the dendritic proeutectic austenite and untransformed austenite in the interface grains transformed to martensite, the melt zone hardening from HV470 to HV630, Fig.2.10b.

TABLE 2.3. Eutectic Spacing and Cementite : Ferrite Phase Ratio

Phase Ratio Given as Fe ₃ C:α		Key-Hole (1.7kW, 1.5mm, 20mm/s)				Conduction Limited 1.7kW, 5mm, 25mm/s	
		HYPOEUTECTIC		HYPEREUTECTIC			
		λ ₃ (μm)	Phase Ratio	λ ₃ (μm)	Phase Ratio	λ ₃ (μm)	Phase Ratio
SEM		0.57	1.72	0.53	2.10	0.28	2.05
		0.72	1.89	0.65	1.84	0.60	2.34
		0.64	2.31	0.52	1.72	0.45	2.10
		0.62	2.05	0.62	1.88	0.43	1.85
		0.52	2.05	0.40	2.21	0.35	1.78
		0.43	1.94	0.55	2.20	0.37	1.80
		0.61	1.82	0.75	1.80	0.54	1.76
		0.42	1.92	0.38	1.92	0.50	1.65
		0.55	2.20	0.47	1.90	0.21	1.95
		0.59	1.93	0.49	1.87	0.27	2.30
	Av	0.57	1.98:1	0.54	1.94:1	0.40	1.96:1
SEM		0.53	2.63	0.57	2.64		
		0.45	2.17	0.32	2.05		
		0.55	2.00	0.47	1.80		
		0.80	1.80	0.71	1.70		
		0.32	1.33	0.65	2.14		
		0.47	1.95				
		0.57	1.88				
		0.62	2.40				
		0.57	2.27				
		0.67	1.51				
	Av	0.55	1.99:1	0.54	2.07:1		
TEM		Pearlite					
		0.05	0.15				
		0.06	0.15				
		0.05	0.15				
		0.06	0.15				
	Av	0.055	1:7				

2.4.2.2. Hypereutectic White Iron

'Protected' processing induces substantially greater alloying than 'painted' processing. One 'protected' processing is approximately equivalent to 5 'painted' reprocessings. Four successive DAG 'protected' reprocessings using the same processing conditions as Section 2.5.2.1. produced a uniformly mixed melt zone of proeutectic cementite plates in a eutectic matrix, Plate 5 (this sample is equivalent to 18 - 24 'painted' reprocessings Fig.2.8.). BCIRA⁹⁶ quantified the wt%C alloyed using a Leco CS244 Automatic C Determination. A section of alloyed track was removed from its substrate using a cold chisel and then analysed. A minimum content of 4.6C for 'Plate 4'-specimen was measured. However, sample size and possible substrate dilution produced differing results and make this figure questionable. Microstructural analysis suggests that the true C content might be ~1wt% greater than that determined by BCIRA.

The track shown, Plate 5, contains 50 vol% of faceted proeutectic cementite plates. These plates grow as families or colonies and vary in sizes from 5 - 30µm width and 20 - 1000µm length. Each family of plates originates from a common source at the melt interface and spreads in an apparently branching manner producing characteristic fan shaped distributions, Plate 5e. Nucleation is heterogeneous and growth is so rapid that a single fan can extend throughout half the track. Growth is competitive and only a few dominant colonies are responsible for the bulk of proeutectic growth. The spreading 'fan' is not significantly distorted by the 'lateral' cooling gradient, created by the traversing beam. Cementite laths, on average, actually grow perpendicular⁸⁹ to the predicted direction of freezing, as shown in a longitudinal section, Plate 5b.

In such multi-run laser processing, each successive run does not necessarily follow the exact path of the preceding run. This is clearly illustrated, Plate 5a, the lower section of the right hand shoulder of the melt zone 'V' not having been melted in the final run. This region consequently contains proportionally far less carbon, hence its structure, primary austenite and eutectic. Plate 5d shows the effect more clearly; ie the complete transition from ferritic iron through martensite (produced from carbon diffusion into the HAZ), interfacing austenite grains, and hypo-eutectic to hyper-eutectic iron.

The eutectic exhibits the same irregular lamellar morphology seen in hypoeutectic samples. Eutectic spacing ranges from $0.3 - 0.8\mu\text{m}$, there being no clear spacing trend from one region of the melt zone to another. Each eutectic colony is orientated to an adjacent proeutectic cementite plate. Polarized light reveals how the eutectic lamellae of each colony lie parallel to themselves and to an adjacent proeutectic cementite plate, Plate 5f, g. Deep etching of fractured surfaces reveals the nucleation and growth relationship of the eutectic to the proeutectic cementite, Plate 6.



a. Eutectic nucleation and '2 dimensional' growth.

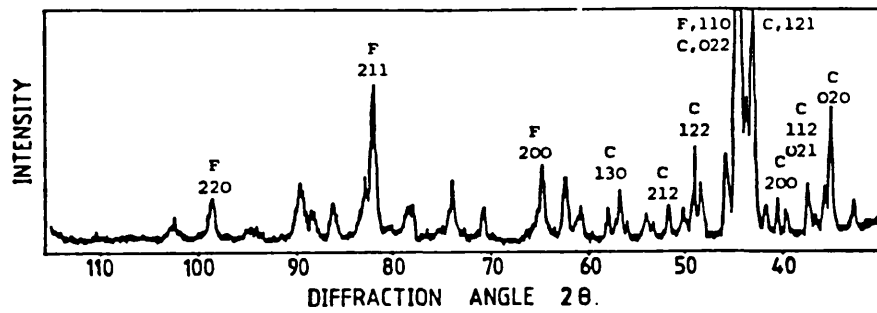


b. Sidewise eutectic growth.

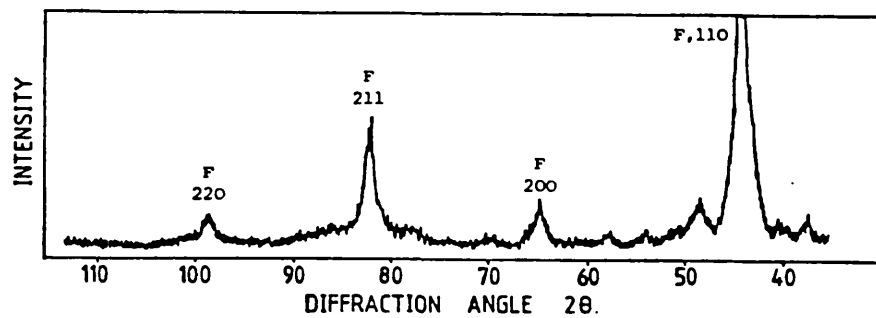
Fig.2.11. Nucleation of Eutectic, from proeutectic cementite, and eutectic growth.

The surface of proeutectic cementite plates contain ridges and steps and this topography, associated with eutectic growth, implies that both eutectic phases nucleate and grow on the proeutectic, Plate 6b, c. Eutectic austenite (transformed to ferrite) has been etched out and the residual surface protrusions shown are eutectic cementite. Plate 6b, c, shows eutectic cementite extending as a series of roughly parallel ribs from a flat eutectic plate. If the rib tips represent the leading edge of the growth front then the rear edge is the point where the ribs 'in-fill' forming a ridge, or eutectic 'plate' Fig.2.11a. Plate 6d, e, illustrate these ribs extending sidewise into the eutectic and, at a distance of $\sim 1\lambda_3$, branch and spread parallel to the proeutectic, either as single two dimensional lamellae or, more likely, as a dendritic network which subsequently 'infills' forming a lamellar morphology. Irregular but continuous sidewise growth and branching leads to the formation of individual broken lamellae colonies related to a single proeutectic plate, Fig.2.11b. Proeutectic plate edges are ill-defined; they 'break-up' extending outward as eutectic cementite lamellae growing in the same plane as the proeutectic and the related eutectic colony, Plate 6.d, e. In areas of disruption, where proeutectic plates impinge the lamellar eutectic is less well defined and formed as an irregular fibrous network, Plate 6f.

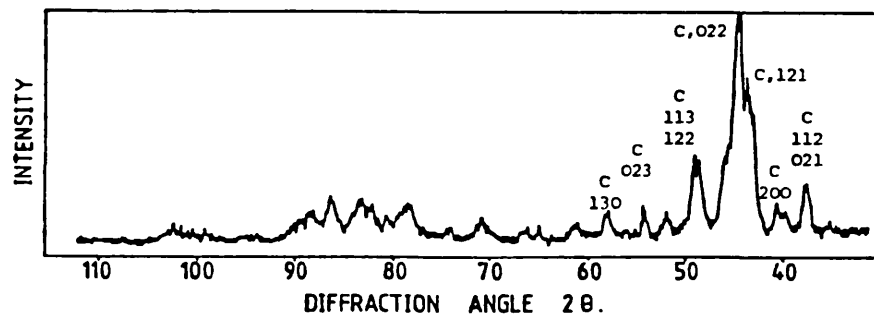
The eutectic phase ratio was consistent with that reported in Section 2.4.2.1. A specimen of suitable size for X-ray analysis was made by overlapping a series of hypereutectic tracks, the substrate being moved laterally between each laser processing generating a white iron layer, Plate 7a. Fig.2.12. shows the X-ray diffraction pattern produced from a Philips Goniometer. The reflections obtained from the as-laser treated surface, Fig.2.12a, were indexed in terms of ferrite and cementite; however, a few lines remained unaccounted for. These lines, evident between $60-65^\circ$ and $78^\circ-88^\circ$, were not austenite, FeC, C nor a non-stoichiometric carbide. Examination of the surface after grit blasting highlighted any ferrite reflections, Fig.2.12b. This effect is attributed to fracturing of the cementite plates and smearing of the ferrite over the surface. Smearing of the ferrite leads to broadening of ferrite reflections. Deep etching removes surface ferrite between the cementite plates and diffractometry reflects the cementite peaks (and the unidentified peaks), Fig.2.12c.



a. As-laser treated surface



b. Surface after grit blasting.



c. Grit blasted surface after deep etching in 10 vol% Nital for 30 secs

Fig.2.12. X-Ray Diffractometry Analysis of Hypereutectic White Iron (Plate 7a.). F = ferrite, C = cementite.

TABLE 2.4. Ferrite Lattice Parameter of Eutectic "Ferrite"

θ , (Fig.2.10)	I	hkl	d, Å	a, Å
44.5	100	110	2.0359	2.8792
64.8	20	200	1.4387	2.8774
82.15	35	211	1.1733	2.8740
98.75	10	220	1.0157	2.8728
116.2	10	310	0.9080	2.8714
Given value for bcc ferrite (pure Iron) ⁹⁷				2.8664

Although the ferrite reflections of the 'eutectic' were of a slightly lower diffraction angle than predicted, the average parameter is quite close to pure iron (average of 3 highest angles, 2.8727Å), Table 2.4. A Guinier camera was used to corroborate the diffractometer results, Table 2.4. A sample of the track illustrated, Plate 5a, was crushed and analysed, Table 2.5. Unfortunately, this method does not measure small d spacings and the unknown high angle reflections seen in Fig.2.11., could not be identified. However, the results are conclusive evidence that the structure comprises of ferrite and cementite.

The average hardness of the hypereutectic track, Plate 5, is HV 930. Quenching in liquid nitrogen has little effect, Fig.2.13, indicating a non-austenite structure.

Fig.2.13. Hardness Traverse through centre axis of hypereutectic track, Plate 5a.

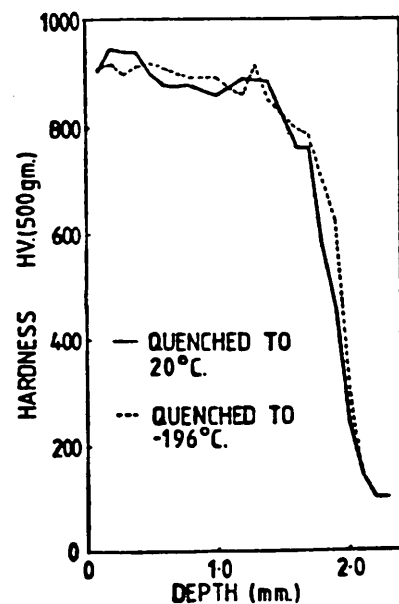


Table 2.5. Guinier Analysis of Hypereutectic White Iron (Co Radiation Source)

Guinier Results		Fe ₃ C ⁹⁷		ferrite ⁹⁷ (pure iron)	
d,Å	Magnitude	d,Å	hkl	d,Å	hkl
2.37	40	2.38	112,021		
2.26	20	2.26	200		
2.20	20	2.20	120		
2.10	50	2.10	121		
2.06	50	2.06	210		
2.02		2.01	103		
2.02	100	2.02	022	2.02	110
1.96	40	1.97	211		
1.87	50	1.87	113		
1.84	50	1.85	122		
1.755	10	1.75	212		
1.68	10	1.68	004,023		
1.58	10	1.58	130		
1.425	60			1.43	200

As a consequence of the brittle nature of hypereutectic tracks it was possible to split the melt/substrate interface revealing the true equiaxed nature of the austenite interface grains, Plate 7c. Plate 7b shows a longitudinal section of the interface and Plate 7d a deep etched SEM view. A plate-like phase has formed within the austenite and along the austenite grain boundaries though whether this is carbide precipitate or martensite is unclear.

Hypereutectic tracks suffer from porosity, due both to gas entrainment and shrinkage, and cracking. Gas pores have smooth 'surfaces' and tend to affiliate to the melt interface. Plate 7e illustrates a section through a pore; the pore is in contact with the melt/substrate interface. Plate 7f shows both types of porosity, the pores in the upper portion of the photo appear to be due to shrinkage. Proeutectic cementite solidifies ahead of the eutectic, hence shrinkage pores are coated with a eutectic 'halo'. The dual beam laser arrangement, previously discussed, had little effect on porosity or cracking; however, its use was seen to modify surface topography, Plate 8a. A laser will usually generate a characteristic 'V' shaped ripple, Plate 5c, on the track surface; however, the post heating beam reverses the ripple direction.

2.4.2.3. Eutectic White Iron

Wholly eutectic tracks were never produced; however, tracks containing large eutectic regions were generated. Plates 8b - e illustrate various aspects of 'unconstrained' eutectic growth (eutectic regions at a distance from any proeutectic phase so as not to be affected by that phase). Unconstrained eutectic has a quasi-regular morphology and is generally seen to grow either as:

1. Lamellar colonies expanding outward, fanlike, from a common source apparently via edgewise growth^{65,84}. Where colonies intersect the lamellae break down into fibrous rod-like networks, Plate 8b ($\lambda_3 = 0.8\mu\text{m}$).
2. Under more rapid cooling eutectic grows as rods or 'directional dendrites', Plate 8c ($\lambda_3 = 0.3\mu\text{m}$). Each 'dendrite' grows as a network. Although solidification is dominated by thermal gradients, 'secondary arms' grow, tangentially, from the primary arms. Such morphology is not typical and was only found near key-hole tips where 'critical' quenching occurs.

Interface nucleation is apparently independent of epitaxial effects. Both eutectic phases nucleate at the melt/substrate interface and grow at angles that range from perpendicular (90°) to almost parallel (15°), Plates 8d, e.

2.5. DISCUSSION

The kinetics of Fe-C solidification have been extensively studied under unidirectional conditions and it has been found that systematic changes in constitution, morphology and spacing occur with change of growth velocity and composition⁶⁰⁻⁷³. Because of the experimental difficulties involved in measuring temperatures and cooling rates during laser processing, researchers have attempted to predict the thermal cycle by either heat flow modelling⁹⁹⁻¹⁰³ or by dimensional measurement of microstructural features^{59, 104, 105}. The work reported can be related to earlier studies of ferrous alloys, cooled under various conditions of G and R (Section 2.2.), and is discussed in terms of microstructural refinement and morphology.

2.5.1. Hypoeutectic Solidification

2.5.1.1. Conduction Limited Melt Zones

Cooling rate is shown to decrease with ^{increasing} fusion zone penetration Molian¹⁰⁴ estimated cooling rates for Cr laser alloyed to Fe-1C by heat transfer modelling and by microstructural refinement. A 1-dimensional model¹⁰³ was employed when the depth/width ratio of the fusion zone was less than 1. A 3-dimensional model¹⁰² was applied to fusion zones where the ratio exceeded 1. Cooling rates based on microstructural refinement were determined according to Flemings¹⁰⁶:

$$\lambda_2 = 60 (GR)^{-0.4} \quad (2.38)$$

Molian¹⁰⁴ accepted that Cr alloyed composition changes with penetration, though he assumed that composition would have minimum effect on dendrite spacing. Molian's comparison of heat flow models and solidification structures is shown in Fig.2.14. Fig.2.14 illustrates how cooling rate decreases with melt track penetration. For Plate 2 where penetration $\approx 200\mu\text{m}$, GR is predicted $1 \times 10^5 - 5 \times 10^6$ K/s.

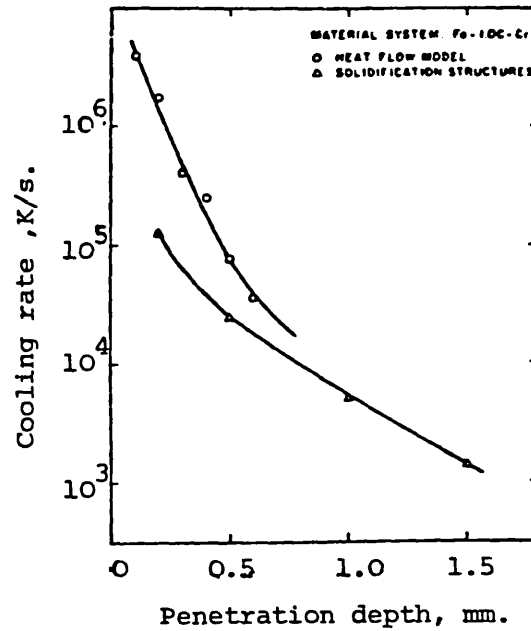


Fig.2.14¹⁰⁴ A comparison of heat flow models and solidification structures to predict the relationship between cooling rate and laser melted penetration depth.

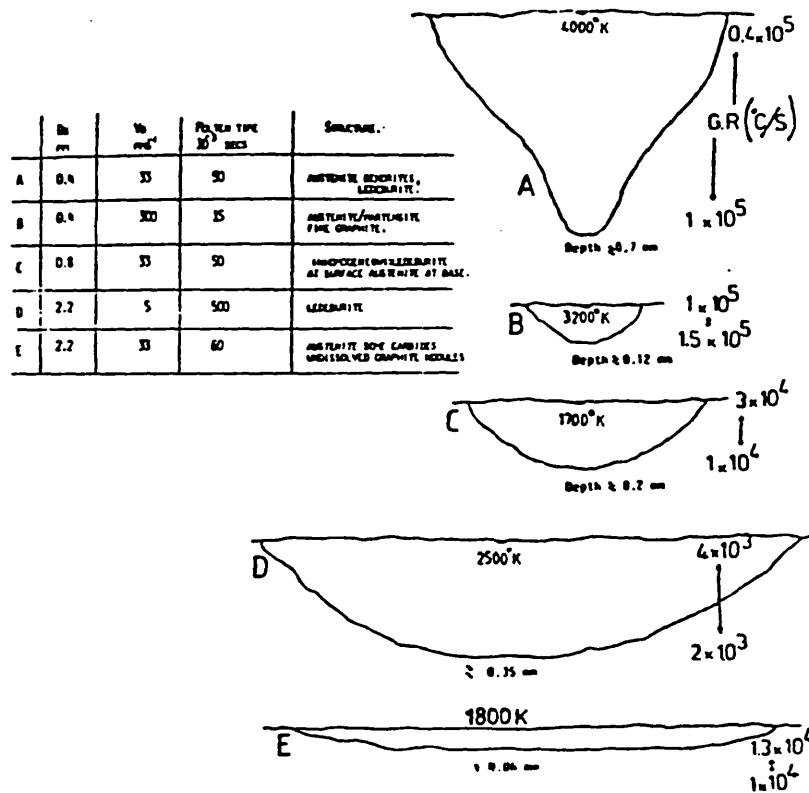


Fig.2.15. Thermal Cycles of Laser Melted SG Iron¹⁰⁷. Data calculated from 3-dimensional heat transfer model, including peak melt temperature, molten time and cooling rates for various laser surface melting conditions.

Hawkes¹⁰⁷ calculated the thermal cycles of laser melted SG Iron using a 3-dimensional heat flow model, Fig.2.15. A cooling rate gradient exists across the depth of the fusion zone; this is reflected in microstructural coarsening¹⁰⁵. Microstructure is more refined in regions of most rapid cooling.

Uneven C alloying causes microstructural anomalies in shallow melt tracks, Plate 2. Cellular-epitaxial growth initiates at the melt/substrate interface. With increasing distance from the interface, the structure becomes cellular dendritic and finally fully dendritic, Plate 2a - d. Increasing microstructural refinement, from the melt/substrate interface towards the track surface, is presumably effected by C concentration. This effect is seen elsewhere. Lundburg^{108, 109} illustrates a Hadfield manganese steel LSA with C. Epitaxial growth of columnar austenite turns to dendritic growth, and λ_2 decreases with increasing distance from the point of initial growth.

Hypoeutectic λ_2 refinement may be due, partly, to an increasing C concentration, and partly to increasing GR. Since it is difficult to accurately determine the C gradient the exact GR can-not be determined. Hawkes's⁸⁹ 3-dimensional heat transfer model indicates that GR might typically increase from 1×10^5 K/s at the melt/substrate interface to 2×10^5 K/s near the surface (for the processing conditions given in Plate 2). These GR values can then be inserted into Okamoto's equation⁷³(eq 2.14) to give an approximation of the C gradient. Okamoto's equation indicates that C might increase from 2.9C at the melt/substrate interface to 4.2C near the surface. λ_1 decreases slightly from $\lambda_1 = 8.5 \mu\text{m}$ at the melt/substrate interface to $\lambda_1 = 7.0 \mu\text{m}$ at the furthest extent of dendritic growth. Kishitake et al^{64, 70} (eq 2.6) indicate that λ_1 should increase with C alloying and decrease with increasing cooling rate (hence one factor will off-set the other). If the C gradient and GR values calculated above are inserted into eq 2.6. then λ_1 should decrease 'slightly' as solidification proceeds. This is seen to occur, λ_1 decreases by a lesser fraction than λ_2 .

2.5.1.2. Key-holed Melt Zones

'Near' key-hole melt pool geometry induces more efficient mixing (discussed Section 2.5.4.); C is "more" homogeneously distributed and hence a more uniform microstructure is produced. Fig.2.9. shows the effect of DAG reprocessing on λ_1 and λ_2 (since reprocessing conditions are unaltered any microstructural changes are assumed to be due to C alloying). λ_1 decreases slightly with C alloying. Kishitake et al^{69,70} predict that λ_1 should increase with increasing C alloying. It is not apparent whether there are other factors controlling λ_1 . λ_2 does decrease with C alloying from $\lambda_2 = 4.6\mu\text{m}$ after 4 reprocessings to $\lambda_2 = 2.1\mu\text{m}$ after 12 reprocessings, as predicted by eq's 2.12 and 2.14. If any change in thermal properties of the Fe substrate with increased C alloying is neglected then GR will be constant, hence eq 2.12 can be used to calculate the magnitude of C alloying. If this were so then C alloying would increase after 12 reprocessings by 1.5 times the percentage of C alloyed after 4 reprocessings. If the percentage of C alloyed were the same for each reprocessing then C alloying should increase 3 times. Strutt et al¹¹⁰ report that when electron beam melting 1.48C steel up to 12% of the C content was vaporised. Since ratios are being considered here, any losses should cancel out. The estimate of a 1.5 times C increase is an approximation and incurs various errors (as discussed). Microstructural observation used in conjunction with the phase diagram (Lever rule) Fig.2.1. indicates that the C content increases from $\sim 1.3\text{C}$ after 4 reprocessings to $\sim 2.6\text{C}$ after 12, an increase of 2 times.

TABLE 2.6. Cooling Rate of Hypoeutectic White Iron, Plate 3

	$\lambda_2, \mu\text{m}$	Cooling Rate (GR), K/s				
		Ibaraki ⁶⁴	Okomoto ⁷³	Hawkes ¹⁰⁷	Artinger ¹⁰⁵	Molian ¹⁰⁴
Key-hole 'tip'	1.5	4.1×10^7	3.9×10^5	$\sim 1 \times 10^5$	$\sim 1 \times 10^5$	
Track Centre	3.0	3.5×10^6	6.0×10^4		$\sim 1 \times 10^4$	$\sim 1 \times 10^4$
Near Track Surface	2.2	1.7×10^7	1.4×10^5	4×10^4		$1 \times 10^5 - 5 \times 10^6$

λ_1 and λ_2 also vary across individual melt track sections, Fig.2.10a. It is proposed that these structural changes reflect diminishing GR with increased distance from the 'initial' melt/substrate interface^{89, 107}. The cooling rate for the specimen reprocessed 12 times, Plate 3, has been calculated according to Ibaraki⁶⁴, Okamoto⁷³, Hawkes¹⁰⁷, Artinger¹⁰⁵ and Molian¹⁰⁴ the alloy content is assumed to be Fe-2.6C.

Of the four sets of results, the data of Hawkes¹⁰⁷, Artinger¹⁰⁵ and Molian¹⁰⁴ are based on laser surface melting. Ibaraki did not rapidly quench 'low C' hypoeutectic white irons (a 2.5C, $\lambda_2 = 32\mu\text{m}$ alloy was the nearest). Consequently the results given in Table 2.6 are based on an extrapolated formula which may not be applicable to the LSA hypoeutectic specimen (Plate 3). The inordinately high GR values compared with the other results makes the Ibaraki data suspect. Molian's 'comparison' of cooling rates¹⁰⁴, Fig.2.14, reflects decreasing cooling rate with increasing penetration but does not account for increased cooling rate in the keyhole. According to Molian¹⁰⁴ GR varies from 1×10^4 K/s near the track centre to either 1×10^5 K/s (calculated from λ_2 ¹⁰⁶) or 5×10^6 K/s (calculated from heat flow model¹⁰³) near the track surface. Hawkes^{89, 107} used a three dimensional heat transfer model to calculate the thermal cycle of laser melted spheroidal graphite cast iron. His results indicate that GR will fluctuate from $\sim 1 \times 10^5$ K/s at the keyhole to $\sim 4 \times 10^4$ K/s near the surface. It seems likely that a realistic cooling rate regime for Plate 3 is $10^4 - 10^5$ K/s.

2.5.2. Eutectic Solidification and Decomposition

2.5.2.1. Nucleation and Growth

The type of proeutectic phase is important since it controls eutectic nucleation and influences growth. In near eutectic alloys the eutectic nucleates at the melt/substrate interface and spreads outwards as an irregular lamellar structure. The eutectic can grow at any angle to the interface. Plate 8e illustrates the eutectic nucleating and growing almost parallel to the interface. The usual mode, however, is to see eutectic grow 'near' perpendicular to the interface, Plate 8d.

The eutectic appears to perpetuate in the same manner as described for proeutectic cementite growth⁵⁷ (Section 2.2.2.). It nucleates at the melt/substrate interface and ideally spreads as slightly fan shaped lamellar colonies, Plates 2c, 8b. The spreading appears to be produced by a slight distortion of the lamellae rather than tip fracture and regrowth as described for proeutectic cementite growth. Eutectic growth is stopped where two or more eutectic colonies intercept. At this point the lamellae become unstable and break up as an irregular rod network, in the manner described by Ibaraki et al⁶⁴ and Hunt and Chilton⁸⁴ (Sections 2.2.3.2., 2.2.3.3.).

Proeutectic austenite does not nucleate the eutectic nor does it appear to influence its growth. Plates 3c and e show how the eutectic grows in an unrelated mode. As proeutectic austenite grows it should expel C, increasing the C content of the surrounding melt. Following^{the} Hillert and Steinhaüser model⁵⁷ for eutectic nucleation on cementite it might be thought that eutectic cementite would nucleate on the austenite when undercooled below the eutectic temperature. As we can see this does not occur. In certain instances proeutectic austenite does appear to be surrounded by a greater proportion of eutectic cementite than is seen in eutectic regions of the melt, Plate 3c, e, g. Deep etching has caused specimen topography to exaggerate this effect in Plate 3c. A 'halo' rich in eutectic/eutectoid cementite could form since C will be rejected to the liquid as proeutectic austenite precipitates, which should initiate preferential eutectic cementite formation. The proeutectic austenite should reject C during solid state cooling and deposit proeutectoid cementite. This would presumably form as a surface layer. Visible observations, Plate 3c, e, indicate that a cementite 'halo' of less than $1\lambda_3$ may form. Close to the melt/substrate interface where fine austenite arm spacing occurs, the eutectic appears to form as a divorced eutectic, Plate 3g. Proeutectic austenite dendrites are interspaced by carbide. Proeutectic austenite spacing is sufficiently 'fine' for preferential precipitation of eutectic austenite on the proeutectic, despite the possibility of local C enrichment (due to C rejection from precipitating proeutectic austenite). Hillert and Steinhaüser⁵⁷ have shown that the eutectic nucleates preferentially on flat surfaces and grows as a lamellar or rib structure. Proeutectic austenite is dendritic and has a curved interface and this may reduce its suitability as a site of eutectic nucleation.

Proeutectic cementite preferentially nucleates the eutectic and influences its growth. Both eutectic cementite and eutectic austenite nucleate on the proeutectic. Plate 6b, c, shows how eutectic cementite has spread as a two-dimensional dendrite across the surface of the proeutectic. 'In filling' behind the advancing eutectic dendrite arms forms surface ridges of eutectic cementite. If the advancing dendrite arms grow co-operatively then eutectic austenite will form between them. Plate 6b, c, indicates that nucleation of these two dimensional cementite dendrites is heterogeneous. Presumably steps or defects in the proeutectic plate act as sites. It appears that specific austenite regions (in addition to eutectic austenite produced by co-operative growth) do nucleate on the proeutectic phase, Plate 6.b, c. The liquid layer surrounding the proeutectic phase is not sufficiently depleted in C (the C having diffused to the proeutectic cementite (Section 2.2)⁵⁷) so as to produce a near complete austenite halo around the proeutectic phase. The situation appears unstable and eutectic phase growth may be partly governed by available nucleation sites. Eutectic cementite perturbations stimulate sidewise growth (as described by Hil¹ert and Steinhaüser (2.2.)⁵⁷). Sidewise growth would appear to be co-operative and occurs as one-dimensional dendrites or two-dimensional ribs, Plate 6d, e. Sidewise growth of individual rods/ribs rarely extends more than three lamellar widths. Perturbations develop on these sidewise ribs and grow edgewise as lamellae parallel to the original proeutectic plate and at constant spacings. At the plate edge of the proeutectic, eutectic cementite nucleates and extends as lamellae in the same plane as the proeutectic, Plate 6d, e. Sidewise growth of these 'extended lamellae' does occur. The eutectic grows by a co-operation of sidewise and edgewise mechanisms, growing outward from the proeutectic phase by sidewise steps and then spreading edgewise, Fig.2.14. Thus each proeutectic cementite plate is orientated to an individual eutectic colony, Plate 5g. At points of constraint, where eutectic colonies interface, the lamellar structure breaks down into a rod network. The irregular rod network shown, Plate 2e, may be partially due to impurities or alloy additions (eg Cr in S135 steel; Section 2.2.3.3.).

2.5.2.2. Eutectic Spacing

The rapid solidification in a laser melt zone depends in a complex manner on thermal conditions and epitaxial effects; the growth rate will vary with the position in the melt zone and with the solidification direction relative to the liquid/solid interface. The present observations of longitudinal sections (using a 1.5mm beam) at the zone centreline show that, for hypoeutectic white irons growth tends to be upward from the base within 10° of vertical. Proeutectic phase growth is not significantly affected by lateral cooling, Plate 5b. In extreme cases it can grow tangentially to the expected thermal gradient, although 'average' growth tends to be within 10° of vertical.

Hawkes^{89, 107} introduced a schematic representation of melt zone solidification, Fig.2.16. This may be used to calculate an approximate 'average R' from the melt pool centre line. Hawkes¹⁰⁹ suggested that the maximum melt pool length is 2 - 3 times the beam diameter; however, it seems unlikely that the melt pool of a conduction limited melt produced by a ~5mm diameter defocused beam, Plate 2, could extend over 10 - 15mm.

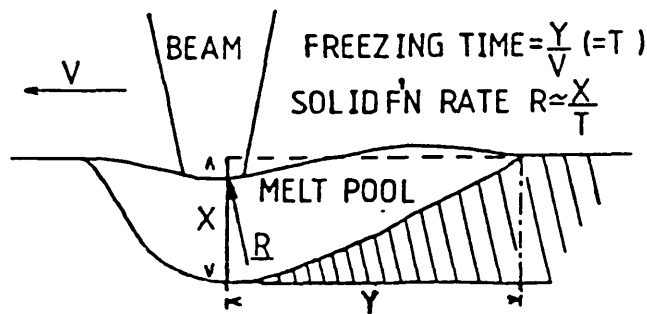


Fig.2.16¹⁰⁹ Schematic Representation of Melt Zone According to Hawkes.

TABLE 2.7. Prediction of λ_3 as a Function of R

	λ_3 (μm)	T (S)	R (mm/s)	$\lambda_3 \sqrt{R}$ ($\mu\text{m}^{3/2}/\text{s}^{1/2}$)
Conduction Limited Plate 2	0.4 ± 0.2	0.20	1.0	6 - 19
Key-hole Plate 3	0.55 ± 0.25	0.22	7.5	8 - 22

Takeda¹¹¹ has studied laser cladding of Ni-Cr powder, continuously fed on to En3 (0.2C) steel. He measured the melt pool length over a range of scanning speeds (at 1.86kW, 4.0mm beam dia, 0.315 g/s powder feed). For $V = 7\text{mm/s}$ pool length was 3.5mm and for $V = 19.5\text{mm/s}$ pool length was 1.7mm. A laser melted substrate, or one where small amounts are LSA, is likely to have a longer melt pool since high flow rates of cladding powder will reduce melt pool length. In the present study a 5mm diameter beam was found to melt 4.9mm wide tracks; it seems unlikely that the melt pool length is less than its width. In predicting λ_3 as a function of R (Table 2.7) it has been assumed that for conduction limited melts produced by defocused beams, pool length is equal to beam diameter. Jones and Kurz⁸³ reported that Fe-Fe₃C eutectic growth at a given velocity can occur over a range of interlamellar spacings (Section 2.2.3.1.). Measured values of the product $\lambda_3 \sqrt{R}$, Table 2.7, lie in the range 6 - 22 $\mu\text{m}^{3/2}/\text{s}^{1/2}$, while the value predicted⁷⁹ for the extremum condition is 17 $\mu\text{m}^{3/2}/\text{s}^{1/2}$. The measured values, Table 2.7, correlate well with those reported elsewhere⁸³, 11 - 29 $\mu\text{m}^{3/2}/\text{s}^{1/2}$. The use of a focused beam producing a keyholed melt track will fundamentally affect the product of R. According to Fig.2.16, freezing time will be minimised, hence any increased pool penetration caused by beam focussing could cause a magnitude increase in R, increasing the product $\lambda_3 \sqrt{R}$ by a root ratio; hence the product of $\lambda_3 \sqrt{R}$ will be greatest for keyhole melt tracks. The allowance of a decreased melt

pool length (ie melt pool length = beam diameter) for conduction limited melt tracks produced by defocused beams helps minimise any error used to calculate R (according to Hawkes⁸⁹, Fig.2.16¹⁰⁹).

2.5.2.3. Eutectic Decomposition

The experimental results suggest that the eutectic, ledeburite, undergoes equilibrium transformation ie diffusional decomposition of austenite to ferrite + cementite. Table 2.8. indicates phase changes, according to the equilibrium diagram Fig.2.1.⁵⁶, during cooling. On cooling below the eutectic temperature the austenite of the eutectic will reject C and deposit proeutectic cementite; hence, the $\gamma : \text{Fe}_3\text{C}$ phase ratio will change in favour of Fe_3C with cooling. This deposition continues until eutectoid decomposition sets in, with the formation of pearlite.

Table 2.8. Equilibrium Phase Changes of the Eutectic During Cooling
(as calculated from Phase diagram Fig.2.1.)

wt% °C	LEDEBURITE		PEARLITE		Wt Ratio $\text{Fe}_3\text{C}:\gamma+\alpha$
	γ	Fe_3C	α	Fe_3C	
1150	52.2	47.8			~ 1:1 6:4 13:7
≥727	40.4	59.6			
20		59.6	35.7	4.6	
	TOTAL Fe_3C		TOTAL α		Vol Ratio $\text{Fe}_3\text{C} : \alpha$
20	64.3		35.7		17 : 9

$$(\rho_{\text{Fe}_3\text{C}} = 7.4^{112}, \rho_{\alpha} = 7.86^{112})$$

The equilibrium volume phase ratio at 20°C approaches $\text{Fe}_3\text{C} : \alpha$, 2 : 1 (Table 2.8.); this compares with a measured average volume ratio of $\sim 2.0 \pm 0.5 : 1$ determined by SEM and TEM (Table 2.3).

2.5.2.4.C Diffusion

C occupies interstitial solute sites in the iron lattice. These solute atoms diffuse by random jumping between interstitial positions. Classical equations which describe the process of diffusion in solids generally express the diffusion coefficient in terms of lattice geometry, temperature and energy. A form of determining diffusivity may be expressed:

$$D = D_0 \exp \left[- \frac{\Delta H}{R_G T} \right] \quad (2.39)$$

where D_0 and ΔH are constants.

Wert¹¹³ measured D for C in α -iron over the range -35 to 200°C and fitted the results to eq 2.39 and so obtained values of D_0 and ΔH to give:

$$\text{For } \alpha \text{ (bcc iron) } D = 0.02 \exp \left[\frac{-20,100}{R_G T} \right] \quad (2.40)$$

Wells and Mehl¹¹⁴⁻¹¹⁵ measured D for C in γ -iron over the range 750 - 1250°C and so obtained values of D_0 and ΔH to give:

$$\text{for } \gamma \text{ (fcc iron) } D = 0.07 \exp \left[\frac{-32,000}{R_G T} \right] \quad (2.41)$$

Wert and Mehl's¹¹³⁻¹¹⁵ equations (2.40, 2.41) have been extrapolated over a wider range of temperatures than the temperature range over which their results were based, to illustrate the effect of phase morphology on C diffusivity as temperature decreases from the eutectoid, Table 2.9. At temperatures below the eutectoid diffusion rates in ferrite are of the order 100 times more rapid than in austenite.

TABLE 2.9 C Diffusivity in Ferrite and Austenite

Temp °C	Ferrite cm ² /s	Austenite cm ² /s
1530	7.2 x 10 ⁻⁵	-
1150		8.5 x 10 ⁻⁷
727	8.1 x 10 ⁻⁷	7.1 x 10 ⁻⁹
700	6.1 x 10 ⁻⁷	4.5 x 10 ⁻⁹
570	1.4 x 10 ⁻⁷	4.1 x 10 ⁻¹⁰
500	4.1 x 10 ⁻⁸	1.1 x 10 ⁻¹⁰
20	4.5 x 10 ⁻¹⁷	3.4 x 10 ⁻²⁵

2.5.2.5.A Decomposition Theory

The decomposition of austenite to form pearlite occurs by nucleation and growth. Some undercooling below the eutectoid temperature is required to initiate pearlite transformation. Ridley¹¹⁶ recently reviewed the topic of pearlite transformation. Current concepts¹¹⁷⁻¹¹⁹ are based on a theory introduced by Mehl¹²⁰. Mehl¹²⁰ assumed that the transformation initiated at austenite grain boundaries where a small lamella of cementite might grow into one austenite grain. This lamella thickens and grows in length, depleting C from the surrounding austenite. A C concentration occurs in the austenite, Fig.2.17a. When the composition of the austenite next to the cementite reaches a 'fixed' value, ferrite nucleates and grows along the surface of the cementite. The ferrite will reject C so causing a C build-up at the ferrite-austenite interface, Fig.2.17b. This build-up continues until a new cementite layer is nucleated, which will in turn induce the formation of a new layer of ferrite. As this process proceeds, a pearlite colony of many lamellae forms. Pearlite growth will occur both (sidewise) by the nucleation of additional lamellae and (edgewise) as the lamellae edge advances.

In the specimens reported (Section 2.4.) the eutectic austenite is seen to decompose, by a third route, diffusively during cooling to room temperature by rejection of C to the existing cementite eutectic lamellar. Flower's⁹² observation that ferrite typically exhibits a single orientation in association with a family of cementite plates and is related to cementite by the Bagaryattski relationship, implies that eutectoid ferrite nucleates on eutectic cementite plate surfaces and grows into the remaining austenite.

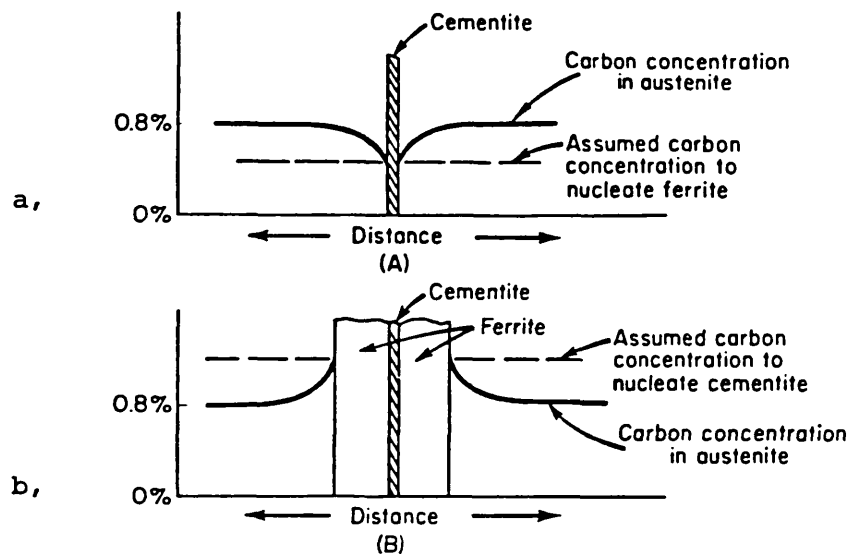


Fig. 2.17¹²⁰ Schematic Sketch of Classical Nucleation a), and Growth Mechanisms of Pearlite b).

Consider a section through a eutectic austenite lamella and its adjacent eutectic cementite lamella. Undercooling below the eutectoid temperature will induce the austenite to transform to ferrite and cementite. If interface nucleation is kinetically favourable C will diffuse from the austenite to the cementite causing ferrite to nucleate at the cementite interface, Fig.2.18a. This might be expected to produce an increasing C concentration in the austenite at the advancing ferrite/austenite interface. However, since C diffusion in ferrite is very much faster than in austenite, Table 2.9, the concentration at the ferrite/austenite interface is probably controlled by the transport of

C through the ferrite to the eutectic cementite. Thus, the C gradient in austenite is so shallow, there is insufficient C concentration to promote cementite nucleation within the austenite; hence the ferrite interface advances from opposing cementite plates replacing the austenite, Fig.2.18b. The maximum diffusion distance involved is half the austenite plate width and must, therefore, be less than 0.2 μ m. The time required for austenite transformation is that time required for C diffusion from the centre of the austenite lamellae:

$$t \approx x^2 / D_{\alpha} \quad (2.42)$$

x = half austenite lamellae width

D_{α} = ferrite diffusivity

The time required for austenite transformation increases with decreasing transformation temperature. Based on the data of Table 2.9. applied to (eq 2.42); $t_{700} = 6.6 \times 10^{-4}$ s, $t_{650} = 1.1 \times 10^{-3}$ s, $t_{570} = 2.9 \times 10^{-3}$ s. Transformation will, however, occur over a range of temperatures below 727°C and will be dependent upon cooling rate. According to Table 2.6 a realistic cooling rate for solidification might be $10^4 - 10^5$ K/s. If the most critical solidification cooling rate were applied over the eutectoid transformation range, GR = 10^5 K/s, then the entire austenite/ferrite transformation should be complete at $\sim 650^\circ\text{C}$ (in actual fact GR will decline after solidification and the austenite/ferrite transformation be complete at a higher temperature). This supports the findings of Table 2.4. (that the ferrite contains negligible C), that there is sufficient time for the transformation to complete.

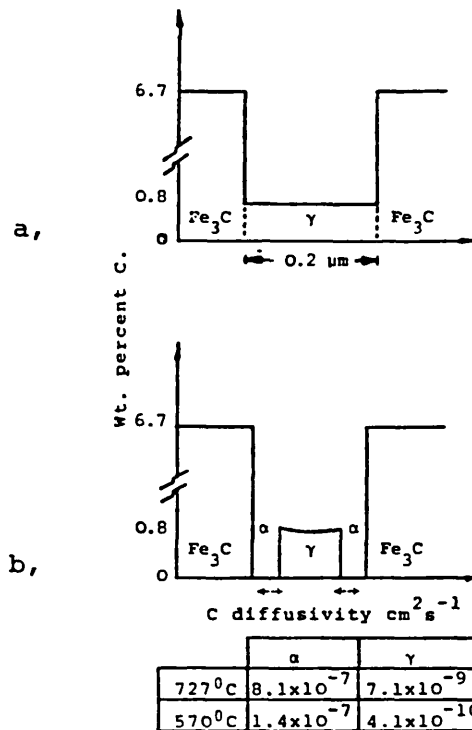


Fig.2.18^{9,2} Austenite-Cementite Eutectic Decomposition Profiles at a. 727°C and, b., between 727°C and 650°C.

Newcomb et al⁷⁸ who melt spun Fe-3.5C alloy (Section 2.2.3.) and suggested that 'a eutectoid rather than a eutectic cooling path has been followed' did not discuss the possibility of eutectic solidification and a divorced eutectoid.

2.5.2.6. Pearlite Formation

The decomposition mechanism which leads to a divorced eutectoid, although dominant, is not exclusively followed. Small regions of extremely fine pearlite were observed between well ordered eutectic colonies, Plate 4e. The cementite/ferrite lamellae width ratio was close to that predicted for pearlite, 1 : 7 (Table 2.3), produced from an equilibrated eutectoid steel^{11,2}. The fine lamellar spacing, ~55nm, implies that the austenite must have been substantially undercooled when it transformed. Mehl's work¹²¹ (Appendix IV) indicates a transformation temperature of ~590°C while Zener's work¹²² (Appendix IV) indicates a transformation temperature of ~400°C (the inaccuracies of

extrapolating a limited formula, for eutectoid spacing, over a wide temperature range are discussed in Appendix IV). Bolling¹²³ introduced a relationship between eutectoid spacing and R (Appendix IV) which indicates that for $\lambda = 55\text{nm}$, $R \sim 10\text{mm/s}$. For pearlite transformation to occur GR must be of the order 100 K/s. Even though M_s is depressed by rapid quenching^{46-48, 124} and microstructural refinement, a higher cooling rate would cause martensite or bainite to form, a lower cooling rate would cause a coarser pearlite to form. If these assumptions are true then G decreases, not unexpectedly, with cooling. GR is therefore much less than 10^5 K/s during solid-state austenite decomposition (Section 2.5.2.5.).

2.5.3. C Diffusion at the HAZ Interface

The layer of equi-axed austenite interface grains, and martensitic HAZ, are notable features of the melt/substrate interface. It is postulated that heating transforms melt/substrate ferrite grains to austenite and that C diffusion and grain growth causes this austenite to be retained as equiaxed austenite when cooled to room temperature. These equi-axed austenite grains in turn act as nuclei for track solidification. In hypoeutectic irons this leads to epitaxial growth of proeutectic austenite; hence the interface grains must have transformed (not unexpectedly) to fcc austenite before solidification. The interface microstructure is C content controlled (C diffusion controlled) and hence represents a C gradient. TEM indicates that regions of equi-axed austenite contain $\sim 0.9C^{92}$. This estimate is supported by regions of transformed 'butterfly' martensite¹²⁵. The band of plate martensite which bounds the equi-axed austenite is indicative of a content $< 0.6C^{125}$.

The problem of calculating C diffusion in this situation is enormous. C diffusion is temperature dependent, yet the heating cycle is not fully understood. As the C content of the interface rises so the melting point of the alloy falls and melt back of the interface should occur. Diffusivity will change as the structure changes from bcc ferrite to fcc austenite. A basic diffusivity approximation can be determined thus:

$$D = \frac{x^2}{t} \quad (2.43)$$

where x = carbon penetration = $30\mu\text{m}$

t = diffusion time = 0.22s

C penetration is estimated as the nominal thickness of the equi-axed austenite grains plus the martensite. It is known that martensite does not necessarily contain C^{121} but it is assumed to do so because of the simplicity of our equation. Diffusion time is taken to be the freezing time, t (Table 2.7). The average diffusivity at the interface over the processing cycle is $D \sim 4 \times 10^{-5} \text{ cm/s}$ (eq 2.43).

2.5.4. Melt Zone Geometry and its Effect on Thermal Fluid Flow

To increase the concentration of C alloying a defocused beam (5mm diameter) was used to produce wide-shallow melt zones. Since the alloyed C is preplaced, C concentration would ordinarily be related to the melt track, surface area/melt track volume ratio; ie a wide-shallow track implies a high alloying ratio (vol alloyed/vol of substrate melted). Surface alloying appeared to be caused by 'impingement' and diffusion; C was unevenly dispersed causing local microstructural differences, Fig.2.19a⁴² (Section 2.4.1.). Laser beam focussing increases melt penetration and decreases melt track width causing the surface area/volume ratio to decrease. In such tracks, having hemispherical or near-keyhole cross-sectional profiles, C dispersion is far more homogeneous. This is attributed to convective mixing of the molten pool.

Convective flow is attributed to surface tension gradients in the melt pool^{7,127}. Pool temperature will be highest at the central point of gaussian beam impingement (along the central axis of the melted track) and hence surface tension is lowest. Surface tension increases with decreasing temperature along a line from the pool centre to the pool edge. Any volume element of the surface experiences a net force parallel to the surface causing it to move from the centre to the edge of the pool. This in turn causes a 'return' flow deep within the pool from the pool edge to the pool centre, Fig.2.19.b,c.^{110,128} Where the melt pool is stationary under the beam the convection pattern is, logically, symmetrical about the impingement point.

As a substrate traverses through a focused or near focused beam regular, intermittent, liquid surges from the puddle front to the puddle rear occur, leaving coarse track ripples in its wake^{129, 130}. Cline and Anthony¹²⁷ suggest that coarse rippling can result from surface vapour pressure depressing the pool combined with surface tension gradients, Fig.2.20. The substrate melts near its leading edge, thereby increasing its volume, while near its trailing edge it cools and contracts. It is suggested that periodic surges from the front to the rear stabilise the pool.

Various authors have commented upon the problems of achieving homogeneous alloy distribution during LSA of conduction limited tracks^{7, 33, 131, 132}. Chande and Mazumder³³ observed compositional fluctuations when alloying Ni into AISI 1020 steel. Weinman et al¹³¹ and Gnanamuthu¹³² report compositional differences in alloying AISI 1018 steel substrates. Gnanamuthu¹³² attempted to analyse the problem and suggested that by locally oscillating the beam at rapid rates, the localised liquid flow is spread out and over the wider region radiated by the beam. The author assumes that as the beam sweeps the same incremental area of the liquid surface several times, potentially beneficial mixing occurs. Molian³² LSA Cr into AISI 1018 steel, and demonstrated that in laser tracks with hemispherical melt sections homogeneous alloy distribution occurred. In key-holed melt tracks Cr composition in the key-hole region was reduced. Certainly there is a microstructural change in the "key-hole regions" of C alloyed ferrous substrates, Plate 4a, 5a. However, it is not apparent whether this is a function of local solidification conditions or C depletion. The reduction in volume fraction of proeutectic cementite, Plate 5a, suggests the latter.

Whether convection enhances the total amount of C alloyed, is not clear, since it is difficult to compare an unevenly alloyed, conduction limited, high surface/volume ratio track with a homogeneous, near key-holed, low surface/volume ratio track. Strutt et al¹¹⁰ reports a 12 wt% loss of C from laser melted 1.5C steel. If 'decarburisation' does occur then C loss either from the track surface or from a point in the pool near the track surface is more likely in conduction limited tracks.

Coarse surface rippling may be dependent, to the same degree, upon the same conditions that are required for convection, since neither characteristic occurred without the other. Fig.2.21. illustrates how convection and rippling occur together. The effect of lower temperature gradients, and by implication, lower surface tension gradients, caused by beam defocusing is not fully realised, though it must clearly reduce the likelihood of convection. For homogeneous distribution of C LSA to Fe the optimum cross-sectional shape for a laser melted track is that where the melt width is approximately equal to half ^{The} melt depth (as demonstrated by Molian³²).

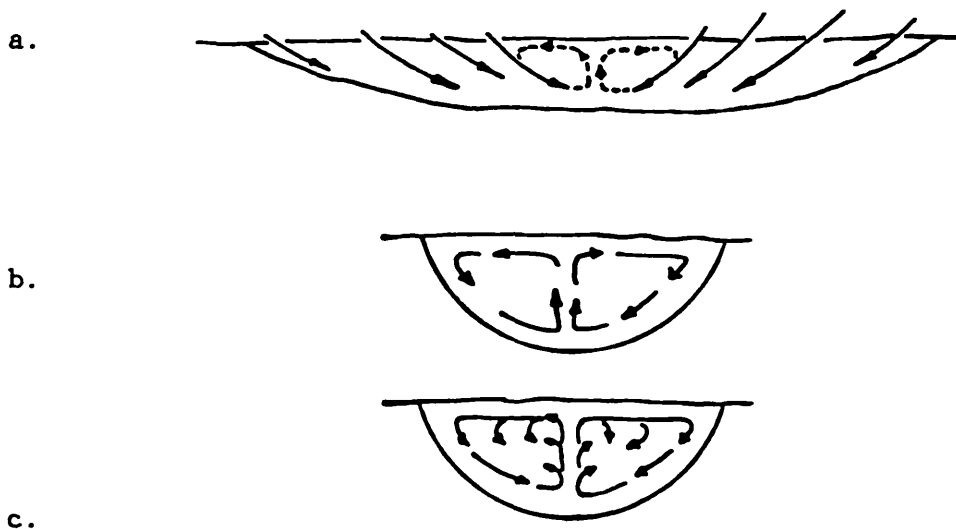


Fig.2.19. Possible Convection cycles for laser melted pools

- a. for shallow melt zones⁵²
- b. and c. for hemispherical melt zones¹¹⁰

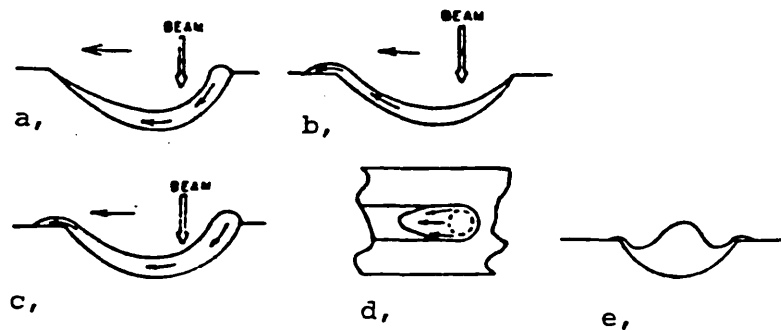


Fig.2.20¹²⁷ A schematic diagram showing the formation of the depression beneath the beam and liquid flow to form; a, b, surface ripples and c, d, e, a continuous central ridge and side troughs.

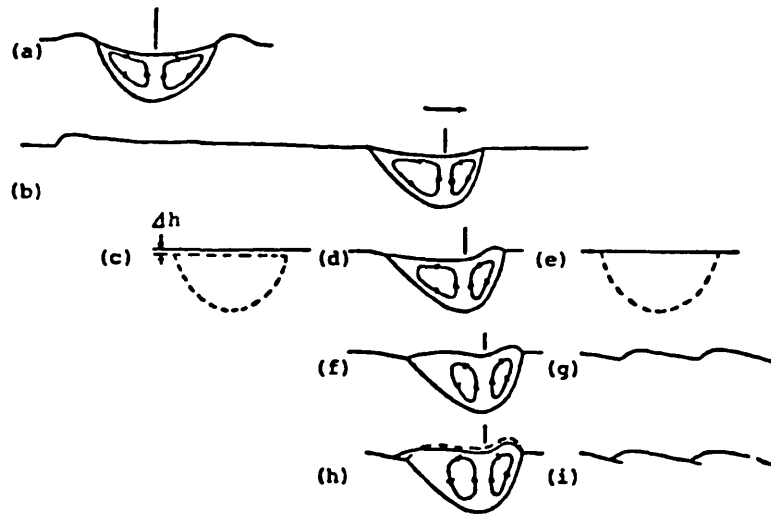


Fig.2.21¹²⁹ Mechanism of ripple formation: (a) velocity equals zero; (b) and (d) velocity not equal to zero; projected area of back side of pool (c) less than that at front edge of pool (e); (f) and (g) ripples without back flow; (h) and (i) ripples with back flow.

PLATE 2 C Alloying into S135

(1.7kW, 5mm, 25mm/s 5 successive DAG painted runs)

- a. General view taken from cross-section of laser alloyed track (width 6.1mm, depth 0.2mm). Uneven mixing of alloyed C causes microstructural variations throughout the track.
- b. Section through melt/substrate interface; Martensitic HAZ, layer of equiaxed austenite interface grains, proeutectic austenite grains grow upwards through the melt track.
- c. Section through upper portion of melt track; Proeutectic austenite + eutectic growth is superseded by eutectic growth (note the 'fan-like' morphology of unrestricted eutectic growth) and in turn superseded by proeutectic cementite (etching as opaque plates) + eutectic growth near the melt surface.
- d. General view taken from upper portion of cross-section of laser alloyed track; lower portion of melt zone hypoeutectic, upper portion of melt zone hypereutectic.
- e. High magnification SEM view of Plate 2d; proeutectic cementite and associated irregular eutectic (deep etched in 10% nital)

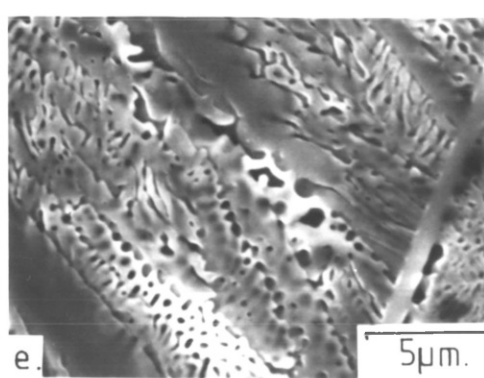
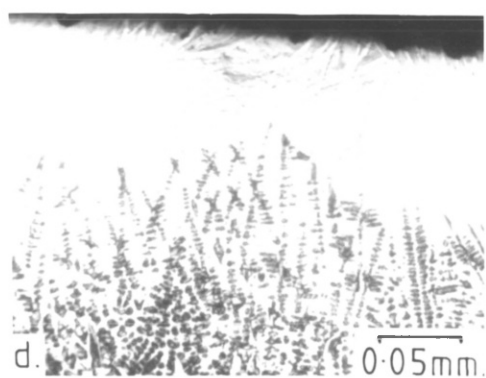
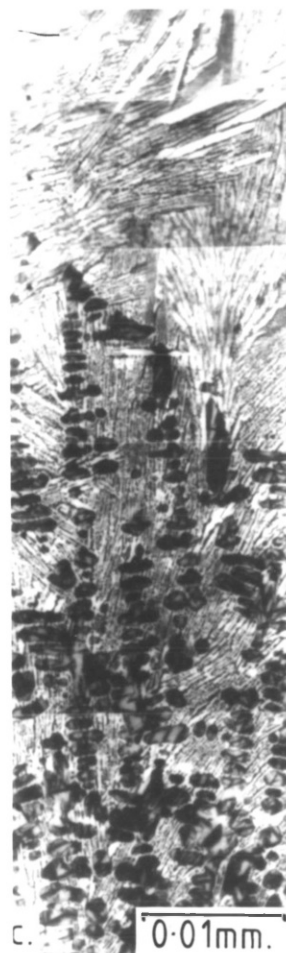
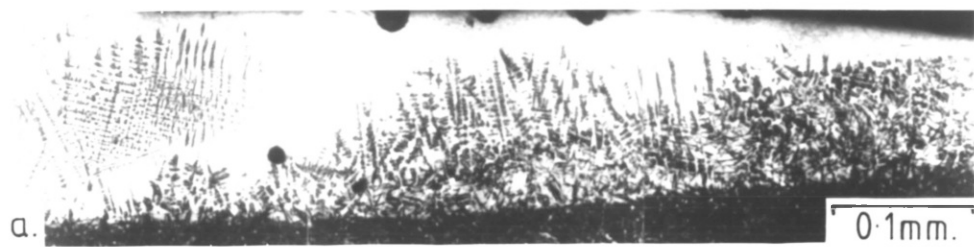


PLATE 3 C Alloying to Pure Fe, Hypoeutectic Alloy

(1.5kW, 1.5mm, 20mm/s, 12 successive DAG 'painted' runs).

- a. General view of cross-section of laser alloyed track. The track consists of a uniform hypoeutectic structure with localised porosity. The dark region at the key-hole base is an etching characteristic (the final laser run did not penetrate as deep as a previous run, the previous run was 'tempered' and hence etched differently).
- b. Section through melt/substrate interface, Plate 3a, proeutectic dendritic austenite grows perpendicular to the interface.
- c. SEM view of section near melt/substrate interface, top corner Plate 3a, illustrate nucleation site and growth of proeutectic austenite. (This specimen has been deep etched in 10% nital to remove any austenite).
- d. SEM view of section near melt/substrate interface, Plate 3a, illustrating the dendritic morphology of proeutectic austenite.
- e. High magnification SEM view of melt/substrate interface, Plate 3a. There is no apparent growth relationship between proeutectic austenite and eutectic.
- f. High magnification SEM view of fractured melt/substrate interface illustrating proeutectic austenite growing epitaxially from the substrate.
- g. High magnification SEM view of melt/substrate interface, Plate 3a, illustrating equiaxed austenite interface grains partially transformed to martensite (right) and expitaxially growing proeutectic austenite (left).

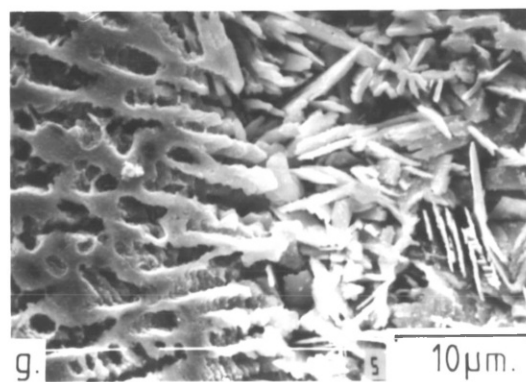
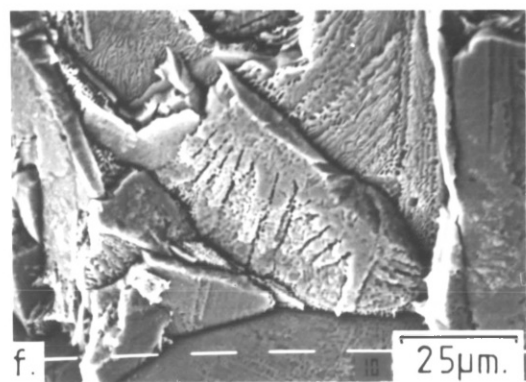
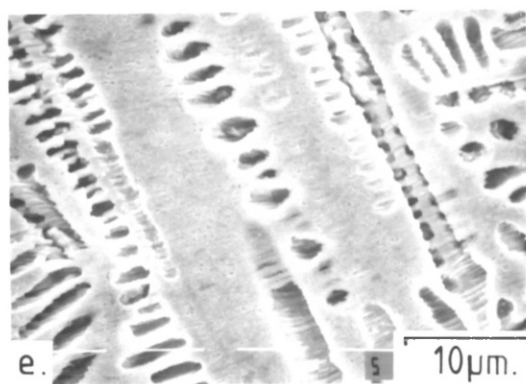
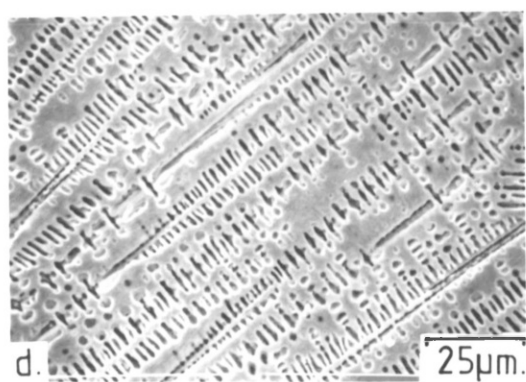
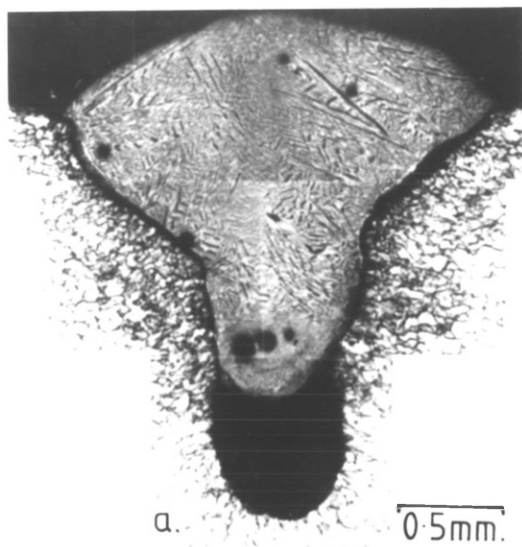


PLATE 4 C Alloying to Pure Fe. TEM Analysis of Hypoeutectic Alloy
(Plate 3)

In the most perfectly lamellar regions of the eutectic the width ratio of the carbide - 'austenite' phases was found to be $2.0 \pm 0.5 : 1$

- a. & b. Analysis of selected area diffraction patterns showed that the carbide is exclusively Fe_3C , which in many cases contained stacking faults.
- c. & d. The metallic phase was identified as ferrite rather than retained austenite or martensite. The ferrite contained subgrains and was highly dislocated.
- e. In regions between well ordered eutectic colonies austenite was observed to have locally decomposed into pearlite of extremely fine lamellar spacing.
- f. TEM image of martensite plate in equiaxed melt/substrate austenite interface grain.

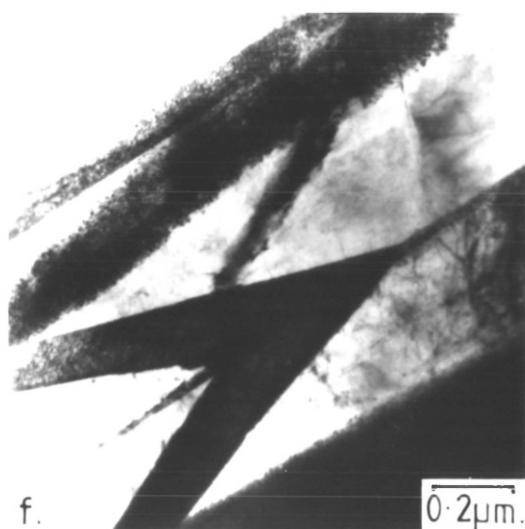
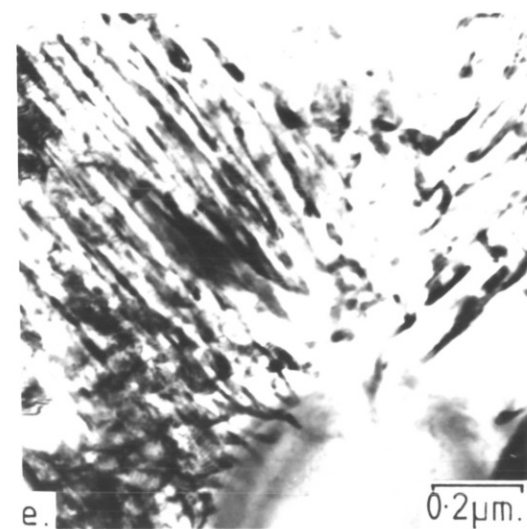
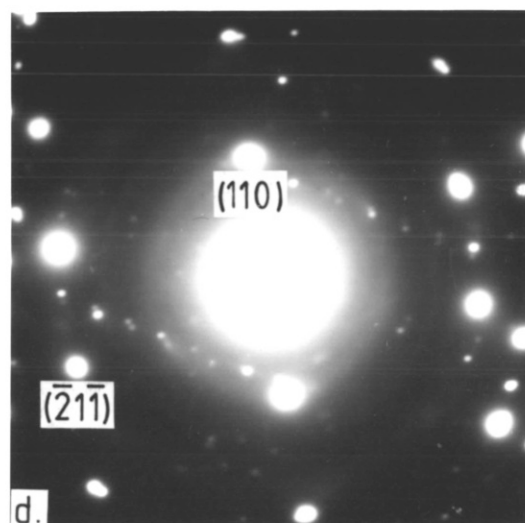
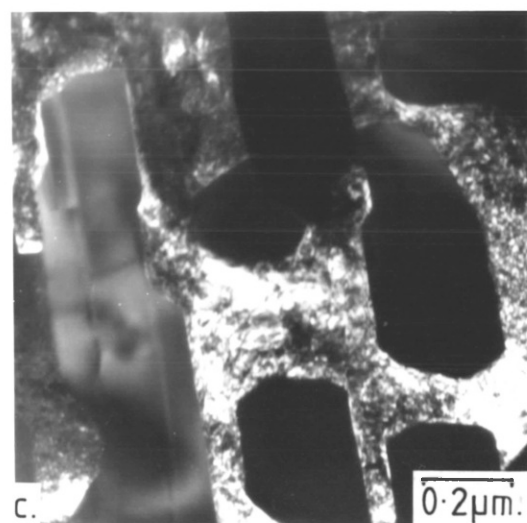
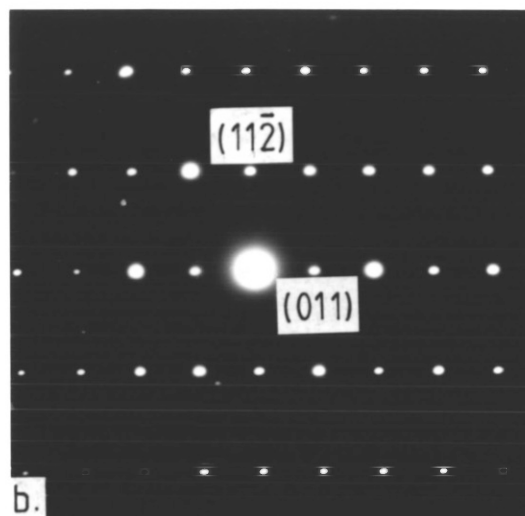
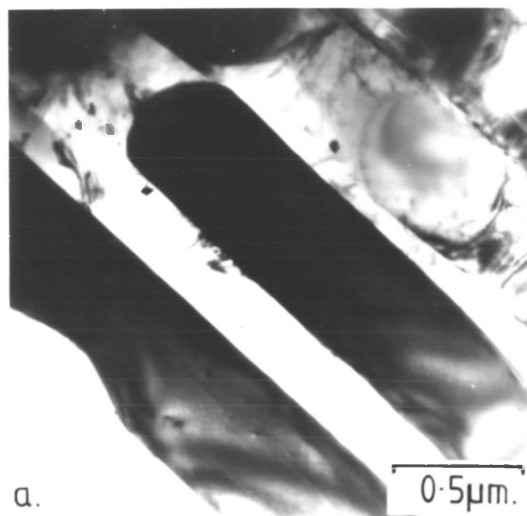


PLATE 5 C Alloying to Pure Fe, Hypereutectic Alloy

(1.5kW, 1.5mm, 20mm/s, 4 successive DAG 'protected' runs)

- a. General view of cross-section of laser alloyed track. The track comprises a 'fairly' uniform hypereutectic structure with regional porosity and severe cracking.

- b. Polarized view of longitudinal section of laser alloyed track. Polarizing highlights individual proeutectic cementite 'fans'.

- c. Plan view of laser alloyed track. The laser has traversed from left to right producing a characteristic ripple pattern.

- d. Region spanning part of melt zone and HAZ. In multi-pass alloying each successive melt track does not follow the exact path of the preceding track. This has occurred at the lower right hand shoulder of the key-hole, Plate 5a. The melt track ranges from hyper- to hypo-eutectic, while the HAZ spans retained austenite, martensite and ferrite.

- e. Section of Plate 5a showing proeutectic cementite nucleation at melt/substrate interface and subsequent fan-like growth.

- f. High magnification view of alloyed microstructure, Plate 5a, proeutectic cementite and broken lamellar eutectic.

- g. High magnification polarized view of alloyed microstructure, Plate 5a, illustrating the parallelism of individual eutectic colonies to proeutectic cementite plates.

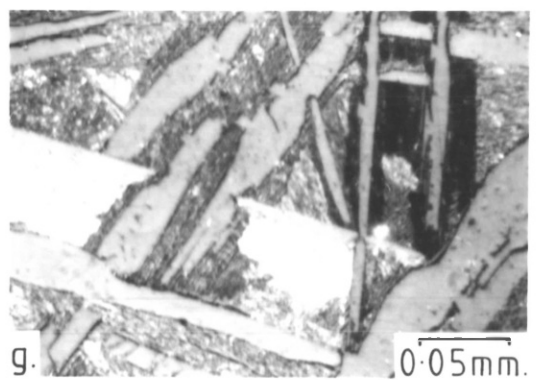
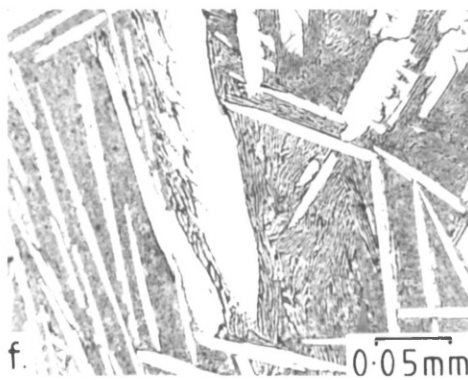
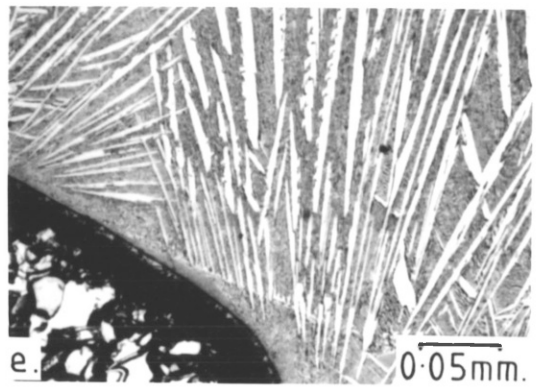
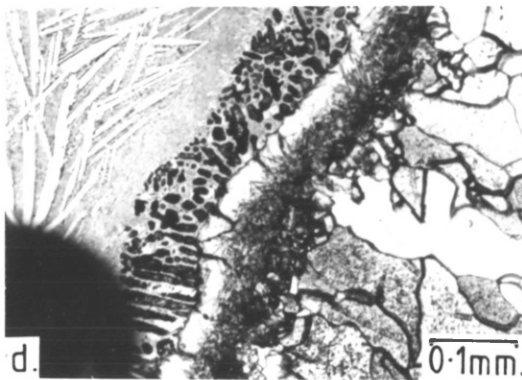
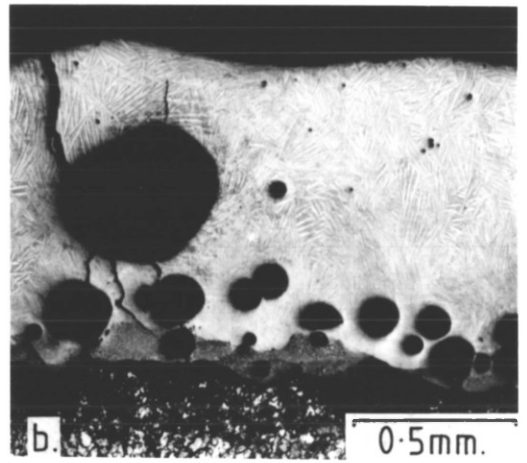
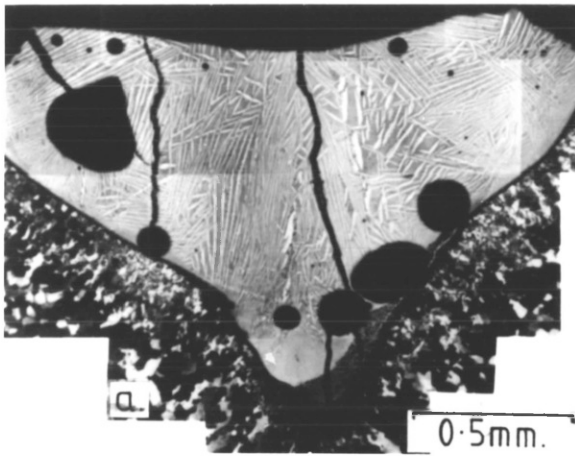
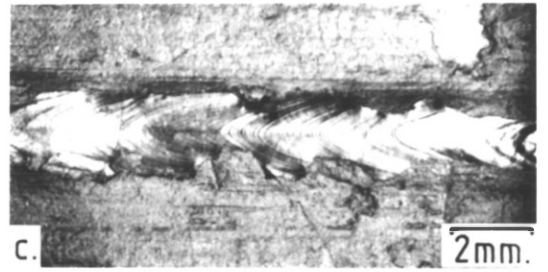


PLATE 6 C Alloying to Pure Fe - SEM Study of Fractured Hypereutectic Alloy (Plate 5)

- a. General view of proeutectic cementite plates and associated eutectic (deep etched in 10% Nital)

- b. Surface of proeutectic cementite plate containing ridges and steps, due to eutectic nucleation and growth.

- c. Surface of proeutectic plate showing ridges, steps and interrelated 'local' eutectic region.

- d. Two faces with near 90° corner, illustrating edgewise growth of the eutectic, nucleating, and growing as a rib on the proeutectic and then spreading throughout the eutectic.

- e. Two faces with near 100° corner, proeutectic cementite 'breaks-up' at plate edges extending outward as eutectic cementite lamellae.

- f. In areas of disruption where proeutectic plates interface the lamellar eutectic is less well defined and forms an irregular fibrous network.

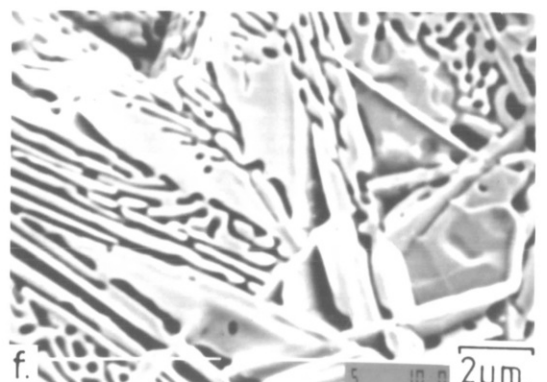
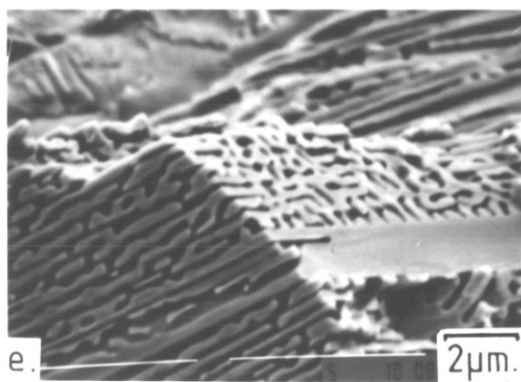
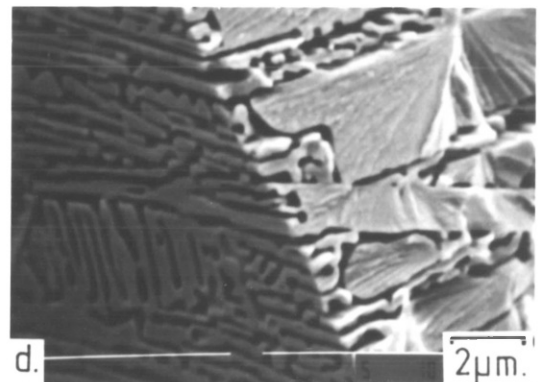
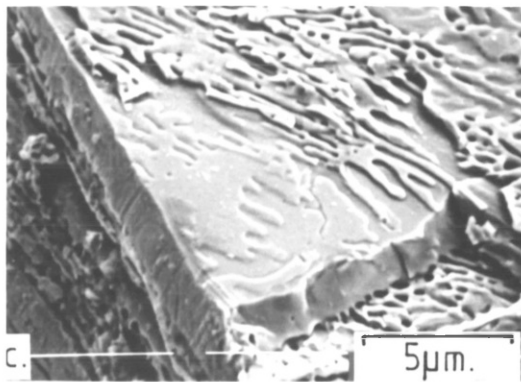
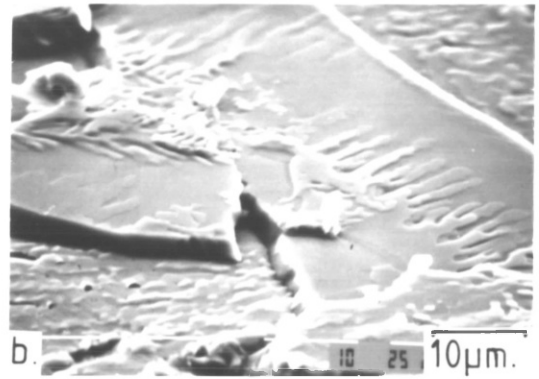
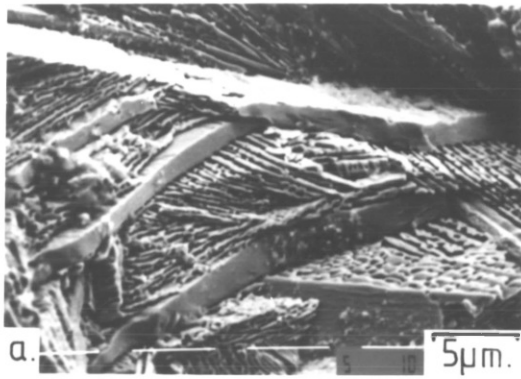


PLATE 7 - C Alloyed to Fe, Hypereutectic Alloys

- a. ^{ns}
Λ Traverse section through white iron surface, generated by overlapping a series of hypereutectic tracks. (1.7kW + 1.5kW glancing, 3.5mm, 10mm/s, 4 protected runs per track).
- b. High mag longitudinal view of melt/substrate interface (Plate 7a).
- c. SEM view of melt/substrate interface (Plate 7a). The laser track has been removed revealing the equi-axed nature of the austenite at the interface.
- d. Deep etched transverse SEM view of equi-axed interface grains. Austenite grain boundaries, highlighted by carbide precipitation and individual martensite lathes are revealed (Plate 7a).
- e. SEM view of gas pore; sectioned in half by fracturing and showing interface adherence (Plate 7a).
- f. High mag transverse section through hypereutectic track; showing shrinkage porosity, (upper pores), and gas entrainment (lower pores), (1.7kW, 3.5mm, 10mm/s, 4 protected runs).
- g. ^{ns}
Λ High mag traverse section through hypereutectic track: 'Massive' C alloying leads to the retention of free graphite flakes in a matrix of proeutectic cementite and eutectic (1.7kW, 2.5mm, 10mm/s, 8 protected runs).

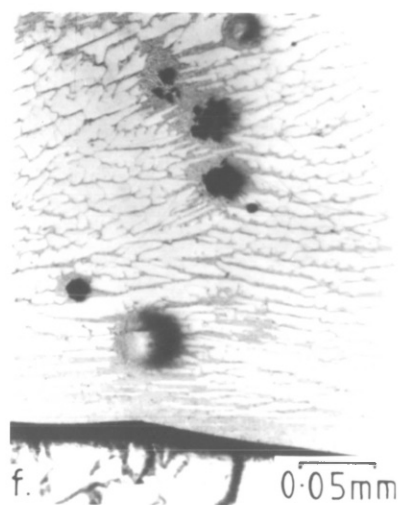
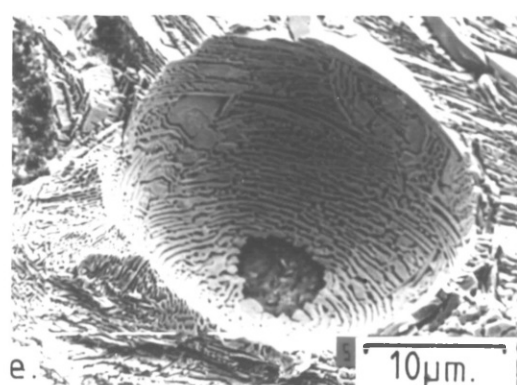
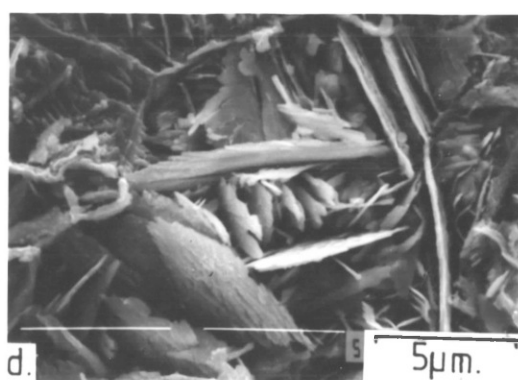
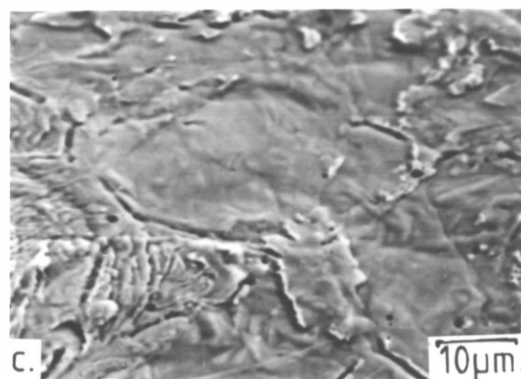
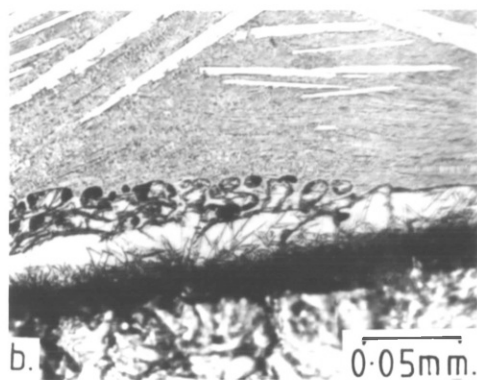
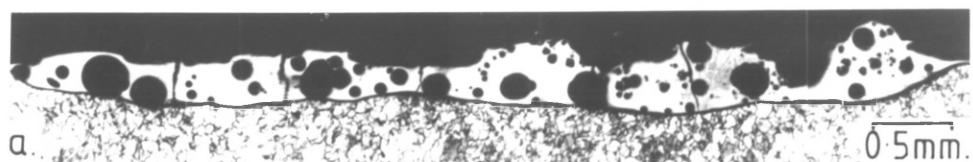


PLATE 8 C Alloying to Fe

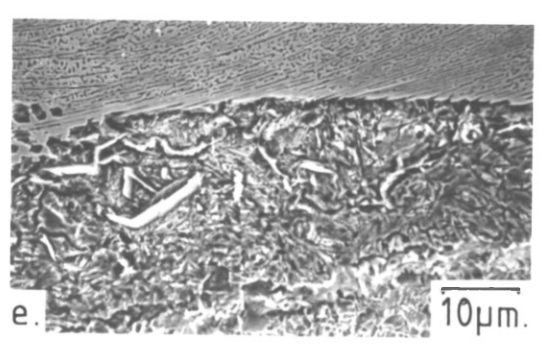
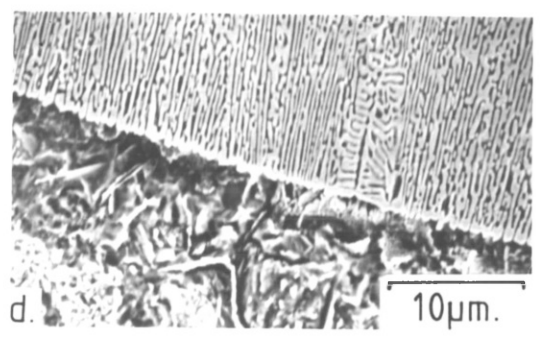
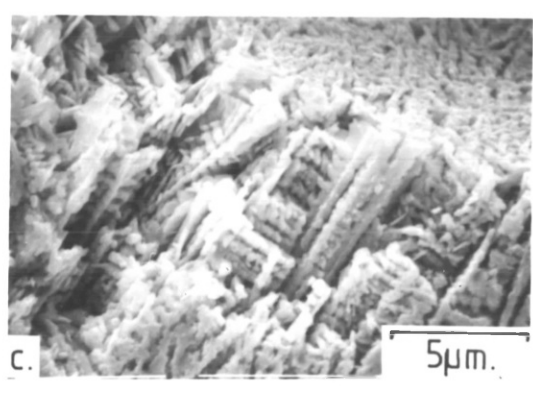
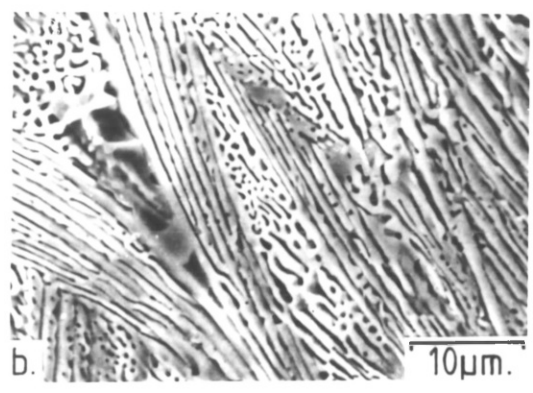
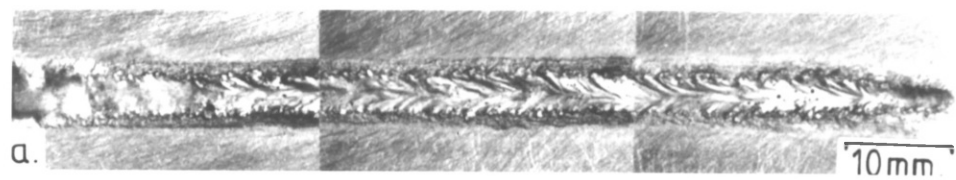
- a. Plan view of laser alloyed track produced by twin beam arrangement; beams move from left to right, and the glancing beam 'pushes' the surface ripples in the opposite direction Plate (7a).

- b. SEM transverse view of irregular lamellar eutectic (1.7kW, 1.5mm, 20mm/s 2 protected runs, single beam processing).

- c. SEM view of irregular dendritic like eutectic of key-hole region (Plate 8b), (deep etched in 10% nital).

- d. SEM transverse view of melt/substrate interface; irregular lamellae and 'chinese script' eutectic nucleates and grows perpendicular to interface (1.7kW, 2.5mm, 10mm/s 2 protected runs).

- e. SEM transverse view of melt/substrate interface; irregular lamellar eutectic nucleates and grows 'within 15°' of the interface (1.7kW, 3.5mm, 10mm/s 2 protected runs).



3. SURFACE MELTING OF Al-Si ALLOYS AND SURFACE ALLOYING OF Si TO Al ALLOYS

3.1. INTRODUCTION

In an effort to minimize material costs, recycled Al is commonly used in commercially manufactured Al alloy components. As a result of continual recycling, Al alloys contain tramp elements, typically Fe or Si. In conventional chill castings these elemental impurities form coarse dispersoids, which limit fracture toughness and formability. Conventional Al alloys lack thermal stability. Age-hardenable alloys tend lose their strength at temperatures above the 100 - 200°C range, as a result of precipitate coarsening. Al alloys have a low elastic stiffness, approximately 1/3 that of steel¹³³. Li additions are used to increase the modulus; however, these high strength alloys are associated with reduced ductility and reduced fracture toughness. Rapid solidification refines or extends the level of solid solution of impurity dispersoids, age-hardening intermetallics and high modulus intermetallics. Atomization and splat quenching has been shown to increase strength, modulus and thermal stability² (raising possible operating temperatures) without impairing ductility or fracture toughness, Table 3.1¹³⁴.

Table 3.1.¹³⁴ Effect of Cooling Rate during Solidification on Wrought 2024-T4 (Al - 0.4 Cu - 0.6Mn - 1.5Mg)

	Ingot	Air-Atomized	Splat-quenched
Cooling rate K/s	0.1	100	10 ⁵
Dendrite spacing μm	60	7	0.7
Metallic inclusion size μm	10 to 20	4 to 6	0.5 to 1
Lattice Parameter Å	4.049	4.047	4.044
0.2% yield strength MPa	80	290	330
Ultimate Strength MPa	460	480	540
Elongation to fracture %	23	25	24
Reduction in area %	37	33	39
Fatigue life at 200MPa, cycles	10 ⁵	3 x 10 ⁵	7 x 10 ⁵

Si additions to Al alloys enhance alloy rigidity, hardness, corrosion resistance and reduces thermal expansion (coefficients of expansion for Si and Al are 7.36×10^{-6} and $28.7 \times 10^{-6} \text{cm}/^{\circ}\text{C}$)¹⁹. Al-Si alloys might be used where high strength or good wear properties are required. High Si alloys are used as engine bearings. A typical alloy, 11Si - 1Cu, is manufactured so as to produce finely divided, $2\mu\text{m}$, Si particles in a Al-Cu-Si solid solution. Another example is the use of hypereutectic alloys to cast Al alloy engine blocks. In such alloys it is necessary to precipitate sufficient quantities of hard proeutectic Si particles so as to provide the hard wear resistance of cylinder bores. The bores are sometimes deep etched so that the Si precipitates ride proud of the Al matrix. Si content is limited by its embrittling effect in high Si Al-Si alloys, and by serious machining problems associated with high Si alloys. It is desirable to ensure that the proeutectic Si is well refined; this enhances physical properties and can extend the range of Si alloying.

The refinement of Si particle size resulting from atomization of Al-Si alloys permits alloys containing up to 25Si to be satisfactorily extruded, forged and stamped. Elongation to fracture for Al-25Si increases from 0.2% in the cast condition to 8% for extrusions made from atomized alloy powder¹³⁵. Compositions beyond the range of conventional casting technology have been processed. Hot pressed Al-45Si alloy atomized powder has a thermal expansion similar to that of Cast Iron² and with its improved wear resistance would be suited for high temperature cylinder liners.

In this chapter laser surface melting of Al-Si alloys and laser surface alloying of Si to Al alloys is investigated. This study seeks to describe the solidification mechanism and phase morphology of rapidly solidified hypoeutectic and hypereutectic Al-Si alloys. The physical problems of laser beam coupling with Al, notorious for its reflectivity and high conductivity, are reviewed and the physical processing parameters associated with the LSA Si evaluated.

The effect of symptomatic rapid solidification on Al-10Si has been discussed. Proeutectic Al is greatly refined and shown to grow as 'limited two dimensional' dendrites. The Si content of the fibrous Al-Si eutectic increases with quenching. LSA of Si to pure Al, C817 (a commercial Al alloy), and Al-10Si has been considered. Sufficient Si was alloyed so as to produce hypereutectic alloys. Rapid solidification induced two morphological forms of proeutectic Si, plate-like/idiomorphic and dendritic Si. Dendritic hypereutectic alloys with fibrous Al-Si eutectic were shown to fracture in a ductile mode up to 40Si. Alloys containing up to 72Si, HV460, were subsequently produced.

3.2. REVIEW

3.2.1. The Al-Si System

The Al-Si system is a simple eutectic, a combination of fcc metal and a non-metal diamond cubic structure¹³⁶⁻¹⁴⁰. Figures for the eutectic composition are controversial, determinations suggest that it lies between 11.7¹³⁶ and 12.7¹³⁷ Si, at 577°C, Fig.3.1. Mn additions are 'typically' added to commercial alloys (C817). Mn increases high temperature strength and improves creep resistance through the formation of high melting point compounds. Mn also corrects for the embrittling effect of Fe which is commonly present as an impurity. When Fe is present thin platelets of hard, brittle, FeSiAl₅ form. The addition of 1 - 2 Mn to a 0.7 - 0.8 Fe alloy transforms FeSiAl₅ into [FeMn]₃Si₂Al₁₂ which typically adopts an hexagonal morphology.

Alloys having a coarse eutectic exhibit low ductility because of the brittle nature of eutectic Si plates; cracks propagate through a specimen across the 'plane' of flakes. Rapid cooling or alloy modification (Appendix V) refines the microstructure and Eutectic Si assumes a fibrous form which minimises crack propagation. Both ductility and tensile strength are improved, Table 3.2.

TABLE 3.2.¹³⁸ Mechanical Properties of Al-13wt% Si

	Tensile Strength (MPa)	Elongation (%)	Hardness (Rc B)
Normal Sand Cast	125	2	50
Na Modified Sand Cast	195	13	58
Normal Chill Cast	195	3.5	63
Na Modified Chill Cast	220	8	72

3.2.2. Solidification Mechanisms

3.2.2.1. Eutectic Growth

In a eutectic system liquid may freeze by the independent growth of relatively large crystals or by co-operative growth. The latter process is kinetically more attractive, since it minimises diffusion distances. Equilibrium solidified eutectic Al-Si conventionally forms with a 'flake' morphology, but rapid quenching produces a fine fibrous-duplex structure^{139-148, 75}. This 'coupled' growth process occurs in a region below the eutectic.

In the Al-Si system Si tends to grow anisotropically to give faceted crystals. Si growth is kinetically more difficult and hence the coupled region is asymmetric about the eutectic, Fig.3.1. Thall and Chalmers¹³⁸ conceived the idea that eutectic Si grows ahead of eutectic Al, Fig.3.2. Skewing of the coupled zone has been explained in terms of constitutional undercooling¹⁴⁰. The equilibrium freezing point of the liquid in contact with the Al is lower than the liquid in contact with the Si. Undercooling ahead of the Si phase will be much larger than ahead of the Al, and because of the difference in equilibrium temperatures, the Al phase will grow ahead of the Si.

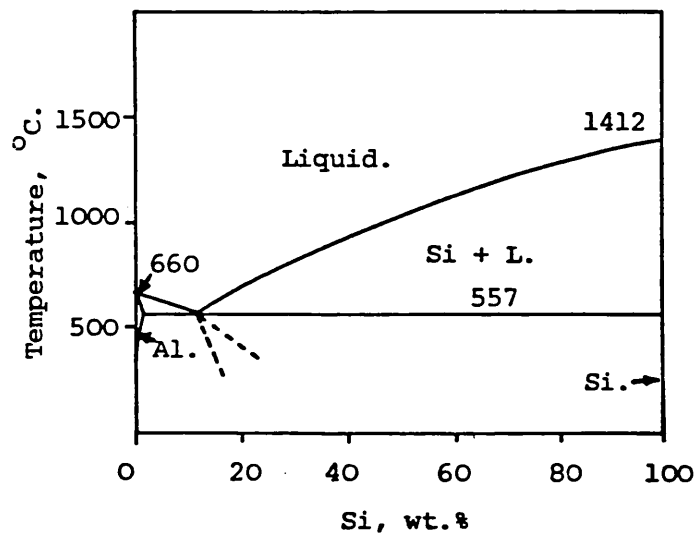


Fig.3.1.¹³⁷ The Al-Si Equilibrium Phase Diagram (with superimposed skewed coupled zone).

Steen and Hellawell¹⁴⁹ report that multiple twinning occurs with increasing density in fine eutectic Si. Fibrous Si is commonly twinned on two {111} systems. They speculate that with increased freezing velocity 'the kinetic undercooling for Si must increase sharply so that eventually there occurs an inversion of the front such that in profile the Si grows behind the Al front', but (since the network is now known to be continuous) without the Si being enveloped completely.

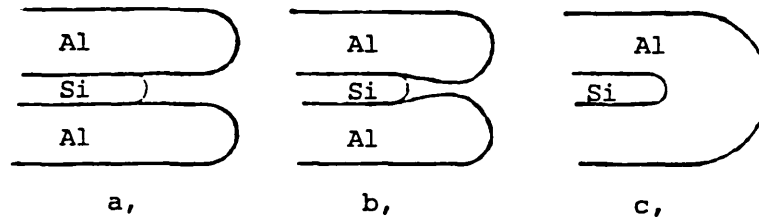


Fig.3.2. The Al-Si Eutectic Growth Mechanism According to Thall and Chalmers¹³⁸. Thall and Chalmers¹³⁸ concluded that the Al interface would advance more rapidly than the Si. They postulated that the rate of advance of the interface depends on the balance between the rate of heat flow from the liquid to the solid through the interface and the magnitude of the heat evolved during solidification. 'Since Al has a higher thermal conductivity and a lower latent heat of fusion, it will advance ahead of the Si'. It was suggested that; 'if the Al phase leads the Si phase by a sufficient distance, then the Al will completely enclose the Si, sealing it off from the melt'. Further growth would occur through fresh nucleation.

Day and Hellawell¹⁴³ have attempted to classify the eutectic Al-Si growth mechanism in terms of growth rate, R , and temperature gradient, G . Fig.3.3. shows a summary of these findings. At high G and low R , region a, the two phases grow independently and Si solidifies in a faceted manner. Decreasing G , region b, causes breakdown of the Al-interface and the Si forms rods with a $\langle 100 \rangle$ texture. Region C corresponds to typical casting conditions; Si grows as a twinned irregular interconnected flake network via the twin plane re-entrant

edge mechanism (TPRE)¹⁵⁰. Controlled rapid cooling produces steep G and high R necessary to form fibrous Si, region d. Fine twins 500Å apart extending along the length of the fibres have been reported¹⁴⁹. Frequent twinning allows a more flexible growth mechanism which can approach the diffusion-controlled growth of a non-faceted/non-faceted system. It is suggested that the Si-liquid front must be a jumble of serrated edges and grooves. Atasoy et al¹⁴⁸ have, however, shown that twins are not essential for fibrous growth and attribute the transition in morphology to change from layer to continuous growth. The quenching associated with laser processing ($\sim 10^5$ K/s) would produce fibrous structures, region d.

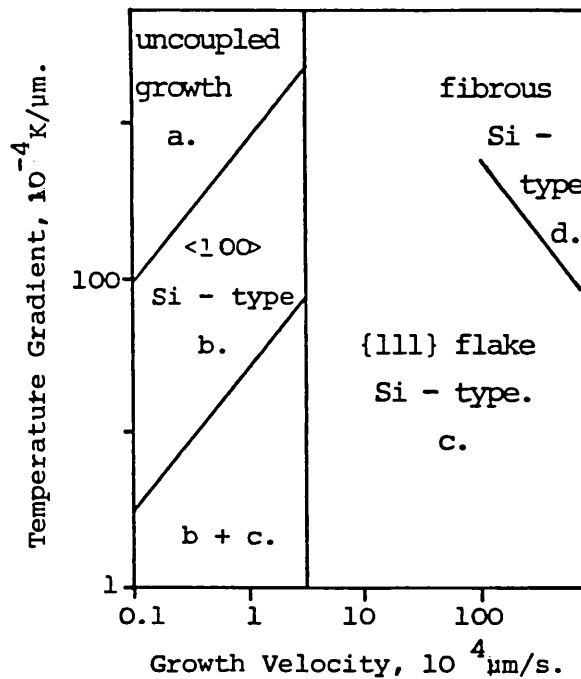


Fig.3.3.¹⁴³ Range of microstructures observed in directionally solidified Al-Si eutectic alloys.

3.2.2.2. Proeutectic Si Growth

Proeutectic Si crystals with {111} facets form from hypereutectic alloys. The true perfect shape would be octahedral bounded by 8 {111} planes¹⁵¹, the planes of closest packing and lowest free energy in the diamond lattice, Fig.3.4a. However, crystals with twin planes are often found. If the twin has the effect of removing a portion of the crystal and reflecting the remaining solid then a bicrystal similar to

Fig.3.4b will result. The twin boundary has a hexagonal shape; thus twin planes which bound the lamellae produce in the sides of the growing crystal a self-perpetuating system of grooves in which nucleation and growth readily occur. Preferred growth has been described¹⁵⁰ as being due to the twin plane re-entrant edge mechanism (TPRE). Growth takes place at these edges and the twin boundary would approach a triangular shape, Fig.3.4c, bounded by the 3 other sides. However, this tendency is not generally seen to occur. Fredriksson et al¹⁵² have demonstrated that there is no indication that twin boundaries have any decisive influence on crystal growth. Atasoy et al¹⁴⁸ remark that twins which form during growth do not necessarily contribute to the growth process.

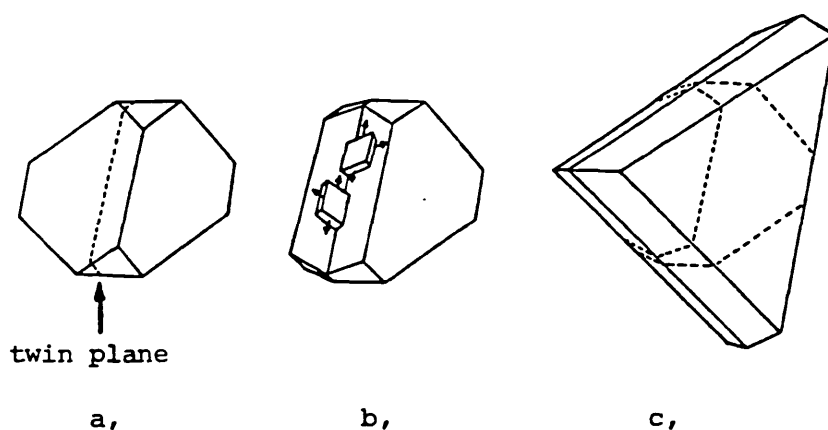


Fig.3.4. The Si Crystal¹⁵³

- a. The equilibrium form of Si, an octahedron bounded by $\{111\}$ surfaces.
- b. A twinned crystal derived from the equilibrium form by reflection across the twin plane.
- c. The 'triangular' solid that is formed if the three-reentrant corner sites in the bicrystal are allowed to grow.

In hypereutectic alloys Si nuclei grow by advancing tips of Si plates to form a skeleton, which is then slowly in-filled to produce idiomorphic crystals¹⁵⁴. Crosley and Mondolfo¹⁵⁵ claim that this is typical of slow growth in slightly supersaturated liquid. Kim and Heine¹⁵⁴ have defined the shape of Si particles as being temperature dependent. An increasingly hypereutectic melt causes nucleation to occur at higher temperatures, favouring idiomorphic and coarse plate Si.

Wagner¹⁵⁰ showed that the growth of the Ge crystals in contact with a supercooled melt may either be polyhedral or dendritic depending on whether they are grown slowly or rapidly. Wagner¹⁵⁰ artificially grew a faceted Ge dendrite with a network of saw tooth sides. Si dendrites of a similar morphology have been observed elsewhere¹⁵². Only if thermal conditions are so severe that the reentrant corners are reduced below a minimum size, can primary Si be expected to grow in a truly dendritic fashion.

Atasoy et al¹⁴⁸ report the changing morphology of Si in terms of alloy content and growth velocity, Fig.3.5. A high G/R ratio suppresses proeutectic Si growth in favour of dendritic Al. In an 11Si alloy proeutectic Si is suppressed at $R < 10\mu\text{m/s}$. In region B proeutectic Si grows as 'skeletal-complex-regular' or 'star-like' formations. Massive proeutectic Si precipitates occur in alloys containing > 14.5 Si, both in region B and in smaller quantities in regions C and D. The growth rate anisotropy of Si is such that massive geometric proeutectic Si grows from the melt by layer growth and is bounded by slow growing $\{111\}$ faces giving an octahedral growth habit. Atasoy et al¹⁴⁸ suggested that proeutectic Si grows from an untwinned nucleus by layer deposition on $\{111\}$ faces to develop geometric faceted precipitates. Fredriksson et al¹⁵² showed that increasing cooling rate causes nucleation to occur at edges and corners. Atasoy et al¹⁴⁸ confirmed that at higher growth velocities edges and corners become preferred growth sites and demonstrated that extended layer growth occurs producing ragged dendritic networks. If these observations are true then TPPE is not the dominant growth mechanism that some authors suggest.

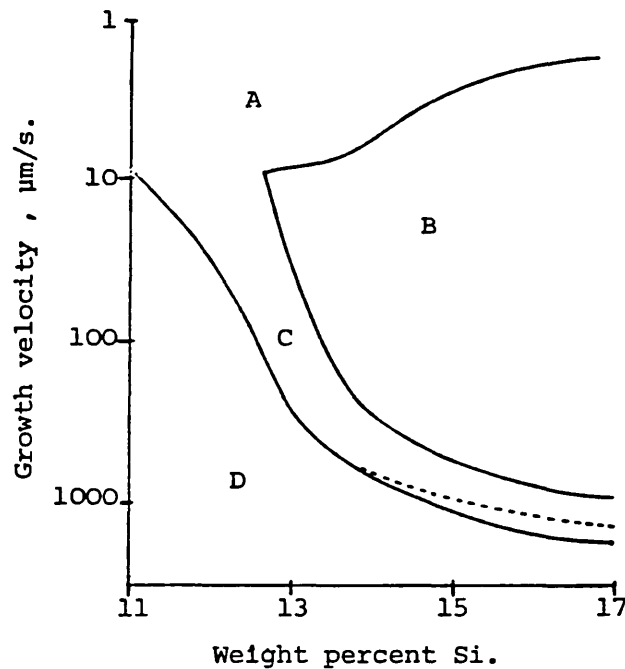


Fig.3.5.¹⁴⁸ Relationship between structure, Si composition and growth velocity

Region A: angular, rod, flake eutectic Si.

Region B: eutectic, complex regular, star-like and massive primary Si (Si>14.5%).

Region C: eutectic Si, some primary Si(Si>14.5%).

Region D: α -Al dendrites, eutectic Si and some primary Si(Si>14.5%).

3.2.3. Determination of Solidification Conditions

3.2.3.1. The Eutectic

3.2.3.1.1. Undercooling, Thermal Gradients and Growth Velocity

Modification produced by rapid chilling is most likely to be the consequence of diffusion control. However, in systems where one or more of the phases grows in a faceted manner, the influence of G cannot be neglected, because the growth fronts are non-isothermal¹⁵⁶. Steep thermal gradients would force the growth front to be more planar, making solute rejection more difficult so promoting morphological instability. This increases the frequency of branching, therefore increasing the interphase spacing, and hence facilitating the flake/fibrous transition. Steen and Hellawell¹⁴⁹ demonstrated that the flake/fibrous transition is primarily dependent on R and hence the kinetic undercooling for Si must increase with increasing R , so that eventually there occurs an inversion of the growth front.

Toloui and Hellawell¹⁵⁶ have plotted actual values of eutectic spacing, λ_3 , for G and R, Fig.3.6, showing the flake/fibrous transition at rates approaching 1mm/s. Only two values of fibrous spacings are included and any discontinuity in slope with transition requires substantiating. Toloui and Hellawell¹⁵⁶ concluded that the freezing point during growth will be determined by the contributions of ΔT_d , ΔT_c and ΔT_k . Estimates of ΔT_c and ΔT_k led Steen and Hellawell¹⁵⁷ to conclude that they were small, less than 10%; hence insufficient solute diffusion causes undercooling. Toloui and Hellawell used Zener's expression¹⁵⁸ to determine ΔT_d :

$$\Delta T_d = \frac{(C_E(1-k)mR\lambda_3)}{D} \quad (3.1)$$

For the Al-Si system:

$$\begin{aligned} C_E &\sim 13 \\ (1-k) &\rightarrow 1 \\ m &\sim 10K/wt\% \\ D &\sim 3 \times 10^{-3} \text{mm}^2/\text{s} \end{aligned}$$

$$\underline{\Delta T_d = R\lambda_3 \ 4 \times 10^6 K} \quad (3.2)$$

Eq (3.2) used in conjunction with Fig.3.6 gives undercoolings within <20% of measured values¹⁵⁶. (Although C_E is dependent upon R any increase in C_E will be offset by a decrease in m). That the measured undercoolings and those estimated should coincide so closely is perhaps fortuitous but the estimate does serve to emphasise the relative order of contributions from compositional effects.

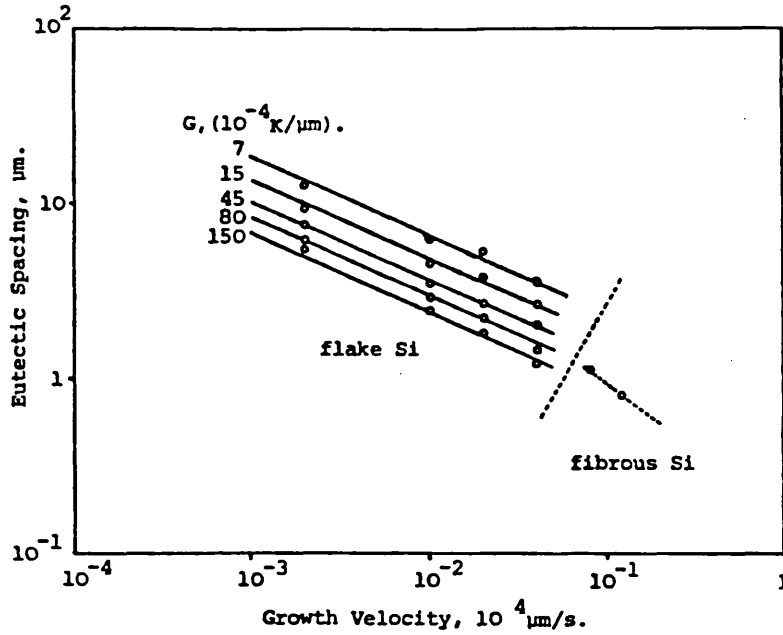


Fig.3.6.¹⁵⁶ Variation of Eutectic Spacing as a Function of Growth Rate and Temperature Gradient.

Elliott and Glenister¹⁵⁹ have demonstrated that the undercooling/velocity relationship changes with increasing R and have explained their results in terms of Hunt and Jackson's⁷⁹ steady state theory:

$$\Delta T^2/R = \text{Const} \quad (3.3)$$

$$\lambda_3^2 R = \text{Const} \quad (3.4)$$

Elliott¹⁵⁹ accepts that the mechanism of Si growth changes with growth conditions and suggests:

$$\Delta T = 2.24 R^{0.25} \text{ at low velocities for coarse Si} \quad (3.5)$$

$$\Delta T = 0.8 R^{0.5} \text{ at high velocities for fine Si} \quad (3.6)$$

Kurz and Fisher¹⁴⁵ have developed an analogous mathematical model for solidification. They have considered proeutectic Al to have a needle like morphology and proeutectic Si to have a plate like morphology.

$$\Delta T_{\text{needle}} = GDR + mC \left[1 - 1/[1 + (k - 1)\Omega_n] \right] + 2 \theta/R \quad (3.7)$$

$$\Delta T_{\text{plate}} = GD/R + mC \left[1 - 1/[1 + (k - 1)\Omega_p] \right] + \theta/R \quad (3.8)$$

The solution to Kurz and Fisher's model compares favourably with the results of Steen and Hellawell¹⁴⁹, Fig.3.7. The two sets of results do illustrate a discrepancy with regard to the degree of skewness of the zone. Kurz and Fisher¹⁴⁵ suggest that this may be due to the naivety of their model but it may equally be due to the fact that the experimentally determined coupled zone has been placed in doubt by later research¹⁵⁶ (K has been found to depend on G).

Kurz and Fisher's¹⁴⁵ analysis has been approximated to:

$$\Delta T = A R^{0.5} \quad (3.9)$$

This is in accord with Elliott and Glenister's results¹⁵⁹.

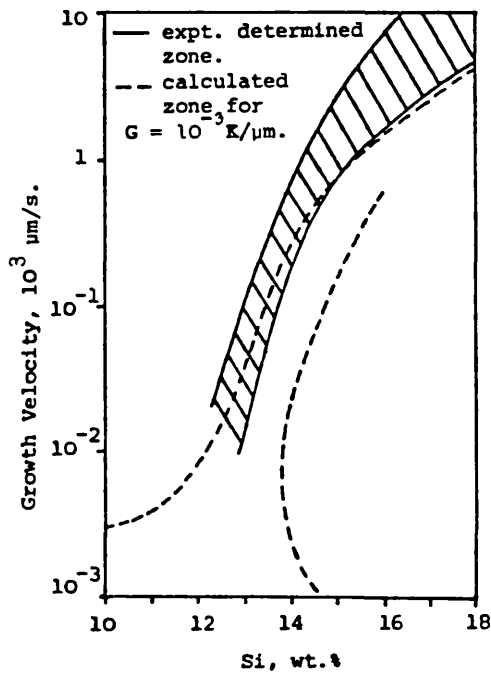


Fig.3.7 Coupled zone of directionally grown Al-Si eutectic. The calculated zone predicted by Kurz & Fisher¹⁴⁵ is compared with the experimentally determined zone found by Steen and Hellawell¹⁴⁹.

Armstrong and Jones¹⁶⁰ experimenting with a Al-10.5Si alloy observed that the interdendritic eutectic has a composition appropriate to the prevailing growth conditions and that this relationship extends to regimes of high growth velocity. The composition of the residual eutectic was shown to increase from 19.5Si to 37Si as cooling rate increases from 1.8×10^3 to 1.2×10^6 K/s. These values are reasonably consistent with those given for coupled growth by Steen and Hellawell¹⁴⁹. Armstrong and Jones¹⁶⁰ expressed their relationship:

$$C_{Eu} = (10.9 \pm 0.7)(GR)^{0.091 \pm 0.007} \quad (3.10)$$

As the composition of the eutectic changes so the volume fraction present must also change. For a Al-10.5Si alloy Armstrong and Jones concluded:

$$f_{Eu} = (1.25 \pm 0.1)(GR)^{-0.13 \pm 0.01} \quad (3.11)$$

Providing the eutectic composition (or the total average composition) can be accurately measured then cooling rates can be predicted. Any relationship for fibrous eutectic spacing drawn from Toloui and Hellawell's¹⁵⁶ results will need substantiating. For coupled eutectic growth λ_3 is normally associated with the relationship $\lambda_3 = A R^{-1/2}$; while this has been validated for the Al-Al₂Cu eutectic² no supportive evidence is available for the Al-Si eutectic. If, however, a reasonable value for R can be predicted then undercooling can be determined.

3.2.3.1.2. Thermal Analysis

Laser processing involves a prime interest in quenching properties; however, the effect of alloy composition and presence of modifying elements (Appendix IV) should not be ignored. The temperature of the eutectic arrest depends on cooling rate. The eutectic plateau temperature falls as quenching rate increases.

Crosley and Mondolfo¹⁵⁵ have conducted a detailed thermal analysis of various Al-Si alloys. Their findings, summarised in Fig.3.8a., have been used in conjunction with metallographic evidence to construct a nucleation diagram, Fig.3.8b. They showed that primary Al would nucleate the eutectic at undercoolings of 6K in unmodified alloys and 12K in Na modified alloy, proeutectic Si apparently having no nucleating effect. Rapid cooling of a hypereutectic alloy produces an undercooling; proeutectic Si precipitates and the liquid composition moves to the 'left' whereupon an Al 'halo' forms around the Si. The remaining liquid will then be displaced along the Al liquidus to a point where proeutectic Al^{and} eutectic will nucleate.

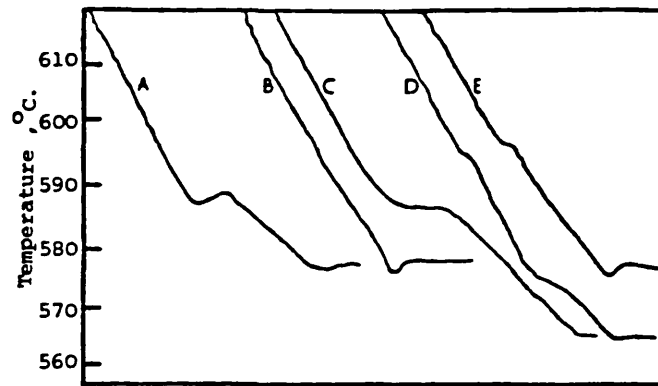


Fig.3.8a¹⁵⁵ Cooling curves for Al-Si alloys, cooling rate 5°C/min.
 A. sodium-free hypoeutectic: B. sodium-free hypereutectic: C. sodium-modified hypoeutectic:
 D. sodium-modified hypereutectic: E. phosphorus-modified hypereutectic.

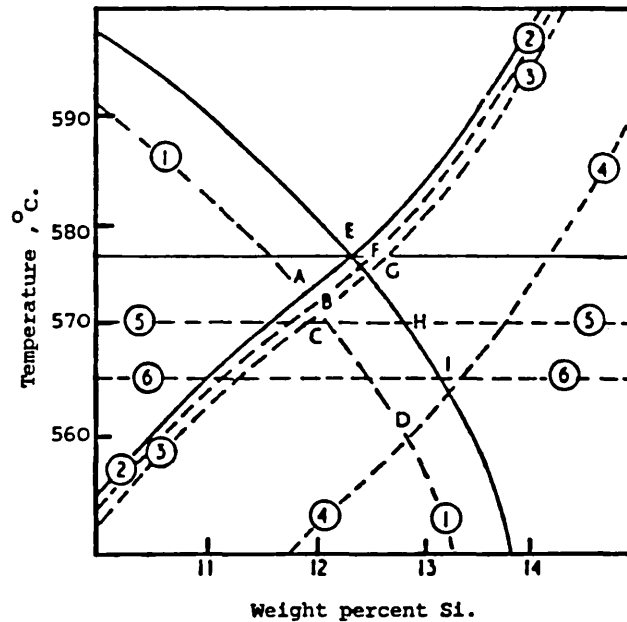


Fig.3.8b¹⁵⁵ Eutectic zone of Al-Si diagram with nucleation lines. Line 1 - nucleation of aluminium by impurity X: line 2 - nucleation of silicon by AlP particle: line 3 - nucleation silicon by AlNaSi particle: line 4 - nucleation of silicon by impurity Y: line 5 - nucleation of silicon by aluminium: line 6 - nucleation of silicon by aluminium in presence of Na

3.2.3.2. Proeutectic Al Dendrite Spacing

It is generally accepted¹⁶¹⁻¹⁶³ that, for hypoeutectic alloys, increased cooling rates usually increase tensile strength and

elongation to fracture, and this is normally related to decreasing dendrite spacing. It has since been shown that dendrite arm spacing can be used to accurately determine solidification rates. Horwath and Mondolfo¹⁶⁴ were probably the first to represent this relationship empirically, for Al alloys:

$$\text{ie } \lambda_2 = A(GR)^{-n} \quad (3.12)$$

Their results extended to λ_2 values no smaller than $8\mu\text{m}$ and (GR) values no higher than 30 K/s. Spear et al^{165, 166} observed similar relationships in spacings up to $1\mu\text{m}$, in given splats cooled at 10^7 K/s.

Young and Kirkwood¹⁶⁷ solidified Al-Cu alloys under steady-state conditions and measured primary and secondary arm spacings as separate functions of G and R. Primary arm spacing was found to increase with solute content and it was concluded¹⁶⁷ that, to a reasonable approximation, the equation may be written:

$$\lambda_1 = k(GR)^{-1/2} \quad (3.13)$$

Young and Kirkwood¹⁶⁷ also demonstrated that secondary arm spacing is a function of distance from the primary dendrite tip. Secondary arm spacings increase with time in the solid/liquid region, θ , and change approximately according to a $\theta^{1/3}$ relation (as described previously, 2.2.1.2.). The authors indicated that λ_2 can be reduced by increasing the solute content or increasing R (for the same value of θ).

Armstrong and Jones¹⁶⁰ explored the effects of cooling rates on Al-10.5Si in the range 400 to 10^6 K/s and dendrite arm spacings in the range 5 to $0.5\mu\text{m}$. Using Horwath and Mondolfo's original relationship¹⁶⁴ they demonstrated that $\log \lambda_1$ and $\log \lambda_2$ varied linearly with $\log(GR)$ ie:

$$\lambda_1 = 55 \pm 12 (GR)^{-0.25 \pm 0.002} \quad (3.14)$$

$$\lambda_2 = 47 \pm 6 (GR)^{-0.33 \pm 0.001} \quad (3.15)$$

In reviewing aspects of rapid solidification, Jones^{2, 168} considered the value of secondary arm spacing, Fig.3.9., and concluded that it could be used to determine surprisingly accurate values of cooling rate:

$$\lambda_2 = 50 (\text{GR})^{-1/3} \quad (3.16)$$

Microstructural refinement of proeutectic Al can be used to complement eutectic composition and eutectic spacing as a method of determining GR.

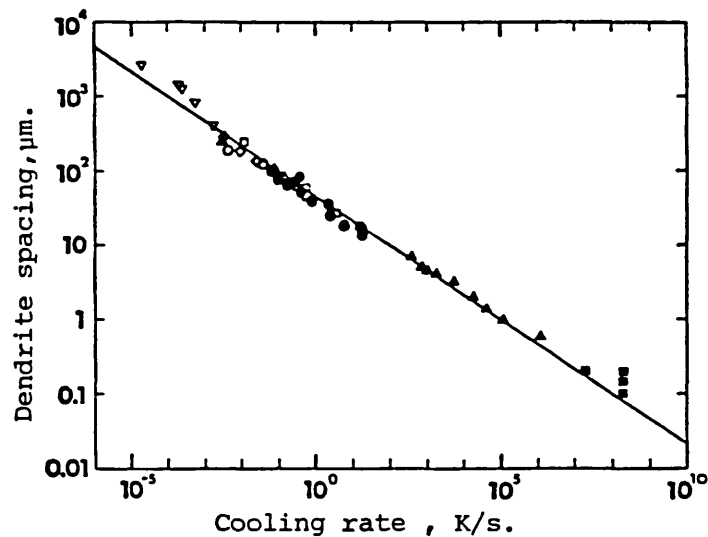


Fig.3.9² Dendrite spacing λ_2 as a function of cooling rate, ϵ , for Al-4 to 5wt%Cu (open points) and Al-7 to 11wt%Si (filled points). Line shown is $\lambda_2 \epsilon^{1/3} = 50 \mu\text{m (K/s)}^{1/3}$.

- Horwath and Mondolfo, Acta Met., 1962, 10, 1037.
- Michael and Bever, Trans. AIME, 1954, 200, 47.
- △ Bardes and Flemings, Trans. AFS, 1966, 74, 406.
- ▽ ditto, but sand cast rather than chill cast.
- ◇ Kaneko, J. Mat. Sci., 1977, 12, 1392.
- Spear and Gardner, Trans. AFS, 1963, 71, 209.
- Matyja et al, J. Inst. Met., 1968, 96, 30.
- ▲ Armstrong and Jones, in 'Solidification and Casting of Metals', Metals Society, 1979, p.454.

3.3. EXPERIMENTAL PROCEDURE

Some 350 laser alloyed tracks combined various combinations of processing parameters from beam diameters 1.0 - 5.0mm, scan velocities 2-250mm/s and powers 0.95 - 2.00 kW. The effects of beam intensity, interaction time and alloy coatings on melt track shape, size and microstructure have been studied. The substrates used were Al (CP Al), Al-10Si and C817(a commercial alloy). All specimens were grit blasted then soaked for 1 hour at 400°C (to produce a thick oxide surface layer) before processing. Their compositions as determined by wet analysis are given in Table 3.3.

TABLE 3.3. Compositions of Al Alloy Substrates

wt%	Si	Fe	Mn	Zn	Ti	Na	Sr
Pure Al	<0.05	0.016	<0.02	-	-	0.013	<0.02
10Si	10.3	0.32	<0.02	-	-	0.008	<0.02
C817	0.21	0.63	1.14	0.01	0.01	-	-

30mm thick specimens, clamped to a cold steel plate, were given single and multipass treatments using the 2kW CO₂ laser (described Section 2.3.) with a Gaussian beam. He rather than Ar was used to shroud the melt and suppress plasma generation. Preplaced surface alloying was carried out. Coatings of either Si or DAG graphite diluted with methanol were preapplied with a small brush. The Si used was 'Silicon special product 80/00 flame spraying powder' lot 4345 supplied by METCO, Woking, Plate 9a. The DAG was the same as that used for alloying to ferrous substrates (2.3.). The amounts of preplaced coatings (after methanol evaporation) for all the samples listed, were determined by weight as:

METCO Si $0.045 \pm 0.007 \text{ g/cm}^2$

DAG Graphite $0.010 \pm 0.001 \text{ g/cm}^2$

The use of DAG as an absorbant coating is discussed (its alloying effects are reported elsewhere, Appendix VI). The problems of laser

beam reflectivity and thermal conductivity dominate Al processing. Beam absorptivity varied with surface coating. DAG coated specimens melted preferentially to uncoated specimens. C was seen to alloy to laser melted tracks. In studying LSA of Al alloys it was originally proposed to make a microstructural study of C alloying. Diamond 'dust' which reduces to C was used as a direct comparison for DAG. 40 μ m diamonds mixed in ethanol were painted on Al substrates. When processed the diamond decomposed and reformed as Al carbide or free carbon. Beam coupling was found to be inferior and since there were no apparent advantages the process was abandoned in favour of less expensive DAG.

A detailed microstructural study of the laser processed tracks has been made. The shape and size of the proeutectic phases, the form of the eutectic and the effect of eutectic skewing have all been investigated. Three techniques were utilized, optical microscopy, SEM and TEM. Laser processed tracks were sectioned in three planes (vertical, longitudinal and cross-sectional), polished with diamond pastes, and then examined, firstly in an unetched condition and then after etching in 1 vol HF, 9 H₂O for ~15s, at magnifications of x10 - x1500.

The JEOL T200 scanning microscope was used to study both polished and fractured specimens at magnifications of x35 - x10,000. The polished 'optical' specimens were re-etched in 1 vol HF, 9H₂O for ~45s to permit topographic identification of the microstructure. Primary and secondary dendrite arm spacing were measured by the method previously described (2.3). Other specimens were fractured and then deep etched in a solution of 1vol HF, 1 HNO₃, 5 acetic acid for 10-30s or 1 vol HCl, 1 H₂O, 1 C₂H₅OH for ~15s. HCl was added slowly to H₂O + C₂H₅OH while the specimens were etching to avoid excessive reaction destroying the fine structure. After acid leaching the specimens were thoroughly washed by repeated immersion in alcohol, then by a 30min ultrasonic wash in alcohol changing the washing solution after 1, 2, 5 and 10 mins.

A TEM examination was made of the eutectic. Thin foils were made by the method previously described (2.3.). The morphology of the eutectic and the presence of any 'trace phases' (eg Mn₃Si₂Al₁₂) were studied at magnifications up to x100,000.

X-ray diffractometer examinations of the surface of various melted and alloyed specimens were carried out using the Philips Goniometer, Model PW1050, fitted with a Cu K α radiation source (2.3.). The experimental spacings given in the results are mean high angle spacings.

The concentrations of alloyed Si were quantified using a JSM-35 scanning microscope fitted with a probe analyser and by 'wet' chemical analysis. Some 20 different specimens were tested on the JSM-35. Transverse sections of individual laser tracks were mounted in bakelite, polished with diamond paste and then examined. Despite the lack of etching it was possible to identify both track contours and individual microstructural features. Low magnifications, $\sim$ x100, were used to identify average compositions. Higher magnifications, x500, were used to determine compositional changes through tracks. Very high magnifications, $\sim$ x8,000, were used to identify the compositions of microstructural features, ie eutectic composition. Wet analysis was used to determine the average composition of over 15 different specimens. Sections of Si alloyed track were first carefully removed using a 'sharp-edged' cold chisel and then dissolved in a warm caustic soda solution (typically 100mg of sample per 1g NaOH + 1ml H₂O). After cooling the solution was poured into a 1 vol HCl + 9 H₂O solution. Up to 10 samples from each solution were then measured by atomic absorption against a Si standard using a PERKIN-ELMER 2380 Atomic Absorption Spectrophotometer, and an average result determined.

Melt depth, width, volume of molten substrate, and total track volume (vol molten substrate + vol alloyed) were determined for all specimens. Depth and width were measured, from previously polished and etched track cross sections, using the moving stage of an AKASHI microhardness machine. Depth is measured from the substrate surface, to the furthest extent of melt penetration. Substrate sectioned areas were determined by tracing magnified views of the cross sections, using a Projectina Model 4011-4016/MMA projector. The tracings were cut out, weighed and directly compared with a previously weighed, known, magnified area.

Hardness tests were carried out using either the AKASHI microhardness machine fitted with 100 or 500g loads or using a Vickers machine fitted with a 5kg load.

In an attempt to evaluate abrasive wear, a simple pin and disc test apparatus was constructed along the designs used by Sanvik AB¹⁶⁹, for 'dry' wear resistance, and originally based on DIN 50330. Test samples ground on 400 grit discs so as to produce flat specimens with a nominal 'rubbing' area 3mm x 2mm. The specimens were then pressed against a rotating disc whose surface was covered with a dry abrasive paper. The silicon carbide grit discs were changed after each test. The samples were given a motion like a gramophone stylus and wear was defined as the distance travelled in metres for 0.1mm³ of sample lost, Fig.3.10.

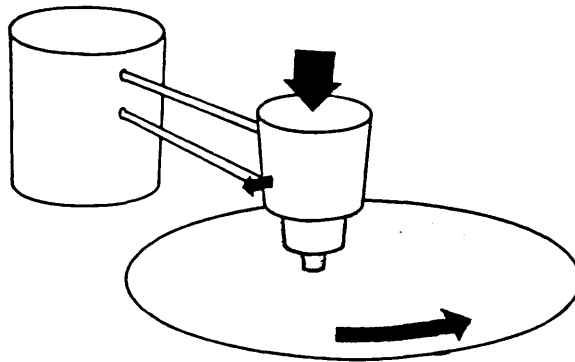


Fig.3.10. Test Equipment for Determining Abrasive Wear

3.4. RESULTS

3.4.1. Operating Parameters

3.4.1.1. Alteration of Scan Velocity

Controlling velocity allows interaction time effects to be studied at constant power intensities.

3.4.1.1.1. Surface Melting

Grit blasted and oxidised substrates of pure Al and Al-10Si alloy were processed at various scan velocities using power combinations of 0.95 or 1.65kW with beam diameters of 1.5 or 3mm. The Al-10Si alloy melted more readily than the CP Al. Indeed, using 0.95kW, only the Al-10Si alloy could be induced to melt under scanning conditions. It is not clear whether this preferential melting is due to improved coupling through reduced reflectivity and melting point, or whether it is due to reduced thermal conductivity, or a combination of the effects.

Fig.3.11.a,b, illustrates the effect of 1.65kW, 1.5mm beam processing. Preferential melting of Al-10Si occurs across the whole range of scan velocities. Reducing velocity causes a relatively slight increase in melt depth and width, though the effect is more evident when considered in terms of cross sectional melt area (CSMA), Fig.3.11.b. Melting of CP Al does not occur at velocities faster than 100mm/s. Reducing velocity increases heating time and, hence, surface melting occurs. Melt width increases uniformly to ~1.4mm at 25mm/s; further widening by reducing velocity is minimal. Melt depth increases gradually to a maximum ~0.4mm at 2mm/s. The changes cause a 'steady' increase in CSMA as velocity decreases. The slopes of the CSMA plot for both substrates are similar and any difference in substrate properties would appear independent of scan velocity.

Use of 1.65kW, 3mm beam conditions showed improved melting for similar velocities, Fig.3.11.c,d. Melting of CP Al initiated at 160mm/s. Melting trends were otherwise similar, ie: preferential melting of Al-10Si and a gradual increase in melt depth and width with reducing velocity.

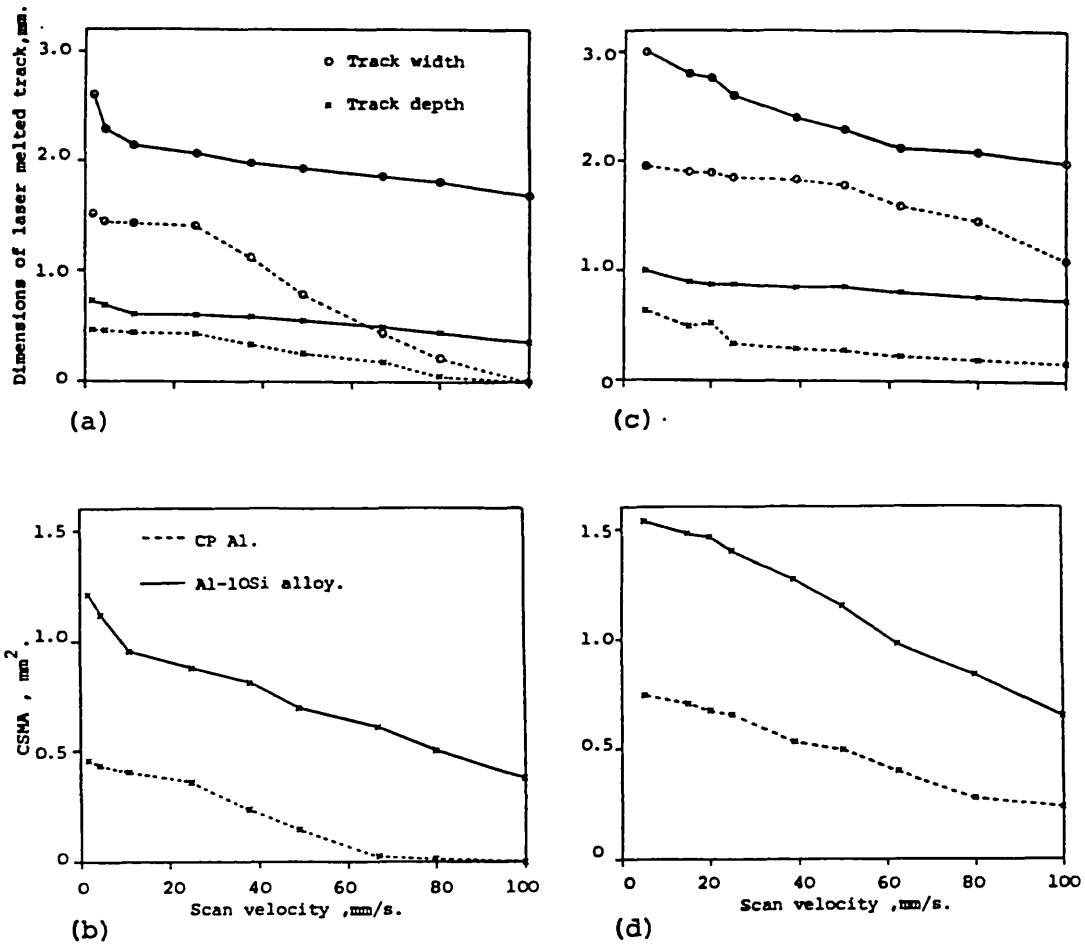


Fig.3.11. The effect of Scan Velocity on the surface melting of Uncoated Substrates.

(a) and (b) 1.65kW, 1.5mm.

(c) and (d) 1.65kW, 3.0mm.

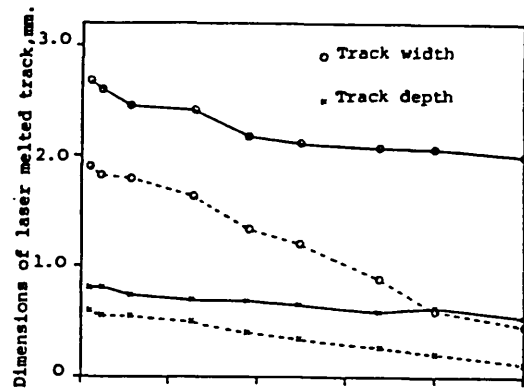
3.4.1.1.2.DAG Coating

Grit blasted and oxidised pure Al and Al-10Si alloy substrates were DAG coated and processed under the same conditions as previously described (3.4.1.1.1.). The objective was to observe the effects of DAG coating with changing velocity, and compare the results with previously processed uncoated specimens.

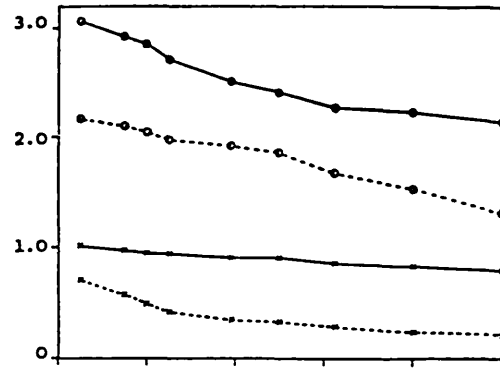
DAG precoating does induce greater melting, Fig.3.12.a-d. Melt widths, depths, and hence, CSMA, for both CP Al and Al-10Si alloy were seen to increase when DAG was used. The CP Al substrates are more sensitive to use of DAG coatings than the Al-10Si. CP Al was induced to melt at 160mm/s using a 1.65kW, 1.5mm beam and at 200mm/s using a 1.65kW, 3mm beam. CP Al was also induced to melt at low beam powers; at 25mm/s using 0.95kW, 1.5mm beam, and at 20mm/s using 0.95kW, 3.0mm beam. Reversal of melting efficiency with beam defocusing at low powers is discussed elsewhere (3.5.1.1.3.). Fig.3.12. illustrates the effect of DAG coatings using a 1.65kW, 1.5 and 3mm beams over a range of scan velocities. Melt depth and width show the same steady increase with decreasing velocity, the effect as mentioned being more prominent in CP Al substrates. Although DAG precoating alters the 'position' of the CSMA plots, it does not greatly alter their 'slopes', Fig.3.12.b,d. These same trends were observed on specimens processed at 1.45kW, 1.5mm and 1.56kW, 3.0mm.

3.4.1.1.2.Si Alloying

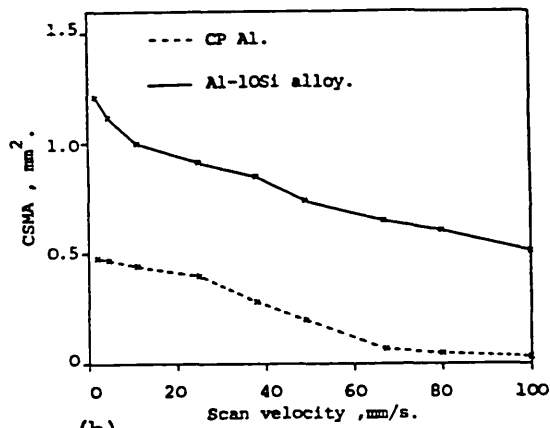
Grit blasted and oxidised substrates of CP Al, Al-10Si and C817 alloy were precoated with Si powder and processed at various scan velocities using power combinations of between 0.97 and 1.85kW with a range of beam diameters, 1.5 to 3.0mm. The level of Si alloying could be readily controlled by altering beam diameter and scan velocity.



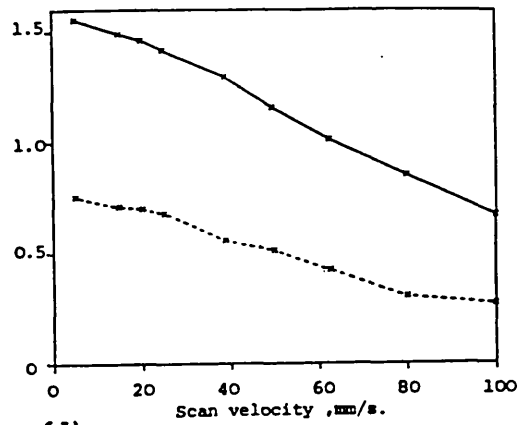
(a)



(c)



(b)



(d)

Fig.3.12. The effect of Scan Velocity on the surface melting of DAG coated substrates.

(a) and (b) 1.65kW, 1.5mm.

(c) and (d) 1.65kW, 3.0mm.

For a 1.5mm beam Si alloying was generally found to increase with decreasing velocity. This was particularly evident for samples processed at 1.85kw, 1.5mm beam, Fig.3.13. In processing at these conditions melt width was seen to increase evenly with decreasing velocity, but melt depth did not increase to the same degree, Fig.3.13.a. As velocity declined below 18mm/s melt penetration halved; below 6mm/s penetration recovered. Melt penetration is limited by the high thermal conductivity of Al alloys; neither hemispherical melting nor key-holing occurs: ie conduction limited melting dominates. Reducing velocity widens the melt zone but does not significantly deepen it, hence increasing the surface/volume ratios, so increasing the surface alloying ratio (previously discussed 2.4.1.1.). The ratio is further enhanced by preferential melting of the Si layer, ie: the Si melt track is wider than that of the melted substrate, Fig.3.13.c. At velocities 100 - 20mm/s this increases proportionally to the increasing substrate melt width, below 20mm/s the Si track widens at a greater rate. The level of alloying in the 100 - 20mm/s range is significantly less than might be expected, Fig.3.13.d, it is ~5wt%Si at 20mm/s while at 100mm/s negligible alloying occurs. If all the Si melted had alloyed with the track it should be ~30wt%Si at 20mm/s and considerably more at 100mm/s. In this velocity range alloying has been reduced by more than a magnitude; either it has been blown away by the shroud gas, vapourised, or insufficient melting has not allowed it to adhere to the substrate. At velocities below 20mm/s the amount of Si alloyed dramatically increases.

The fluctuation in Si alloying was initially assumed to be a freak result. However, the experiment was repeated six times (twice on each of the three types of substrate) and the fluctuation was seen to occur in each set of results, where beam diameters <2.0mm, at ~1.8kW. Fig.3.14. illustrates one series of Si alloyed tracks. The cross-sectional profiles of the individual tracks have been included and show the change in alloying mode and melt penetration with decreasing scanning velocity Fig.3.14.d.

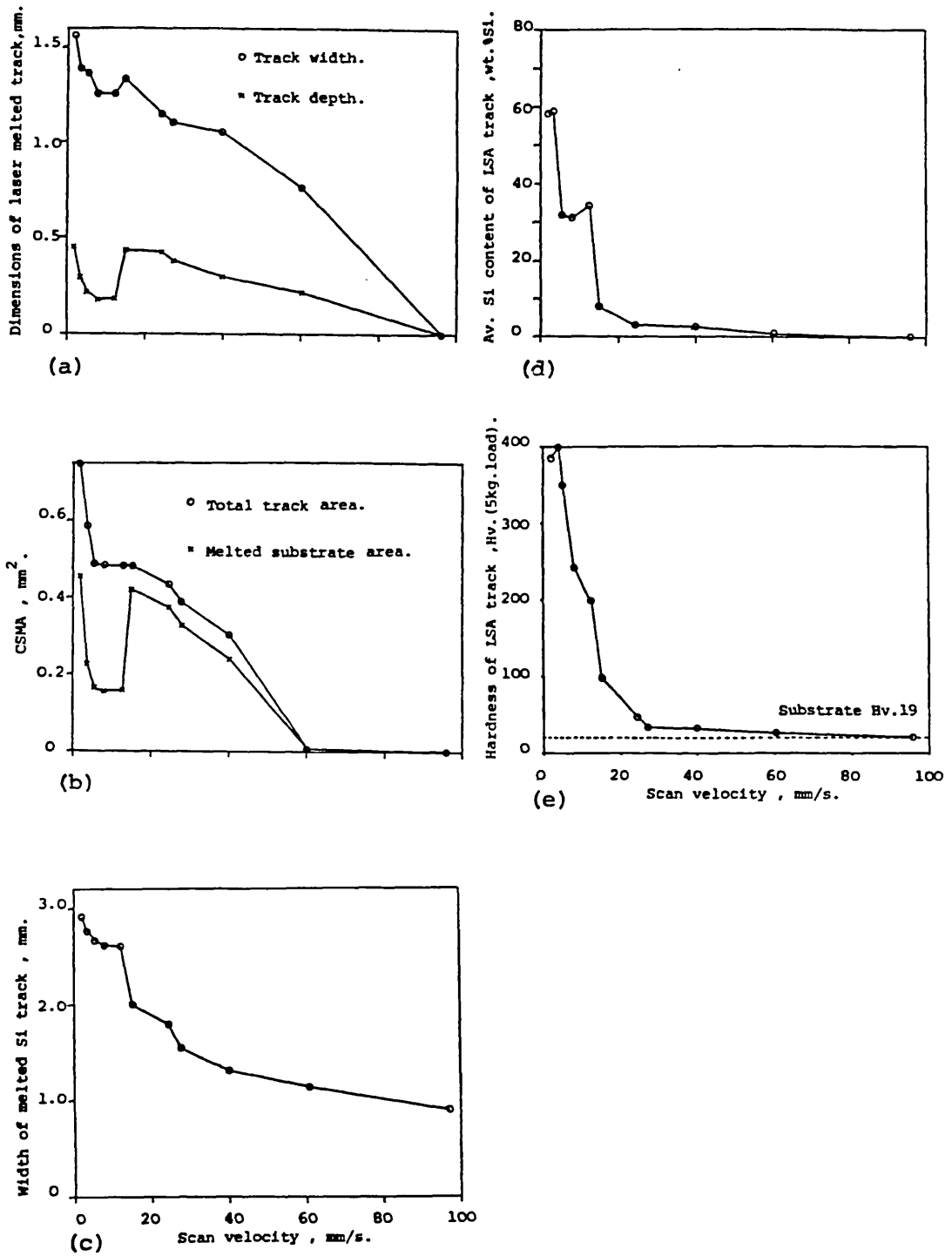
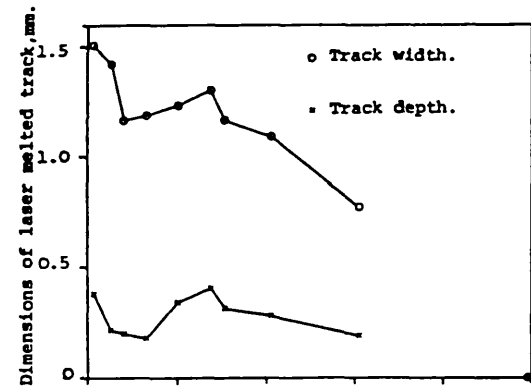
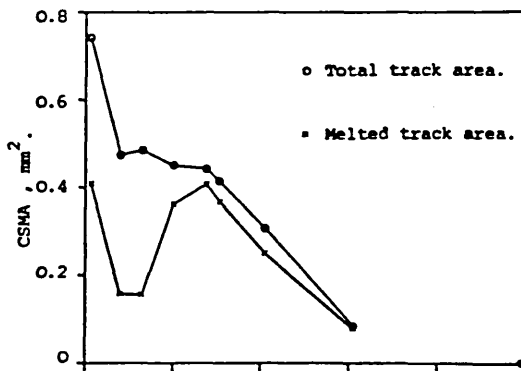


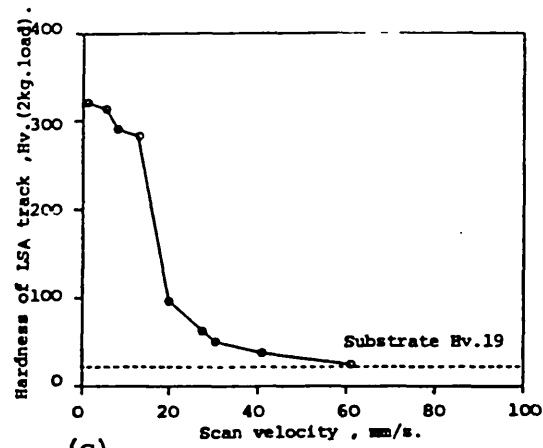
Fig.3.13. The effect of Scan Velocity on Si Alloying of C817 using 1.85kW and 1.5mm beam



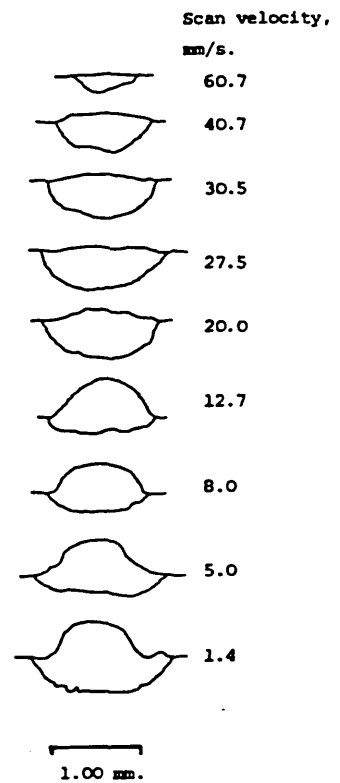
(a)



(b)



(c)



(d) Cross sectional profile of LSA tracks.

Fig.3.14. The effect of Scan Velocity on Si Alloying of C817 using 1.80kW and 1.9mm beam

It would appear that the fluctuation in melt penetration is a product of this high ratio alloying. It has been suggested¹⁷⁰ that at lower velocities the melt puddle may advance ahead of the beam drawing Si from in front of the shrouding gas flow. The true influence of an advancing melt puddle or the widening Si track is unknown. Surface tension does, however, draw greater amounts of Si into the 'substrate' melt track, the presence of which inhibits substrate penetration which in turn accentuates the increased alloying ratio. Reducing velocity (<6mm/s) further induces improved penetration which would locally reduce alloying, but other processes dominate, and the overall effect is for increased Si alloying. Figs.3.13.d,e, illustrate the regimes of Si alloying; low alloying, low hardness, above 20mm/s; high alloying, increased hardness, below 20mm/s. At 6mm/s, track composition was Al-60 Si, Hv 400.

Fig.3.15 illustrates the effect of using 1.8kW, 3mm beam, processing conditions. Substrate melting initiates at 140mm/s and steadily widens with decreasing velocity to a maximum of ~2.0mm at 5mm/s, penetration increases more gradually to a maximum of ~0.5mm at 5mm/s, Fig.3.15a. Fluctuations in penetration did not occur. The total volume of Si alloyed increased with decreasing velocity, Fig.3.14b. This increase is more gradual than when processing at 1.8kW, 1.5mm, since significant amounts of Si are alloyed at high velocities. While the 'high volume' Si alloying mechanism, previously seen to operate at low velocities, does not function under these conditions. As the velocity decreases the volume of substrate melted increases more rapidly than the volume of Si alloyed. Therefore, because of the dilution effect, the actual alloying ratio declines with decreasing velocity, Fig.3.15c. This is reflected in a decreasing hardness with decreasing velocity. Processing under these conditions is seen to be more effective at higher velocities and less effective at lower velocities. Similar results were obtained when processing was repeated on both CP Al and Al-10Si, using the same laser power and beam diameter.

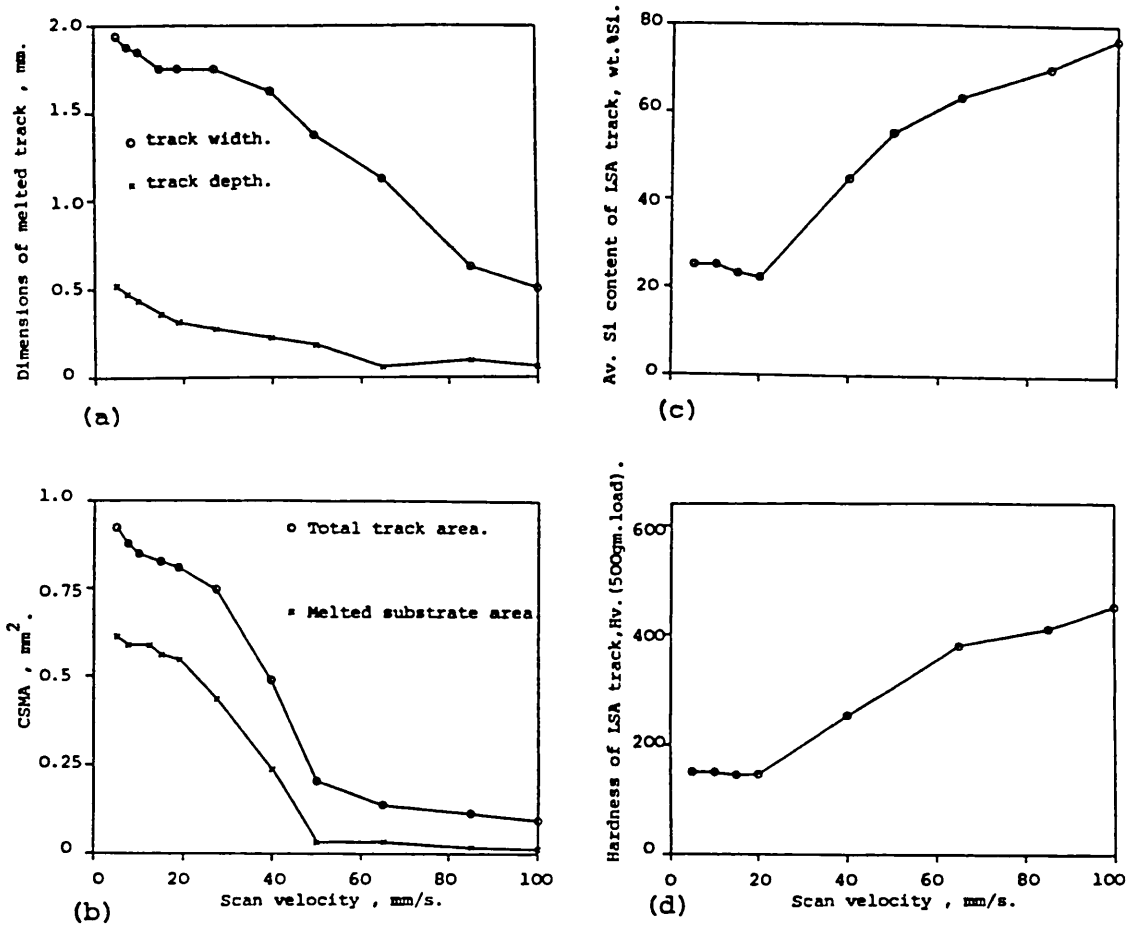


Fig.3.15. The effect of Scan Velocity on Si Alloying of C817 using 1.85kW and 3.0mm beam.

3.4.1.2. Recoating and Reprocessing

3.4.1.2.1. DAG Coating

CP Al and Al-10Si alloy substrates were recoated with DAG and reprocessed up to 8 times, the specimens being coated between successive processings. Both types of substrate behaved similarly, hence only one set of results is reported, Fig.3.16 (Al-10Si). The melt track width and penetration in pure Al was, predictably, less than that in Al-10Si alloy processed under the same conditions (3.4.1.1.2.). Successive reprocessing does enhance the volume of substrate melting, Fig.3.16a. The melt track widens with each reprocessing. Melt penetration is less sensitive and increases only slightly. However, the overall effect is for a general increase in CSMA, Fig.3.16b. The effect was seen to occur at various beam diameters. The more defocused the laser beam the greater the width and depth of the melted track, hence the greater the CSMA.

3.4.1.2.2. Si Alloying

C817 and Al-10Si alloy substrates were recoated with Si and reprocessed up to 8 times, the specimens being cooled between successive reprocessings. Both types of substrate behaved similarly and hence only one set of results is reported, Fig.3.17 (Al-10Si). The critical effect of 'beam focus' condition, reported elsewhere (3.4.1.1.3.) is illustrated. A 5mm diameter beam melts a wider and deeper track in the substrate than a 1mm beam. Slight widening and deepening of the melt track occurs with reprocessing, this being most evident in melt widening using a 5mm beam. In all cases the total Si amount alloyed increases with reprocessing, Fig.3.17b. Use of a 1mm beam induces 'high' volume Si alloying, reduced substrate melting enhances the 'alloying ratio'. Use of a 5mm beam induces low volume Si alloying; the alloying ratio is further reduced by increased substrate melting. Fig.3.17c illustrates the change in percentage Si alloyed. Using a 1mm beam Si alloying increases from ~19Si after 1 processing to 70Si after 8 processings, while using a 5mm beam Si alloying increases from 15Si to 28Si. Increased Si alloying is reflected by increased hardness, Fig.3.17d.

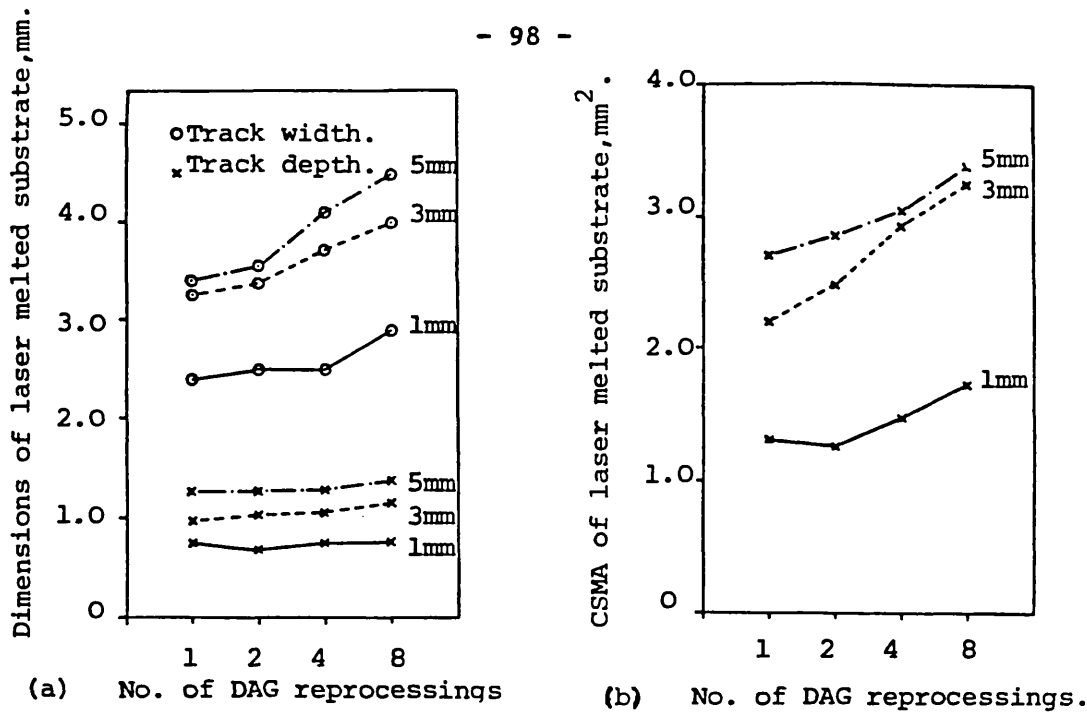


Fig.3.16 The Effect of DAG Reprocessing on Al-10Si Alloy Substrate,

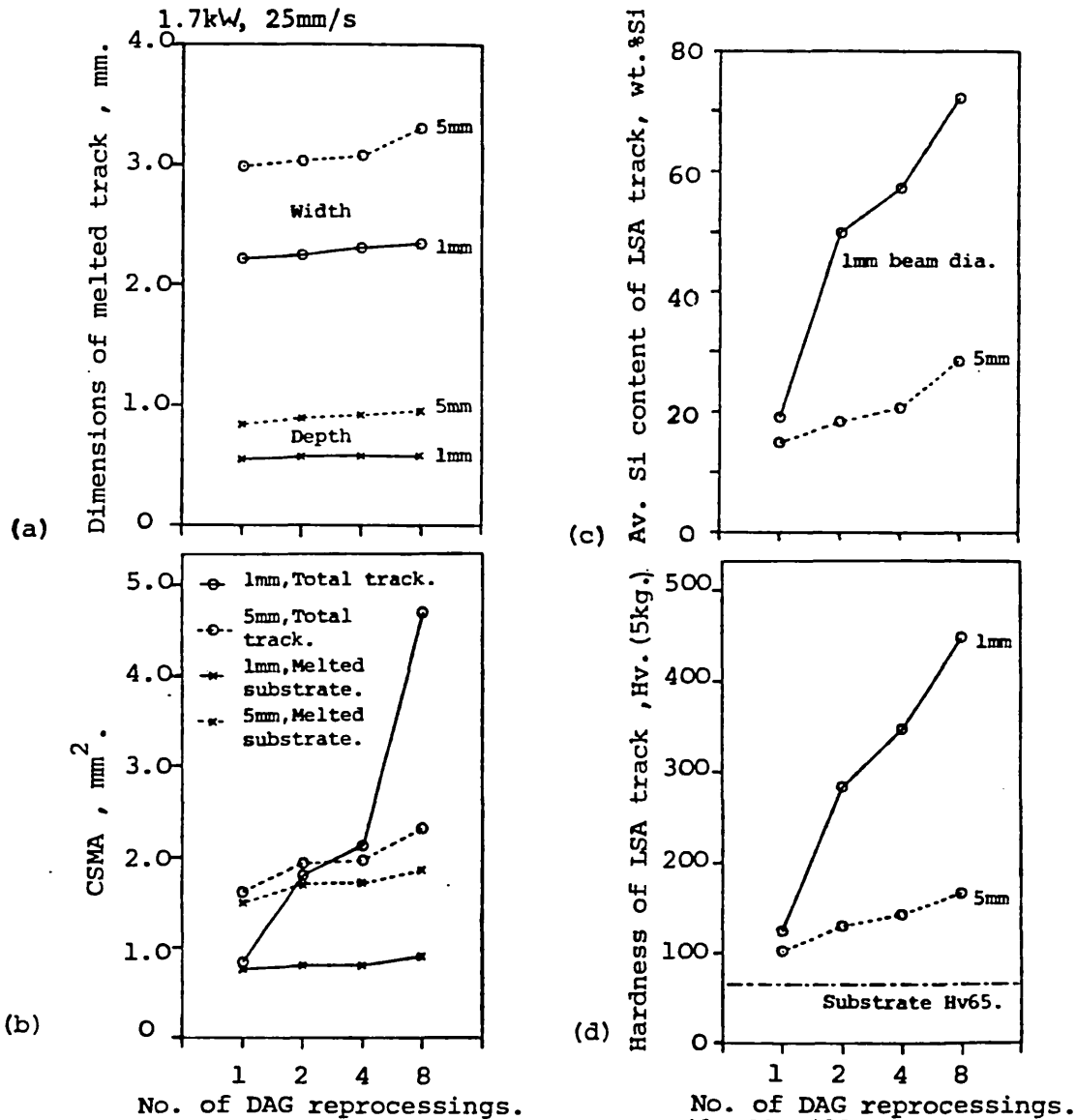


Fig.3.17 The Effect of Si Reprocessing on Al-10Si Alloy Substrate

1.7kW, 25mm/s

3.4.2. Microstructural Analysis

3.4.2.1. Hypoeutectic Al-Si Alloys

Limited Si alloying (using $\sim 1.8\text{kW}$, $< 2.0\text{mm}$, $> 25\text{mm/s}$), to either CP Al or C817, produced hypoeutectic alloys with a microstructure of superfine proeutectic Al dendrites in fine fibrous eutectic of Al + Si, Plate 9b. Identical microstructures were produced by laser melting Al-10Si alloy. Al-10Si was supplied as chill cast ingots with a microstructure of relatively coarse proeutectic Al in a coarse fibrous eutectic matrix. Laser melting refines the microstructure by $\sim 1/100$, Plate 9c-e.

3.4.2.1.1. Proeutectic Al

Fine proeutectic Al produced by laser processing grows directionally in individual colonies with a 'disfigured' dendritic morphology. On a microscopic scale these colonies solidify as lamellar sheets, which are tilted so as to freeze at an oblique angle to the vertical when viewed in both the longitudinal and transverse section, Plate 9f. Dendrites nucleate individually at the melt/substrate interface. Dendrite colonies are of consistent width, typically $9\mu\text{m}$, and extend over $100\mu\text{m}$ in both longitudinal and cross section, Plate 9e.

The growth front of the proeutectic Al comprises of many dendrite lamellar colonies advancing in a 'cellular' manner along a single front. Each colony behaves as an individual growth 'cell', Plate 10a. 'Belling' of dendrite branches and increasing secondary arm spacing indicates that the growth rate across individual colonies is not consistent but decreases as a function of distance from centre. This decrease in λ_2 is difficult to quantify although it can visibly be observed, Plate 10a. Since the branches grow, where possible, normal to the Al + liq - liq front, it follows that curvature of the branches increases progressively towards colony boundaries, Plate 10b. Each colony has a central 'spine' aligned perpendicular to the growth front where maximum growth velocity occurs. Side branches, growing at a curvature, lie in a plane of less favourable growth, hence their growth rate slows and they are overcome by new side branches nucleating on the advancing 'spine'.

There was a significant difference in secondary arm spacing for laser melted tracks produced using the same same laser beam conditions (ie fixed power and focus) but with varied scan velocities, specimens melted at higher velocities having finer spacings, Table 3.4.

Rapid cooling induces undercooling which, because of the skewing of the coupled zone, causes the volume of proeutectic Al to increase. Laser processing trebled the volume of proeutectic Al, Table 3.4.

TABLE 3.4. Microstructural Refinement of Laser Melted Al-10Si Alloy

The Vol Fract of Proeutectic Al was determined by Grid Measurement of Optical and SEM photos	Chill Cast Ingot	Laser Melted (1.65kW, 1.5mm)		
		12.5mm/s	27.5mm/s	60.5mm/s
Secondary Arm Spacing, μm	25 $\pm$ 1.5	1.43 $\pm$ 0.2	1.20 $\pm$ 0.2	1.04 $\pm$ 0.2
Vol of Proeutectic Al, %	20	60	60	60
Fibrous Eutectic Spacing μm	1.0 $\pm$ 0.12	0.14	0.10	0.08
HV (500gm)	64.0	67.5	69.5	68.0

3.4.2.1.2. Eutectic

The eutectic Si forms a continuous fibrous/rod network, Plate 10d. It is not possible to identify any nucleation relationship between the proeutectic and eutectic. However, it does appear that a Si rich eutectic 'band' forms preferentially around proeutectic Al, clearly seen in Plate 10d. Eutectic spacing was seen to change with changing scan velocity, Table.3.4. Increasing scan velocity increases R and refines the eutectic. Composition analysis of the eutectic using the JSM-35 probe analyser indicated that the eutectic composition had shifted significantly from equilibrium. The 'highest' eutectic composition measured for laser melted Al-10Si alloy (1.65kW, 1.5mm, 27.5mm/s), using the probe on an unetched specimen, was 24.7 Si. It was assumed that any low Si content values had been produced by analysing regions containing proeutectic Al. In comparison, a rough approximation of the SEM results, Plate 10a,b, indicates that the same

laser track consists of a minimum, ~60vol%, proeutectic Al. Therefore, the eutectic composition must consist of ~25Si.

3.4.2.2.Hypereutectic Al-Si Alloys

Highly alloyed tracks were readily produced by preplaced Si alloying. Plates 10e, 11a and 21a, illustrate the characteristic, 'rib-like', surface protrusions of these deposits. All tracks were totally free of cracking and virtually free of porosity. These hypereutectic alloys had a microstructure of proeutectic Si, proeutectic Al and fibrous eutectic Al + Si. Proeutectic Si was found to exist with either plate or dendritic morphology depending on the level of Si alloying. A distinctive Al shell coats the proeutectic Si and separates it from the eutectic. Inhomogeneous mixing of alloyed Si can result in an uneven distribution of proeutectic Si. This is seen to occur both as a function of track depth and as a function of relative position to track 'ripples'.

3.4.2.2.1.Proeutectic Si

The morphology of proeutectic Si was found to vary with the amount of Si alloyed rather than differing processing conditions. Where the amount of proeutectic Si exceeds 30vol% the proeutectic phase occurs as large directionally orientated plates (>500 μ m long) Plate 11, 12a. Individual grains nucleate at points near the melt/substrate interface, and grow upward at a 'slight' angle to the vertical (when viewed in the longitudinal section, Plate 11f.). 'Plate-like' Si growth is anisotropic and initially grows along the most favourable plane closest to the optimum thermal gradient. Further Si growth may cause this direction of growth to become less favourable. New Si plates nucleate on the edges of the existing plates. Growth favours these reorientated plates which grow more closely to the thermal gradient. The actual freezing rate of the idiomorphic plates illustrated, Plate 11f, can be 'geometrically' approximated as being greater than 3mm/s for a sample traversing at 10mm/s, Fig.3.18.

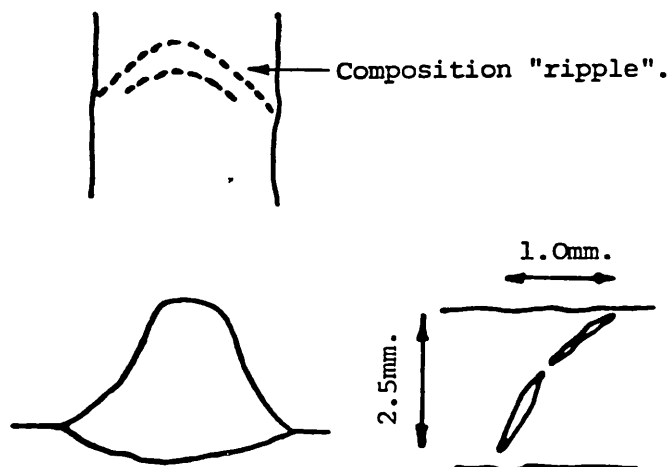


Fig.3.18 Rough Determination of Freezing Rate of Melt Track, Plate 11 (1.8kW, 2.5mm, 10mm/s). The max melt pool length according to Hawkes¹⁰⁹ is 2-3 times beam diam, therefore (from Fig.2.16) solidification rate >3.3mm/s. Although this track is for a multi-processed track, metallurgical analysis suggests that melting during the final run extended to 0.9 of the full length of the alloyed track.

Where the amount of proeutectic Si is less than ~30vol% the proeutectic phase forms as dendrites. Melt track rippling causes uneven mixing of the alloyed Si. This is seen in plan sections of highly alloyed specimens, Plate 11a,b. Proeutectic Si is seen to form as rosettes in regions of depleted Si content (in regions of low volume fraction proeutectic Si, Plate 11a,b.). Faceted dendrites of the form described by Wagner and Fredriksson¹⁵⁰⁻¹⁵² have nucleated and grown 'almost' vertically from near the melt/substrate interface and are, therefore, only evident in the plan view. Close to the melt/substrate interface polyhedral Si and twinned polyhedral particles are observed, Plate 10e, 11d.

The growth mode of 'dendritic' Si is illustrated, Plate 12c-f, 13a. It appears that Si forms as a polyhedron (Plate 12c), twinning occurs (Plate 12e), producing a star-shaped crystal (Plate 12f), which grows as a faceted dendrite (Plate 13a).

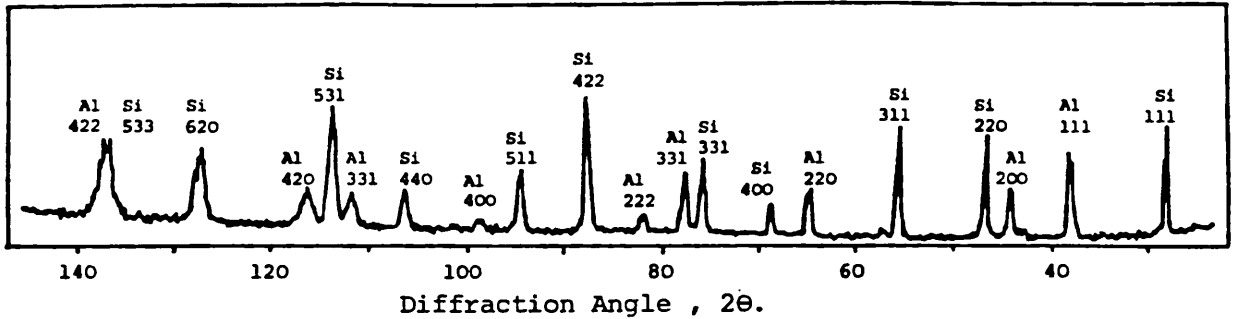


Fig.3.19 X-Ray diffractometer analysis of 72Si alloyed to Al-10Si, 8 reprocessed runs (1.7kW, 1mm, 25mm/s). Radiation source: Cu.

3.4.2.2.2. Proeutectic Al (in Hypereutectic Alloys)

As proeutectic Si precipitates the liquid composition approaches the eutectic. A consequence of rapid cooling is that undercooling below the eutectic temperature occurs. The Al-Si eutectic exhibits a skewed-coupled zone and undercooling induces proeutectic Al dendrite formation. In hypoeutectic alloys proeutectic Al nucleates at the melt/substrate interface and grows in dendritic colonies, Plate 9.e. In low Si hypereutectic alloys (<5vol% proeutectic Si) proeutectic Al grows in a similar fashion, independently as undistorted dendrite fronds, Plate 13c. Where a front intercepts a proeutectic Si crystal, local misgrowth occurs, the obstacle is 'by-passed' and growth continues in the original direction, Plate 13c. In high Si alloys, where plate-like Si forms, 'disruption' is greater and proeutectic Al appears to nucleate from a Si depleted Al 'shell' surrounding proeutectic Si, replacing the directional 'frond' network with a localised dendritic network, Plate 12b-f. Disruption due to the presence of proeutectic Si makes measurement difficult. It is not possible to assess whether secondary arm spacing varies with composition.

3.4.2.2.3. The 'Al Shell'

As solidification proceeds the liquid surrounding proeutectic Si becomes depleted in Si. Cooling below the eutectic temperature causes Al to nucleate and grow preferentially. This produces scalloped Al zones around proeutectic Si, Plate 12c-f. The variation in shell thickness on any one specimen is so large as to make any mean variation with scan velocity or composition unmeasurable. For Plate 12c-f the

shell thickness is $1.0 \pm 0.4\mu\text{m}$. The Al 'shell' is not part of the eutectic, it is proeutectic Al and a product of proeutectic Si growth.

3.4.2.2.4. Eutectic

Eutectic Si nucleates from proeutectic Si and grows as rods, $0.1 - 0.2\mu\text{m}$ diameter, through the Al 'shell'. The nature of initial eutectic growth suggests that eutectic Si either precedes or grows in unison with the Al shell. These eutectic Si rods appear to 'penetrate' the Al shell at regular intervals, though it is not clear whether this regularity is due to a concentration gradient or to the availability of nucleation sites (fault sites) on proeutectic Si. Edges and corners act as preferential growth sites, Plates 12c-f.

Eutectic Si radiates in 'fan-like' networks from the tips of the Si rods that 'penetrate' the Al 'shell', Plate 12c, d. Colonies expand by continual branching and outward growth. Colony size varies with proeutectic Si spacing but typically grow to $3 - 5\mu\text{m}$. Eutectic spacing does vary considerably with total alloyed Si composition. The nature of eutectic growth makes measurement difficult; however, spacings for differing compositions processed under the same conditions have been estimated, Table 3.5. This is also shown in the relative difference in refinement between Plates 10d and 12d.

C817, as mentioned (3.3), contains both Mn and Fe. In the case of the binary Al-Si alloy a simple Al-Si binary eutectic formed. Mn and Fe additions produce a ternary compound $\text{Mn}_3\text{Si}_2\text{Al}_{12}$ in which Fe may replace a proportion of the Mn. Crystals tend to be bounded by {111} faces and appear as well formed hexagons¹⁷¹ within the eutectic, Plate 13d.

TABLE 3.5. The Effect of Alloy Composition on Fibrous Eutectic Spacing
Si alloyed to Al-10Si (1.7kW, 1.0mm, 25mm/s)

Measurements Taken from Deep Etched SEM's (Average Taken from up to 20 m'ments)	Average Track Composition (wt % Si)	Average Eutectic Spacing (μm)
Surface Melted	10	0.10
1 alloyed run	19	0.17
2 " runs	50	0.30
4 " "	57	0.37
8 " "	72	0.48

3.4.3. X-Ray Diffractometry

Si alloyed tracks that had been reprocessed 1, 2, 4, and 8 times were analysed. fcc Al peaks 'weakened' with increased Si alloying while cubic Si peaks 'strengthened', Fig.3.19. The average lattice spacings for either Al or Si did not vary between samples¹⁷⁴ and was found to be:

For Al

Expt.Spacing 4.050°A (using CuK α = 1.5405)
Ref.Spacing¹⁷² 4.0494°A (using CuK α = 1.5405)

For Si

Expt.Spacing 5.434°A (using CuK α = 1.5405)
Ref.Spacing¹⁷³ 5.4301°A (using CuK α = 1.5405)

While solid solution of Al in Si is unlikely¹³⁷, that of Si in Al is known to occur. The experimental results for Al are considered to be within an acceptable experimental error indicating that solid solution does not occur. If the experimental results are taken at 'face-value', since solid solution of Si in Al would decrease lattice spacing rather than increase it, Si solid solution is not apparent.

3.4.4. Wear Results

Abrasive pin and disc tests were carried out on laser alloyed specimens containing 50Si, 32Si, laser melted 10Si, as supplied 10Si and as supplied CP Al. Increased Si alloying was a major factor in reducing wear, Table 3.6.

TABLE 3.6. The Effect of Alloyed Si on Abrasive Wear

Load: 3kg Disc: 800 grit		As Supplied CP Al	As Supplied Al-10Si Alloy	Laser Melted Al-10Si Alloy	32 Si (alloyed to CP Al	50Si (alloyed to Al-10Si Alloy)
Distance travelled to wear 0.1mm ³ of sample (m)	1	0.020	0.101	0.106	0.320	0.650
	2	0.021	0.089	0.110	0.405	0.681
	3	0.023	0.095	0.115	0.385	0.672
	4	0.023	0.098	0.111	0.390	0.690
	5	0.021	0.100	0.112	0.402	0.655
	6	0.021	0.100	0.106	0.401	0.003*
	7	0.020	0.097	0.108	0.382	0.671
	8	0.020	0.100	0.110	0.390	0.676
	9	0.022	0.095	0.106	0.300	0.667
	10	0.020	0.097	0.109	-	0.670
Average(m)		+0.0019 0.0211 -0.0011	+0.0038 0.0972 -0.0082	+0.0057 0.1093 -0.0033	+0.0267 0.3783 -0.0583	+0.0198 0.6702 -0.0202

*Sample fractured, data not used in average value.

Five Al-72Si wear specimens were manufactured but all specimens failed by brittle fracture before testing was complete.

3.5 DISCUSSION

Although interrelated three distinct topics for discussion emerge, processing parameters, microstructure and physical properties. The first considers the parameters affecting substrate melting, Table 3.7, and any associated effect on Si alloying. The second examines the salient microstructural features of laser melted and Si alloyed Al-Si alloys. The third considers the effect of Si alloying on physical properties, in particular wear rates.

3.5.1. Processing Parameters

3.5.1.1. Substrate Melting

3.5.1.1.1. Substrate Composition

The depth and width of the laser melted track is always greater for Al-10Si alloy substrates than for CP Al substrates, processed under the same conditions. Preferential melting of Al-10Si alloy occurred at all processing conditions, on both non 'DAGed' and 'DAGed' samples.

Preferential melting was most noticeable when using a more focused beam on 'non DAGed' samples; significant melting of CP Al only occurs at low scan velocities, Fig.3.11a, b, Table 3.7. A magnitude decrease in scan velocity doubles the melt volume of Al-10Si alloy but causes a magnitude increase in CP Al melting. The lower melting point and reduced thermal conductivity of Al-10Si alloy appear to enhance melting. This does not explain the magnitude rise in melt volume of CP Al, which is presumably due to improved beam coupling. Al-10Si, as a metal alloy, is 'less' reflective and couples at higher scan velocities, hence coupling efficiency is less susceptible to changes from fast to slow velocity. Decreasing scan velocity increases beam coupling with CP Al and so causes a dramatic increase in melting. At lower traverse velocities beam coupling of the two alloys more closely approaches 'unison', and the melting point and thermal conductivity difference becomes a more important factor, Table 3.7. Snow and Breiman²² commenting on a laser welding study of Al alloys observed an increase in penetration in higher Mg alloys. Whether this is due to reduced reflectivity or reduced melting point temperature is not clear.

TABLE 3.7 EFFECT OF PROCESSING PARAMETERS, SUBSTRATE COMPOSITION AND DAG COATING ON SURFACE MELTING

		1.65kW, 1.5mm		1.65kW, 1.5mm DAG Coated		1.65kW, 3.0mm		1.65kW, 3.0mm DAG Coated	
Traverse Velocity		CP A1	Al-10Si	CP A1	Al-10Si	CP A1	Al-10Si	CP A1	Al-10Si
100mm/s	Melt Width (mm)	-	1.68	0.43	2.00	1.09	2.00	1.32	2.15
	Melt Depth (mm)	-	0.36	0.12	0.54	0.17	0.74	0.22	0.80
	CSMA (mm ²)	0.02	0.37	0.03	0.505	0.235	0.65	0.27	0.67
	% of Largest Melt Vol	3.0	55.2	4.5	75.4	35.1	97.0	40.3	100
10mm/s	Melt Width	1.44	2.16	1.80	2.48	1.92	2.89	2.14	3.00
	Melt Depth	0.43	0.61	0.54	0.675	0.56	0.94	0.64	0.99
	CSMA	0.41	0.98	0.445	1.02	0.73	1.52	0.74	1.53
	% of Largest Melt Vol	26.8	64.1	29.1	66.7	47.7	99.3	48.4	100
% Vol Difference between 10 and 100mm/s		2,050	265	1,483	202	311	234	274	228

3.5.1.1.2. DAG Coating

DAG coatings reduce reflectivity and enhance substrate melting, Fig.3.11, 3.12, Table 3.7. DAG coatings are most effective where beam coupling is poor, eg where a 1.5mm beam is traversed at high speed. In such cases DAG coating enhanced melting by up to 50%; elsewhere, where coupling was more efficient, eg where a 3mm beam is traversed at low velocity, melting was enhanced by less than 5%. Repetitive DAG processing further enhanced substrate melting, Fig.3.16. Since Al and C do not produce a low melting point eutectic as do Al and Si, it is assumed that the increased melting is due to a change in substrate reflectivity induced by a changing substrate composition, or by reduced conductivity due to graphite inclusions (Appendix VI).

3.5.1.1.3. Power Density and Interaction Time

The threshold energy required for keyhole melting does not occur under the conditions examined; all melted/alloyed tracks are conduction limited. A real increase of melt width and penetration occurs as the laser beam is defocused. Widening of the melt zone is readily explained as a function of defocusing; however, it is usually assumed that a focused high power density beam produces a deeper melt track than a defocused lower power density beam.

Defocusing the beam lengthens interaction time, t , but reduces beam intensity, I . As t increases linearly with defocusing, I decreases by a factor r^{-2} since:

$$t \propto \frac{d}{V} \quad (3.17)$$

$$I \propto \frac{P}{\left[\frac{d}{2} \right]^2 \pi} \quad (3.18)$$

This effect is illustrated 'experimentally', Fig.3.20.

As conditions never approach keyholing and since the substrate melting point is comparatively low (CP Al 660°C, Al-10Si alloy 590°C), it may be argued that high beam intensity is superfluous. Presumably longer interaction time lengthens preheating, enhances absorptivity, and so increases melting. Under more focused conditions, melt zone superheating must take place. Indeed, substrate vaporisation was seen to occur when preheated CP Al was melted with a 0.6mm focused beam, nearly 20 vol% of the melted substrate being lost (Table 1.3). Although interaction time is, clearly, important, it seems unusual that deeper melt zones can be produced with a power of an order of magnitude less than at focus. High thermal conductivity must have a critical effect, minimising melting, enhancing the importance of absorptivity, so causing interaction time to be dominant.

There are other less plausible explanations. Penetration may be directly related to the melt zone, whether it be a function of geometry and mixing cycles, or by implication, that a wide melt caused by greater heat transfer should be a deeper melt. A focused beam may possibly enhance reflectivity, prematurely removing the oxide layer or preferentially 'smoothing' the substrate, although this seems unlikely to happen at specific beam conditions.

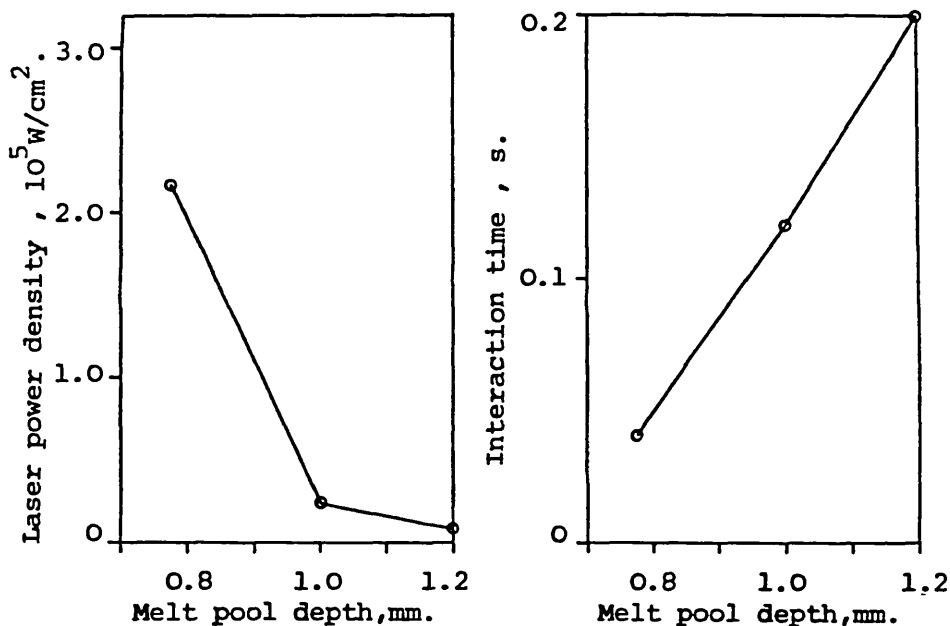


Fig.3.20. Relationship of Power Density and Interaction Time to Surface Melting DAG Coated Al-10Si
1 run, 1.7kW, 25mm/s (Fig.3.16)

3.5.1.2. Si Alloying

Increasing t by reducing scan velocity widens and deepens the melt track of uncoated and DAG coated substrates. When substrates are precoated with Si and processed using a $<2.0\text{mm}$ beam, this effect can be reversed. At rapid scan rates minimal Si alloying occurs and substrate coupling and melting dominate. At slow scan rates, critical coupling is achieved, the Si melt path widens and Si alloying increases. Reduced substrate melting further accentuates the Si alloying ratio, although because of increased Si alloying the total melt track volume remains 'roughly' constant, Fig.3.13b. Processing, using a 1.5mm beam ($I = 1.02 \times 10^5 \text{ W/cm}^2$) Fig.3.13, occurs over 3 regimes:

t, sec

- | | |
|---------------|--|
| <0.08 | <u>Substrate melting.</u> Minimum Si melting and minimum Si alloying, $<10\text{Si}$ alloyed. Substrate melting increases with decreasing scan velocity. |
| $0.08 - 0.35$ | <u>Si alloying.</u> Si alloying increases and substrate melting decreases. High Si alloying, $\sim 50\text{Si}$. |
| >0.35 | <u>Substrate melting and Si alloying.</u> Volume of Si alloyed stabilises, substrate melting increases with decreasing scan velocity. |

The region of greatest superheat lies along the centreline of the melt track; it is suggested that surface tension draws the molten Si inward producing highly alloyed tracks which form as smooth protruding ribs. Si has a relatively low density and when preplaced it is vulnerable to 'erosion' by the shrouding gas. If Si is lost in this way then it would explain the loss of Si at high velocities. At lower velocities Si is presumably melted outside of the nozzle shroud, either at the sides (widening the Si melt path), or ahead of the advancing beam ahead of the (advancing melt puddle). The molten Si is then drawn into the shroud as liquid and is, therefore, not lost.

A different alloying situation exists when processing Si precoated substrates with a 3mm beam, Fig.3.15. Melt track penetration and width increase with decreasing scan velocity. The amount of Si alloyed also increases with decreasing scan velocity, but because Si alloying increases at a slower rate than substrate melting, the Si alloying

ratio declines (2.5.4.). Megaw et al¹⁷⁵ experimented with surface alloying of preplaced Si to Al. They reported that the percentages of Si in the alloyed track increases with scan velocity, Fig.3.21. Likewise, hardness increases with the percentage of Si alloyed. Megaw et al describe this as being caused by dilution of the substrate:

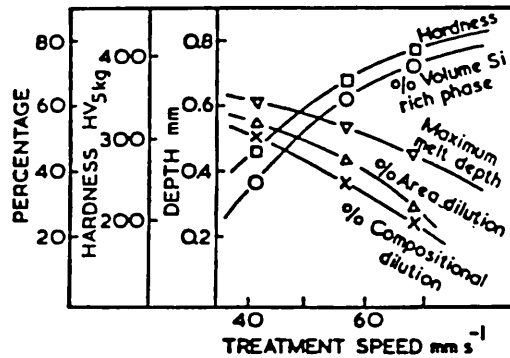


Fig.3.21.¹⁷⁵ Variation of Si alloying and properties with scan velocity; according to Megaw et al.

Defocusing the laser beam from 1.5mm to 3mm diameter involves raising the laser head from the work table, increasing the distance from the 'nozzle' to the substrate. This may sufficiently reduce shroud gas impingement so as to prevent it eroding the preplaced Si layer before processing.

A simple experiment was carried out to assess this hypothesis. A specimen block of CP Al coated with Si was traversed at various velocities under the beam exit nozzle. The shrouding gas was blown through the nozzle at gas velocities used in previous experiments. The nozzle was adjusted to different heights above the workpiece, representing different focusing conditions. The laser was not 'fired', thus any loss of Si was due to gas erosion.

Gas erosion of the Si layer occurred at conditions equivalent to a 1.5mm focus condition. An unmeasurable, thin surface layer, was seen to be 'blown away' at velocities over the range 5 - 100 mm/s. No erosion was apparent at the 3.0mm focus condition.

If the erosion supposition were true, the results of specimens processed with a 1.5mm beam will be 'distorted'. However, this does not fully explain the high Si alloying regime at low velocities. In an

ideal situation, for decreasing velocity, the total percentage Si in the track would decrease because of substrate dilution, pass into the high alloying regime and so increase again.

The potential offered by optimising I and t, and the regimes of alloying were combined to determine the effect of beam focus condition on 'multi-realloying' of a single track, Fig.3.16. With repetitive use of a 1mm beam at 25mm/s the process operates in the Si alloying mode. The evidence that each successive alloying increases proportionally with each successive track is not clear. While reflectivity and thermal conductivity decreases with reprocessing (increased alloying) liquidus temperature rises. A 5mm beam at 25mm/s operates in the regime of high dilution so reducing the alloying ratio, hence successive reprocessing will allow only a gradual increase percentage Si alloyed.

3.5.2. Microstructure

3.5.2.1. Proeutectic Si

It has been suggested^{148, 152, 154} that the morphology of proeutectic Si is dependent on both alloy content and cooling rate. This report confirms a composition dependence and by implication a temperature dependence (since the liquidus temperature rises with composition). Different morphologies grow in discrete regions throughout the same melt, apparently determined by regional composition, Plate 11. In high Si regions massive proeutectic Si plates precipitate. Atasoy et al¹⁴⁸ suggest that these form by layer growth being bounded by {111} giving an octahedral growth habit. Fredriksson¹⁷⁶ suggested that the plates are made up of many 'thin' twins and that growth via TPPE could occur.

While the plate growth mechanism is unclear, that of dendritic proeutectic Si is more easily defined. Star-like Si, Plate 12f, originates from a nucleus with low energy {111} surface facets, that occurs as a decahedron formed by five tetrahedra in twin relationship¹⁷⁷. Undercooling induces anisotropic growth at corners and the precipitate grows as a star-like skeleton. If the leading edge of each arm were indented then this would provide a re-entrant edge for the TPPE mechanism; however, there is no evidence of this. It has been suggested elsewhere^{148, 152, 178} that with increased supersaturation

edges and corners become preferred growth sites causing the dendritic networks to propagate by layer growth.

Assuming growth velocity fluctuations are marginal then Atasoy et al's observations¹⁷⁸, Fig.3.5., suggest that Si composition is critical. Highly alloyed hypereutectic regions begin to solidify at higher temperatures than lower alloyed regions; hence the two proeutectic Si morphologies will nucleate and begin to grow at different temperatures. Although it is not possible to state the mechanisms of growth it is known that growth does occur by more than one mechanism.

3.5.2.2.Eutectic Formation

The eutectic grows as 'fibrous eutectic bushes'. Crosley and Mondolfo¹⁵⁵ suggested that proeutectic Si does not nucleate the eutectic, being isolated by the Al 'shell'. However, this is not so, Plates 12c-f illustrate how corners, edges and faults nucleate the eutectic. Fredriksson et al¹⁵² have demonstrated how the Al 'shell' spreads as a two-dimensional dendrite, eutectic Si nucleating between dendrite arms. Smith¹⁴² illustrates this in a 'classical' photograph of growth morphology, but does not comment on its relevance. Proeutectic Si contains twin planes and it seems not unreasonable that the intercepts of these twins at crystal faces should act as nucleation sites. The nucleation site illustrated in Plate 12d initiates at a fault or twin site. Plate 12e illustrates two Si crystals where eutectic initiation along individual faces are interrelated, possibly by 'regular' twin sites. Fredriksson et al¹⁵² have observed similar relationships over greater range in slow cooled alloys. The shape and location of the Al dendrite 'lobes' which comprise the Al 'shell' are clearly related to corners, edges and faults of the proeutectic Si. The interconnecting fibrous eutectic rods which extend through the Al 'shell' must, therefore, grow slightly ahead of the 'shell'.

Eutectic spacing is affected both by scan velocity, Table 3.4., and total Si alloy content, Table 3.5. It seems plausible that where eutectic spacing is controlled by Si alloy content it is the reduced thermal conductivity induced by increased Si alloying that reduces cooling rate, so reducing freezing rate and hence, increasing eutectic

spacing. It must, therefore, be assumed that the most rapid cooling rates are associated with low Si alloys. Consequently the eutectic composition of hypoeutectic alloys should have a higher Si content than hypereutectic alloys (assuming that the high Si content in hypereutectic alloys reduces GR).

3.5.2.3. Solidification Conditions

Eutectic composition, volume fraction of residual eutectic, and microstructural refinement can be used to estimate the cooling rate, freezing velocity and temperature gradient of the solidifying laser melted track. Secondary dendrite arm spacings and eutectic spacings are particularly sensitive, their spacings decrease with increasing beam scan velocity, Table 3.4. The solidification determinations previously reviewed, (3.3.), are used to estimate the conditions for solidification of laser melted Al-10Si alloy, Table 3.8. (The experimental data are listed, Table 3.4., 3.4.2.1.1., 3.4.2.1.2.)

The three methods of determining cooling rate produce different results, Table 3.8., but these differences are explainable. The experimentally measured eutectic Si composition is probably less than the true composition. Despite great care it is almost inevitable that a proportion of proeutectic Al was analysed (3.3.). Consequently the calculated cooling rate is less than the true rate. The fraction of eutectic is a visual 'approximation' and not an accurate measurement. A small discrepancy in f_{Eu} greatly affects the determined cooling rate value. It would appear that our estimation ($f_{Eu} = 0.4$, Table 3.4.) is greater than the true fraction, which is probably nearer $f_{Eu} = 0.3$. Secondary arm spacing measurements are extensive, Fig.3.9. Arm spacing was measured and is probably the most accurate method of determining cooling rate. Secondary arm spacings indicate that cooling rate increases with scan speed over the range $10^4 - 10^5$ K/s.

TABLE 3.8. CONDITIONS OF SOLIDIFICATION OF LASER MELTED Al-10Si ALLOY 1.65kW, 1.5mm

			Ref	As Supplied Chill Cast	LASER MELTED		
					12.5mm/s	27.5mm/s	60.5mm/s
Cooling Rate (GR) K/s	(1)	$\lambda_2 = 50 \text{ (GR)}^{-1/3}$	2	8.0 K/s	4.27×10^4	7.23×10^4	1.1×10^5
	(2)	$C_{Eu} = 10.9 \text{ (GR)}^{0.091}$	160	-	-	8.05×10^3	-
	(3)	$f_{Eu} = 1.25 \text{ (GR)}^{-0.13}$	160	31.0 K/s	6.40×10^3		
(R)mm/s		R=1.55 (Hawkes Value)	109 Fig.2.16	-	3.9	8.5	10.1
G K/mm	(1)	Using above		-	1.1×10^4	8.5×10^3	1.1×10^4
	(2)	Data where		-	-	9.5×10^2	-
	(3)	R is known		-	1.64×10^3	7.5×10^2	6.3×10^2
ΔT K		$\Delta T = 25 R^{0.5}$	145	-	50	72.5	80

An extrapolation of Steen and Hellawell's results¹⁴⁹ and Kurz's and Fisher's prediction¹⁴⁵ indicates that, for $C_{Eu} = 24.7\text{Si}$ (27.5mm/s), R lies in the range 10 - 100 mm/s, Fig.3.7. A rough approximation for eutectic spacing against Toloui and Hellawell's data¹⁵⁶, Fig.3.6., corroborates this estimation. Plate 9f illustrates the solidifying direction. Assuming that R is approximately the 'longest diagonal of a cube', then $R = 1.55$ times Hawke's value (2.5.2.2.). For surface melting of Al alloys melt depth is shallow. Assuming that melt pool is 2 times beam diameter then R will be less than scan velocity, Fig.2.16. If this assumption is correct then it can be shown that G is always very steep though it appears to decrease slightly with increased scan velocity. Laser melted tracks will always freeze as described by region d, Fig.3.3., with a fibrous eutectic.

Undercooling can be determined from R using Kurz and Fisher's relationship¹⁴⁵. Using this relationship, ΔT is found to increase with increasing scan velocity, Table 3.8. Crosley and Mondolfo¹⁵⁵ indicated that primary Al would nucleate the eutectic at undercoolings of 6K in unmodified alloys and 12K in Na modified. Laser processing produces undercooling far in excess of these values.

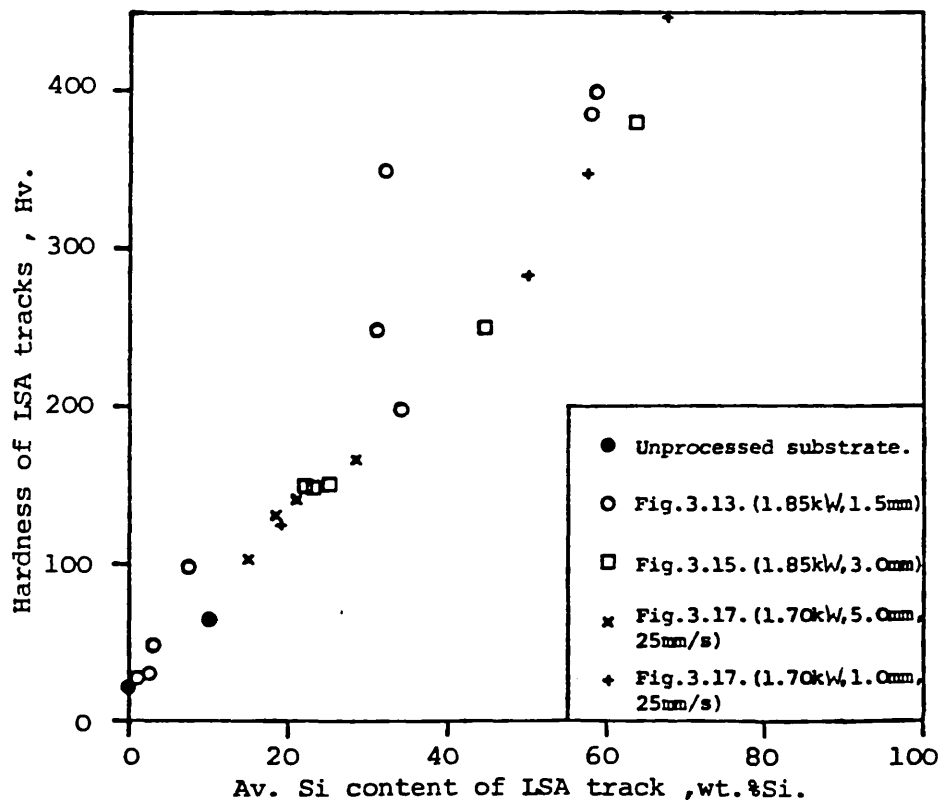


Fig.3.22 Effect of Increasing Si Content on Hardness
(Summary of all Si composition analysis)

3.5.3. Physical Properties

Rapid freezing imparts microstructural refinement which enhances strength and extends fatigue life, Table 3.1. Si alloying has been shown to increase surface hardness, Fig.3.13, 3.15, 3.17 (Fig.3.22. summarises all the experimental results of Si composition analysis) and wear resistance, Table 3.6, illustrating the precept that abrasive wear decreases as hardness increases. Fig.3.22. indicates that hardness increases linearly with Si content. The relationship is not affected by either hypo or hypereutectic, nor by the morphology of the proeutectic (dendritic or plate). An approximate value for hardness can be determined from the formula; $HV = 5.7wt\%Si + 20$. These results are in general agreement with those reported by Megaw et al¹⁷⁵, Fig.3.21, 3.23. Megaw reports that wear rates for laser Si alloyed Al-4.5Mg alloy approach 1/4 of the level of unprocessed substrate. Our results indicate that Si alloying to Al-10Si alloy can reduce wear to 1/6 of chill cast Al-10Si alloy. Using CP Al for comparison is unrealistic since its wear properties are extremely poor.

Very high Si alloys are associated with brittle fracture during wear. This could in part be related to the physical morphology of the proeutectic Si; dendritic proeutectic Si has been shown to fracture in a ductile dimple fracture, Plate 13b. Idiomorphic or plate Si found in chill cast high Si alloys is inherently more susceptible to brittle failure.

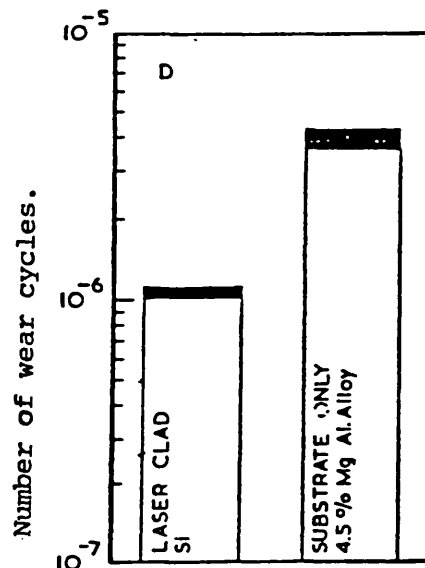


Fig.3.23¹⁷⁵ Relative wear performance of Laser Si alloyed Al-4.5Mg and unprocessed Al-4.5Mg

PLATE 9

- a. Si flame spraying powder 80/00 (used for preplaced alloying composition 99.995wt% Si, particle size $0.40 \pm 0.3 \mu\text{m}$)
- b. 5Si alloyed to C817 (1.8kW, 1.5mm, 17mm/s, unetched)
Porosity present in the substrate is reduced by laser processing.
- c. Al-10Si alloy (etch: 1 vol HCl, 1H₂O, 1C₂H₅OH). As supplied, chill cast condition, proeutectic Al dendrites in a fibrous Al-Si eutectic.
- d. High magnification section taken from centre of Plate 9c showing interface between proeutectic Al and eutectic Si. Deep etching has removed eutectic Al.
- e. Laser melted Al-10Si alloy. (1.65kW, 1.5mm, 27.5mm/s, etch: as 9c)
Interface of melt zone and substrate. Melt zone, (top left), fine proeutectic Al in a fine eutectic. Substrate, (bottom right), coarse proeutectic Al in a coarse eutectic.
- f. Topographic view of transverse section of alloyed track, Plate 9e, illustrating the growth morphology of proeutectic Al colonies.

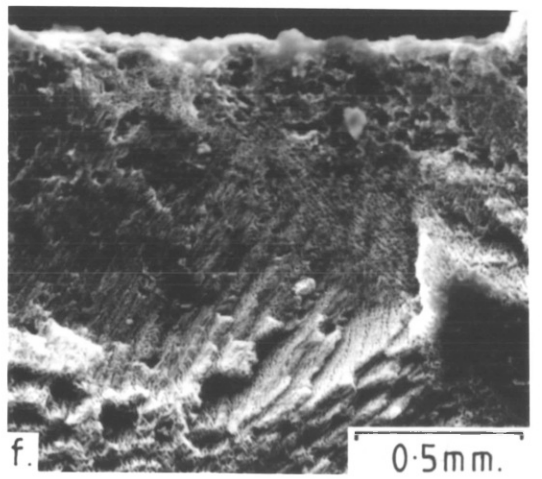
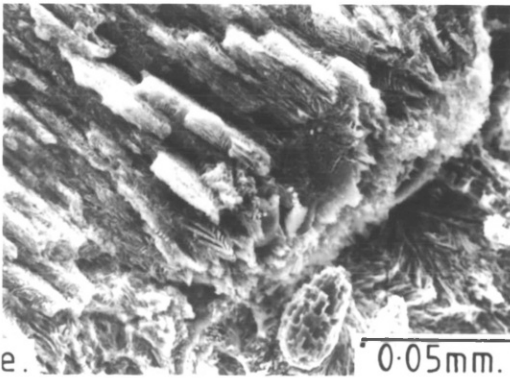
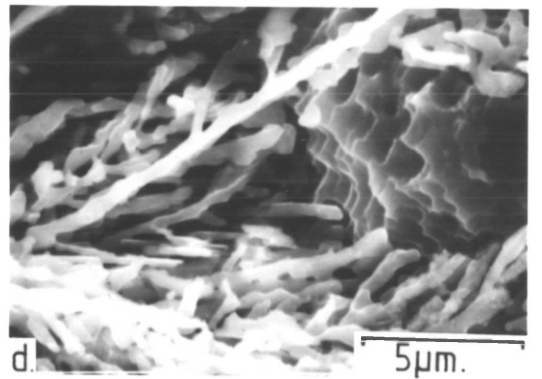
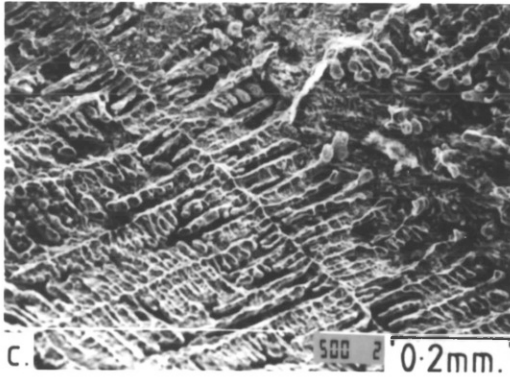
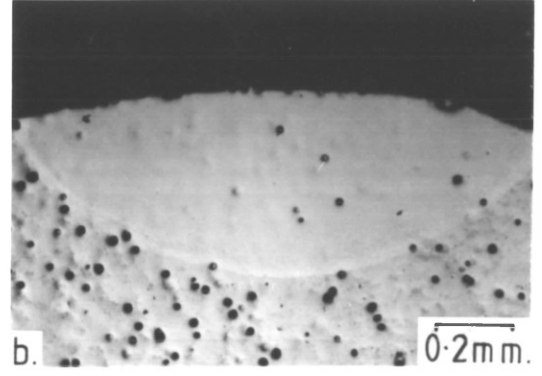
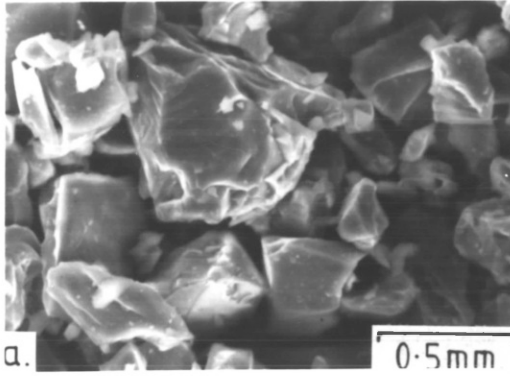


PLATE 10

- a. Laser melted Al-10Si (1.65kW, 1.5mm, 27.5mm/s, etch: as Plate 9c)

Proeutectic Al dendrite colonies near interface with surface.
The 'curved' growth fronts of individual colonies can be identified (top centre).

- b. High magnification view of Plate 10a, showing secondary dendrite arm growth of proeutectic Al.
- c. High magnification view of internal surface of 'pore' in laser melted track Plate 10a.
- d. Very high magnification section, taken from centre of Plate 10a, showing the fibrous eutectic and its relationship to proeutectic Al.
- e. ~50Si alloyed to C817 in a single run. (2.00kW, 2.0mm, 5mm/s)
Precise control of processing conditions can induce massive alloying with a single run, Fig.3.13, 3.14.
- f. High magnification view of melt/substrate interface, Plate 10e. Photograph shows transition from hypoeutectic (proeutectic Al, middle section) to hypereutectic (proeutectic Si, top section).

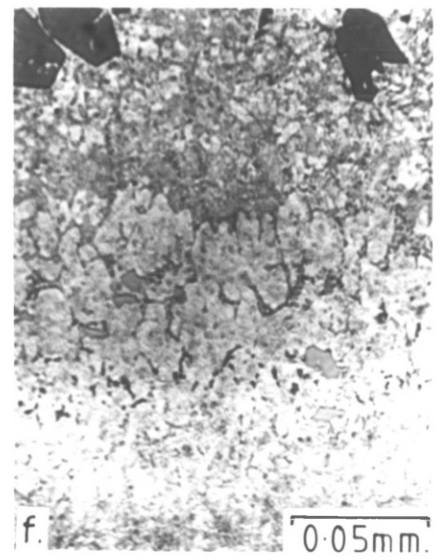
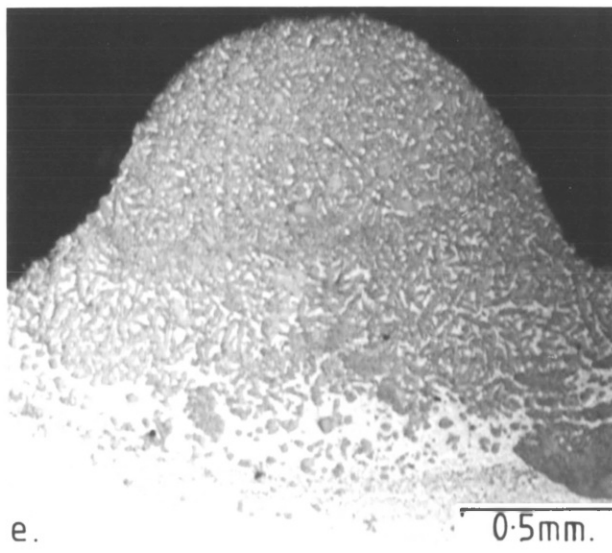
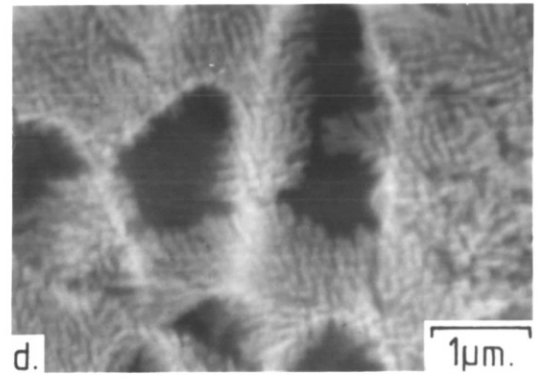
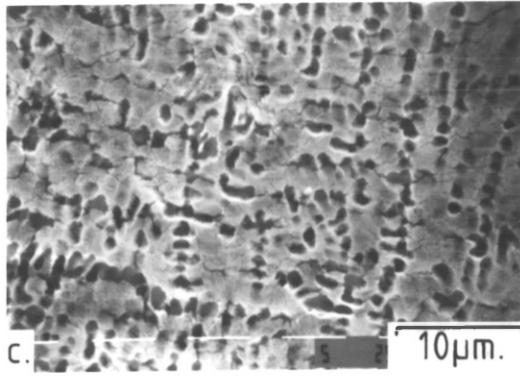
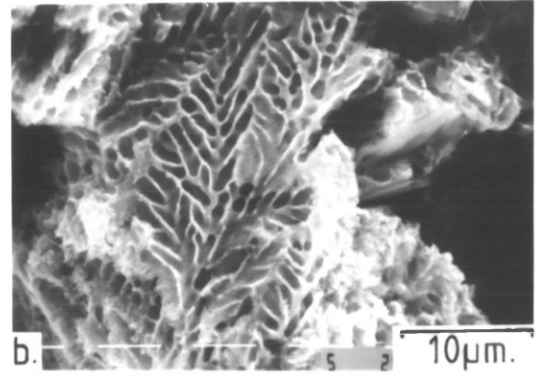
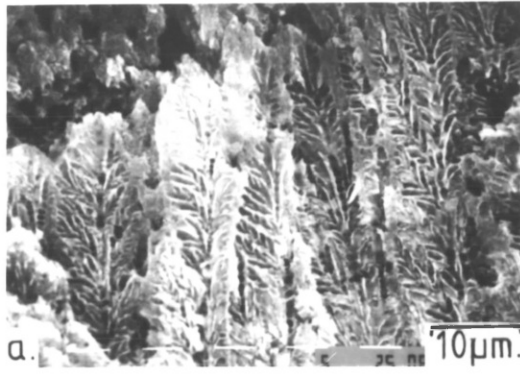


Plate 11

>50Si alloyed to C817 8 alloying runs (1.8kW, 2.5mm, 10mm/s, all specimens unetched).

- a. Plan section of alloyed track, subsurface rippling leaves 'horseshoes' of high Si, idiomorphic plates, interspersed with regions of low Si faceted dendrites.
- b. High magnification taken from centre of melt track, Plate 11a.
- c. Very high magnification taken from centre of melt track, Plate 11a, illustrating the characteristic rosette appearance of dendritic proeutectic Si.
- d. Transverse section of alloyed track, large 'plate-like' proeutectic Si precipitates.
- e. High magnification section taken from centre of melt track, Plate 11d, illustrates the faceted nature of 'plate-like' proeutectic Si.
- f. Longitudinal section of alloyed track, proeutectic 'plate-like' Si 'grows' towards the receding laser beam.
- g. High magnification section taken from centre of melt track Plate 11f.

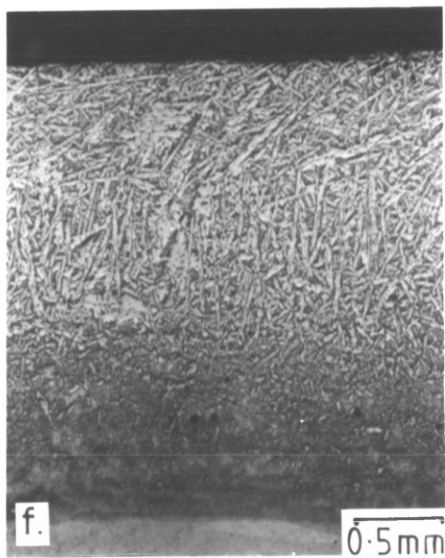
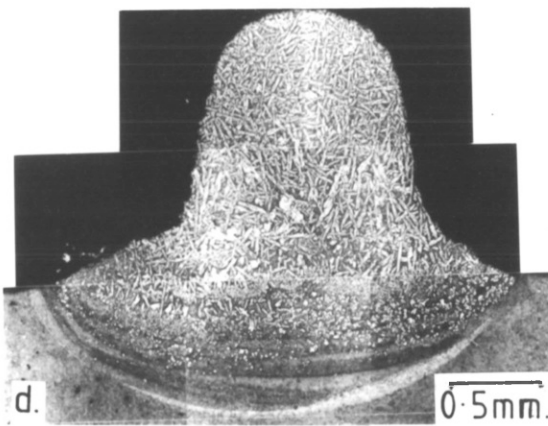
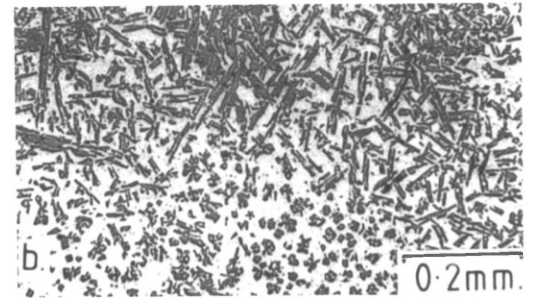
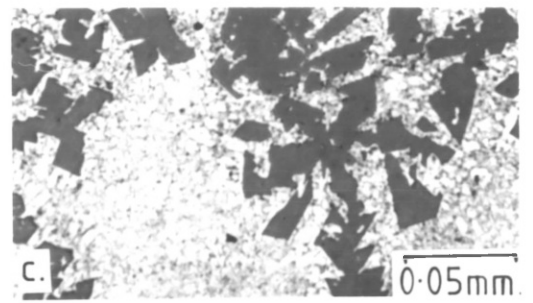
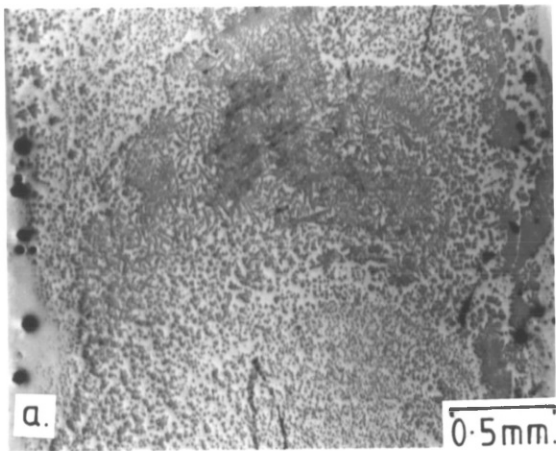


PLATE 12

>50 Si alloyed to C817. 8 alloying runs (1.8kW, 2.5mm, 10mm/s)

- a. Fractured longitudinal section of alloyed track illustrating the 'plate-like' nature of idiomorphic proeutectic Si (unetched).
- b. Fractured plan section of alloyed track illustrating proeutectic Si, proeutectic Al and eutectic (etch: 1 vol Hf, 1HNO₃, 5 Acetic)

32 Si alloyed to CP Al. 1 alloying run (1.8kW, 1.5mm, 8mm/s)
etched as Plate 12b).

- c. Proeutectic Si polyhedron, coated with an Al 'shell' in a fibrous eutectic.
- d. High magnification section of proeutectic Si/eutectic interface. Eutectic Si nucleates preferentially on proeutectic Si and spreads fan like.
- e. Twinned proeutectic Si polyhedrons. The Al 'shell' is particularly noticeable.
- f. 'Star-like' proeutectic Si precipitates, produced by multiple twinning.

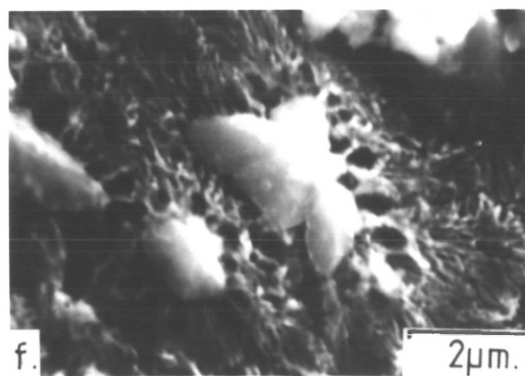
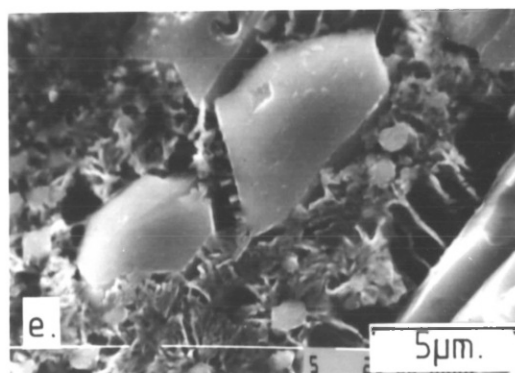
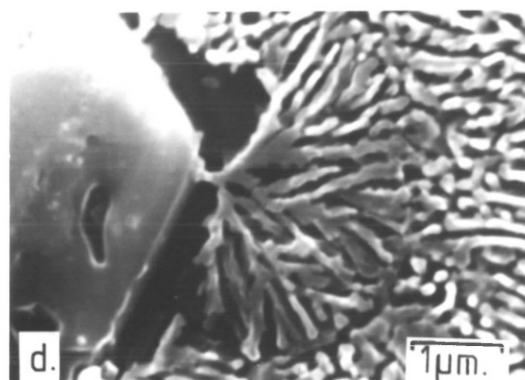
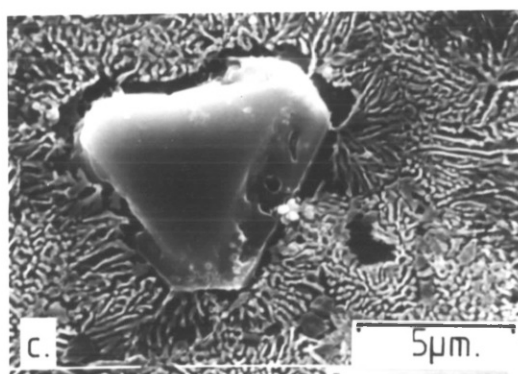
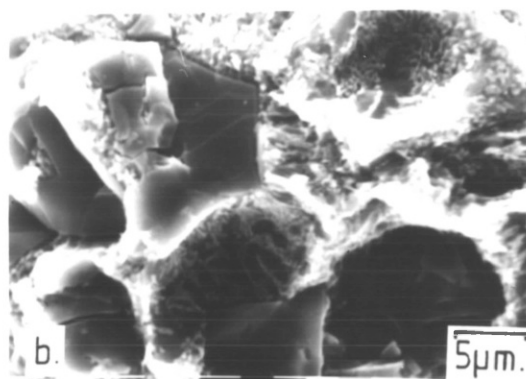
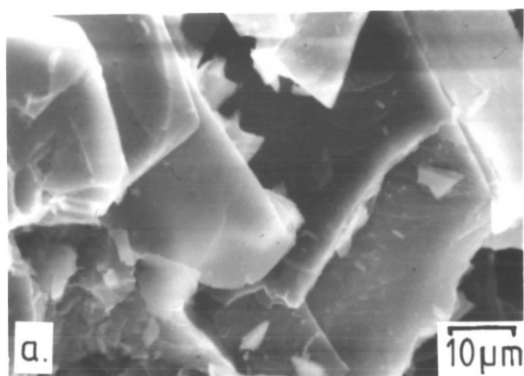
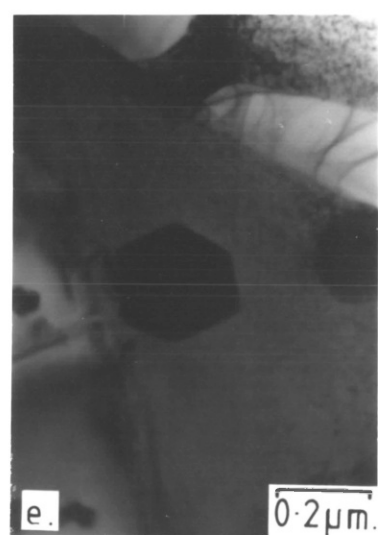
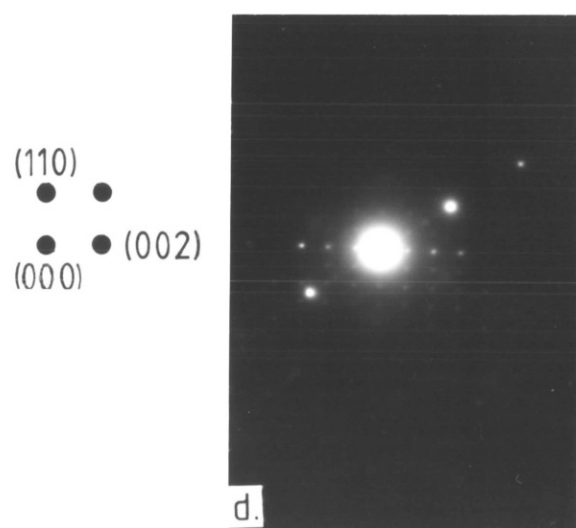
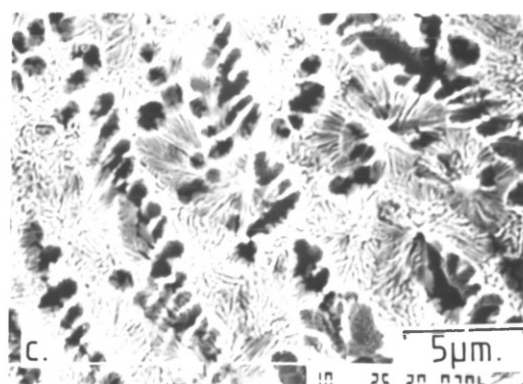
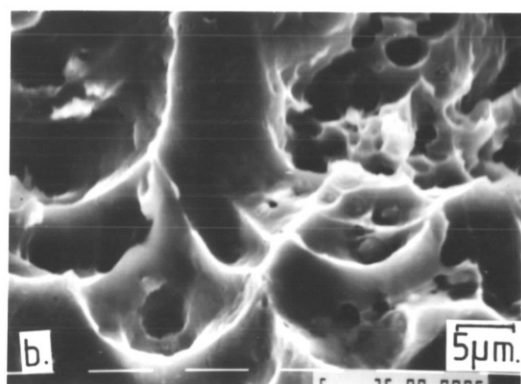
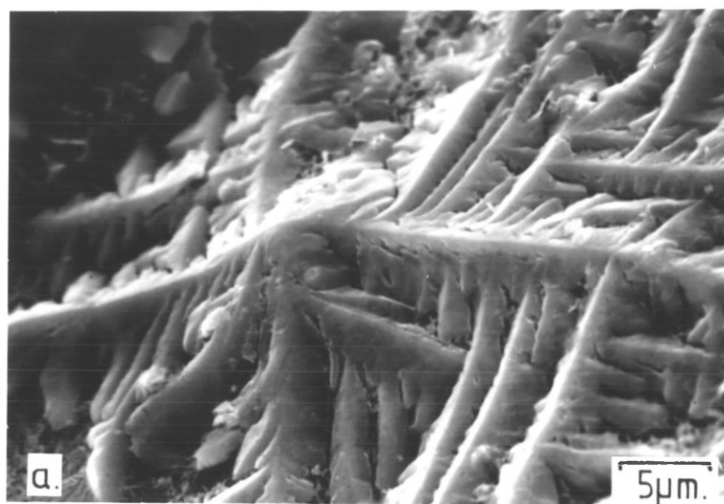


PLATE 13

32Si alloyed to CP Al. 1 alloying run (1.8kW, 1.5mm, 8 mm/s, etch as Plate 12b).

- a. Proeutectic Si precipitated with a faceted dendritic morphology.
- b. In hypereutectic tracks where proeutectic Si forms as faceted dendrites, the alloy track fractures in a ductile dimple fashion rather than a brittle cleavage.
- c. Si alloyed to Al-10Si alloy. 1 alloying run (Av composition ~ 19Si, 1.7kW, 1mm, 25mm/s, etch as Plate 12b).
The eutectic does not appear to nucleate on proeutectic Al.
This specimen contains small proeutectic Si 'precipitates' which are seen to act as nucleation sites for eutectic 'fans'.
- d,e. 36Si alloyed to C817. 4 alloyed runs (1.8kW, 2.5mm, 25mm/s)
TEM image of hexagonal $\text{Mn}_3\text{Si}_2\text{Al}_{12}$ inclusion in eutectic and associated diffraction pattern of $\text{Mn}_3\text{Si}_2\text{Al}_{12}$ inclusion.



4. SURFACE MELTING AND C ALLOYING OF Ti AND Ti-6Al-4V

4.1. INTRODUCTION

Development of Ti alloys for aerospace applications has expanded enormously over the past 30 years. Their use has revolutionized turbine engine manufacture and plays an increasingly important role in advanced air-frames. The high strength/weight ratio of Ti makes it particularly attractive. Conventional Ti alloys are unsuitable for moving contact faces¹⁷⁹, since high wear rates occur under conditions of sliding or fretting. While phase modification or solid solution strengthening can be used to improve fatigue life, ductility or yield strength, only limited solutions to reducing wear have been developed; ie hard particle surface injection. A method of laser surface alloying to enhance wear resistance is described here. Commercial purity (CP) Ti and Ti-6Al-4V alloy substrates were precoated with DAG graphite and laser surface melted. Structural studies including X-ray diffraction and electron microscopy showed how C alloyed to form TiC particles in a martensitic (hexagonal) matrix. Crack free surface layers up to HV650 were formed.

4.2. REVIEW

Ti undergoes an allotropic phase transformation from low temperature α (hexagonal) phase to high temperature β (bcc) phase at $\sim 880^\circ\text{C}$.

Alloying elements may be grouped as α or β stabilizers depending upon their effect on transformation temperature, ($T_{\alpha/\beta}$). Al, O, and C are α stabilisers and tend to raise $T_{\alpha/\beta}$, while V, which is a β stabilizer, depresses $T_{\alpha/\beta}$.

Inman and Gilmore¹⁸⁰ showed the the properties of Ti-6Al-4V (an $\alpha+\beta$ alloy) could be enhanced by heating to $843-1065^\circ\text{C}$ and then water quenching. Fatigue life increased by a factor of ten; in addition this treatment resulted in high ductility and tensile strength. Above a critical temperature ($\sim 820^\circ\text{C}$) β transforms to martensite during quenching. The authors concluded that these improvements were a results of strain induced transformation of retained β to martensite. In an earlier publication Williams and Blackburn¹⁸¹ reported two forms of martensite in Ti-6Al-4V, fcc or fct (α'') and hexagonal (α'). Ti-6Al-4V quenched from above 1000°C consisted of $\beta + \alpha'$. α' was seen to be highly dislocated although it contained only a limited number of stacking faults and twins. Lipscombe et al¹⁸² laser glazed IMI500 (an $\alpha+\beta$ alloy) and described the solidification mechanism where initial dendritic β solidification undergoes solid state transformation to martensite. TEM showed fine martensite plates, twinning and stacking faults. O contamination favoured stacking fault formation. Mazumder and Steen^{183, 184} produced high quality welds in Ti-6Al-4V. They carried out fatigue and tensile testing, and subsequently reported little difference in mechanical properties as compared with unwelded Ti-6Al-4V. O pick-up was minimised by He shielding. Breinan and Snow¹⁸⁵ introduced powder-feed LAYERGLAZE/Narrow-gap laser welding whereby Ti-6Al-4V powder was used as a filler in gap welding Ti-6Al-4V plates. The mechanical properties of Breinan's welds are comparable with Mazumder's¹⁸³. Bayles et al¹⁸⁶ report a decrease in fatigue life of laser melted Ti-6Al-4V. None of these workers appear to have optimised the improvement in mechanical properties by precise control of the β/α' transformation¹⁸⁷. Breinan¹⁸⁵ and Mazumder¹⁸³ report minimal O contamination; Bayles et al¹⁸⁶, who utilized He shielding, did not comment upon its effects. Limited O contamination can impart solid solution strengthening; however, excessive oxidation is

detrimental. If Bayles et al¹⁸⁶ allowed their specimens to cool outside the inert gas shield, surface oxidation (in addition to any O contamination during the 'molten/shielded' period) may have occurred. Above ~550°C Ti will absorb O and will form both an oxide scale and brittle sub-surface layers which can initiate surface cracking.

Elemental additions such as Be, Ce, Co, Er, Fe, Nd, Th and Y have been shown to induce the formation of fine incoherent dispersoids in rapidly solidified Ti alloys¹⁸⁸⁻¹⁹¹. Rapid solidification of Ti-1C produces a large volume fraction of such dispersoids which have been shown to increase the yield strength of Ti by 100% and modulus by 30%¹⁸⁹⁻¹⁹¹. Extended high temperature properties are attributed to the effectiveness of dispersoids as barriers to dislocation motion.

Ayers et al¹⁹²⁻²⁰⁰ impregnated substrates with carbide particles (size range 40-150µm) by laser melt/particle injection. Ayers used a 10kW laser, typically focused to ~3mm diameter, to surface melt shallow tracks across traversing specimens. At the same time TiC or WC particles, carried in He, were blown into the melt puddle^{192,196}. By overlapping successive runs extended surface areas were treated. The particles were generally retained in the injected form, though limited dissolution was reported. The processed layer consisted of particulate carbides in a martensitic matrix. Ti-6Al-4V injected with 30-50 vol% TiC showed a hardness of 460HV¹⁹⁵. The coefficient of friction of Ti-6Al-4V (0.4 measured in sliding contact with a 52100 steel) decreased with increasing content of TiC, reaching a minimum of 0.18 at 50 vol% TiC¹⁹⁴, Fig.4.1.²⁰⁰. Fine surface cracking occurred where tracks overlapped, while catastrophic cracking was prevalent in samples containing high volume fractions of TiC.

Although WC is the most widely used dispersion hardening carbide in wearfacing applications (Appendix II), TiC offers some obvious advantages²⁰¹. It has a higher heat of formation and is less likely to dissociate. Where WC dissociates Ti-W carbides form, the properties of which are unknown. TiC melts congruently and has a much wider range of homogeneity than WC, Fig.4.2. TiC is harder than WC and is sometimes regarded as 'over-brittle'; retention in a soft matrix should minimise this. TiC has a lower density than WC (TiC, $\rho = 4.93 \text{ g/cm}^3$ WC, $\rho = 15.70 \text{ g/cm}^3$)¹⁹ and on a volume basis it is less expensive.

This chapter considers the rapid solidification mode of Ti alloys and the advantageous effects of forming TiC particles. Graphite powder is laser alloyed to Ti alloys and TiC particles form either as proeutectic dendrites or as particulates precipitating via solid state diffusion along β grain boundaries. The matrix comprises of β transformed to martensite. Dendritic TiC is thought to be preferential to Ayer's arrangement of 'individual carbides' since the dendritic networks are more firmly embedded and ^{so} more resistant to abrasive wear. In addition this process appears less susceptible to cracking.

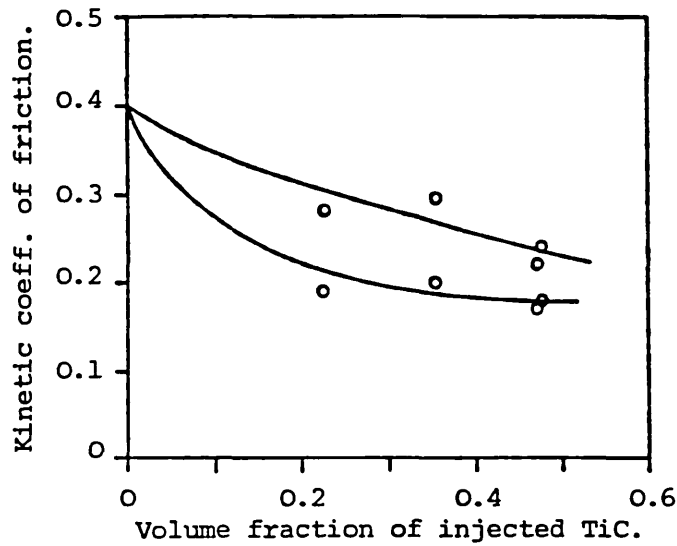


Fig.4.1.²⁰⁰ Kinetic Coefficient of friction for Ti-6Al-4V laser injected with different volume fractions of TiC. The lower values are from early measurements. The upper values are averages of more recent measurements.

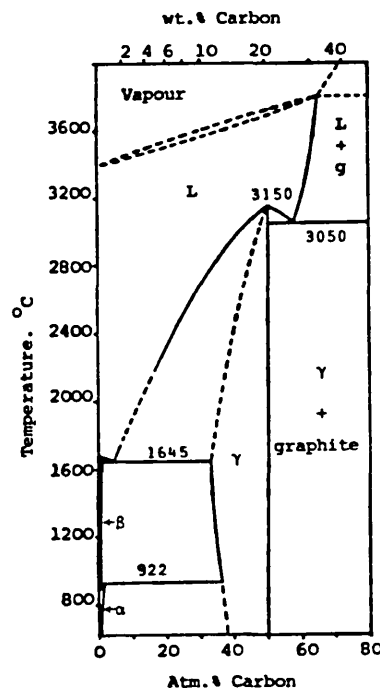


Fig.4.2. TiC Phase Diagram (combining data from Refs.202 and 203).

4.3. EXPERIMENTAL PROCEDURE

60 laser alloyed tracks were produced. Scan rates of 5-100mm/s were used in conjunction with beam diameters of 1.5-4mm and powers of 1.2-1.8kW. Interaction time and power density are discussed. The substrates used were commercially pure (CP) Ti and Ti-6Al-4V.

10mm thick grit blasted specimens, clamped to a cold steel plate, were painted with a DAG graphite/methanol solution (DAG coat, $0.010 \pm 0.002\text{g/cm}^2$ after methanol evaporation), and then laser melted using the 2kW CW CO₂ laser with a Gaussian mode. Successive overlapping laser treatments (up to 16) were given, a DAG coating being reapplied between each treatment.

Microstructural observations and microhardness measurements (100g load) were made on transverse longitudinal and vertical sections of laser alloyed tracks (as 2.3., 3.3.). For optical microscopy specimens were etched in 1 vol HF, 4 vol HNO₃ and 6 vol H₂O for ~5 sec. An SEM examination using the JEOL T200 scanning microscope was made of the same specimens after 'deep etching' in the same solution for ~30 sec. Primary and secondary dendrite arm spacings of TiC were measured in the same way as previously described (2.3.).

Dr H M Flower²⁰⁴ using the 1MeV AEI EM7 microscope undertook a TEM analysis of a high C alloyed Ti-6Al-4V track to identify phases and phase relationships; subsequently a microanalysis of the foil was made. 3mm TEM discs were cut parallel to the top surface of the alloyed track and thinned by the method previously described (2.3.).

Microstructural phases were initially identified by X-Ray diffraction, using the Philips Goniometer, fitted with a Co radiation source (2.3.). (TiC lattice distortions were observed and are discussed in terms of stoichiometry and TiC-VC binary carbide formation).

Wear tests using the same test apparatus as described elsewhere (3.3.) were carried out on a limited sample of specimens.

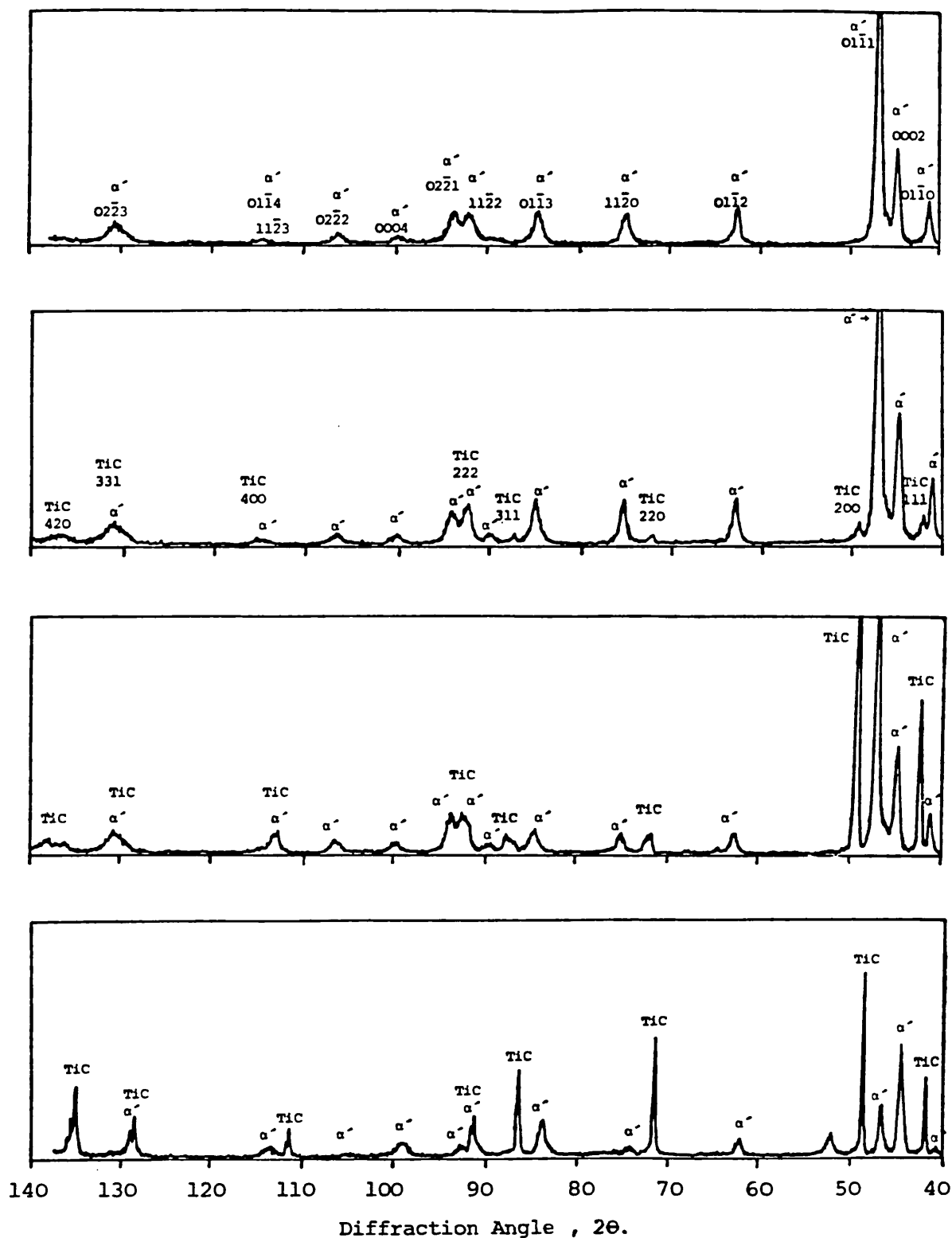


Fig.4.3. X-RAY DIFFRACTOMETER ANALYSIS OF LASER PROCESSED Ti SUBSTRATES

a) Laser melted Ti-6Al-4V b) 'Low' C alloying (1 DAG run) of Ti-6Al-4V c) 'High' C alloying (8 successive DAG runs) of Ti-6Al-4V d) 'High' C alloying (16 successive runs) of C.P.Ti.

4.4. RESULTS

4.4.1. Surface Melting

Laser melted Ti-6Al-4V solidifies as β which in turn undergoes solid state transformation to martensite. The β grains are a magnitude coarser than those of the HAZ, or unaffected substrate, and grow as large columnar grains, nucleating at the melt/substrate interface and extending to the track surface, Plate 14a. The martensite originally indexed as hexagonal martensite (α')²⁰⁵, Fig.4.3., forms as regular, near parallel, plates within individual β grains. β grain boundaries can be identified as the interface between contrasting regions of α' plates, (see upper portion Plate 14b).

The HAZ is a transition zone, $\alpha' + \beta \rightarrow \alpha + \beta$, Plate 14b. Close to the melt interface it consists almost entirely of α' transformed within the 'substrates' original unmelted β matrix. The β grain boundaries are less clearly defined. The exact boundary between the melted region and the HAZ is taken as the 'line' where the fine β grains of the HAZ are no longer identifiable. Moving away from the interface through the HAZ, β grain boundaries are more easily defined. The volume of α' decreases in favour of increasing β . At the visible extent of the HAZ the structure is presumed to consist of $\alpha + \beta$.

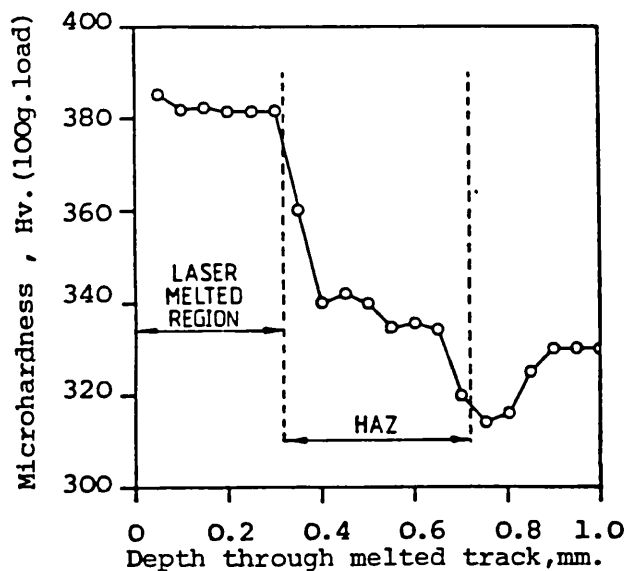


Fig.4.4. Microhardness traverse through centre axis of Ti-6Al-4V laser melted track (data is for track illustrated Plate 14a, av. hardness taken from 5 traverses).

A micro-hardness traverse through the centre axis of a laser melted track indicates that the melted region is slightly harder than the HAZ or unaffected substrate, Fig.4.4. (The HAZ region indicated is the apparent visible HAZ).

4.4.2. C Alloying

4.4.2.1. Processing Parameters

The amount of C alloyed can be controlled by the thickness of DAG precoat, the laser alloyed track profile (surface/volume ratio) or by the number of successive DAG reprocessings.

Fig.4.5a illustrates how a laser alloyed 'thick' DAG precoat (0.041 g/cm^2) induces greater hardening than a laser alloyed 'thin' precoat (0.01 g/cm^2). Track hardening reflects the volume fraction of TiC present, ie the level of C alloyed. DAG precoat thickness has little apparent effect on track width, depth or cross-sectional melted area (CSMA), Fig.4.5b,c.

Increasing scan velocity decreases the volume of melted track and alters the track profile. Melt puddle depth decreases at a faster rate relative to decreasing puddle width, Fig.4.5b, 4.7b, thus increasing the track surface/volume ratio. Hence, track hardness (vol % C alloyed) increases with increasing scan velocity, Fig.4.5a, 4.7a. 'Thick' DAG precoating accentuates this effect, Fig.4.5a. A laser alloyed 'thick' precoated track increases by a greater hardness than a laser alloyed 'thin' precoated track, over the same increasing range of scanning velocities. Track profile can also be controlled via laser beam focusing. Where surface melting can be maintained, then defocusing spreads the beam, reducing beam intensity, and induces wide/shallow melted tracks with high surface/volume ratios. Providing pool stirring is established the volume %C alloyed should increase (as described 2.5.4.).

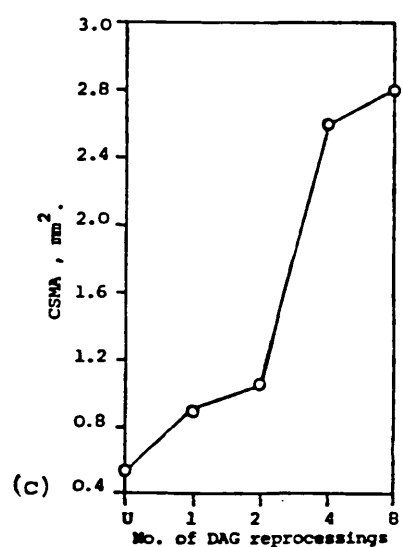
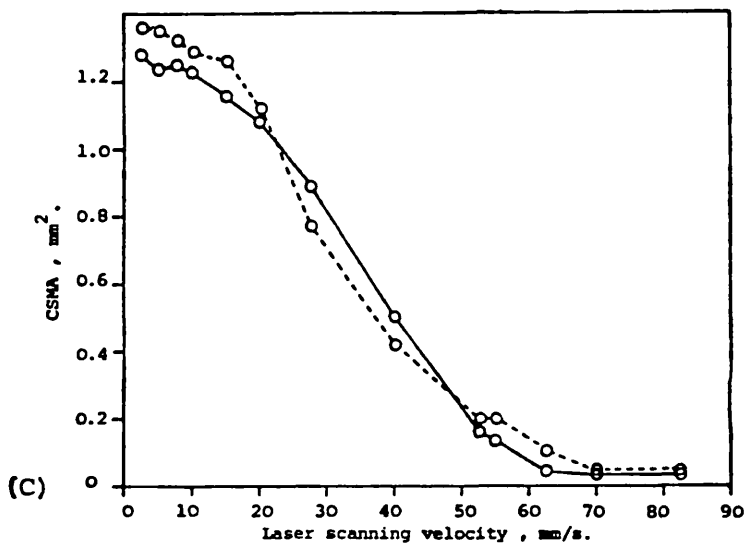
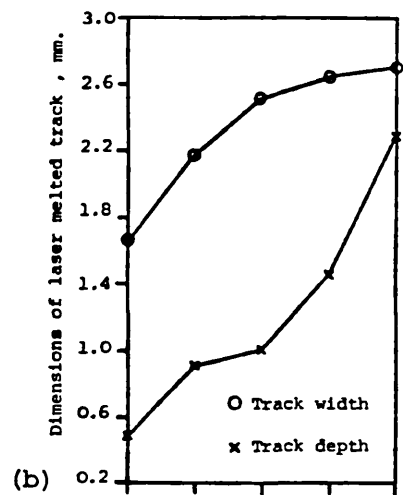
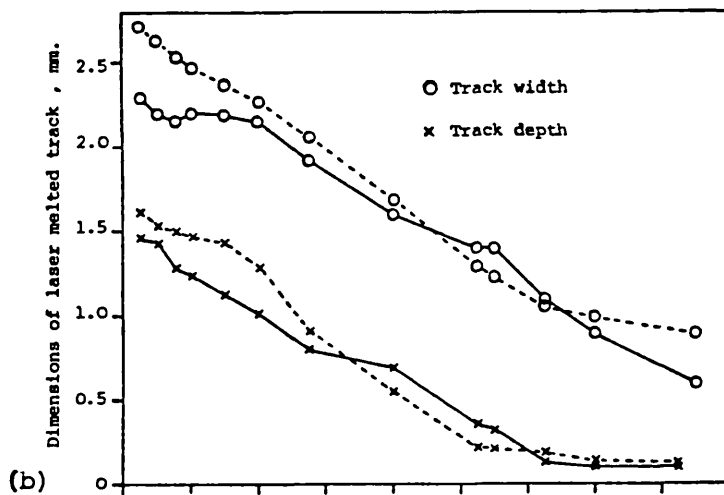
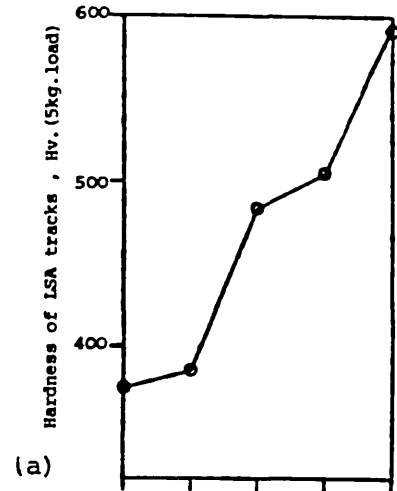
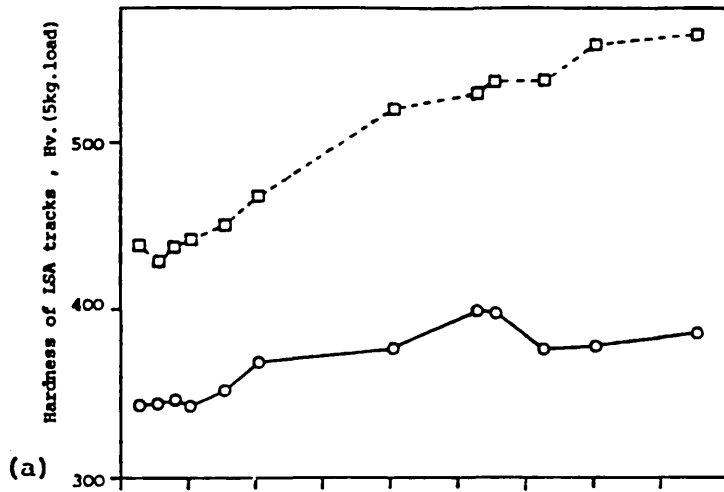


Fig.4.5. The effect of scan velocity and DAG precoat thickness on C surface alloying of Ti-6Al-4V substrates (1.8kW, 2.0mm) broken line (0.041gm/cm² C precoat) unbroken line (0.01gm/cm² C precoat) (Av values taken from 4 sets of measurements).

Fig.4.6. The effect of successive DAG reprocessings on C surface alloying of Ti-6Al-4V. (1.8kW, 2.5mm, 20mm/s) u = uncoated. (Av values taken from 4 sets of measurements).

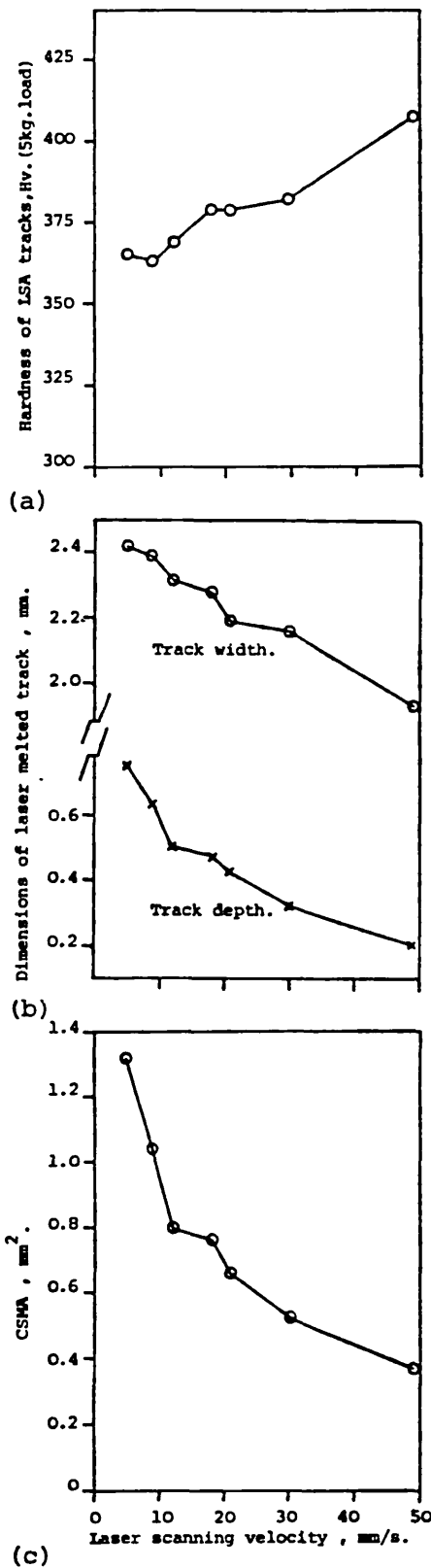


Fig.4.7. The effect of Scan velocity on C surface alloying of C.P.Ti substrates (0.01gm/cm^2 C precoat) (1.7kW, 3.0mm)(Av values taken from 4 sets of measurements)

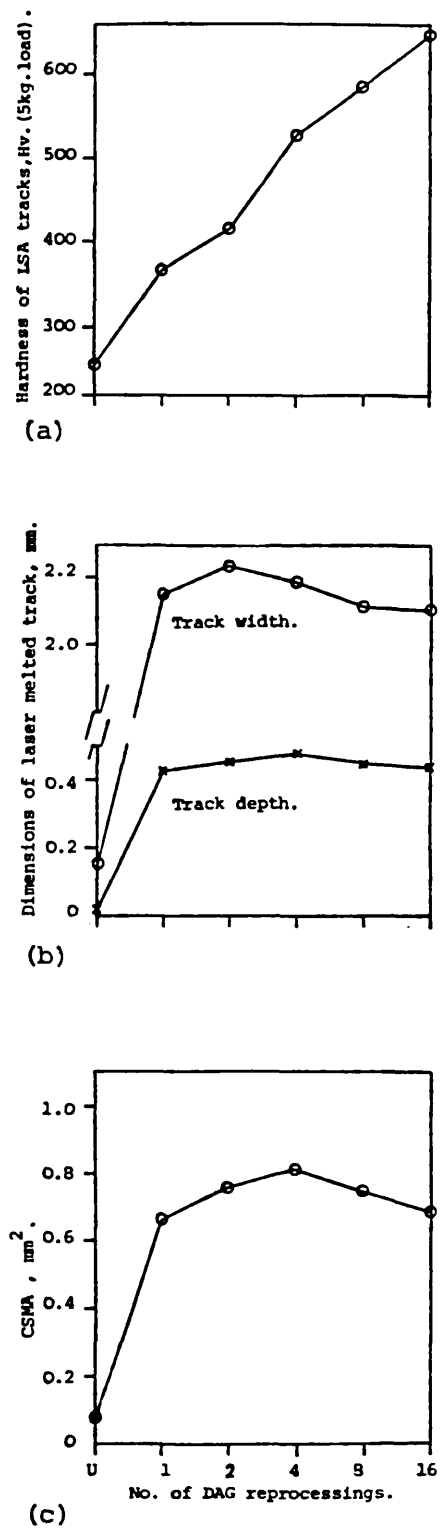


Fig.4.8. The effect of successive DAG reprocessings on C surface alloying of C.P.Ti (1.7kW, 3mm, 20m/s) u = uncoated. (Av values taken from 4 sets of measurements).

Figs.4.6. and 4.8. show how track hardness increases with successive DAG reprocessing. The two sets of tracks were processed at different times and illustrate the problem of producing repeatable conditions; the data for these results differ. Melt penetration of Ti-6Al-4V increases with successive reprocessings approaching a near key-holed condition after eight reprocessings, Fig.4.6b, Plate 16a. Laser alloyed C.P.Ti melts in a conduction limited mode and melt penetration is unaffected by reprocessing, Fig.4.8b, Plate 17c. Relatively greater volumes of Ti-6Al-4V are melted compared to C.P.Ti, CSMA = 0.3mm^2 ($1.7 \times 0.5\text{mm}$) for uncoated Ti-6Al-4V compared with CSMA $<0.1\text{mm}^2$ ($0.15 \times 0.05\text{mm}$) for uncoated C.P.Ti. The melt volumes of the two substrates after the 1st and 2nd reprocessings, partially resemble each other (though track width, depth and CSMA for Ti-6Al-4V is greater) Fig.4.6b, c, 4.8b, c. Where pool depth increases with successive reprocessing, CSMA increases. For Ti-6Al-4V reprocessed 8 times CSMA $\sim 2.8\text{mm}^2$. For C.P.Ti, where pool depth is unaffected by reprocessing CSMA = $\sim 0.7\text{mm}^2$, Fig.4.6c, 4.8c. Realloyed C.P.Ti tends to be harder when compared with equivalent reprocessed Ti-6Al-4V reflecting the decreased surface/volume ratio of Ti-6Al-4V. The drastic difference in melting modes of the two substrates is unlikely to be solely due to either different processing conditions or alloy composition. Both substrates were grit blasted before processing yet surface melting (particularly for uncoated sample) of C.P.Ti is limited. The laser calorimeter may have malfunctioned. Reduced coolant flow to the calorimeter is known to give a higher, false, laser power reading. Though the indicated power was 1.7kW a truer value may be $\sim 1.4\text{kW}$. Successively increasing track penetration with reprocessing is a function of preheating. The time between reprocessings of Ti-6Al-4V was insufficient to allow the substrate to cool to ambient. This effectively preheated the substrate causing successively deeper melts. In subsequent experiments substrate quenching before reprocessing eliminated this.

4.4.2.2. Microstructural Analysis

4.4.2.2.1. Solid State TiC Precipitation

Microstructure varies with the level of C content in the melt zone. In 'low C' alloy melts (single thin, 0.01 g/cm^2 C, prepainted DAG runs) β solidification is followed by TiC formation, Plate 15. Coarse columnar β grains (up to $0.3 \times 0.05\text{mm}$) nucleate at the substrate interface and

grow, 'tangentially', towards the surface. Particles, presumed to be TiC, precipitate along β grain boundaries and along the crystallographic planes of β grains in a 'Widmanstätten fashion', Plates 15c,d. In the example illustrated pool stirring has ensured homogeneous C mixing and an 'even' dispersion of TiC precipitates. Solid state TiC precipitation induces limited hardening, from Hv380 for non-alloyed laser melted Ti-6Al-4V, Fig.4.4., to Hv 395 for C alloyed, Fig.4.9. The HAZ exhibited the same microstructural transition as previously discussed (4.4.1.), from β transformed to martensite near the interface, Plate 4.2b, to $\alpha + \beta$ at the HAZ limit. The HAZ indicated in Fig.4.9 is the visible HAZ; it is not clear whether the apparent softening at a depth of 0.8mm is a real feature.

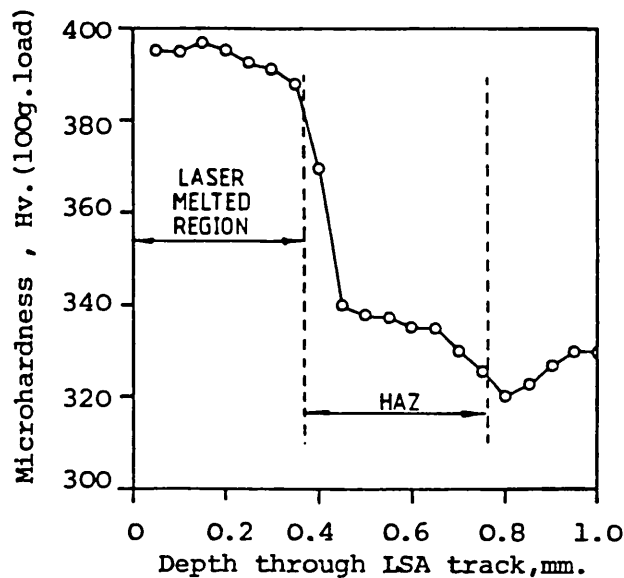


Fig.4.9. Microhardness traverse through centre axis of Ti-6Al-4V laser alloyed with a single (0.01g/cm² C) DAG precoated run, (data is for track illustrated Plate 15a. Av.hardness taken from 5 traverses).

An X-ray diffraction analysis of the track shown, Plate 15a, is illustrated, Fig.4.3b. fcc TiC and martensite (indexed as hexagonal α') were identified. The carbide lattice parameter was measured as 4.318Å. A suggested lattice parameter for TiC is 4.3274Å²⁰⁶. Although the measured TiC lattice parameter lies within an acceptable experimental tolerance, the slight deviation could be interpreted as lattice distortion.

The conduction limited melt track profile and microstructural features discussed were typical of all 'low C' tracks, both for C.P.Ti and Ti-6Al-4V substrates, where TiC was seen to precipitate from the solid state.

4.4.2.2.2. Proeutectic 'Dendritic' TiC

In 'high C' alloy melts (single 'thick' $0.041\text{g}/\text{cm}^2$, or multi preapainted $0.01\text{g}/\text{cm}^2$, DAG runs) proeutectic TiC nucleates and grows dendritically. Microstructures consist of proeutectic TiC in a matrix of β which has transformed to martensite. Three examples are shown each illustrates a different feature of dendritic growth, Plates 16, 17.

Plate 16 shows a transverse section through a 'key-hole' track produced by reprocessing with DAG eight times. Proeutectic networks tend to grow in a 'equiaxed' fashion, though aligned columnar dendritic regions do exist near interfaces where thermal gradients are strong and stirring effects minimised, Plate 16b. λ_2 varies across the depth of the track from $1.15 \pm 0.35\mu\text{m}$ at the surface Plate 16c, $0.97 \pm 0.2\mu\text{m}$ at 1/3 melt track depth, to $0.4 \pm 0.1\mu\text{m}$ at 3/4 melt track depth (in the keyhole) Plate 16d. While it was difficult to measure accurately the volume fraction of TiC dendrites it was possible to establish (by comparison) that there were more dendrites in the upper portion of the track than in the lower. This is reflected in decreasing hardness through the track, Fig.4.10.

Dr H M Flower²⁰⁴ analysed a thin foil of the track, Plate 16e, and identified small amounts of retained β . α' exhibits a Burgers relationship with this retained β . A possible, but not unique, orientation relationship between TiC and β close to the Kurdjumov Sachs relationship was also observed. Microanalysis of the foil showed the carbide to contain 0.5 ± 0.4 Al and 1.4 ± 0.3 V. Carbide formation has depleted the matrix of Ti so raising the Al and V concentration in β . An analysis of the matrix indicated 7.5 ± 3 Al, 6.4 ± 0.8 V.

An X-ray diffraction analysis of the track is illustrated, Fig.4.3c. fcc TiC and α' were identified. The carbide lattice parameter was measured as $4.305\text{\AA}$, a greater distortion than reported elsewhere (4.4.2.2.1.).

Etching highlighted a layer (0.1mm thick) in the HAZ adjacent to the melt interface where limited solid state grain boundary precipitation of fine plates occurred in a α' matrix, identical in appearance to those reported elsewhere (4.4.2.2.1.). C diffusion into the HAZ may have resulted in TiC formation. Beyond this layer the HAZ is the same as described elsewhere (4.4.1.).

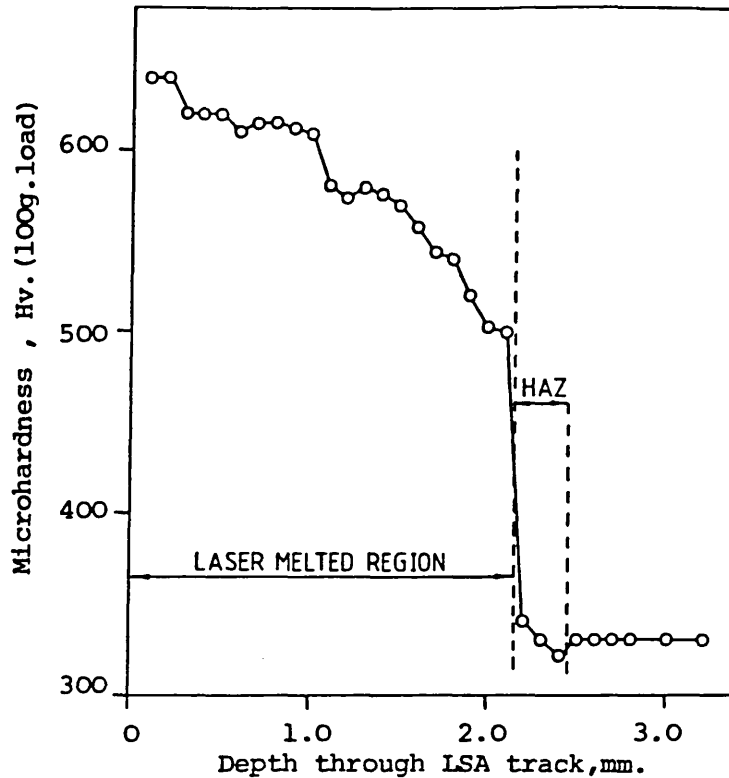


Fig.4.10. Microhardness traverse through centre axis of Ti-6Al-4V laser alloyed with eight successive (0.01g/cm^2 C) DAG precoated runs (data is for track illustrated Plate 16. Av. hardness taken from 5 traverses).

Plate 17a shows a conduction limited track, surface hardness, HV420. Alloying is limited to a region near the track surface. TiC dendrites extend downward to a depth of $\sim 0.05\text{mm}$ ($\lambda_2 = 1.05 \pm 0.4\mu\text{m}$). Below the layer of dendrites TiC solid state precipitation appears to extend to the full depth of the melt track. This example, where a C gradient exists, clearly illustrates how carbides grow downwards from the surface. In 'high C' alloys both melt/substrate interface and surface nucleation can occur. TiC dendrites grow both upward and downward.

When excessive C is alloyed, and where poor melt pool stirring occurs, large irregular TiC particles (up to $100\mu\text{m}$ in diameter) form heterogeneously, Plate 17c,d. TiC forms as irregular particles surrounded by a regular 'fibrous' TiC network (coarser than dendritic TiC), Plate 17d. In 'lower C' regions of the same track TiC dendrite networks form, Plate 17e ($\lambda_2 = 1.2 \pm 0.5\mu\text{m}$). Most of the irregular TiC particles are near the surface, only one significant particle is situated in the track core. A gap in the TiC 'surface crust' indicates that it may have formed at the surface and subsequently drawn downwards. An X-ray diffraction analysis is illustrated Fig.4.3d. The TiC lattice parameter was measured as $4.329\text{\AA}$.

C alloying appears to affect surface topography; fine rippling is eliminated in 'high C' alloys (where dendritic TiC forms) though intermittent 'humping' occurs, Plate 17f.

4.4.3. Wear Results

Abrasive pin and disc tests were carried out on the series of C alloyed Ti-6Al-4V substrates given, Fig.4.6. The wear apparatus is described elsewhere (3.3.) Although it was not possible to quantify the volume of TiC, the relative increasing surface hardness of the track reflects an increasing proportion of TiC. TiC formation reduces wear significantly, Table 4.1.

TABLE 4.1 The Effect of Laser Alloyed C on Abrasive Wear Resistance of Ti-6Al-4V Substrates

Load: 5kg 800 grit		Substrate Ti-6Al-4V (1.8kW, 2.0mm, 20mm/s, 0.01g/cm ² C precoat)				
		Surface Melted	1 DAG processing	2 DAG processings	4 DAG processings	8 DAG processings
Surface (500g) Micro Hardness		HV385	Hv395	Hv480	HV520	HV650
Distance travelled to wear 1mm ³ of sample , m.	1	0.102	0.108	0.407	0.755	0.850
	2	0.090	0.105	0.425	0.694	0.855
	3	0.092	0.095	0.392	0.720	0.832
	4	0.115	0.120	0.392	0.741	0.820
	5	0.095	0.104	0.400	0.705	0.860
AVERAGE , m.		+0.016 0.099 -0.009	+0.014 0.106 -0.011	+0.023 0.403 -0.011	+0.032 0.723 -0.029	+0.017 0.843 -0.023

4.5. DISCUSSION

4.5.1. Microstructure

The structures produced are similar to those described by Ayers et al ^{195, 196} who found that TiC dendrites formed from dissociation and reformation of TiC particles in particle injected laser melted Ti alloys. In the laser tracks described here TiC forms either by solid state precipitation from β or by direct solidification from the liquid.

The Ti-C system, Fig.4.2., undergoes a eutectic reaction at 1645°C, liq (4.4 at %C) $\rightarrow \beta$ (0.55 at %C) + TiC (33 at %C). Where limited amounts of C are alloyed (<4.4 at %C) hypoeutectic solidification occurs. For example if the fraction TiC in Plate 15 were ~5vol% then the C content would be ~1wt%, equivalent to 3.9 at %C (C constitutes ~16wt% of TiC). Quenching may skew the eutectic to higher C compositions extending the hypoeutectic region. The equilibrium phase diagram, Fig.4.2., does not indicate a change in solid solubility of β . Solid state TiC precipitation does apparently occur. Decreasing solid solubility with decreasing temperature could be due to non-equilibrium cooling or may normally occur (previous work reported a peritectic reaction at 1750°C and a decrease in C solubility in β with decreasing temperature). It is presumed that the alloy shown, Plate 15, is hypoeutectic and solidifies as β which nucleates at the melt/substrate interface and grows as 'coarse columnar' grains, as described (4.4.2.2.1.). C is rejected from the β and forms TiC plates at grain boundaries and along crystallographic planes. The β then transforms to martensite near the peritectoid. The martensite has been indexed as hexagonal martensite (α') though it is not easy to distinguish the diffraction pattern of from that of orthorhombic martensite. (Positive identification of the martensite phase morphology was not possible).

In 'high' C alloy tracks hypereutectic solidification occurs. Dendritic proeutectic TiC growth initiates. At the eutectic any remaining liquid solidifies as β . Solid state TiC precipitation does not occur between proeutectic TiC dendrite arms. It is presumed that any TiC precipitated by C rejection from β nucleates on existing TiC dendrites. Plate 17c shows a TiC crust formed on top of a melt track

(the argument that TiC floats doesn't hold, since TiC ($\rho = 4.93\text{g/cm}^3$)¹⁹ has a greater density than Ti ($\rho = 4.51\text{g/cm}^3$)¹⁹ or Ti-6Al-4V ($\rho = 4.42\text{g/cm}^3$)¹⁹. Elsewhere TiC dendrites nucleate and grow downward from the surface. Good pool stirring is needed to ensure homogeneous mixing of alloyed C. Wide/shallow melt zones do not establish such stirring cycles, C appears to alloy through surface impingement (2.5.4.). A C gradient through the depth of the melt track was established, hence surface layers contain preferentially more C. The closer the Ti-C composition is to stoichiometric TiC the higher the solidification temperature, Fig.4.2. On quenching 'preferred' undercooling may occur in high C regions, hence TiC solidification initiates near the surface (possibly nucleated by Ar quenching from the shroud gas, or C particles). The solidification front proceeds downward with decreasing C and meets the advancing upward solidification interface (β phase) which has nucleated at the melt/substrate interface and grown with the thermal gradient. In plate 17a, b the upward interface has solidified as a hypoeutectic and the downward as a hypereutectic; consequently the β grains below the TiC dendritic network have undergone solid state TiC precipitation. In plate 17c, where C has been alloyed to such an extent that a solid layer of TiC formed, a section of this layer has fragmented and been drawn into the pool where it acts as nuclei for TiC dendritic growth, Plate 17d. Plate 17e shows an unusual TiC dendrite network, probably produced by a 'high C swirl' drawn in from the surface. Where a laser melted track has a hemispherical profile, convective stirring cycles are established and C is homogeneously mixed (2.5.4.). Where TiC dendrite growth initiates from the pool centre it is presumed that TiC dendrite tips are swept inward from the solidification interface and act as nuclei. In keyhole melting C mixing is not homogeneous. The keyhole tends to have a lower alloying content²⁰⁷. This is reflected in the declining hardness with pool depth of Plate 16, Fig.4.10.

Peng et al²⁰⁸ laser surface melted Ti-15V-3Al-3Sn-3Cr and correlated the observed dendrite arm spacing with cooling rate, where:

$$\lambda_2 = 80 (\text{GR})^{-0.34} \quad (4.1)$$

Their calculated cooling rate was based on Cline and Anthony's three dimensional heat-transfer model²⁰⁹. Although Peng's relationship

(eq.4.1.) was based on a different Ti alloy, it has been applied to our results to obtain a rough GR approximation. For Plate 16, GR varies from 2.6×10^5 K/s (surface), 4.3×10^5 K/s ('core') to 5.9×10^6 K/s (keyhole). For Plate 17a, GR is 3.4×10^5 K/s, and for Plate 17c, GR is 2.3×10^5 K/s. These cooling rates are higher than those predicted for either cast irons, $10^4 - 10^5$ K/s (2.5.1.2) or Al-10Si, $10^4 - 10^5$ K/s (3.5.2.3.). TiC dendrites do, however, solidify at higher temperatures than these other alloys and a greater GR might be expected.

X-ray diffraction patterns indicate a slight distortion of the TiC lattice (4.4.2.2.). Cubic carbides are liable to varying departures from stoichiometry. The TiC lattice parameter is known to be composition dependent. Any decrease in C content below the stoichiometric value would lead to a decrease in lattice parameter²¹⁰. If the lattice 'contraction' of the 'high C alloyed' Ti-6Al-4V ($a = 4.305\text{\AA}$) were due totally to deviation from stoichiometry then the carbide would be of the form $\text{TiC}_{0.9}$. Lattice distortion is not seen to occur in C alloyed C.P.Ti. Microanalysis indicates that where TiC forms from C alloying to Ti-6Al-4V, the carbide dendrites contain amounts of Al and V. For the 'high C' Ti-6Al-4V track Plate 16 ($a = 4.305\text{\AA}$), this comprises 0.5 ± 0.4 at % Al and 1.4 ± 0.3 at % V. The binary carbide system TiC-VC is known to contract the TiC lattice. If the lattice distortion of the high C alloyed Ti-6Al-4V were totally due to V then it would be caused by 10 mol % solute VC²¹⁰ (5 at % V).

4.5.2. Physical Properties

Where the volume of TiC (produced by laser C alloying) increases, laser track hardness increases and abrasive wear rate decreases.

Hypoeutectic Ti-C alloys containing TiC precipitated from solid solution has a minimal improvement in wear resistance. Only the presence of dendritic TiC has any significant effect on abrasive wear resistance, ie where sufficient C is alloyed to produce a hypereutectic structure with a continuous dendritic TiC network near the surface. Table 4.1. shows how abrasive wear of C alloyed Ti-6Al-4V can be reduced to 15% of laser melted Ti-6Al-4V.

Ayers reports²⁰⁰ surface cracking in alloys containing high volume fractions of TiC. No apparent cracking was observed in any Ti-C samples although the brittle TiC layer, Plate 17c, is suspect.

PLATE 14 LASER MELTED Ti-6Al-4V
(1.8kW, 2.0mm, 20mm/s)

- a. General view of transverse section through laser melted track.
The track comprises of β transformed to α' .

- b. Region spanning part of melt zone and HAZ, Plate 14a. 'Upper'
regions of HAZ, near interface, comprise $\alpha' + \beta$. 'Lower'
regions comprise $\alpha + \beta$.

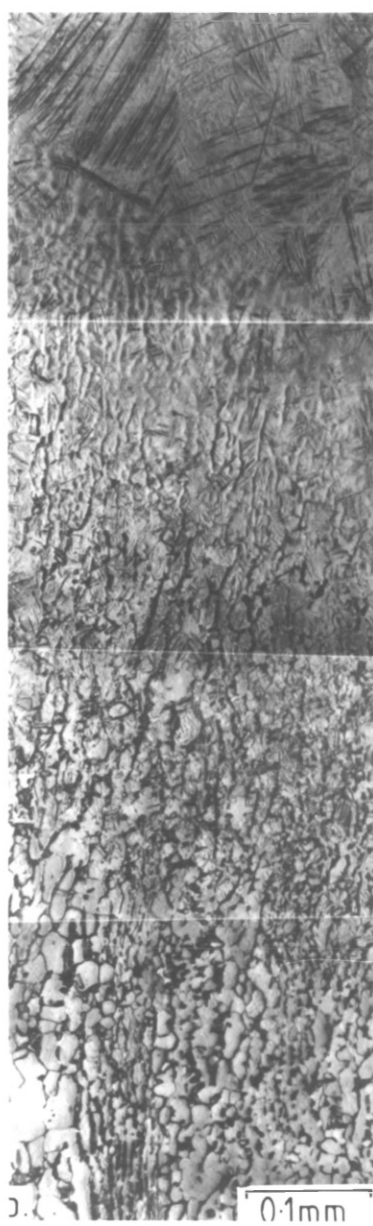
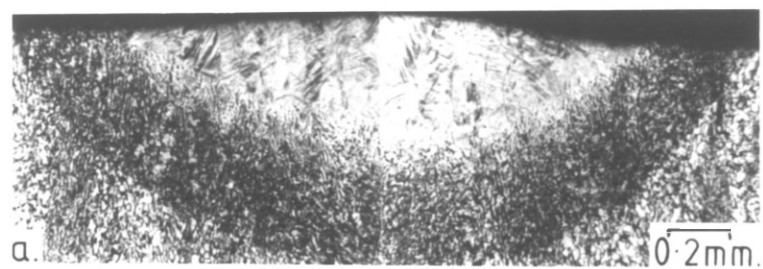


PLATE 15 C ALLOYING TO Ti-6Al-4V, HYPOEUTECTIC ALLOY

(1.8kW, 2.0mm, 20mm/s; one 0.01 g/cm² DAG reprocessing).

- a. General view of transverse section through laser C alloyed track. The track comprises of large columnar β grains (particularly noticeable) transformed to α' . Solid state TiC precipitation has occurred.

- b. Region spanning part of melt zone and HAZ, Plate 15a. Etching has pitted the α' structure of the melt zone, though HAZ α' is clearly identified.

- c. SEM view of melt zone, Plate 15a. Solid state precipitation at β grain boundaries and along specific crystallographic planes in β has occurred.

- d. SEM view of β grain boundary TiC precipitate, Plate 15c.

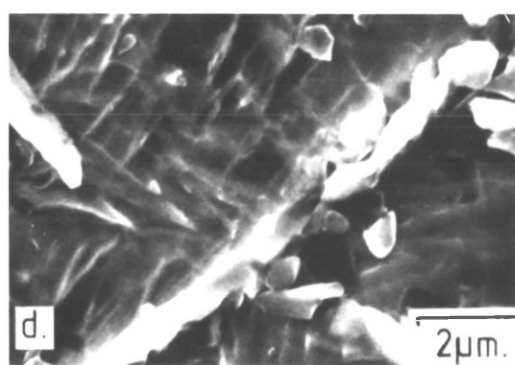
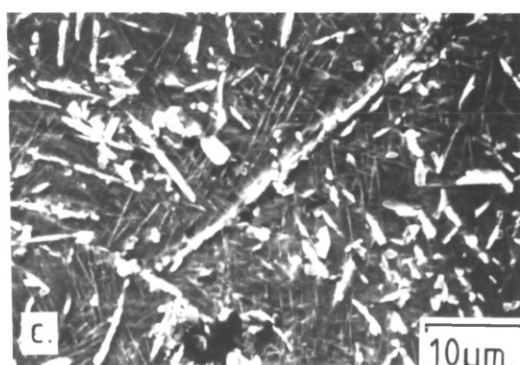
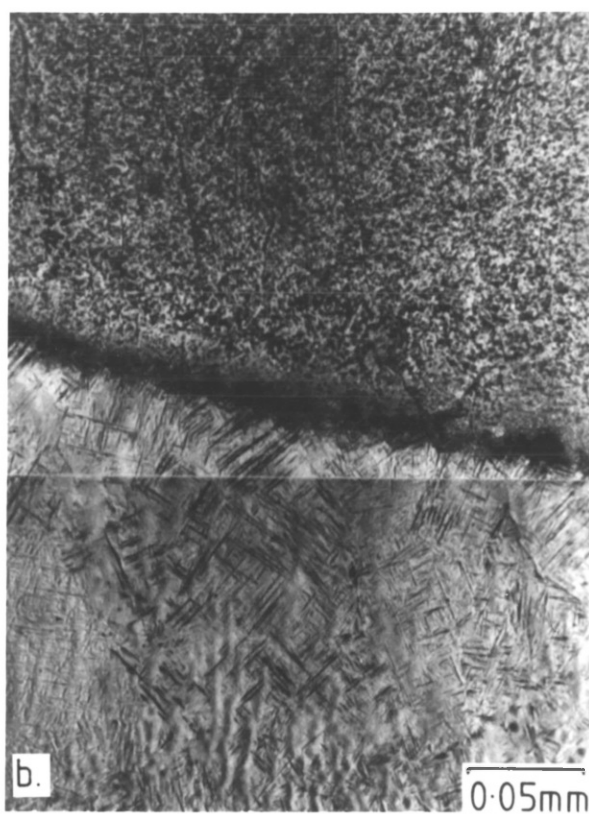
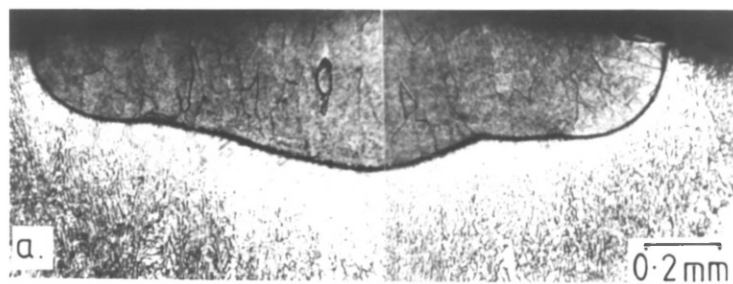


PLATE 16 C ALLOYING TO Ti-6Al-4V, HYPEREUTECTIC ALLOY

(1.8kW, 2.0mm, 20mm/s, eight 0.01g/cm² DAG reprocessing).

- a. General view of cross section through laser C alloyed track.
The track comprises of proeutectic TiC dendrites in a matrix of β transformed to α' .
- b. Region spanning part of melt zone and HAZ, Plate 16a. Growth patterns of TiC dendrites are highlighted.
- c. SEM view of melt zone/surface interface, Plate 16a. Deep etching reveals the TiC dendrite networks ($\lambda_2 = 1.15 \pm 0.35 \mu\text{m}$).
- d. SEM view of melt zone at '3/4 of track depth' (in keyhole). TiC dendrites are more refined than, Plate 16c ($\lambda_2 = 0.4 \pm 0.1 \mu\text{m}$)
- e. TEM view of foil (foil taken from longitudinal section parallel with surface at approximately half track depth) showing TiC dendrites.

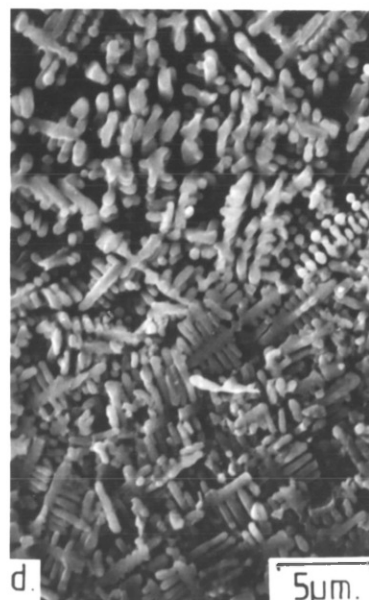
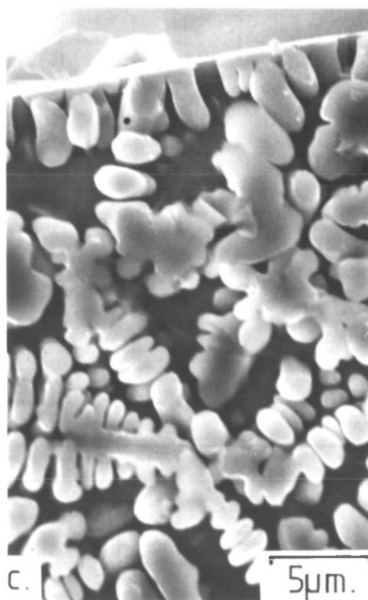
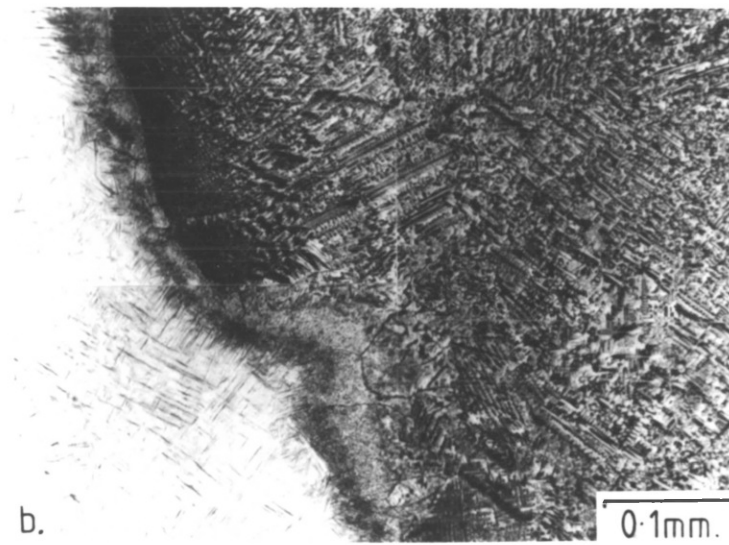
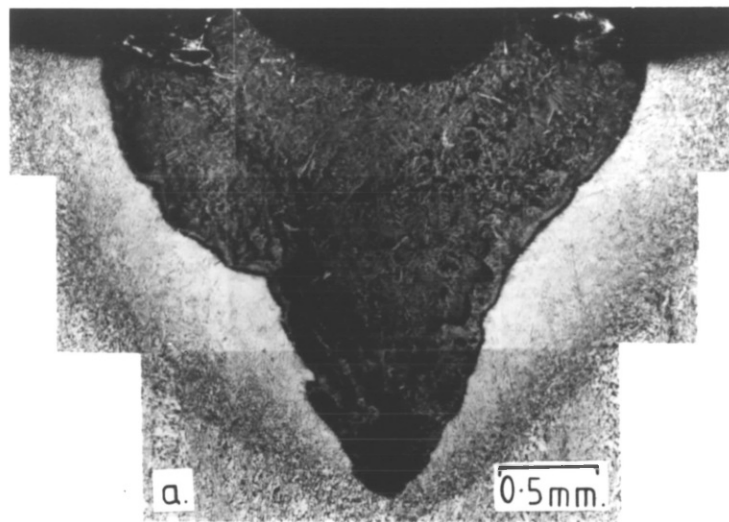
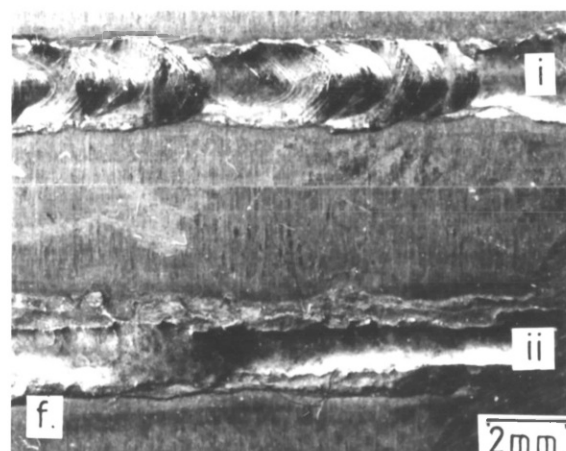
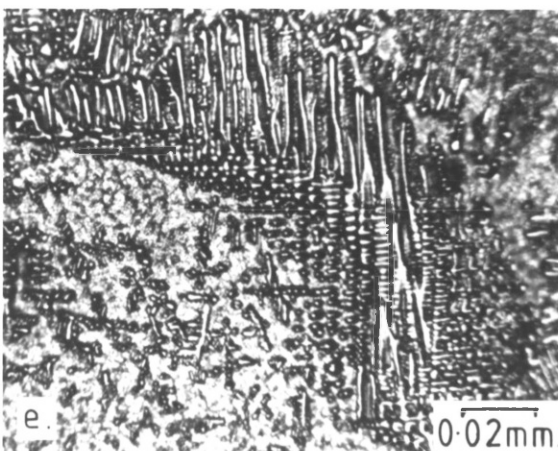
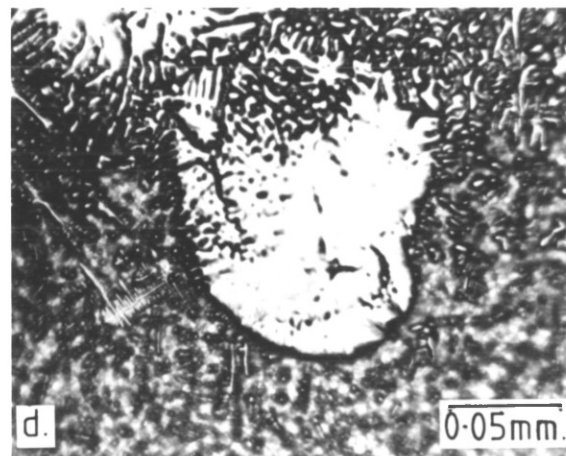
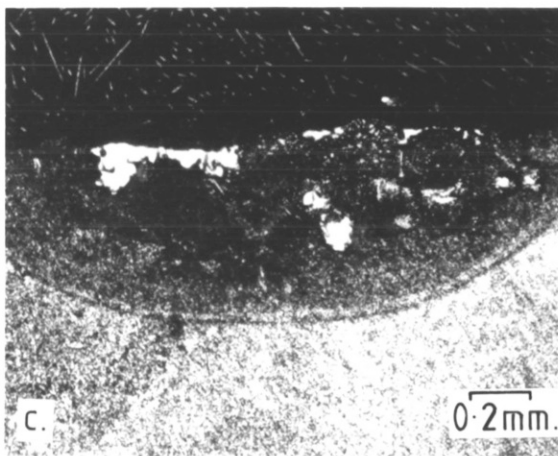
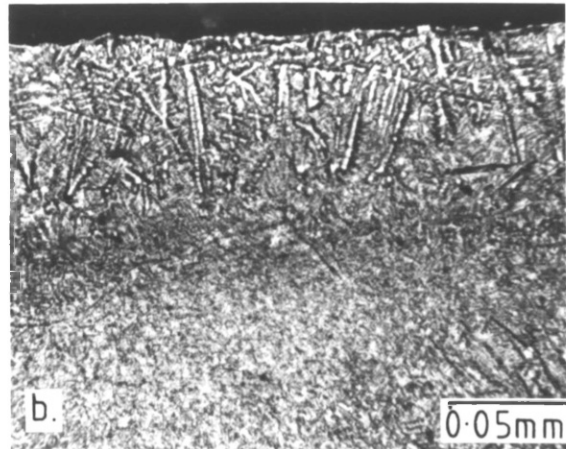
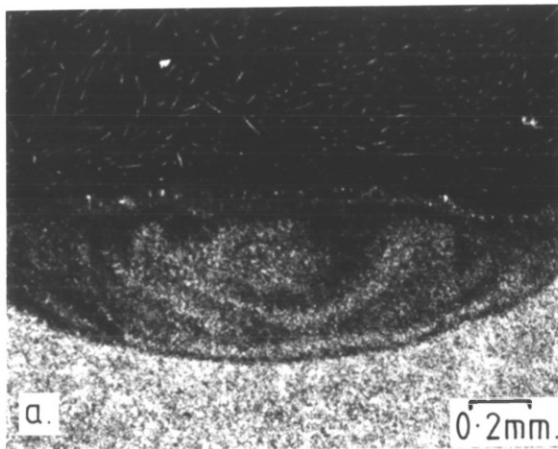


PLATE 17 C ALLOYING TO C.P.Ti, HYPEREUTECTIC ALLOY
(1.7kW, 3mm, 20mm/s)

- a. General view of transverse section through laser C alloyed track (two 0.01g/cm² DAG reprocessings).
- b. View of melt zone/surface interface, Plate 17a., showing TiC dendrites growing downwards from the surface.
- c. General view of cross section through laser C alloyed track (sixteen 0.01g/cm² DAG reprocessings). Large TiC particles occur at the surface.
- d. View of melt zone, Plate 17c, showing a large TiC particle (0.1mm dia) and 'coarse' interrelated 'fibrous' TiC network.
- e. View of melt zone, Plate 17c , showing unusual dendrite network.
- f. Plan view of (i) laser surface melted Ti-6Al-4V and (ii) C alloyed Ti-6Al-4V (Plate 16). C alloying eliminates 'fine' rippling, so 'smoothing' track topography.



5. CONCLUSIONS

The suitability of three different metal systems to LSA has been investigated. The relative importance of processing parameters vary between different substrates. The cross-sectional profile of the melted track affects pool stirring and, hence, alloying homogeneity. Rapid cooling causes non-equilibrium solidification. In Fe alloyed with C the growth mechanism of ledeburite and its decomposition to a divorced eutectoid of ferrite and cementite has been observed. Si alloyed to Al, to hypereutectic levels, forms proeutectic Si dendrites in a fine fibrous eutectic. Dendritic Si imparts both wear resistance and ductility. C LSA to Ti forms TiC. Proeutectic TiC dendrites in a martensitic matrix significantly improves abrasive wear resistance over non C alloyed Ti.

5.1. PROCESSING PROPERTIES

5.1.1. Substrate Parameters

Substrate reflectivity has a critical effect on beam coupling. The high reflectivity of Al makes it less susceptible to melting than either Fe or Ti alloys. Thermal conductivity controls the cross sectional profile of the melted track. The high thermal conductivity of Al alloys inhibits key-hole melting. For Al, beam interaction time rather than beam intensity is seen to be more important. Al has a relatively low melting point (compared to Fe or Ti) and, since it was not found to key-hole, increased beam intensity above a fixed threshold is unnecessary. Beam coupling is critical in melting Al, and increased heating time enhances coupling. Beam defocusing increases interaction time and so increases heating time (3.5.1.1.3.), hence defocusing increases melt penetration and CSMA.

Fe alloys and Ti alloys have higher emissivities and lower thermal conductivities than Al. Beam coupling conditions are less critical and melting readily occurs. Both types of alloys are susceptible to key-hole melting under focused conditions. For Fe alloys and Ti alloys beam focusing enhances both penetration and CSMA.

Cooling rates of LSA hypoeutectic white irons have been calculated from microstructural refinement and heat transfer models. Results vary between methods, however it may generally be concluded that cooling

rates occur in the range $10^4 - 10^5$ K/s. Cooling rates vary across individual track sections. Where key-hole melting occurs the cooling rate is higher in the key-hole, decreases in the central track region and increases near the surface (Table 2.6.). In shallow melt tracks (where no key-hole exists) cooling rate decreases from the melt/substrate interface to the surface.

For laser melted Al-10Si solidification rates occur over the region $\sim 10^4$ K/s and increase with increasing scan speed. Undercoolings in excess of 50K are found to occur.

Al alloy substrate could be melted with powers of less than 1kW. The depth, width and CSMA of the laser melted track is always greater for Al-10Si alloy than for CP Al substrates processed under the same conditions. All laser melted Al alloy tracks were conduction limited.

The level of Si alloying can be controlled by altering beam diameter and scan velocity. For a <1.9mm dia beam alloying increases with decreasing scan velocity (Fig.3.13, 3.14). At near focused conditions the laser nozzle is close to the workpiece. Shroud gas may erode the precoated Si layer so reducing the possible amount alloyed. Reducing scan velocity allows the melt puddle to advance ahead of the beam, hence Si is melted ahead of the shroud. At low scan speeds <20mm/s large "volumes" of Si are drawn into the melt track. This inhibits substrate melting, further increasing the alloying ratio. For a >2.0mm dia beam alloying decreases with decreasing scan velocity; as scan velocity decreases the volume of substrate melted increases more rapidly than the volume of Si alloyed (Fig.3.15).

5.1.2. Melt Zone Geometry

In LSA melt pool profile is critical. A near hemispherical melt pool cross-sectional profile is required to induce stirring. Pool stirring transports alloying additions from the surface and homogeneously distributes them throughout the melt zone. Convective flow occurs from the centre to the edges of the pool, while return flow occurs deep within the pool (2.5.4, Fig.2.19). Where high volume fractions are alloyed surface ribs protrude. Although melt penetration is shallow substrate metal is distributed throughout the alloyed track (Plate 10f). Convective stirring occurs in the protruding rib (Plate 18f). It is the hemispherical profile which induces convective flow and it does not matter whether this profile is melted into the substrate or inverted as a surface protrusion.

Wide/shallow melt pools exhibit high alloying ratios (high surface/volume ratios). Alloying occurs by surface impingement and an alloying gradient usually occurs through the pool. Such tracks can not establish convective stirring and this can minimise the effect of a high alloying ratio.

5.2. PHYSICAL PROPERTIES

5.2.1. Ferrous Alloys

In hypereutectic white irons proeutectic cementite nucleates at the melt/substrate interface and spreads as plates throughout the liquid pool. Each proeutectic cementite plate is associated with an individual eutectic colony. The eutectic is lamellar and is aligned parallel to the proeutectic. Both eutectic cementite and eutectic austenite nucleate heterogeneously. Eutectic cementite spreads as two dimensional dendrites across the surface of the proeutectic, 'in-filling' behind the advancing dendrite arms and forms surface ridges of eutectic cementite. Specific austenite regions, in addition to austenite produced by co-operative growth, occur on the proeutectic. Eutectic cementite perturbations stimulate sidewise growth. Sidewise growth is co-operative and occurs as one-dimensional protrusions or two-dimensional ribs (Plate 6d,e). Eutectic growth then spreads edgewise parallel to the proeutectic. The eutectic continues to spread outwards by simultaneous sidewise and edgewise growth until one eutectic colony interfaces with another.

The ledeburite eutectic undergoes diffusional decomposition from austenite plus cementite to ferrite plus cementite. It is postulated that transformation initiates at austenite/cementite grain boundaries where a cementite lamellar might grow. As this lamella grows, C is depleted from surrounding austenite. Where the composition of the austenite adjacent to the cementite reaches a fixed value ferrite nucleates. Thus, the austenite is transformed to ferrite plus cementite, eutectoid cementite forming on existing 'eutectic' cementite. A divorced eutectoid occurs.

5.2.2. Al Alloys

Laser produced hypoeutectic Al-Si alloys consisted of superfine proeutectic dendrites ($\lambda_2 = \sim 1-2\mu\text{m}$) in a fine fibrous/rod eutectic of Al + Si ($\lambda_3 = \sim 0.1\mu\text{m}$). Al dendrites grow directionally in colonies.

These colonies form as lamellar sheets which are tilted so as to freeze at an oblique angle to the vertical when viewed in both the vertical and longitudinal direction. Rapid cooling induces undercooling which, because of skewing of the coupled zone, causes the volume of the proeutectic Al to increase (Table 3.4). For laser melted Al-10Si ~60vol% of the alloy was proeutectic. Composition analysis indicates that the eutectic composition has significantly shifted from equilibrium. The most extreme eutectic composition measured for laser melted Al-10Si was 24.7wt% Si (3.4.2.1.2.).

Hypereutectic Al-Si alloys produced by LSA consisted of proeutectic Si and proeutectic Al in a fibrous eutectic. Proeutectic Si occurred with either plate or dendritic morphology depending on the level of Si alloying. Where the amount of proeutectic Si is <30vol% the proeutectic formed faceted dendrites. Where the amount of proeutectic Si exceeds ~30vol% the proeutectic Si occurs as directionally orientated plates. Proeutectic Si is coated with a 'shell' of Al. Dendritic proeutectic Al grows from the Al 'shell'. Eutectic Si nucleates from proeutectic Si and grows as rods, 0.1-0.2 μ m dia, through the Al 'shell'. The eutectic then radiates in fan-like networks from the tip of these Si rods. Eutectic colony size varies with Si rod spacing, but typically grow over 3-5 μ m. Eutectic spacing varies with Si content. Low Si alloys have finer spacings than high Si alloys (Al-19Si λ_3 = 0.17 μ m, Al-72Si λ_3 = 0.48 μ m). Si alloying reduces thermal conductivity and so reduces cooling rate.

Si alloying increases surface hardness and abrasive wear resistance. Hardness increases linearly with Si content according to the formula: $H_v = 5.7\text{wt\% Si} + 20$ (Fig.3.22). Alloys containing up to 50wt% Si were ductile. 50wt% Si LSA specimens were seven times more wear resistant than unprocessed Al-10Si (Table 3.6). Alloys containing 72wt% Si were subject to brittle fracture.

5.2.3. Ti Alloys

The amount of C alloyed to Ti alloy substrates could be controlled by the thickness of the DAG precoat, the laser alloyed track profile (surface/volume ratio), or by the number of successive DAG reprocessings.

Microstructure varies with the C content of the melt zone. In 'low C' hypoeutectic melts β solidification is followed by TiC formation. Particles presumed to be TiC precipitate along β grain boundaries and along crystallographic planes of β grains. X-ray diffraction identified the structure as fcc TiC and martensite.

In 'high C' hypereutectic melts proeutectic TiC nucleates and grows dendritically from the liquid. The microstructure consists of proeutectic TiC in a matrix of β which has transformed to martensite. λ_2 varies from 0.3 to 1.5 μm depending on processing conditions and location within the melt. Where excessive C is alloyed and where poor melt pool stirring occurs, large irregular TiC particles (>100 μm dia) form heterogeneously.

The HAZ of all C alloyed Ti substrates was similar and ranged from β transformed to martensite near the melt interface to α plus β at the HAZ extremity.

Increasing the amount of C alloyed increases the volume fraction of TiC. Where the volume fraction of TiC increases laser track hardness increases and abrasive wear rate decreases. Hypoeutectic Ti-C alloys show a minimal improvement in wear resistance. In hypereutectic alloys, where dendritic TiC forms wear resistance can be considerably improved. Where C is alloyed to Ti-6Al-4V abrasive wear can be reduced to 15% of that for laser melted Ti-6Al-4V.

APPENDIX I

LASER TRANSFORMATION HARDENING

Laser hardening is an economically viable industrial application, capable of competing directly with relatively low cost conventional processes such as induction hardening. The advantages of laser hardening are:

- a. Accurate control of treated depth possible.
- b. Little or no machining required after treatment.
- c. Generally no external quenching is required.
- d. Surface hardening can be achieved with little or no contamination.

Typically, laser hardening is employed where case depths up to 1mm are required. Alloy composition, prehardened microstructure and section thickness affect both final thickness and case depth. In general, all materials which transform and are amenable to surface hardening by conventional techniques are suitable candidates for laser hardening.

Ferrous alloys are prime candidates for laser hardening. A thin surface layer of material is rapidly heated above the austenitizing temperature by the beam. Subsequent self quenching occurs producing a martensitic structure. The most important criteria for laser hardening steels are:

- a. Temperature of the heated substrate must reach into the austenitizing region.
- b. The substrate should be maintained at the austenitizing temperature long enough for carbon diffusion to occur.
- c. There should be enough mass so that the cooling rate by self-quenching is such that it could satisfy the critical quenching rate requirement.

As a result of the very rapid quenching rates plain carbon steels 0.2% C will harden, compared with a practical lower limit of 0.3% C for conventional hardening techniques. Conversely, steels containing spheroidal carbides or graphite cast irons require longer soaking times than is practical with short heating cycles. Since incomplete austenitization occurs, it is generally considered that these types of materials are unsuitable for laser hardening. Cast irons can only be hardened in those cases where the matrix will readily austenitize, the pearlitic matrix hardening as martensite on cooling, while the primary graphite remains unaltered.

APPENDIX II

LASER CLADDING

A.2.1. INTRODUCTION

The cladding of components whether it be for wear or thermal protection is of growing interest²¹¹. Commercial processes, primarily based on either gas welding or electric arc processes are available²¹². Laser cladding of Stellites is applied industrially²¹³, the problems of thermal quenching together with a lack of suitable cladding powders has limited development. In this appendix, laser cladding using a continuous pneumatic powder delivery system is described. This process was developed, and subsequently used to clad Stellite powders and WC-Co powders on to ferrous substrates. The attraction and 'pitfalls' of laser cladding these materials are discussed; in particular the problems of cladding powder (shape and size), interface bonding with substrate, and carbide dissolution.

A.2.2. REVIEW

Laser cladding is a technique similar to conventional hard facing in which the laser beam melts either a preplaced or continuously fed material causing it to flow over the surface of the substrate, to freeze and form a protective or wear resistant layer. Under controlled conditions, the laser melts a very thin surface layer of the substrate; this thin liquid layer mixes with the liquid cladding alloy and subsequently freezes to form a metallurgical bond between clad and substrate.

Cladding is applied where one set of properties is required for surface conditions and another for bulk, all at minimum cost. The main attraction of cladding is the range of material possibilities involved with coating one material on another.

Laser cladding, offers distinct advantages over traditional processes:

- a. High melting point alloys can be clad on low melting point workpieces.
- b. Controlled dilution levels. Dilution of cladding alloy with substrate is generally less than 5%.
- c. Good fusion bonding. The cladding is metallurgically bonded to the substrate.
- d. Uniform chemical composition and microstructure of the clad layer can be obtained. Particularly fine microstructures can be produced by the rapid quenching.
- e. Localised heating reduces the likelihood of thermal distortion of the substrate and allows a greater degree of control over the process.

Cladding alloys are available as cast rods, wires or powders. Alloy selection is based on such factors as service conditions, substrate materials, cladding processes and cost. There are several laser cladding techniques available:

- a. Pre-alloyed powders can be applied to a substrate prior to laser processing.²¹⁴⁻²¹⁶
- b. Alloy powders can be flame sprayed on substrates before laser processing.²¹⁷
- c. Plasma spraying can be used to deposit selected cladding alloys for subsequent laser processing.^{218, 219}
- d. Rods or wires laid on a substrate and then laser processed.²²⁰
- e. Powdered cladding material can be blown directly into the laser beam.²²¹

A.2.2.1. Continuous Pneumatic Powder Cladding

Ayers et al¹⁹⁶ introduced a laser melt/particle injection process during the late 1970's (4.2.). Rolls Royce have since adopted powder blown cladding for production hardfacing of Ni-based superalloy turbine shroud interlocks.²¹³ The tip shrouds of aero blades interlock and vibration of the interfacing edges causes severe wear. These edges are now laser clad with Stellite producing a hard wear-resistant pad. Weerasinghe²²² modified Rolls Royce's simple powder blowing apparatus and developed a feeder box based on an Archimedes screw arrangement which allowed precise control of powder feeding rates. The feeder system used in this study is based on Weerasinghe's concept.

Continuous pneumatic powder cladding is a dynamic process. Powder, fed at a controlled rate, is blown into the laser beam, where it melts and consolidates, Fig.A.2.1. Initial melting occurs at the substrate interface, a shallow melted layer of substrate mixes and bonds with the freezing clad (in preplaced clad processes melting first takes place at the preplaced layer). Hence, for powder fed cladding, dilution is controlled by powder feed rate rather than power density.

Continuously fed powder cladding is inherently more efficient than 'preplaced cladding' techniques which require preparatory descaling of the substrate and deposition of the clad before laser treatment. Continuously fed powder cladding can be carried out on substrates in their 'supplied condition', since substrate descaling occurs during cladding.

Cladding quality is of prime importance; ideally, clad tracks should be free of porosity and cracks. Track cross-sectional profile should reveal a small angle of contact at the clad edge and even melting of the substrate, Fig.A.2.2.a. At low powder feed rates, or high power densities, excessive substrate melting occurs, Fig.A.2.2.b. At high powder feed rates and low power densities, powder is insufficiently 'wetted' to the substrate and large contact angles occur, Fig.A.2.2.c. Interrun porosity can occur when tracks of section profile Fig.A.2.2.c. are laid together with insufficient overlap, Fig.A.2.2.a. For a given traverse speed and power density there is an optimum flow for maximising cladding rates.

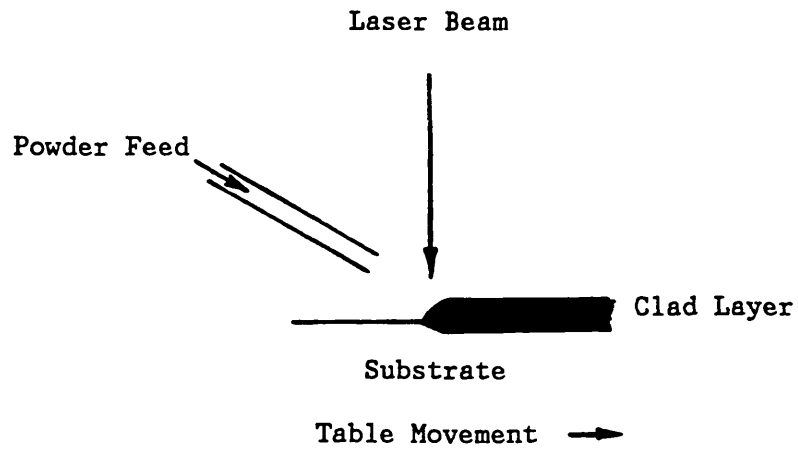


Fig.A.2.1. Continuously fed powder laser cladding

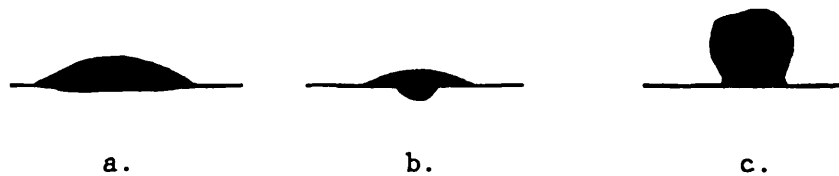


Fig.A.2.2.²²² Sectional profiles of clad tracks
a: ideal profile b: low powder feed rate c: high powder feed rate



Fig.A.2.3. Interrun porosity, caused by poor profile control
(A.2.2.c. above).

A.2.3. CONTINUOUS CLADDING TECHNIQUE

Cladding powder stored in a 'header box' and suspended above the work table was fed via an Archimedes screw arrangement down a 6mm diameter copper tube and into the path of the traversing laser beam, Plate 18a. The 'header box' contains typically 2kg of powder, is pressurised with a carrier gas (usually Ar). At the header box base a stepping motor drives a 3mm screw which in turn feeds powder into the 'equalised' copper pipe and so into the laser beam. Plate 18b shows the experimental hopper box. Increasing the stepping motors speed increases powder flow. Poorly flowing powders (some grades of Sintering WC-Co powders) were pneumatically fed, the box being pressured to a higher level. Excess carrier gas was bled off through small perforations in the delivery tube close to the workpiece.

A.2.4. STELLITE 31

A.2.4.1. Introduction

Stellite 31 has been used to hard face a chisel, by continuously fed powder 'overlap' laser cladding, so illustrating the possible commercial viability of this cladding technique. Stellite powders are readily available in a plasma spray form, a fine free flowing mix, and are ideally suited to powder feeding. Stellite 31 tends to have excellent melting and wetting characteristics.

Co-based alloys²²³ like Stellite 31 are used extensively in wear related applications because of their inherent high-strength, corrosion resistance and ability to retain hardness at high temperatures. Their high cost makes the prospect of cladding rather than casting an attractive proposition and since they are not as susceptible to cracking as Ni-based alloy, when rapidly cooled, a practical one. Gnanamuthu¹⁰ reported that preplaced rods of Stellite 1 could be successfully laser clad. Good interface bonding was accomplished with minimal substrate dilution. Nurminen and Smith²¹⁵ examined the laser cladding efficiency of Stellite 156 in three preplaced forms and concluded that laser beam absorption efficiencies ranged from 20% for fused preforms to nearly 80% for loose powder. Corresponding melting efficiencies ranged from 38% for fused preform to nearly 60% for sintered preforms and loose powder, hence loose powder is preferable to preforms.

A.2.4.2. Experimental Procedure

Stellite 31 powder was laser clad to a 3/4inch wood chisel, Table A.2.1. Having preheated the chisel blade to 650°C, so lowering its subsequent cooling rate and reducing the likelihood of cracking, overlapping Stellite tracks were clad across the blade width. Contraction stresses on the clad layer were reduced by allowing plastic distortion of the chisel. The blade bowed, towards the clad, during treatment. The clad layer was machined flat and a cutting edge ground on the tool, Plate 18c,d. The actual cutting tip of the blade is, therefore, Stellite. The chisel was shot-blasted, for cosmetic reasons, and then put into service. The Stellite chisel was used consistently over a six month period and proved to be tougher and more durable than equivalent hardened and tempered blades.

Table A.2.1. Alloy Compositions

wt%	C	Si	Mn	P	S	Cr	Ni	W
Stellite 31 Powder	0.5	-	-	-	-	25.5	10.5	7.5
Chisel Steel	1.15	0.2	0.3	0.035	0.035	-	-	-

A.2.4.3. Results

A single track of Stellite was clad on to an 'excess' piece of stock, chisel steel. This was sectioned and examined. Etching in nital reveals the substrate's microstructure and the nature of the interface bond, Plate 18e. Incipient melting along grain boundaries minimises alloying with the clad yet allows the clad to 'interlock' with the substrate, Plate 19a. The possibility of interface cracking is reduced and any likelihood of 'peeling' eliminated. Etching in 90vol% HCl, 10vol% H₂O reveals the clad layer, Plate 18f. The track has a good profile and is free of cracking and porosity. Stirring of the molten clad has drawn excess melted substrate into the track. This unintentional alloying modifies the microstructure and causes uneven etching. Convective mixing is in the same direction as that found for surface alloying (2.5.4.). Stellite solidification initiates at the substrate interface and progresses epitaxially as a primary dendrite phase with interdendritic carbides, Plate 19b.

A hardness traverse across a transverse section of the chisel clad revealed a uniform hardness HV460, softer than an equivalent steel blade, HV560. The Stellite tip was sufficiently hard so as not to blunt, with normal use, yet is not 'over' brittle.

A.2.5. CLADDING WC-Co ALLOYS

A.2.5.1. Introduction

WC-Co alloys have been laser clad on to ferrous substrates with limited success. Commercial 'ready-mix' WC-Co sintering powders are unsuitable for hopper feeding; particle fineness and shape irregularity making these powders susceptible to clogging. 'Amdry' and 'Sanvik' powders contain volatile fluxes, ~2% paraffin wax, which react causing severe porosity. In the presence of excessive heating WC dissociated, forming brittle η phase which is detrimental to physical properties. The possibility of dissociation was reduced by opting for a cladding powder containing minimum Fe, precoating the substrate with DAG (increasing free C) and by exact control of the processing parameters.

Very hard wear resisting surfaces, for particularly abrasive applications (for machine tools, mining drills and ore buckets) are always in demand²²⁴. Finish coatings of WC, TiC, TiN or Al_2O_3 are commonly applied to enhance abrasive resistance²²⁵⁻²²⁷. Thin, even, layers (microns) can be applied by chemical vapour deposition or plasma spraying, while thicker layers (mm) are hard-faced by fusion-arc welding. Steel shanked mining drills are hard faced with WC-Co²²⁵; the drill is dipped in WC-Co powder and then heated with an oxyacetylene torch. Ideally the surface layer of the drill tip and the Co melt and form a coherent bond as they solidify, while any WC particles are unaffected. The objective is to retain hard wear resistance WC chips in a 'resilient' Co matrix.

Ayers et al experimented with solid particle injection of TiC and WC into laser melted substrates of Al, Ti and Fe and report a significant increase in wear resistance¹⁹⁶⁻²⁰⁰ (4.2.). Gnanamuthu¹⁰ has illustrated WC-Fe cladding on ferrous substrates, unmelted WC chips being retained in a Fe matrix. Weerasinghe and Steen²²¹ have briefly reported cladding of TiC in a stainless steel matrix. Unmelted TiC particles were retained in the upper layer of a stainless 316 clad. The present exercise was carried out to evaluate the viability of laser cladding WC-Co in preference to existing techniques.

A.2.5.2. Results

Initial trials were carried out using Amdry 983 a WC-17Co spheroidal plasma spray powder clad on a pure Fe substrate, Plate 19c,d. By overlapping layers a 1.7mm thick clad covering an area of 35mm x 60mm was produced. Spherical voids in the range 0.05 - 1.20mm constituted ~30vol% of the clad. Pore inhomogeneity caused hardness variations across the clad surface, Hv950-1150. Carbide dissolution occurred near the substrate interface. High power densities or excessive interaction times causes carbide dissociation in the clad as well as at the interface Plate 20b-d. A 10sec etch in a freshly mixed solution of 10vol% sodium hydroxide, 10vol% potassium ferrocyanide, 80vol% H₂O, revealed characteristic brown cauliflower-like η precipitates (the proper description of η phase is difficult to resolve though it is established that two carbides exist, Co₆W₆C and an M₆C type carbide where composition ranges Co_{3.2}W_{2.8}C - Co₂W₄C). Because of the nature of the process, the molten pool does not exhibit a conventional flow pattern; it appears to behave rather as a 'mush' than a liquid. Although the Co matrix does exhibit directional solidification, any effect is overwhelmed by the bulk of WC. It is difficult to establish conditions where neither carbide spooling nor excessive substrate melting does not occur, the latter, being the lesser of two evils.

Sanvik WC-9Co sintering powder was baked at 350°C for 40min, burning off any volatile fluxes, before use. The resulting powder was extremely difficult to feed; blockages in the hopper caused cavitation around the screw; screw feeding was erratic and delivery pipe clogging resulted in a pulsed delivery mode. Hopper pressurisation improved delivery though this limited the flow rate control. Bed fluidisation, initially by extending the Ar delivery pipe from the box-top to the screw (flushing the screw with Ar at close range), and subsequently by blowing Ar through vents in the flutes of the screw²²² was used. The latter technique was particularly effective; it induced uniform free flowing delivery and permitted flow rate control via screw speed. 'Wax-free' powder produced 'pore-free' clads. Substrate preheating was used to eliminate clad cracking. Process optimisation, beam defocusing (5mm dia), increasing scanning speed (~20mm/s) at a high constant power (1.8kW) eliminated dissolution.

Fig.A.2.4. illustrates an X-ray diffractometer track of an optimised Wc-Co track (at a depth of half the clad thickness). Dissociation has not apparently occurred. (This conclusion was supported by optical microscopy).

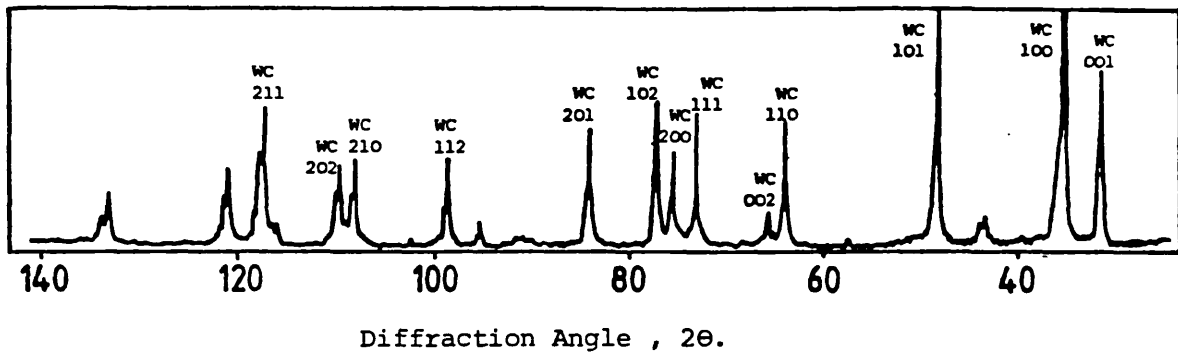


Fig. A.2.4. X-ray diffractometer trace of an optimised WC-Co track.
Unwaxed Sanvik CM clad on pure Fe substrate. Carbide dissociation has not occurred. Radiation source: Cu.

Various Sanvik powders were premixed with additional Co powder and clad. Clad hardness decreases as wt% Co matrix is increased, Fig.A.2.5. The finer the WC grade the harder the clad, though finer WC grades are more susceptible to dissociation. The composition-hardness plot is similar to 'sintered' WC-Co composition-hardness plots,^{2,24} though the clad values are arguably a little on the soft side.

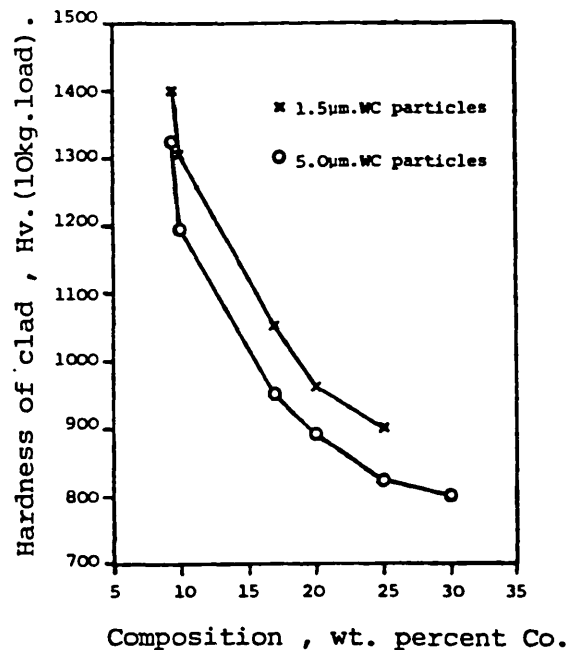


Fig.A.2.5. Hardness Plot of Laser Clad Tracks of Various WC-Co Compositions. (Av hardness value of a range of impressions midway through the clad). Clad alloys: unwaxed Sanvik CM mixed with Co or Sanvik WC mixed with Co, Table A.2.2.

A study of eight different suppliers was instigated to identify suitable commercial ready-mixed powders, Table A.2.2. WC-Co powders form two categories, sintering powders used for pressing machine tool tips etc (Sanvik, Plate 20a), and plasma spray powders (Amdry, Amperit, Metco etc) used for spraying thin finish-coatings. Most powders are supplied in an agglomerated form, ie fine WC chips bonded into spheres. Plasma spray powders, by their very nature, require good flow characteristics and this attraction outweighs their higher costs. Amdry 983 exhibited the best feeding characteristics. It appeared to consist of bonded carbide spheres intermixed with Co spheres, Plate 19g. However, Amdry 983 is waxed. Amperit 526 is a suitable compromise, WC-Co has been agglomerated into $\sim 50\mu\text{m}$ spherical particles and sintered, Plate 20e. The powder could be hopper-fed without fluidization, contained no waxes and the sample supplied was particularly low in Fe content, 0.2Fe (though specification tolerance is 2Fe max, Table A.2.2.). Amperit 526 used in conjunction with a defocused beam (5mm, 1.8kW) and a moderate scanning speed (10mm/s) proved a suitable compromise.

A.2.5.3. Discussion

In sintering accurate weighing and mixing of W and C black is critically important^{229, 228}. The stoichiometric content of 6.12C must be closely maintained in order to avoid either free graphite or the formation of W_2C (which leads to 'brittle' η). Suzuki²²⁹ showed that rupture strength increases with C content to a maximum just before free C appeared. Since the range of homogeneity is so critical a slight C excess is preferable to a slight shortage. Should dissociation occur during laser processing WC reprecipitation is unlikely; thus laser cladding is severely limited by WC stability.

TiC offers an alternative; it has a higher heat of formation (free energy of formation WC -33.5 KJ/mol, TiC -174 KJ/mol, @ 1000°C)¹⁹ and is less likely to dissociate. TiC melts congruently and has a much wider range of homogeneity than WC. The reduced toughness of TiC over WC has in the past limited its advantages (it being unsuitable for tool sintering), though in terms of laser cladding, carbide stability may prove more important. A limited appraisal of TiC cladding has been

made. TiC chips were separately clad in a Co powder matrix on to ferrous substrates and also directly injected into laser melted Ti alloy substrates. Excessive power densities or long interaction time appeared to cause carbide dissociation. Where TiC was injected into Ti alloys, the carbide reprecipitated as TiC dendrites. Reprecipitation did not impair hardness. Interest in TiC suitability led to a review of 'Ayer's work' on TiC injection¹⁹²⁻²⁰⁰ (4.2.). Ayer's findings, together with the implication of TiC reprecipitation, was followed up with a detailed study of laser C alloying of Ti alloys to form hard TiC precipitates (Chapter 4).

Table A.2.2. WC-Co Cladding Alloys

	<u>Manufacturer</u>	<u>Powder Description</u>	<u>WC Grain Size</u>
1.	<u>Amdry</u>	Amdry 983 (Plate 19g) WC-17Co (Agglomerated, waxed)	-
2.	<u>HCST Amperit</u>	Amperit 526.279 (Plate 20e) WC-17.6Co-<0.2Fe (Agglomerated, sintered)	-53µm + 10µm
3.	<u>Carboloy</u>	WC-16.5Co (sintered, granules)	-53µm + 10µm
4.	<u>Cabot</u>	Haystellite 52F WC-16Co (waxed)	-
5.	<u>Metco</u>	Metco 73F-NS-2 WC-17Co-2.1Fe	-53µm + 20µm
6.	<u>Murex</u>	WC-9Co-1.53Fe (sintered, waxed) WC-15Co-1.93Fe(sintered, waxed)	-37µm + 5µm -53µm + 20µm
7.	<u>Sanvik</u>	'N' Grade WC-6Co (waxed) 'CM' Grade (Plate 20a) WC-9.5Co (waxed) WC Powder Co Powder	~1.5µm ~1.5µm 5µm 1µm

PLATE 18

- a. Laser cladding by powder injection. Cladding powder is blown into the beam at the point where the beam melts the work piece. (Photo reproduced by permission of V M Weerasinghe Ref.222.).
- b. Powder feeder box fitted with horizontal screw with attached stepping motor and cooling fin (left) and delivery box (right).
- c. Stellite 31 clad on a 3/4inch wood chisel. The chisel has been ground and grit blasted. Clad layer laid down by overlapping tracks (1.8kW + preheat, 5mm, 6mm/s).
- d. High magnification view of chisel tip.
- e. Transverse sectional view of a single track of Stellite 31 clad on chisel steel substrate (1.8kW + preheat, 5mm, 6mm/s), etched in nital to reveal substrate microstructure.
- f. Plate 18e, etched in 90vol% HCl, 10vol% H₂O₂ to reveal clad microstructure. Substrate alloying has caused uneven etching and so illustrated 'melt pool' motion, Fig.2.19.

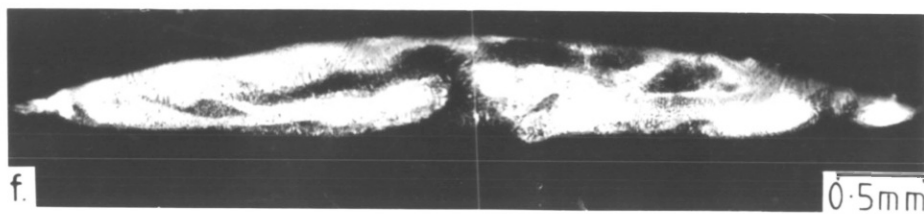
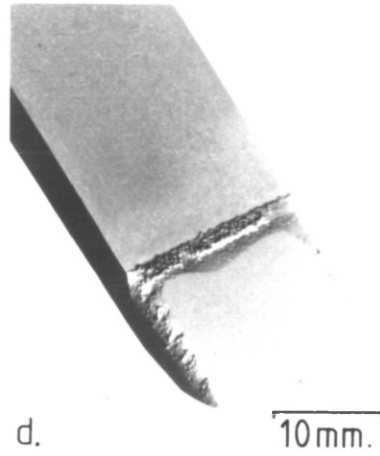
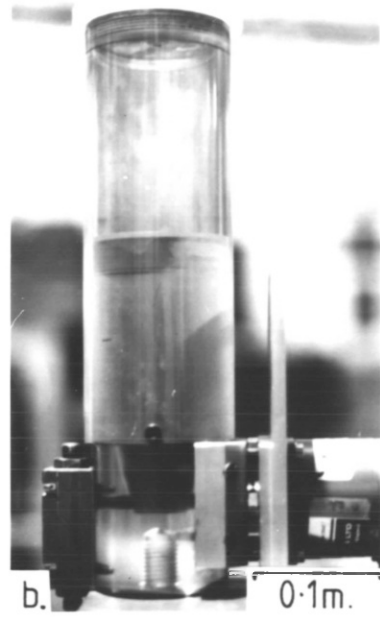
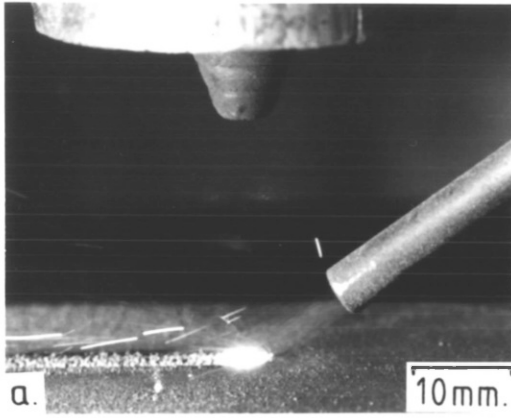


PLATE 19

- a. High magnification view of substrate/clad interface, Plate 18e. Incipient melting along the grain boundaries of the substrate has occurred.
- b. High magnification of substrate/clad interface, Plate 18f. The clad has solidified as epitaxial dendrites with interdendritic carbides.
- c. SEM view of Amdry 983 powder, WC particles held by paraffin wax mixed with Co spheroids.
- d. SEM view of laser clad Amdry 983. Distinctive triangular prism shaped stoichiometric WC particles in a Co matrix.

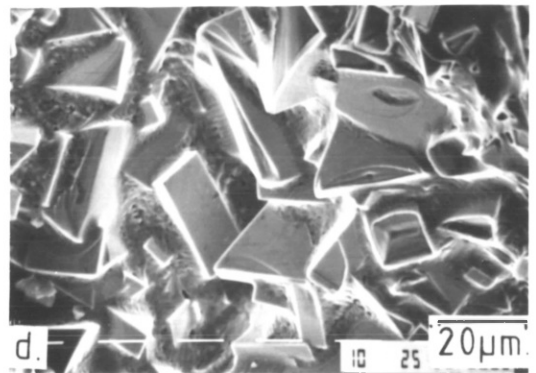
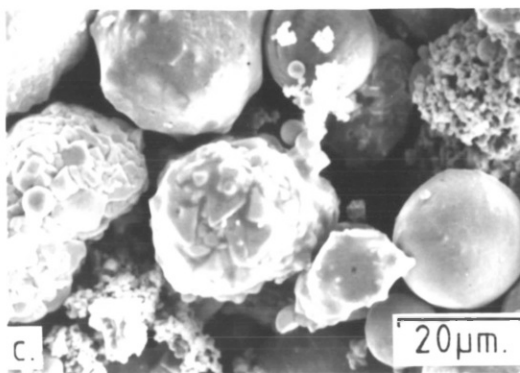
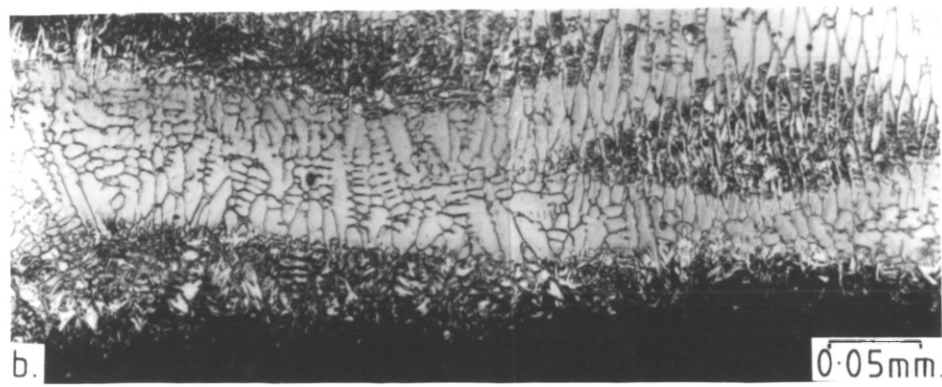
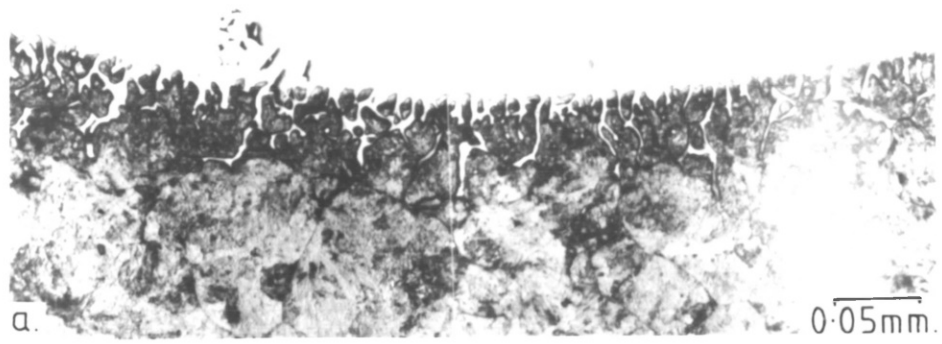
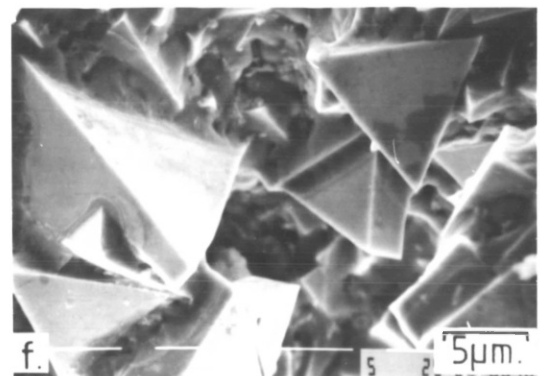
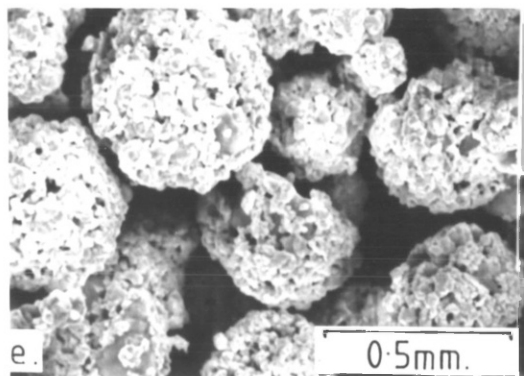
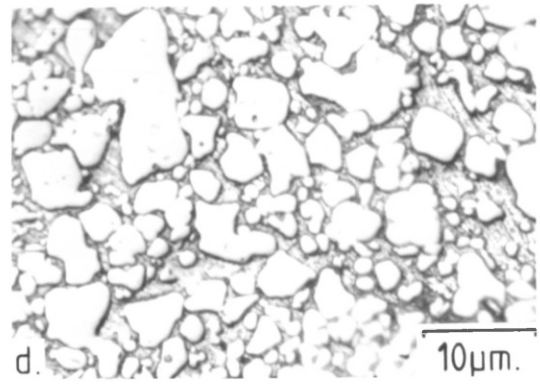
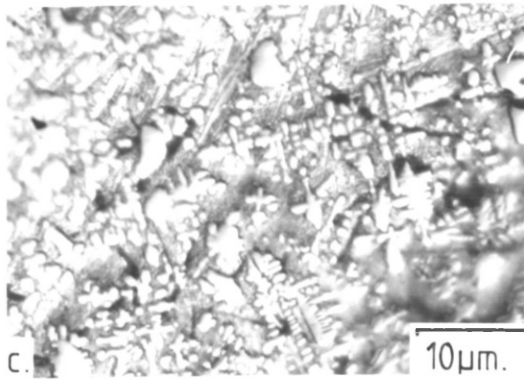
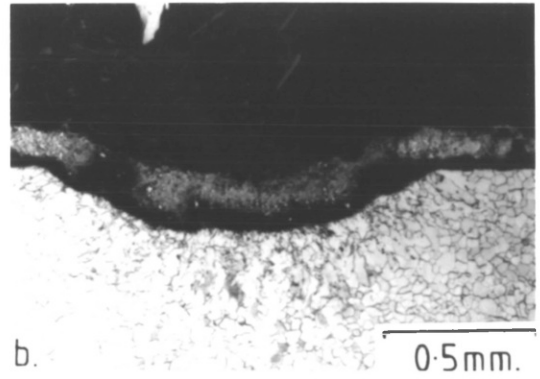
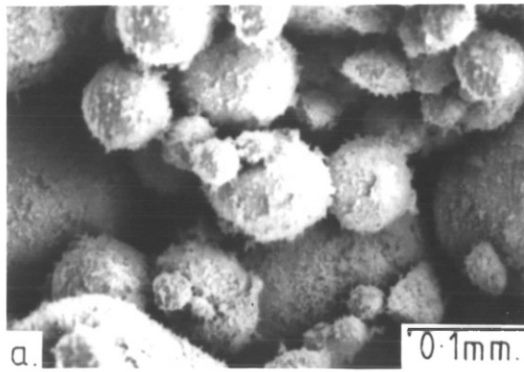


PLATE 20

- a. SEM view of Sanvik WC-9.5Co 'CM' sintering grade powder. Agglomerated spheres of WC-Co and paraffin wax.
- b. Transverse section of laser clad Sanvik 'CM' sintering powder on a ferrous substrate. Excessive power intensity (and insufficient cladding powder) has caused uneven substrate melting (1.75kW, 1.0mm, 20mm/s, unetched).
- c. High magnification view of substrate/clad interface region, Plate 20b. Carbide dissolution has occurred. Graphite together with a proeutectic 'Plate-like' phase (possibly cementite) and an unknown proeutectic dendritic phase have formed together with a lamellar eutectic.
- d. High magnification view 'edge region' of clad (region of minimum heating), Plate 20b. Slight dissolution has occurred giving the WC 'tips' a rounded profile. The matrix has formed as a lamellar eutectic (perhaps a WC-Co pseudobinary eutectic).
- e. SEM view of Amperite 526, WC and Co have been agglomerated into larger spheroids and then sintered.
- f. SEM view of laser clad Amperite 526, stoichiometric WC in a Co matrix.



APPENDIX III

WEAR RESISTANCE

This thesis considers aspects of laser processing and while the prime objective is to make a detailed microstructural evaluation, the indirect objective is to enhance surface properties of alloys. Wear resistance is one important property^{226, 230, 231}.

Wear encountered in industrial situations can be broken down into five categories: abrasive, adhesive, erosion, fretting and chemical. Abrasion accounts for by far the largest share of the wear problems and is due to hard particles or protuberances being forced against a moving surface. Abrasion is characterised by surface scratching or scoring. In alloys designed to resist wear, a dispersed hard phase is commonly induced. Evidence suggests that abrasion resistance of such alloys is controlled by the hard phase volume fraction and by the size and morphology of the hard phase. After a transient stage where the softer matrix is worn down preferentially, the abrasive particles ride on the hard phase, so reducing wear.

Most mathematical or mechanistic approaches to wear suggest some variety of the following relationship:

$$V = \frac{kLd}{P} \quad (A.3.1.)$$

V = Vol of material lost to wear (mm³)

L = Load (kg)

d = Sliding distance (mm)

P = hardness (kg/mm²)

k = Wear Coefficient

The magnitude of k depends on factors such as the wear mode (abrasive or adhesive), the contact material and the conditions of contact. Any change in load, sliding velocity of contacting surfaces or environmental conditions may cause catastrophic changes in wear rate of one or both the contact surfaces. Great care must be exercised in

applying general solutions to specific problems; actual engineering situations are far more complex than equation A.3.1. suggests. This generalised 'wear equation' does, however, illustrate a fundamental precept in wear: wear rate decreases as hardness increases.

Wear caused by the sliding of metallic surfaces is often referred to as adhesive wear. The pressure between the contacting asperities is high enough to cause local plastic deformation. Adhesion occurs between a few asperities which subsequently rupture, usually resulting in metal transfer between surfaces. Wear decreases if the asperity is harder, because the contact area is lower, ie area of contact is inversely proportional to hardness. Adhesion and transfer may also occur where harder surface asperities (steel) ploughing through a softer counterface (Al) cause metal debris to become trapped and embedded in the surface grooves of the harder metal. Wear under metal-to-metal sliding conditions, unlike abrasive wear, is subject to sharp transitions in behaviour. Variations in load and speed will affect 'wear temperatures' and alter wear rates.

APPENDIX IV

ORIGIN OF LEDEBURITE SOLIDIFICATION AND EUTECTOID GROWTH THEORIES

At lower temperatures, residual austenite undergoes a lamellar eutectoid decomposition transforming to ferrite (solubility $\sim 0.02\text{C}$) and cementite. Both eutectic and eutectoid transformations are directly linked, since they are controlled by similar mechanisms of formation (interlamellar spacing is refined by depressing reaction temperatures or increasing GR). For the cast irons, any discussion of the Fe-Fe₃C eutectic reaction must inevitably include the eutectoid reaction.

In 1905 Vogel²³² proposed that growth of lamellar eutectic structures takes place by alternative precipitation of two elemental constituents one upon the other in the form of parallel plates. In 1912 he modified this theory when he demonstrated that the axis of the phases were perpendicular to the solid-liquid interface (growth occurring by an edgewise mechanism). While Vogel's later work was acknowledged eminent scientists of the day, Tammann²³³ and Desch²³⁴ favoured the alternative, sidewise mechanism.

By the early 1920's a greater understanding of solidification led to a revision of these differing theories. Brady²³⁵ and Portevin²³⁶ observed that rapid cooling refined the eutectic and concluded that this was due to edgewise growth. Concepts applied to the formation of lamellar eutectics influenced thinking with respect to pearlite transformations. Hallimond²³⁷ in 1922 described the edgewise growth of pearlite in steels as taking place by the diffusion of C through austenite. Hull and Mehl^{238, 239} expounded a lamellar spacing/undercooling relationship, ie a linear relationship existed between $\log \lambda_{\text{Pearlite}}$ and $1/\Delta T$. This was followed in 1946 by Zener's⁸¹ classical paper 'Kinetics of the Decomposition of Austenite', where he presented a theory for diffusion controlled growth of a two phase structure, ie if a volume of pearlite of depth δ and lamellar spacing λ is advancing in an edgewise mode, and if growth occurs by an amount dx ; the mass transformed per lamellar spacing is $\rho \lambda \delta dx$.

The decrease in free energy resulting from the formation of pearlite is approximately:

$$\Delta G = \frac{\Delta H(T_e - T)\rho}{\lambda} \delta dx \quad (A.4.1.)$$

The formation of this pearlite is accompanied by an increase in ferrite-cementite interfacial energy of $2\sigma\delta dx$, and lamellar growth will only be possible when the increase in surface energy is outweighed by the decrease in free energy resulting from transformation. There is then a minimum possible spacing given by:

$$\lambda_{\min} = \frac{2 T_e \sigma}{\rho \Delta H(T_e - T)} \quad (A.4.2.)$$

In the same way eutectic spacing is determined by balancing the tendency to reduce diffusion distances in the liquid and the tendency to increase it in order to reduce interfacial area.

Zener⁸¹ estimated the effect of diffusion and took into account the surface energy of the lamellar structure. Having found that lamellar spacing was controlled by undercooling he predicted that the product of growth velocity and square of the lamellar spacing should be constant.

$$\text{ie } \lambda^2 R = \text{Const} \quad (A.4.3.)$$

According to (A.4.2.) interlamellar spacing is inversely proportional to the amount of undercooling. Therefore, a log plot should have a slope of -1. Using the data of Pelliser²⁴⁰, Zener⁸¹ plotted this relationship, Fig.A.4.1., together with Mehl's²³⁸ original relationship, Fig.A.4.2. In both cases the experimental points fall in a straight line. However, they give radically differing results, illustrating the danger of extrapolating a formula that fits experimental data over a limited range.

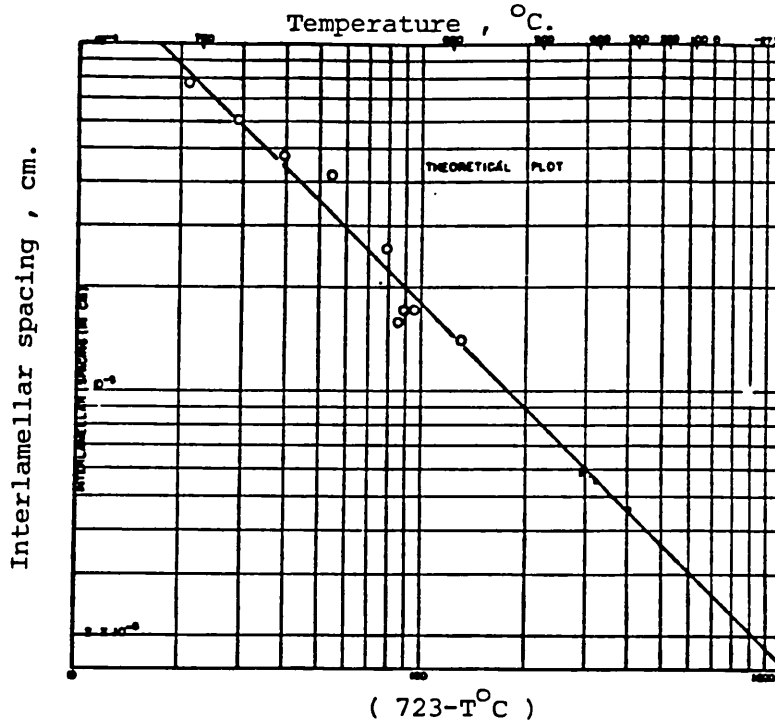


Fig.A.4.1.²⁴⁰ Variation of $\lambda_{\text{pearlite}}$ with T according to Zener. By extrapolating Zener's relationship one surmises that at 400°C $\lambda_{\text{pearlite}} = 550\text{\AA}$

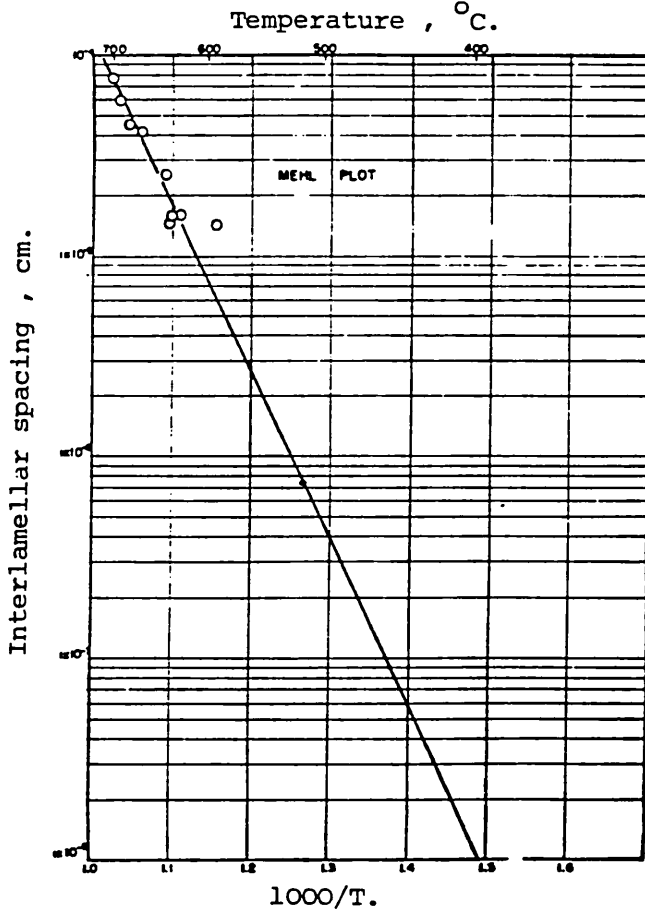


Fig. A.4.2.²³⁸ Variation of $\lambda_{\text{pearlite}}$ with T, according to Mehl. By extrapolating Mehl's relationship one surmises that at 400°C $\lambda_{\text{pearlite}} = 1\text{\AA}$.

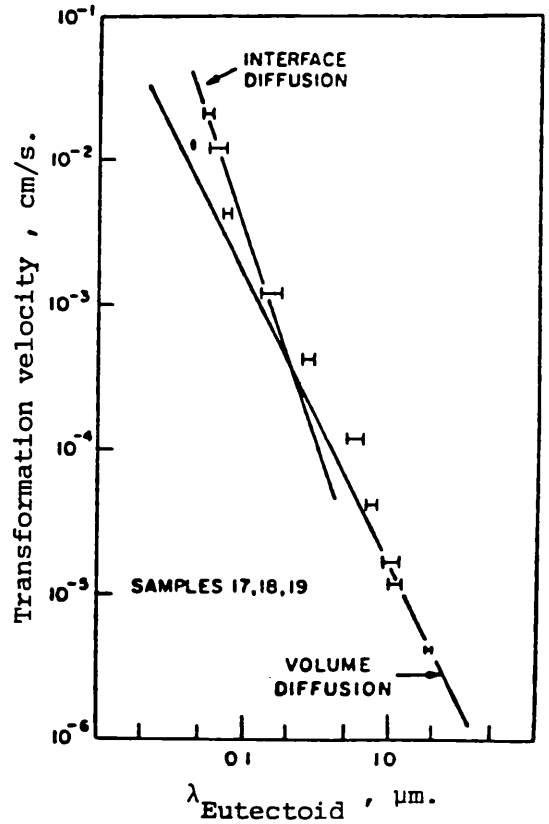


Fig.A.4.3.²⁴⁶ Relationship between transformation velocity and interlamellar spacing for Fe-C eutectoid alloy.

Hillert²⁴¹ extended Zener's model⁸¹ and, after an investigation of the role of interfacial energy, was able to calculate an approximate interface shape. Tillier²⁴² proposed a minimum undercooling condition and solving simple diffusional equations by dimensional arguments and physical reasoning, showed that $\lambda_{\text{Pearlite}}$ varied with R . During the 1960's a number of workers^{243, 244} considered the control of pearlite growth by boundary diffusion. Hillert²⁴⁵ obtained the relationship:

$$R = 12KD_{\beta}\delta \frac{\lambda^2}{\lambda^{\alpha}\lambda^c} \frac{C_e^{\gamma\alpha} - C_e^{\gamma c}}{C^c - C^{\alpha}} \frac{1}{\lambda^2} \left[1 - \frac{\lambda_{\min}}{\lambda}\right] \quad (\text{A4.4.})$$

where: K = boundary segregation coeff.

D_{β} = boundary diffusion coeff.

δ = boundary thickness

λ^{α} = ferrite lamellae thickness

λ^c = cementite lamellae thickness

$C_e^{\gamma\alpha}$ and $C_e^{\gamma c}$ are the equilibrium C concentrations in γ ahead of ferrite and cementite lamellae.

C^c and C^{α} are the C concentrations in cementite and ferrite respectively.

$\lambda_{\min}$ = critical spacing from which the growth rate is zero.

Bolling and Richmann²⁴⁶ measured microstructural refinement in Fe-C eutectoid steels over a wide range of transformation velocities Fig.A.4.3., and concluded that their data fits a relationship:

$$R\lambda_{\text{Pearlite}}^{2.4 \pm 0.1} = \text{Const.} \quad (\text{A.4.5.})$$

APPENDIX V

Al ALLOY MODIFICATION BY ELEMENTAL ADDITIONS

In 1921 Pacz²⁴⁷ reported that refinement or 'modification' could be achieved by adding certain alkali fluorides to the melt before pouring. Na additions at concentration levels of ~0.01wt% are commercially used. The structural change is from one of interconnecting Si flakes in an Al matrix to an apparently finer distribution of irregular fibres. The effect of a soluble addition must involve some change in the equilibrium phase diagram. A report by Kobayashi et al²⁴⁸ based on thermal analysis of normal and modified alloys claimed that Na elevated the Al liquidus temperature by 1-2K so displacing the apparent binary Al-Si eutectic to higher concentrations. Previous discussions suggested that Na may depress the eutectic by as much as 12K,^{151, 152, 249, 250}; a finer microstructure would be expected because the rate of nucleation will be greater in the undercooled conditions. Two mechanisms of modification have been postulated:

- a. Restricted nucleation ie Na retards Si nucleation
- b. Restricted growth ie Na retards Si growth.

Kim and Heine¹⁵⁴ claim that the Si flake/fibrous morphology is purely growth temperature dependent, Na modification reducing the potency of Si nucleation so displacing nucleation to lower temperatures. Flood and Hunt²⁵⁷ used a quenching technique to examine the solidification pattern and concluded that Na modification inhibited nucleation.

The concept of restricted growth involves Na either acting as a mechanical obstruction, forming a precipitate ahead of the interface²⁴⁹, or by being absorbed, poisoning growth sites¹⁴³. Davis^e and West^{252, 253} proposed that undercooling arises from the need for an increased driving force to maintain growth on a poisoned Si/eutectic interface. Crosley and Mondolfo¹⁵⁵ postulated that Na alloying causes Al to grow ahead of the Si. They supported this by suggesting that Si is interconnected in unmodified alloys but discontinuous in modified, Na inducing an exchange of leading phase via Thall and Chalmer's

concept¹³⁸. Thall and Chalmers¹³⁸ considered that eutectic Si trails the α phase and that overgrowth of Si is promoted by a reduction in boundary energy due to Na absorption, or by thermal effects induced by rapid chilling. However, the argument of Crosley and Mondolfo¹⁵⁵ is based on the misconception of a discontinuous modified eutectic, whereas it is now known to be continuous. In a recent study Hanna et al²⁵⁴, reviewing the effects of alkaline earth metals on Al-Si alloys, showed by thermal analysis, that modified growth rather than nucleation causes Si to grow anisotropically.

The use of Na presents founding problems such as reduced fluidity and elemental loss through evaporation and oxidation, hence remelting is impracticable. Development has led to the use of a Sr modifier²⁵⁵. Sr losses during melting are reduced while at the same time proeutectic Si is suppressed, enhancing ductility and toughness.

APPENDIX VI

LASER SURFACE ALLOYING C TO Al ALLOYS

A.6.1. INTRODUCTION

LSA of Si may prove a suitable method of generating high Si faces on the cylinder bores of Al alloy combustion engines. While Si alloying increases hardness it will not enhance piston/cylinder lubrication. DAG graphite was laser alloyed to Al alloys. It was hoped that sufficient free C would be retained in the surface melted layer to reduce surface friction.

Lightweight antifrictional Al-graphite particulate composites have already been invented²⁵⁶⁻²⁵⁸; however, their development has been inhibited by manufacturing problems. Liquid Al does not readily wet graphite. It is reported that graphite is unwettable below 1080°C²⁵⁹. Various foundry techniques have been introduced to prevent graphite rejection. Graphite particles are sometimes coated with Cu or Ni to improve wettability and injected into stirred melts²⁶⁰⁻²⁶². Stirring creates a vortex which enhances particle dispersion. Alternatively, ultrasonic vibration used in conjunction with surface active elements will disperse uncoated particles²⁶³. In a third process graphite particles are injected into an agitated semi-solid alloy²⁶⁴.

There is little information available on the Al-C system though the solubility of C in liquid Al has been determined^{265, 266}, Table A.6.1. A proposed phase diagram²⁵⁶ shows C in equilibrium with liquid solution above ~2050°C. At about this temperature an unidentified phase, tentatively suggested to be Al₂C₂, was indicated to form. At lower temperatures a stable rhombohedral carbide, Al₄C₃, has been shown to form by a peritectic reaction between Al₂C₂ and liquid at ~1850°C²⁶⁶. On cooling, the Al₂C₂ phase undergoes a eutectoid reaction at ~1700°C decomposing to Al₄C₃ and graphite.

TABLE A.6.1. Solubility of C in Al

	Temperature, °C	Solubility, wt%C
Ref 265	800	0.10
	1000	0.14
	1200	0.32
Ref 266	1800	0.90
	1900	2.2
	2000	4.2
	2100	5.2

A.6.2. RESULTS

DAG graphite or diamond dust was preplaced and laser alloyed to pure Al and Al-10Si. In a subsequent exercise C was alloyed in unison with Si, DAG being preplaced and the Si powder being powder fed. A suitable facility for C analysis was not available, so limiting the identification of free graphite or carbides. Consequently, only the physical shape of the tracks, microstructural morphology and precipitate distribution are reported.

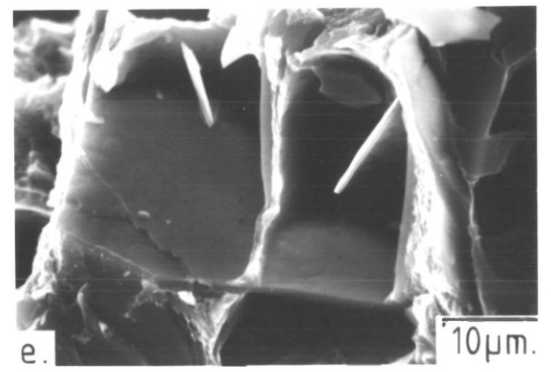
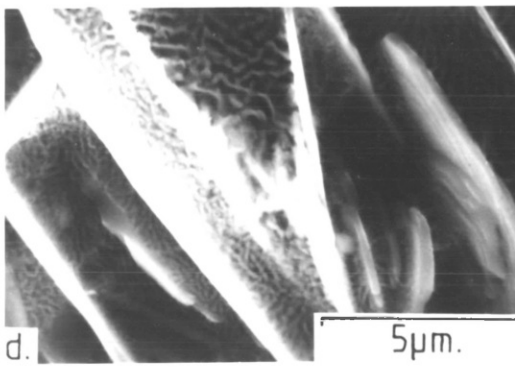
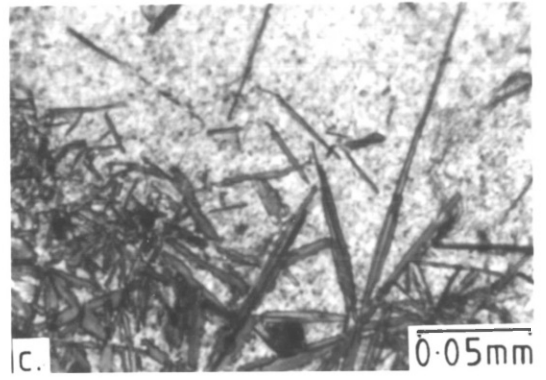
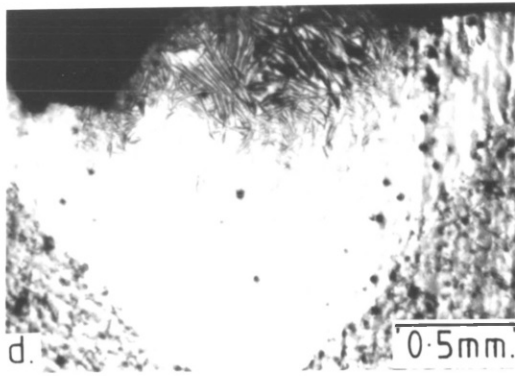
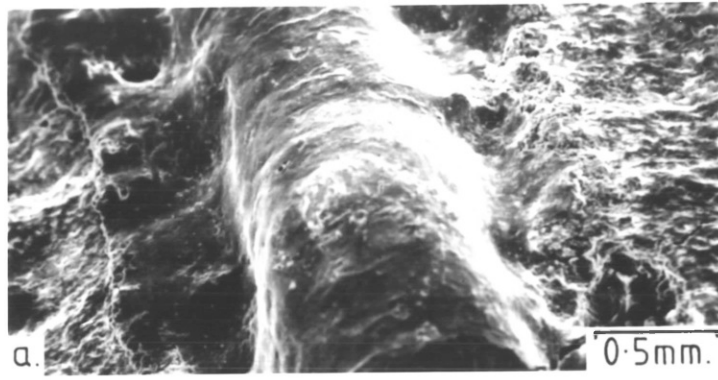
In C-'low' Si alloying situations (C alloying to pure Al or Al-10Si) track surface roughening occurred.. Ripple cycles were erratic both in amplitude and in cycle length. Porosity was prevalent. When alloyed in unison with Si powder (C and Si alloyed to form a 30-50 Si alloy), track surface texture 'smoothed', rippling amplitude harmonised and porosity was eliminated, Plate 21a. C containing phases were presumed to precipitate in two plate like morphologies, discernible by their colouring and shape; larger, darker plates (up to 0.6mm in length) and finer dove-grey plates containing mid-ribs, Plate 21b-e. It is possible that the former is free C and the latter an aluminium carbide. These C containing laths segregate in the upper portion of the track, not unexpectedly since C density $(2.2\text{g/cm}^3)^{19}$ is less than either Al $(2.7\text{gm/cm}^3)^{19}$ or (Si $2.4\text{g/cm}^3)^{19}$. Track hardness was seen to increase with C alloying implying that 'hard' aluminium carbides may have precipitated.

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PLATE 21

- a. SEM view of C and Si alloyed to CP Al (one alloying cycle 1.8kW, 1.5mm, 15mm/s). Smoothly contoured alloyed track.
- b. Transverse sectional view of C alloyed to Al-10Si (1.8kW, 1.0mm, 8mm/s, 4 DAG reprocessings). Particles, assumed to be C containing, have precipitated in the upper portion of the melt track.
- c. High magnification view of melt track, Plate 21b, illustrating dove grey plate-like precipitates; note central plate rib.
- d. SEM view of melt track, Plate 21b (etched in 1 vol Hf, 1 vol HNO₃, 5 vol Acetic acid). Plate-like precipitates and interrelated irregular eutectic.
- e. SEM view of melt track, Plate 21b (etched in 1 vol Hf, 1 vol HNO₃, 5 vol Acetic acid). Plate-like precipitates and interrelated proeutectic Al dendrites.



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