

LASER SURFACE MELTING

OF STAINLESS STEEL

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SUMMARY

This project has investigated the laser surface melting of stainless steels so as to modify their properties, and with a view to a better understanding of the limitations and possibilities of laser surface melting in general. Tests were carried out on two steels, one was martensitic (Fe-12%Cr-0.19%C) and the other was austenitic (Fe-17%Cr-11%Ni-2.5%Mo). The treatment produced a hardened surface layer on the martensitic steel and redistributed chromium in the sensitized austenitic steel restoring the materials intergranular corrosion resistance.

Experimental work was carried out to find treatment conditions that produced treated tracks with shallow profiles of reproducible dimensions. Suitable treatment regimes were identified.

The topographies of resolidified surfaces were studied by a statistical evaluation of digitised profiles.

The microstructures of treated material were studied by optical microscopy, x-ray diffractometry and conventional and scanning transmission electron microscopy; this revealed essentially weld type microstructures. However rapid cooling suppressed δ -ferrite formation in the austenitic steel and the martensitic transformation in the martensitic steel.

Residual stresses were identified to be of primary importance in determining the behaviour of treated material and were measured over a range of treatment conditions in both steels. Subsurface stresses in the austenitic steel were of the order of the tensile yield stress. The stresses in the martensitic steel were highly process sensitive ranging from -500 to 600MPa (tensile). Stress relieving heat treatments were evaluated for both steels.

The fatigue behaviour of treated specimens was evaluated by mechanical testing. The results were interpreted in terms of the hardening and the residual stresses produced by laser surface melting and the defects that initiated fatigue cracks.

The pitting corrosion behaviour of the surfaces was investigated by the potential sweep method. In order to facilitate accurate testing a microcomputer was interfaced with a potentiostat. This system controlled and monitored the behaviour of an electrochemical cell while a series of laser treated and conventionally treated samples were tested. The results were interpreted in terms of residual stress, thermal history and solute distribution as indicated by STEM-EDX. The intergranular corrosion resistance of treated austenitic steel was evaluated by a boil-in-acid test and an improvement over the sensitized condition was observed.

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SYMBOLS

a	Length of major axis
A	Advance between tracks
b	Breadth
c	Initial solute concentration; length of minor axis
d	Interplanar spacing
D	Depth; Diffusivity
E	Young's modulus; potential
E()	Expectation
F	Force
G	Thermal gradient
h	Height
i	Current; integer
I	Moment of inertia; intensity
j	Integer
k	Ratio of solute concentration in solid to solute concentration in liquid; constant
L	Sample length
M	Bending moment
N	Fatigue life; integer
N5	Voltage increment
P	Power
r ²	Determining co-efficient
R	Solidification front velocity; relative peak intensity
R()	Autocovariance function
Sk	Skewness
S1	Potential sweep rate upwards
S2	Potential sweep rate downwards
t	Time
T	Temperature
T2	Oxide stripping time
T3	Time increment
V	Velocity; volume fraction
V1	Maximum potential
V2	Initial potential

x, y, z	Cartesian co-ordinates
α	Direction cosine of stress; ferrite
α'	Martensite
β	Correlation length
β^*	Decay constant
γ	Austenite; surface tension
δ	Delta-ferrite
Δ	Sampling interval
ϵ	Strain
θ	Bragg diffraction angle
λ	Wavelength
ν	Poisson's ratio
σ	Stress
$\bar{\sigma}$	Equivalent stress
τ	Delay
ϕ	Diameter of incident beam; direction of measured stress
ϕ	Angle between specimen surface and diffracting planes
$\angle$	Angle

SUFFICES

C	Carbide
Corr	Corrosion
f	Flow
i	Integer
m	Measured
R	Reference electrode
W	Working electrode
x, y, z	Axes
α'	Martensite
γ	Austenite
ϕ	Direction of measured stress
ϕ	Angle between specimen surface and diffracting planes
1, 2, 3	Directions of principal stresses

INTRODUCTION

High power carbon dioxide lasers provide a high power density heat source than can be used to selectively melt the surfaces of engineering components, after which the melted regions are rapidly cooled by the conduction of heat into the substrate (La Rocca, 1979). Laser surface melting has attracted considerable interest as a means of modifying surface structure and hence properties. This technique has been investigated for various industrial alloys including both austenitic and martensitic stainless steels (Anthony and Cline 1978, David and Vitek 1981, Molian 1982 and Cottrell et al 1983). Other work has explored the possibility of using a laser to melt and alloy chromium into various ferrous substrates (Gnanamuthu 1979 and Moore and McCafferty 1981). Anthony and Cline (1978) have used laser surface melting to restore the intergranular corrosion resistance of sensitized 304 austenitic stainless steel. The 316 steel that is investigated here offers the possibility of showing a similar improvement. With regard to the 420 steel, laser surface melting offers the possibility of selectively hardening the steel while maintaining or possibly enhancing its fatigue strength and corrosion resistance. This may be useful as a means of overcoming a specific industrial problem, the erosion of a turbine component used in the power generating industry. This component performs in a corrosive environment and is subjected to fatigue loading.

The two steels that have been investigated, 420 steel (Fe-12%Cr-0.2%C) and 316 steel (Fe-17%Cr-11%Ni-2.5%Mo) were selected because they are widely used, have different metallurgical behaviours, while both have the potential for showing useful benefits from laser surface melting.

The investigation falls broadly into three parts:-

1. That concerned with the shapes of the tracks and their dependence on the processing conditions. The cross-sectional profiles and the surface profiles are considered in Chapters one and two respectively.
2. That concerned with the make-up of treated layers. The microstructures and the residual stresses of the heated layers and their variation with processing conditions are reported in Chapter three (Microstructures) and Chapter four (Residual Stresses).
3. That concerned with the behaviour of the treated layers. The fatigue and the corrosion behaviour of treated surfaces are dealt with in Chapters five and six respectively. These results are interpreted in terms of the microstructures and the residual stresses of the treated layers.

The experimental work and the context of each chapter in terms of previous work is largely independent of other chapters and each chapter is reported as a self contained investigation.

1.1 INTRODUCTION

1.1.1 The Application of High Power Lasers for the Surface Treatment of Metals

The role of laser surface treatment has been reviewed in the literature eg. Gnanamuthu (1979), La Rocca (1981) and Hicks (1983). Laser surface treatment offers a highly selective process, which can rapidly quench the surfaces of engineering components. This highly selective heating minimizes thermal damage to a component being treated. It also makes for a highly energy efficient process. So although laser light is expensive high grade energy, the energy efficiency of a laser system may be as much as a thousand times higher than for a conventional system such as one suitable for carburising, nitriding or flame spraying, La Rocca (1981).

These possibilities exist because of the high energy densities that may be attained by focussed laser beams. Similar power densities may be attained by focussed electron beams and in this the two processes overlap. The choice of laser or electron beam will depend on a consideration of a particular task, Hicks (1983).

Induction hardening provides a practical means of locally transformation hardening steels and is used for the mass production of AISI 420 steel components, for example in the domestic appliance and automotive industries. The induction hardening of this steel in the solid state requires long soak times to produce full hardening (Hawkes 1984). Such heating does not require or permit the high energy densities that are available from high power laser beams and there is

little reason to use such expensive high grade energy where there is the alternative of induction hardening. The investigation therefore does not consider the possibility of laser surface hardening AISI 420 steel in the solid state, in detail.

1.1.2 The Effect of Process Conditions on the Melt Profiles

In this work a two kilowatt average power, carbon dioxide laser is used as a surface heating device. During surface treatment an object is moved under a focussed laser beam and heated, after which the heated surface region is cooled by the conduction of heat into the substrate. This heating and cooling produces modified tracks of material, which may be overlapped to cover a surface.

The absorbtivity of a metal surface for a focussed laser beam is sensitive to both the temperature of the surface and the power density of the focussed laser beam, see Figure 1.1 (Alexander 1982).

The cold surface of steel reflects ~95% of 28.3GHz radiation incident on it (Duley 1976). However, there is some heating and as the surface is heated its absorbtivity increases, increasing the efficiency of the laser/metal coupling. Surface coating is of interest because it offers the possibility of reducing the reflectivity of metals during the early stages of laser heating. If the metal is heated to its boiling point metal vapour improves the absorbtion of the laser beam. At a sufficiently high vapour pressure a depression will be formed in the melt pool. If there are multiple reflections in the melt pool a keyhole is formed and there is nearly complete absorbtion of the laser beam, see Figure 1.2.

Figure 1.1
The Variation of Absorbtivity with Temperature
for Focussed 28.3GHz Light and a Metallic
Specimen

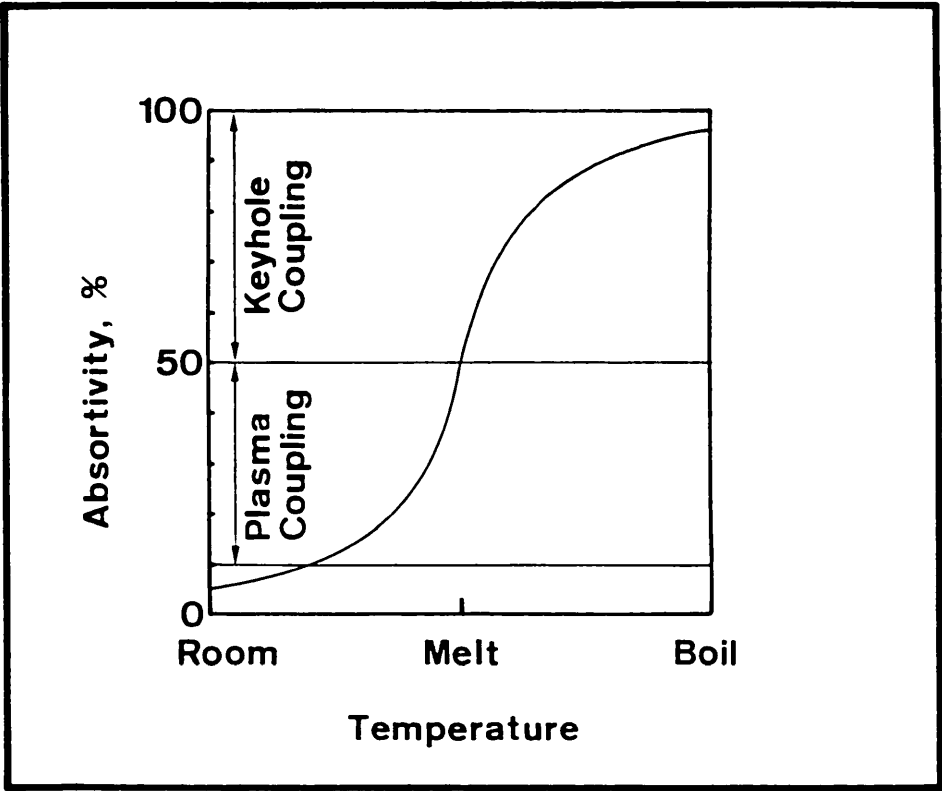
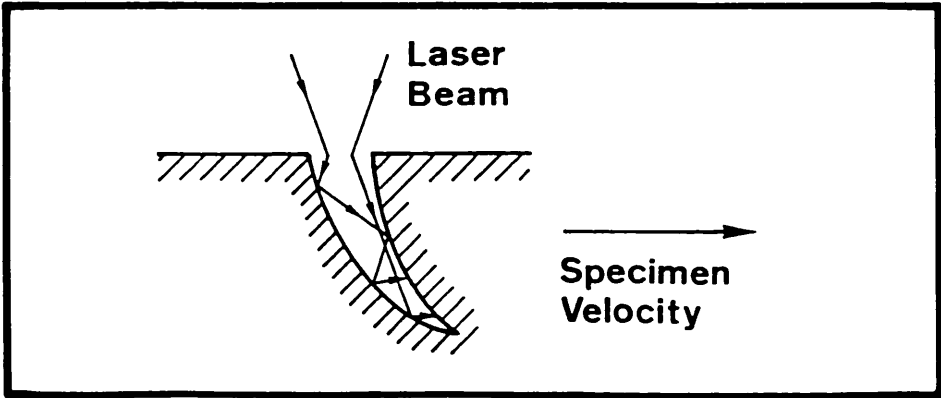


Figure 1.2
The Shape of a Keyhole



The absorbtion of a laser beam is also influenced by the formation of plasma (ionized gas) at high energy densities. At the charged particle densities of the plasmas associated with this project, the plasmas will absorb energy from the laser beam (Cairns and Sanderson, 1979). These high temperature plasmas will give increased absorbtion of the laser beam.

Keyholes can break down where there is extensive plasma formation above the surface of a metal. This can result in energy being blocked out of a keyhole, modifying the track profile. When this happens the nail-like cross-sectional profile of a keyholed track becomes "V" shaped. If plasma formation presents a problem shrouding gas may be used to flush the plasma away.

Defocussing outside the keyhole processing regime produces so called conduction limited cross-sectional profiles. If the beam is defocussed further the effect of mode structure becomes more pronounced. This can show as lop-sided or irregular melt-tracks. The various cross-sectional profiles are shown in Figure 1.3.

1.1.3 The Procesing Parameters

The processing parameters that influence cross-sectional profiles may be divided into three groups, those associated with:-

1. The beam.
2. The specimen.
3. The processing arrangement.

Figure 1.3

Various Cross-Sectional Profiles of Melt Tracks

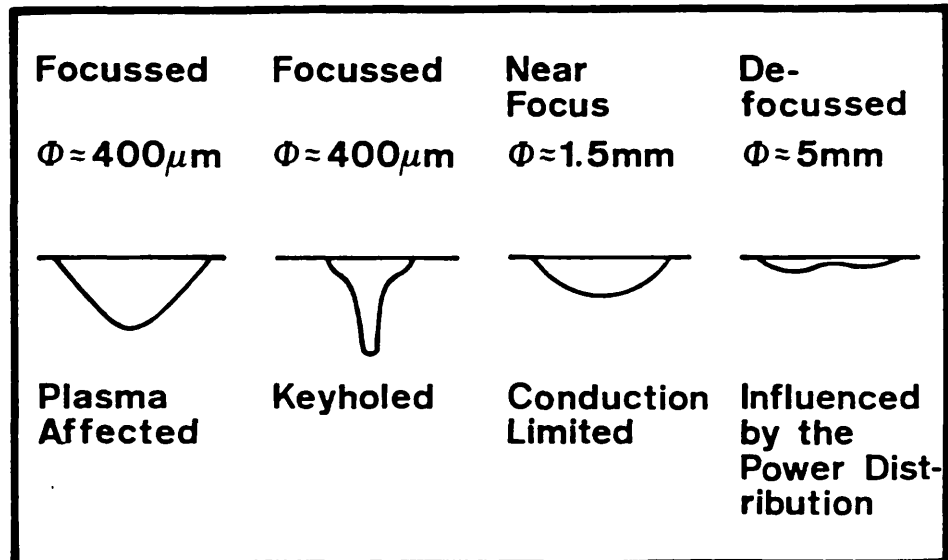
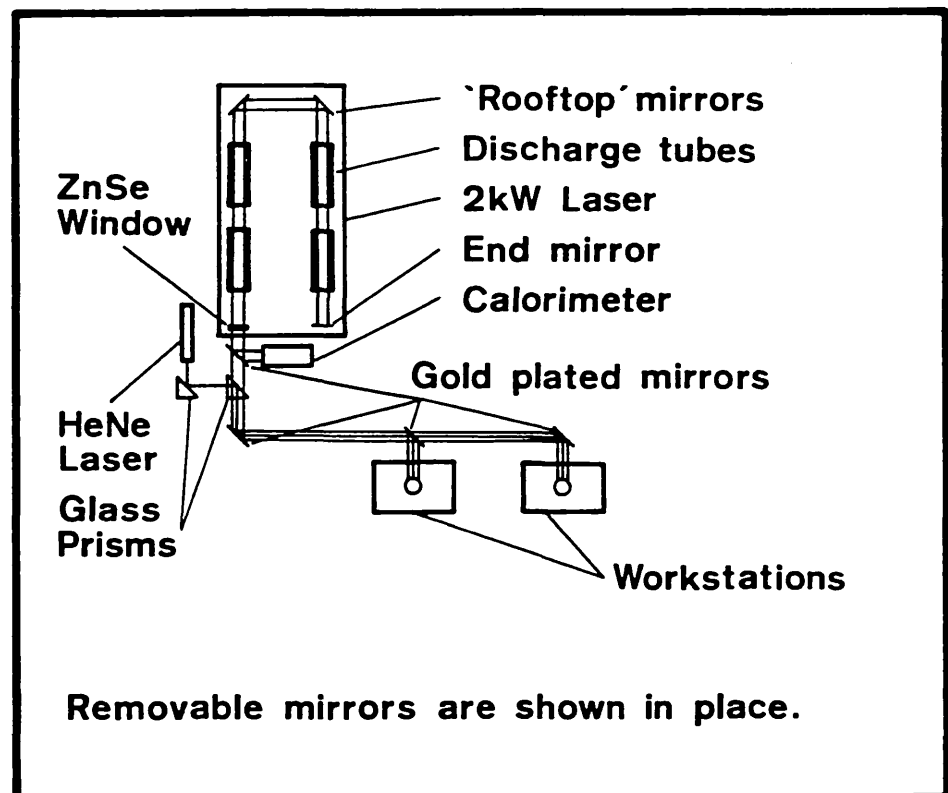


Figure 1.4

Arrangement of the Laser Processing Apparatus



1.1.3.1 Parameters associated with the Laser Beam

These parameters are:

1. Power
2. Divergence
3. Diameter
4. Power Distribution across the Beam
5. Wavelength
6. Plane of Polarisation

Apart from the wavelength which is fixed for the laser used in this work, these parameters may all be varied.

Recent work has pointed to the importance of the power distribution across the laser beam in determining the cross-sectional profiles of laser melt tracks (Sharp et al 1983). Optimal tuning of the laser produces a power distribution across the beam consisting of a single peak with the power falling off in a Gaussian manner (Alexander 1982). This power distribution minimizes the divergence of the beam (down to ~ 1 mrad). During the work reported here the laser was not detuned to evaluate the effect of a range of power distributions, although it would be anticipated that the heating and cooling of the cavity optics during the operation of the laser would introduce some irregularity into the power distribution.

The plane of polarization of the laser beam must always be considered when there is reflection of the laser beam off the specimen onto the specimen as is the case during deep penetration welding and cutting

(Olsen 1980). However for laser surface melting applications conduction limited tracks are generally preferred and the plane of polarization of the laser beam need not be considered.

Processing at less than the full power of the laser is of interest because it offers the possibility of working with less powerful, cheaper machines. Less than full power processing was investigated here.

1.1.3.2 Parameters associated with the Specimen

These parameters are:

1. Absorbtivity and its variation with temperature
2. Thermal diffusivity and its variation with temperature
3. Surface tension and its variation with temperature
4. Ionization potential
5. Bier-Lambert co-efficient
6. Latent heats of transformations

The different surface preparations that were evaluated here will affect the absorbtivity, and, if they are surface active, the surface tension (see Chapter 2). So long as there is not excessive mixing in of the surface coatings the other properties of the specimens will only be changed slightly by these coatings.

As two steels were assessed (AISI 420 and 316) the processing work was carried out for both steels, with their own characteristics.

1.1.3.3 Parameters Associated with the Processing Arrangement

These parameters are:

1. Distance from the specimen to the laser
2. Characteristics of the optics that are outside the laser
3. Shrouding gas
4. Velocity of the specimen relative to the incident beam

The distance from the specimen to the laser will influence any effects due to light reflected from the specimen that finds its way back into the optical cavity. This must be considered for processing where the specimen is close to the focal point so that reflected light is collimated and directed back into the optical cavity where it can detune the laser (Sharp 1984). When this leads to a change in the beam diameter any spherical aberration of the lens will shift the focal point.

The laser that was used for this study produces light with a frequency of 28.3GHz. This light is attenuated if it passes through a humid atmosphere. There will also be power losses associated with the various optical surfaces the laser beam encounters. This will be ~1% for each gold plated mirror and ~5% for a potassium chloride lens.

The characteristics of a focussing system define the power distribution across the specimen. In this study the optical

arrangement consisted of a lens lying normal to and in the centre of the axis of the laser beam.

Alternatives to a simple defocussed beam have been proposed for the laser surface treatment of metals. Possibilities include rastering a beam or folding a beam so as to produce a uniform power distribution across a rectangular treatment zone (Jimbou et al 1981).

It is possible to vary the depths, widths and cooling rates of laser melt tracks by varying the velocity of the specimen relative to the incident laser beam.

1.1.4 Objectives of the Experimental Work

The possible benefits and the problems of a range of surface preparations were evaluated in an initial series of experiments. The tracks that were produced were examined with a view to identifying any adverse metallurgical effects and any inconsistencies of melt profile.

When the most promising condition had been identified (grit cleaned) another more extensive series of melt tracks was produced over a wide range of processing conditions so that operating charts could be consulted for the remainder of the project.

1.2 EXPERIMENTAL

1.2.1 Apparatus

1.2.1.1 The Specimens

The specimens were flat slabs of 420 or 316 steel. They were ground flat with either a

workshop wheel or laboratory silicon carbide papers. A flow of coolant was maintained during grinding. The surface condition of the specimens prior to laser surface treatment was one of the following:

1. As Ground

These specimens were degreased in acetone before treatment.

2. Graphite Coated

A colloidal suspension of fine powdered graphite in acetone was brushed on and the acetone was allowed to dry off.

3. Grit Cleaned

This operation was carried out in a grit cleaning cabinet. The specimens were degreased in acetone before treatment.

4. Coating with Manganese Oxide

This material was supplied as a fine powder which was mixed with acetone and brushed onto a ground surface. The acetone was allowed to dry off before treatment.

1.2.1.2 Processing Apparatus

The overall arrangement of the apparatus is shown in Figure 1.4. After leaving the laser the beam goes to either the water cooled calorimeter or the workstation. The

beam is directed by flat gold plated mirrors. The orientation of these mirrors is adjusted using a visible miliwatt helium-neon laser which is directed to run co-axially with the main beam.

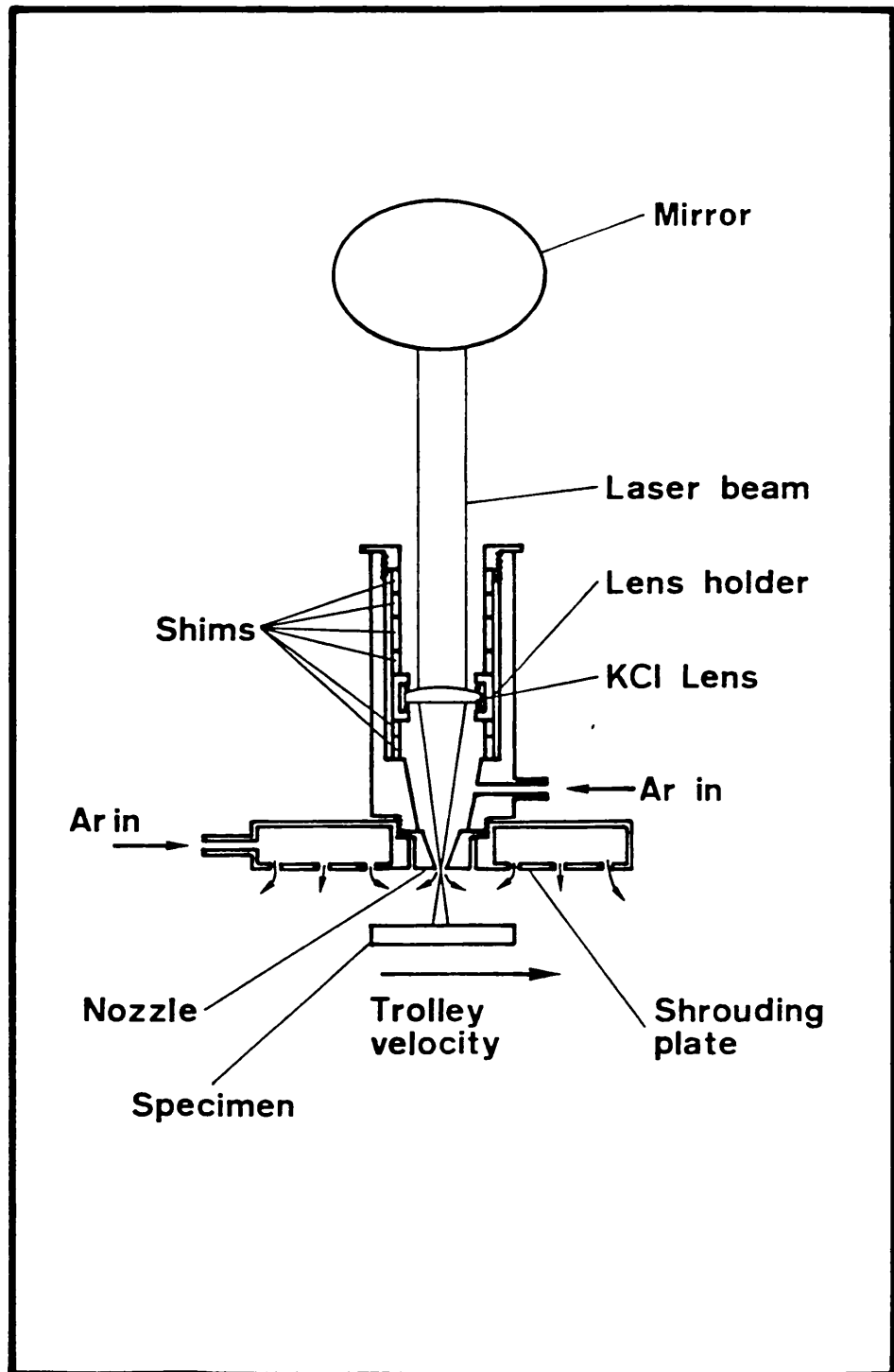
Two workstations were used; one was based around a hydraulic trolley and the other was based around a gas box. The gas box was only used for the earliest investigations when the behaviour of the various surface coatings were being assessed. All the other work that is reported here was carried out with the hydraulic trolley.

The hydraulic trolley moves along guide rails. A hand screw permits shifting perpendicular to the direction of travel and the production of surfaces that are covered with overlapping melt tracks. When a surface was to be covered with overlapping melt tracks it was necessary to clamp the guide rails to a solid object to prevent "crabbing" when the trolley was accelerated. The speed of the trolley was measured with a microswitch which activated a timer while the trolley covered a distance of 100mm.

The shrouding arrangement and the lens holder are shown in Figure 1.5. A gold plated mirror reflects the beam downwards to the lens. The nozzle and the flow of argon through the nozzle protect the lens from debris that is thrown up during laser surface treatment. Shrouding is provided by the flow of argon through the shrouding plate and through the nozzle.

Figure 1.5

Shrouding and Beam Focussing Arrangement



The atmosphere in the transparent gas box is rendered inert by purging the box with argon. This process uses one to one and a half cylinders of argon and takes approximately one day. Specimens were moved under the beam by a turntable inside the box. They were inserted and removed by way of an isolatable side chamber which, like the main box, was rendered inert by purging. This takes about 30 minutes. Rubber gloves fitted to the sides of the box were used to manipulate specimens in the box.

The mirror to reflect the beam downwards to the lens and the protective nozzle with provision for an axial flow of argon were as for the apparatus that were used with the trolley although there was no provision for a shrouding flow of argon outside the nozzle.

1.2.1.3 The Laser

This is a Control Laser "910" fast axial flow, carbon dioxide laser. It is capable of supplying powers in the range from 500W to 2kW. A mixture of carbon dioxide, nitrogen and helium flows through the four discharge tubes. An electrical current flowing through the tubes in the direction of gas flow, pumps the carbon dioxide by way of electron collisions and indirectly by way of vibrationally excited nitrogen (Duley 1976). The helium acts as a coolant and helps to maintain the population inversion that is essential for the lasering action. When the beam is not directed to the specimen it is dumped in a copper cone calorimeter.

The power of the laser is measured by monitoring the temperature rise of the cooling water that flows around the cone.

There is a 300Hz ripple frequency on the laser beam. This gives rise to stitched welds at high traverse speeds (Alexander 1982). This oscillation arises from the rectification of the 50Hz three phase power supply.

Even diffuse reflections from this laser are harmful (ANSI 1976). A number of safety precautions are recommended in the ANSI report. In outline they are:

1. Operator training
2. Eye protection
3. Enclosed beam path
4. Remote firing
5. Key switch interlocks
6. Restricted entry to the laser area

1.2.2 Procedure

1.2.2.1 Laser Processing

Three of the processing parameters were varied, the beam diameter, ϕ , the power, P and the traverse velocity, V.

The diameter of the incident laser beam on the specimen was varied by moving the lens up and down relative to the specimen. The incident beam diameters that are quoted in this work were calculated by assuming that the beam diameter varies linearly from the focal point to its diameter measured at the

workstation before entering the lens. The diameter of the beam at the focal point depends on optical aberrations in the lens and on the diffraction imposed limitation of the beam diameter. The beam diameter at focus was taken to be $400\mu\text{m}$ and the diameter at the workstation before entering the lens was taken to be 20mm, Lim and Steen (1982).

The location of the focal point was found by moving a specimen up and down below the lens and looking for the blue flash that is characteristic of the ionisation that occurs at high energy densities. The highest and the lowest positions that produced blue flash were measured and the focal point was taken to be half way between them.

The beam power was varied by desaturating the discharge tubes. The traverse velocity of the specimen was varied by adjusting a valve leading to the hydraulic ram.

Processing work to find a suitable beam diameter for future experiments was carried out at a power of 1.5kW and beam diameters of 0.4, 1.0, 1.5, 2.2, 3.5 and 5mm for velocities of 10, 25, 75, 200 and 400mms^{-1} .

Further data were produced for twelve traverse velocities in the range from 10 to 400mms^{-1} at a power of 1.5kW for the grit cleaned specimens.

1.2.2.2 Specimen Examination

After treatment the specimens were examined for oxidation. The specimens were sectioned polished and etched as described in

Section 3.2.2. The depths of the melt zones were measured and microhardness measurements were taken on the cross-sections. The widths of the tracks were measured from the track tops.

1.3 RESULTS

1.3.1 Initial Treatment

1.3.1.1 Coated Specimens

The manganese dioxide coated specimens showed wide variations of melt depth for identical treatment conditions. For example, treatment conditions ($P=1.5\text{kW}$, $V=100\text{mms}^{-1}$ and $\phi=1.5\text{mm}$) which melted a track $\sim 150\mu\text{m}$ deep and $\sim 600\mu\text{m}$ wide in 420 steel did not even melt material 20mm further down along the direction of the track; another 20mm further down, the track was $\sim 800\mu\text{m}$ wide.

The manganese dioxide specimens showed an irregular surface topography, comparable to 120 grit grinding paper.

The graphite coated specimens had macroscopically smooth surface profiles.

Carbon contamination was a problem in the graphite coated specimens where increased volume fractions of retained austenite were found in 420 steel melt tracks.

1.3.1.2 As Ground

As with the manganese dioxide coated specimens variations of melt depth and width precluded the production of useful operating charts.

The surfaces of the specimens were macroscopically smooth and did not show oxidation.

1.3.1.3 Grit Cleaned

This technique produced the most consistent depths and widths for given treatment conditions. It also gave macroscopically smooth surfaces.

1.3.2 Processing Results

The results below are all for grit cleaned specimens. The tracks that are shown in the optical micrographs of the "Microstructures" Chapter were produced on as ground surfaces and are narrower and shallower than tracks produced at the same conditions in grit cleaned material.

Keyholing was observed at focus ($\phi=400\mu\text{m}$) at speeds of up to 200mms^{-1} and at 10 and 25mms^{-1} at an incident beam diameter of 1.0mm.

Figures 1.6 and 1.7 show track dimensions for 420 and 316 steel respectively. The beam diameter was 1.5mm. Powers of 1.2, 1.5 and 1.8kW were evaluated for velocities in the range from 15 to 400mms^{-1} .

Figure 1.6
Track Dimensions against Traverse Speed
in 420 Steel for Three Beam Powers

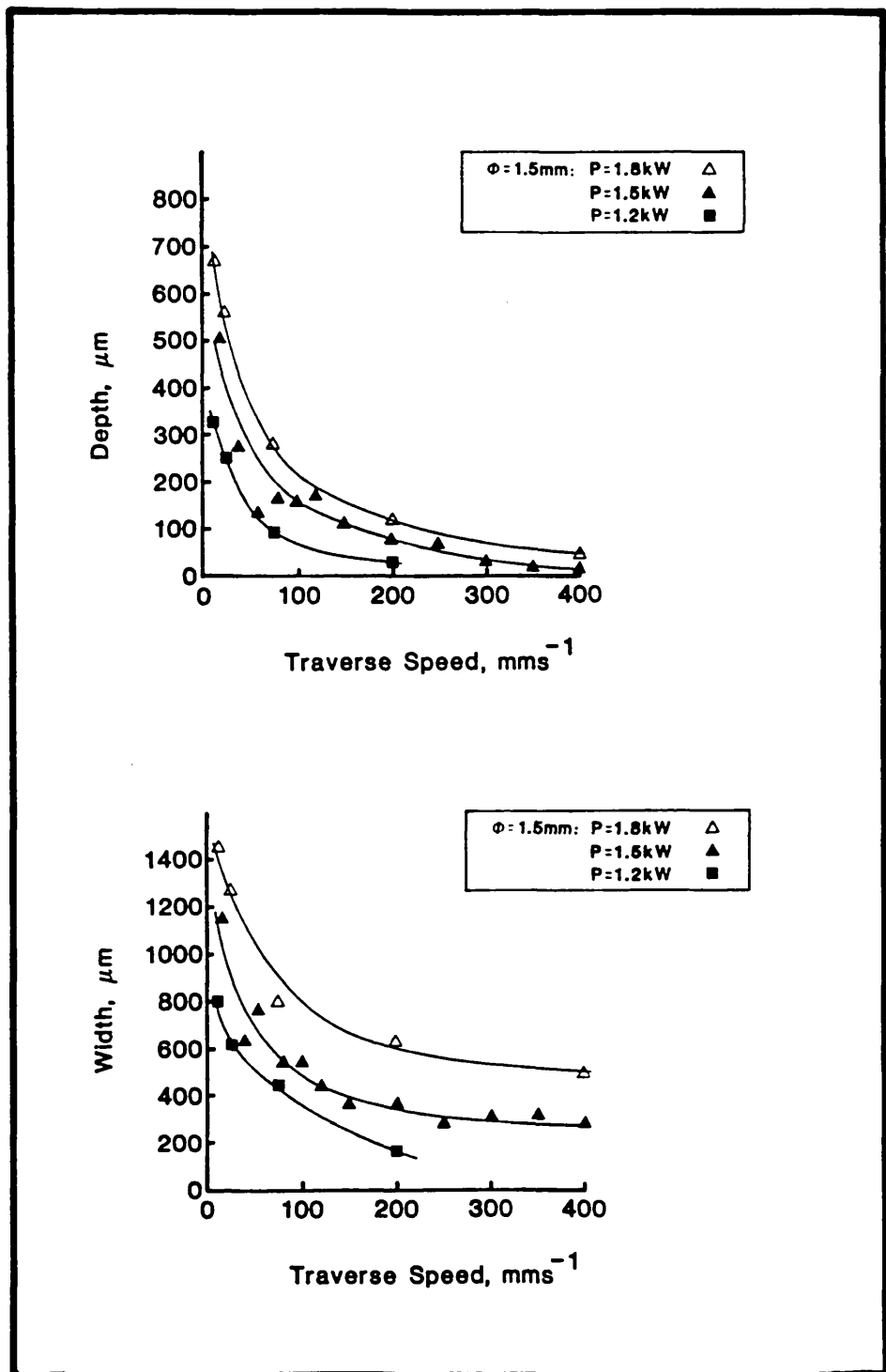
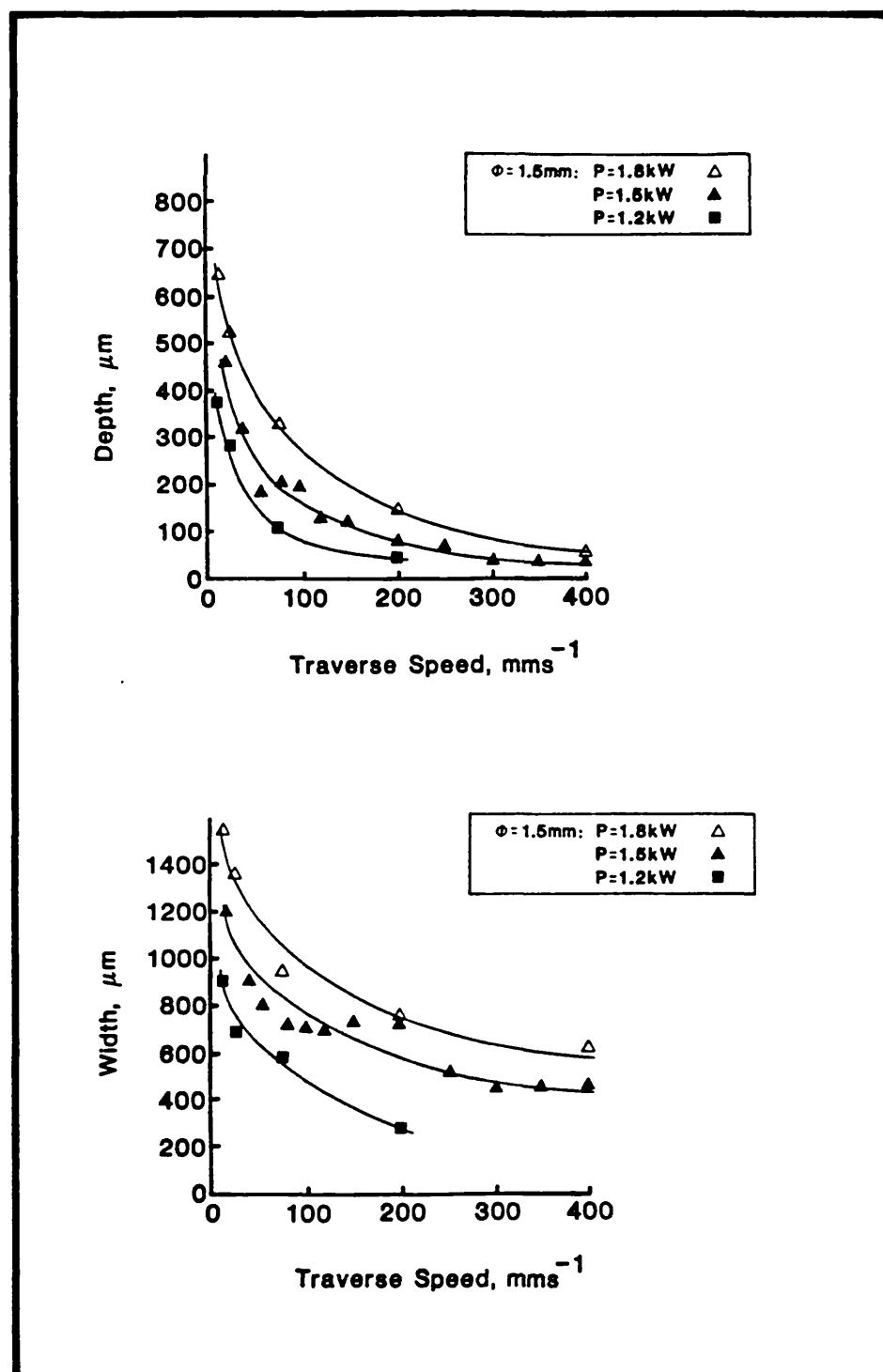


Figure 1.7
Track Dimensions against Traverse Speed
in 316 Steel for Three Beam Powers



1.4 DISCUSSION

1.4.1 Surface Preparation

Grit cleaning offers the most acceptable method of surface preparation combining an absence of contamination with the possibility of producing melt tracks of reproducible dimensions.

The alternative methods of surface preparation were not adopted for the following reasons:

1. Graphite Coating

Although this technique offers the possibility of producing tracks with reproducible dimensions, the problem of unknown quantities of carbon being alloyed into the melt tracks limits the usefulness of the technique.

2. As Ground

The problem here is that only a small fraction of the laser power is absorbed except at very high power densities where there is a risk of keyholing. This ^rsurface preparation is sensitive to small variations in the reflectivity of the metal surfaces because of the small fraction of the incident energy that is absorbed.

3. Manganese Dioxide Coating

This coating does not offer reproducible track dimensions, possibly because of the somewhat coarse and irregular size of the coating particles. It also produces an irregular surface profile.

1.4.2 Processing Conditions

A beam diameter for laser surface melting was chosen which was large enough to avoid keyholing while being small enough to minimize the effects of any irregular distribution of power across the laser beam. A diameter of 1.5mm was chosen, this being the minimum diameter at which no keyholing was observed. This diameter was used for all subsequent work except where the effect of varying diameter was specifically being investigated.

The laser is capable of producing 2kW, but only for optimum operating conditions. Although care was taken to seal leaks so as to minimize contamination of the lasing medium and to accurately align the cavity optics, a considerable time saving was gained by accepting a slight loss of power. These considerations led to a power of 1.5kW being used for subsequent processing except where the effect of varying power was specifically being investigated.

By varying the treatment velocity it is possible to vary the cooling rate through the laser melt tracks and modify the metallurgical structure of the tracks (Kear, Breinan and Greenwald 1979). At a power of 1.5kW and a beam diameter of 1.5mm laser surface melting produces conduction limited tracks over velocities ranging from 15 to 400mms⁻¹, offering a range of cooling rates from $\sim 10^3$ to $\sim 10^6$ °Cs⁻¹ at the higher treatment speeds (Kear, Breinan and Greenwald 1979). This range of cooling rates may offer the possibility of tailoring the microstructure by varying the processing conditions. For example, the amount of retained austenite in martensitic steels is sensitive to cooling rate, generally increasing with increasing cooling rate eg. Ruhl and Cohen (1969). It is possible to suppress

the formation of δ -ferrite in predominantly austenitic steels by rapid cooling eg. David and Vitek (1981). These possibilities are examined further in Chapter 3.

Generally the trends that show are as expected with high ratios of depth to width at near focus conditions and increases in the track dimensions at high powers and low traverse velocities (Alexander 1982).

1.5 CONCLUSIONS

1. A preferred surface preparation of grit cleaning followed by degreasing has been found for the preparation of specimens before laser surface treatment from the viewpoint of the reproducibility of track dimensions and the absence of contamination.
2. A beam diameter of 1.5mm produces only conduction limited tracks over a range of traverse velocities from 10 to 400mms⁻¹ at the three powers that were evaluated (1.2, 1.5 and 1.8kW). Graphs of width and depth against traverse velocity have been produced for these treatment conditions.

2.1 INTRODUCTION

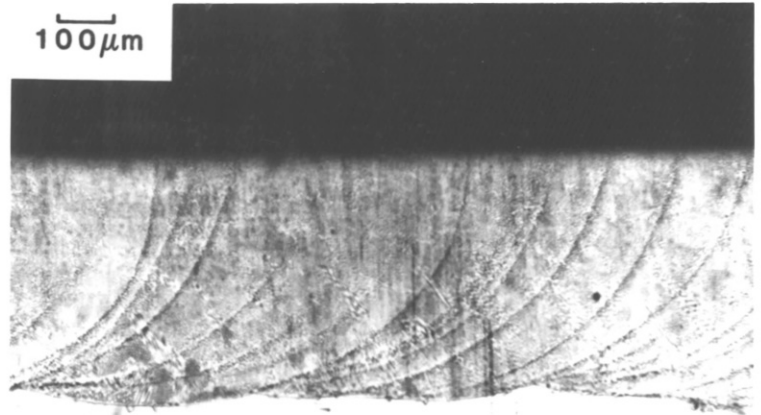
2.1.1 Surface Topography and Fluid Flow in Laser Surface Melting

Surface shape affects many of the properties of materials such as their wear, friction, lubrication, sealing, fluid dynamic and electrical behaviour (Thomas 1982). Where these properties demand a flat surface it is economically desirable to avoid, or at least to minimize, any grinding operations subsequent to laser surface treatment. Fluid flow in laser melted tracks and welds leads to convective heat flow which will modify melt profiles (Heiple and Roper 1981). It also leads to convective mass transfer and the rapid redistribution of solute in laser surface alloying. The periodic movement of material in a melt zone can result in a variation of both the solidification front velocity and the thermal gradients (Hawkes et al 1983). This variation in the solidification conditions can result in segregation which shows as solute banding (see Photograph 2.1). Surface topography must be considered when assessing the properties of materials. For the purposes of this investigation this is particularly important when evaluating the residual stress (Doig and Flewitt 1981) corrosion (Sedriks 1979) and fatigue properties of the materials.

Various kinds of qualitatively different ripples were observed: Photographs 2.1 to 2.3. Experiments were carried out to characterise the surfaces and to show what effects varying the laser treatment conditions has on these ripples. This information can be used to optimize the processing conditions probably with a view to minimising the surface roughnesses. Profiles

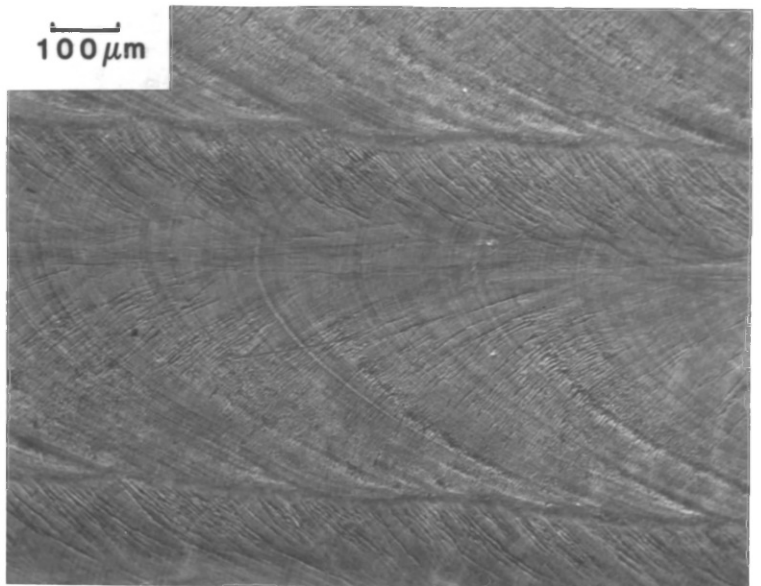
Photograph 2.1

Solidification banding
in 316 steel ($P = 1.6 \text{ kW}$, $V = 5 \text{ mms}^{-1}$ and
 $\Phi = 400 \mu\text{m}$)



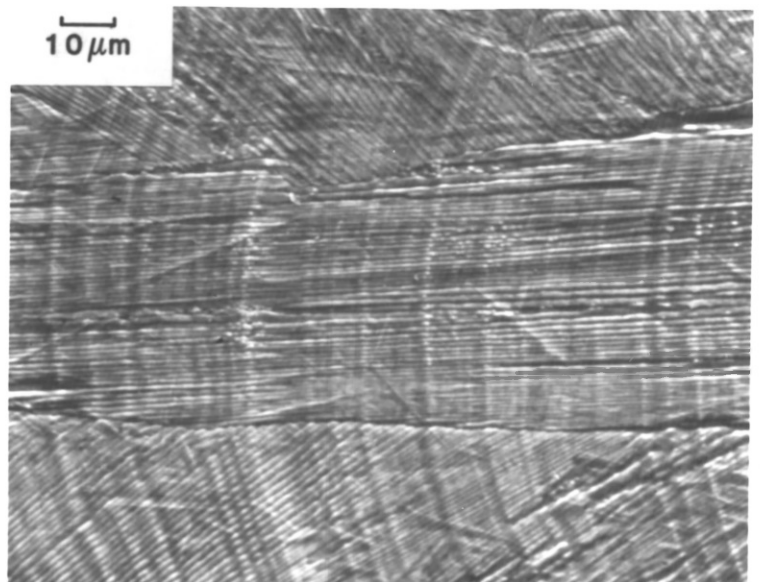
Photograph 2.2

Topography of laser
surface melted 420
steel ($A = 500 \mu\text{m}$,
 $P = 1.5 \text{ kW}$, $V = 30 \text{ mms}^{-1}$ and $\Phi = 1.5 \text{ mm}$)



Photograph 2.3

Topography of laser
surface melted 420
steel ($P = 1.5 \text{ kW}$,
 $V = 30 \text{ mms}^{-1}$ and
 $\Phi = 1.5 \text{ mm}$)



were measured with a "Talysurf" and statistically evaluated with a minicomputer interfaced with the "Talysurf". The profiles were characterised in terms of statistical descriptors of the height distribution. They were also characterised in terms of their autocovariance functions to indicate any periodic rippling and the "openness" or "closedness" of the profiles (see Figure 2.1).

2.1.1 Processes Giving Rise to Surface Rippling

The forces that act on a laser melt pool are gravity, viscous drag, surface tension and vapour pressure (see Figure 2.2).

Generally surface tension will tend to force a surface to its minimum area configuration and this will minimise any distortion of the melt pool (Andrews and Athey 1976). However, this tendency is complicated by local instabilities at the edges of the melt pool and by the dependence of surface tension on temperature.

The rippling process has been modelled in terms of the surface tension at the liquid/solid/gas interface. Ishizaki (1980) has suggested that rippling is set up by the interplay between the solidification direction at the surface of the melt pool and the equilibrium contact angle of the liquid/gas interface. This mechanism only gives rise to local movement of the melt near the solidification front and ripples with wavelengths from $\sim 5\mu\text{m}$ to $15\mu\text{m}$.

The surface tension of metals is usually a function of temperature. When this is so, temperature gradients are associated with surface tension gradients giving rise to fluid flow from regions of

Figure 2.1

Profiles and Autocovariance Functions (ACVFs) of Two Surfaces

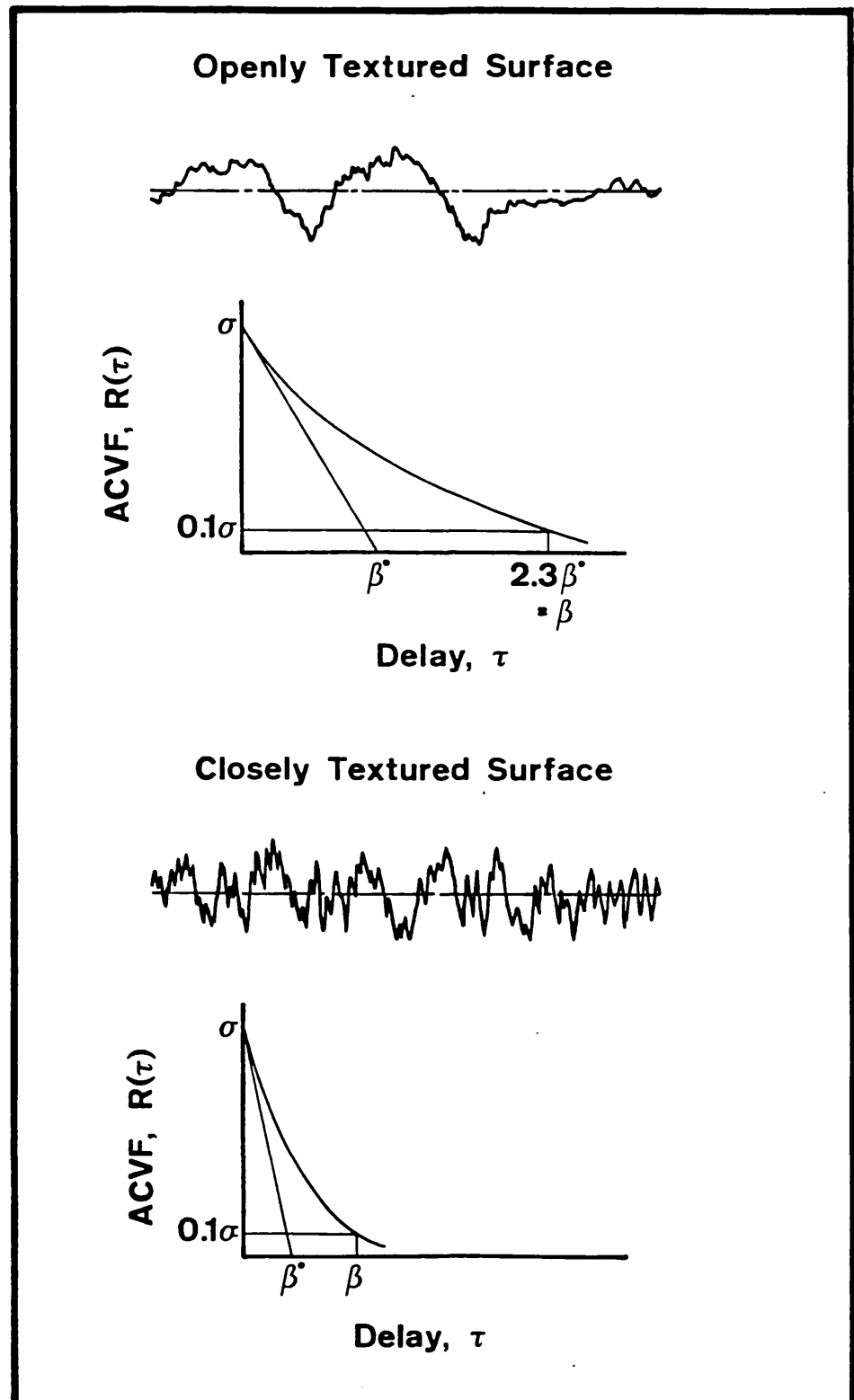


Figure 2.2

Forces Acting on a Laser Melted Pool

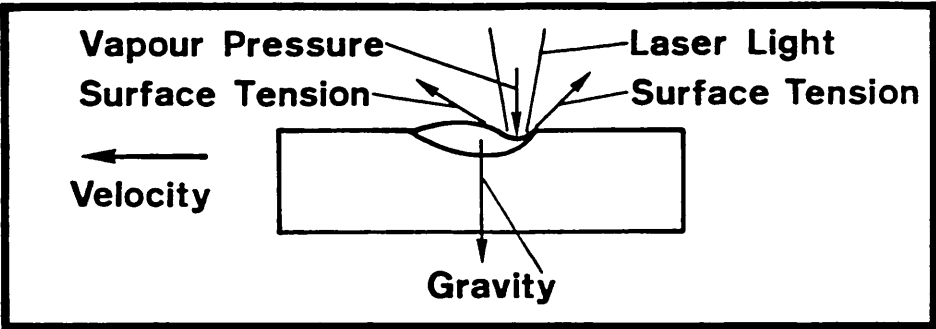
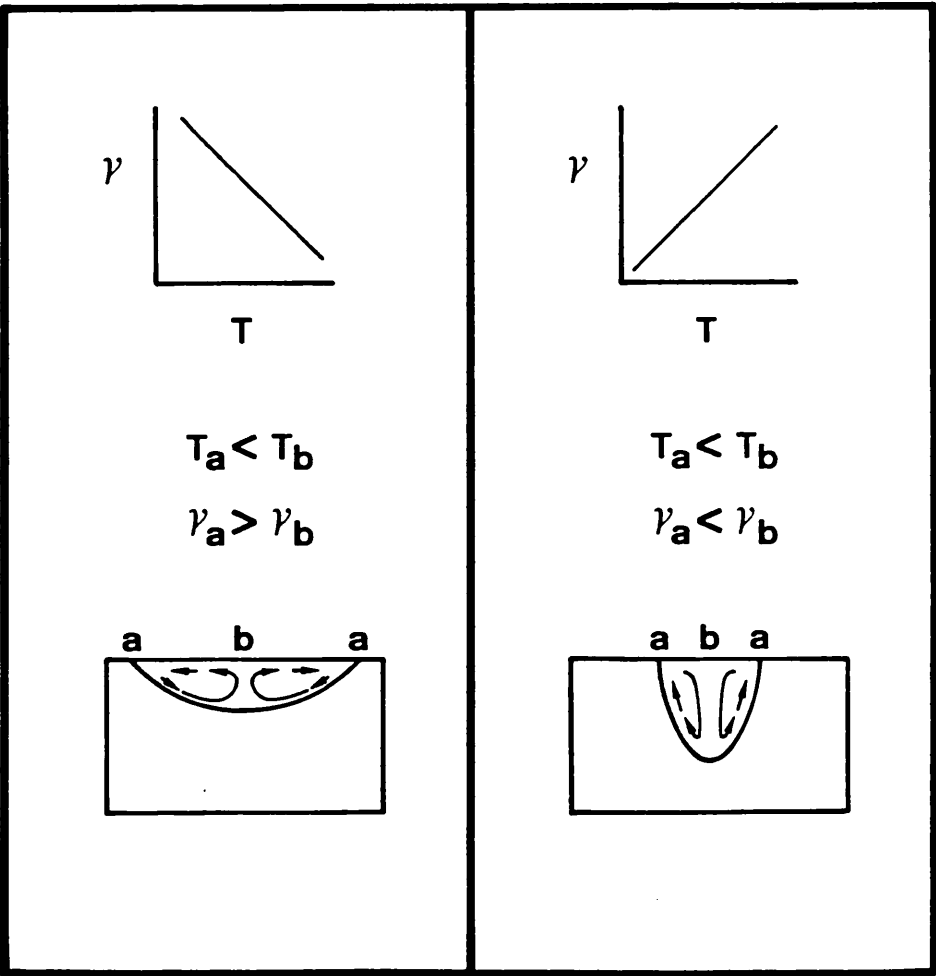


Figure 2.3

Melt Pool Shape and the Variation of Surface Tension with Temperature



low surface tension. This effect is known as Marangoni convection after its discoverer. This flow has been mathematically modelled in two dimensions (Mazumder and Ohji 1982 and Chande and Mazumder 1982). Both these analyses and the earlier work of Ishizaki and his co-workers indicate that surface tension can play an important role in melt pool convection (Ishizaki et al 1965, 1966 and 1967).

It is possible to measure the surface tension of metals by observing the oscillation frequency of a levitated drop. This method prevents oxygen pick-up from a crucible and allows measurement at temperatures of up to 2000°C (Keene 1983). The surface tension of pure metals is almost always found to fall with a rise in temperature. That is the rate of change of surface tension with respect to temperature, $d\gamma/dT$ is negative. Where positive values have been found it is probable that there are impurities in the melt. In alloys however positive values of $d\gamma/dT$ have been found. It has been suggested that the depth of the melt pool in TIG welding depends on the sign and value of $d\gamma/dT$, (Heiple and Roper 1981). The direction of fluid flow at the surface of the melt pool was reversed when sulphur was added (see Figure 2.3). This flow was explained in terms of Marangoni convection and its reversal accounted for by the sign of $d\gamma/dT$. The uncontaminated metal was assumed to have a negative value of $d\gamma/dT$. So the molten metal flowed away from the hot spot in the centre of the melt pool. This convective flow would transfer heat to the periphery of the metal pool giving rise to a shallow profile. The addition of sulphur was assumed to give a positive value of $d\gamma/dT$, reverse the Marangoni flow and transfer heat to the bottom of the melt pool. The importance of surface tension driven flow in

determining melt profiles is confirmed by the correlation of a series of TIG weld penetrations with surface tension values (Keene et al 1983). Deep narrow tracks were associated with low surface tensions and positive values of $d\gamma/dT$. Oxygen and sulphur were found to be highly surface active in iron with increases of oxygen or sulphur content decreasing the surface tension. It was also found that reducing agents such as Al, Ca, Ce and Cr were capable of reducing the oxygen concentration at the melt surface.

Pressure variations can drive fluid flow in melt pools. As material becomes heated and eventually vapourises the vapour is accelerated away from the interaction zone setting up an overpressure. It has been suggested that this mechanism has caused melt pool depressions and rippling in samples treated with focussed high power lasers (Moore et al 1979). Pressure variations can also lead to keyhole formation (Andrews and Athey 1976).

The various forces acting on laser melted pools can cause undercut and humping when material is thrown up behind the melt pool to form beads. This becomes a problem at high weld speeds and can limit the speed of the process.

The mechanisms that have been discussed so far can interact. For example a shape change that is set up by surface tension gradients might alter the incident beam power density at the metal surface, changing the vapour pressure over the melt pool.

It is possible that the melt pool will contain standing waves with wavelengths which are determined by the melt pool dimensions; such standing waves

might influence any rippling (Hawkes et al 1983 and Renwick and Richardson 1983).

2.2 EXPERIMENTAL

2.2.1 Procedure

The topography of a number of laser melted tracks has been evaluated using a Rank Taylor Hobson "Talysurf" interfaced with a Digital "RT11" minicomputer system. The "Talysurf" comprises a stylus which is linked to an electromechanical transducer. A gearbox and motor moves the stylus over the surface at a constant velocity. The signal from the transducer is amplified, electronically digitised and fed into the minicomputer. The digitised information is filed in the form of a series of height measurements. It is possible to use the amplified analogue signal to produce a chart recording of the surface profile and to give a centre line average roughness.

The stylus was traversed over a series of nine tracks of 420 steel. These tracks were produced at speeds in the range from 15 to 400 mms^{-1} with the stylus moving along the centreline of the tracks and parallel to the direction of the tracks. 316 steel tracks that had been produced under identical conditions to three of the 420 steel tracks were tested for comparison.

The stylus was then moved across a series of overlapping tracks to evaluate the profile in this direction. Finally the effects of varying the beam power and the incident beam diameter were evaluated.

2.2.2 Bandwidth Selection

The descriptors of the height distribution and those of the spatial distribution are bandwidth dependent. This is confirmed by observation of Table 2.1 where the ordinate separation and the sample length of the 1000 sample points were varied giving different roughnesses and decay distances. In order to statistically characterise the surfaces of laser melted tracks it is desirable to select a bandwidth that includes all the ripple wavelengths that are observed on the profile. In the stainless steels that are examined in this investigation optical and scanning electron microscopy suggest a range of ripple wavelengths from $\sim 5\mu\text{m}$ to $\sim 2\text{mm}$ (see Photographs 2.1 to 2.3).

The diamond stylus used in this investigation has the shape of a truncated pyramid (see Figure 2.4). The face arising from the truncation is a rectangle with sides of length 2 to $3\mu\text{m}$ parallel to the direction of travel. This shape will raise problems if heights are to be sampled at intervals of less than about $3\mu\text{m}$. As the finest detectable ripples have a wavelength of only about twice the separation of the sample heights it is not possible to detect ripples with the wavelength of the shortest observed wavelength ($\sim 5\mu\text{m}$).

As the system samples a maximum of 1000 heights it is not possible to detect the longest observed ripples while setting the separation of the sample heights to its minimum practical value ($\sim 3\mu\text{m}$). To overcome this problem the stylus was run over most of the tracks twice, firstly to cover the longest observed ripples and secondly to cover the shortest detectable ripples.

Figure 2.4

Diamond Stylus Tip

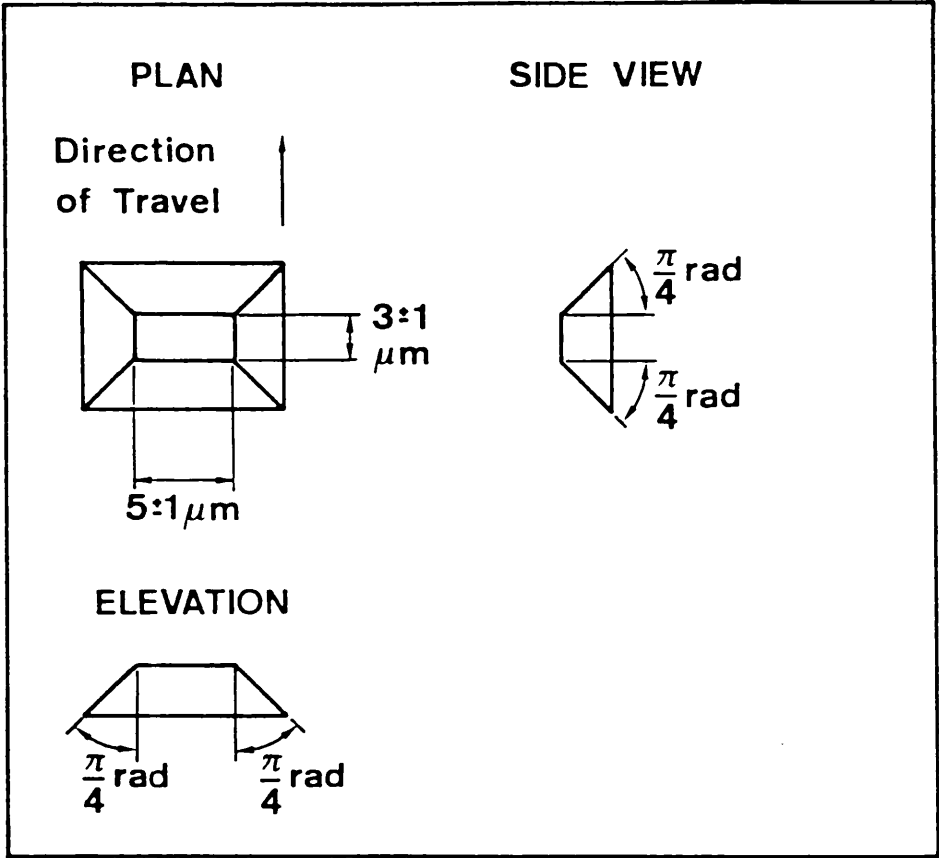
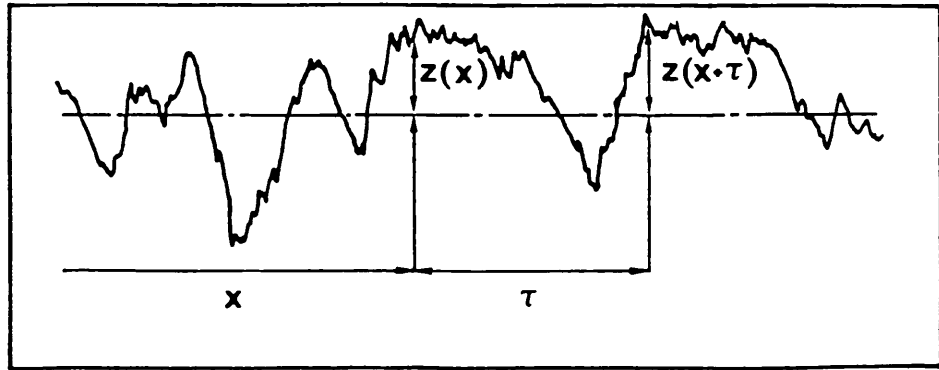


Figure 2.5

Autocovariance Function - Scheme



2.2.3 Statistical Description of the Profiles

The mini-computer system allows a statistical description of the profiles. These descriptions are defined in terms of a mean line which is fitted so as to minimise the sum of the deviations of the profile from it.

2.2.3.1 Height Distribution

The height distributions of the profiles were characterised in terms of their centre line average roughnesses, root mean square roughnesses, skewnesses and kurtosises.

Ra, the centre line average roughness and σ , the root mean square roughness may be defined for surface heights, Z, measured a length, X, along a mean line of length, L:-

$$Ra = \frac{1}{L} \int_0^L |z| dx$$

$$\text{and } \sigma = \left(\frac{1}{L} \int_0^L z^2 dx \right)^{\frac{1}{2}}$$

In practice discrete summations were used:-

$$Ra = \frac{1}{N} \sum_{i=1}^N |z_i|$$

$$\text{and } \sigma = \left(\frac{1}{N} \sum_{i=1}^N z_i^2 \right)^{\frac{1}{2}}$$

where

are N values of z over length L, measured at regular intervals.

For a Gaussian distribution $\sigma = 1.25 \text{ Ra}$.

The distribution of surface heights may also be characterised in terms of their skewness and their kurtosis. The skewness, S_k and the kurtosis, K are defined below:-

$$S_k = \sigma^{-3} \int_0^L z^3 p(z) dz$$

$$\text{and } K = \sigma^{-4} \int_0^L z^4 p(z) dz$$

where the probability that the height z occurs in an interval dz is $p(z)$.

The discrete summations are:-

$$S_k = \sigma^{-3} \frac{1}{N} \sum_{i=1}^N z_i^3$$

$$K = \sigma^{-4} \frac{1}{N} \sum_{i=1}^N z_i^4$$

The skewness is a measure of the lop-sidedness of a distribution and is zero for a symmetrical distribution. The kurtosis is a measure of the peakedness of a distribution and is equal to three for a Gaussian distribution.

2.2.3.2 Spatial Distribution

The spatial distributions of the surface profiles were characterised by their autocovariance functions, ACVFs. For the geometry shown in Figure 2.5 the ACVF, $R(\tau)$ is defined by:-

$$R(\tau) = E \{ z(x) z(x + \tau) \}$$

where $E(a)$ denotes an expected value of a .

The ACVF was evaluated by the step by step method (Bendat and Piersol 1971) which uses the discrete summation form of the ACVF, that is:-

$$R(\tau) = \frac{1}{N-\tau} \sum_{i=0}^{N-\tau} z_i z_{i+\tau}$$

This indicates periodic ripples as maxima at distances corresponding to the ripple wavelengths (see Figure 2.6). This would apply to a series of superimposed periodic ripples which would show similarly. The ACVF can be used to discriminate between different random surfaces, possibly with the same roughnesses, by its decay properties (Sayles 1982) It is found that,

$$R(\tau) = \sigma^2 \exp(-\tau/\beta^*)$$

where $1/\beta^*$ is the decay rate of the ACVF at the origin, for many random surfaces. It is possible to define a correlation length

$\beta = 2.3 \beta^*$ at $R(\tau) = 0.1 \sigma^2$ (see Figure 2.1). β gives a measure of the "openness" of a profile.

2.3 RESULTS AND DISCUSSION

2.3.1 Spatial Distributions

The profiles that have been observed in this work fall broadly into three categories typified by the profiles shown in Figures 2.6, 2.7 and 2.8. Periodic rippling shows in Figure 2.6, a profile taken at right angles to the traverse direction of a series of melt tracks. The surface profiles of the centrelines of melt tracks fall into two groups. Those produced at traverse velocities of 200 mms^{-1} or less resemble Figure 2.7 in that there is no obvious periodicity. The high speed tracks produced at 300 and 400 mms^{-1} show periodic rippling, Figure 2.8. These features show in the forms of the ACVFs. Both the profiles taken perpendicular to the tracks and the profiles of the high speed tracks have periodic ACVFs. The wavelengths of these functions correspond with those that would be anticipated from the observation of their corresponding profiles. This wavelength is the distance the specimen is advanced in between the production of two neighbouring tracks in the case of the profiles taken perpendicular to the tracks. In the high speed tracks the ripple wavelength^g is determined by the ripple on the power supply to the laser, and the traverse speed. The rectified three phase power supply has a 300 Hz ripple which gives rise to a ripple with the same frequency on the power beam (Lim and Steen 1982).

Figure 2.6

Surface Profile and its ACVF, across
Overlapping Tracks in 420 Steel

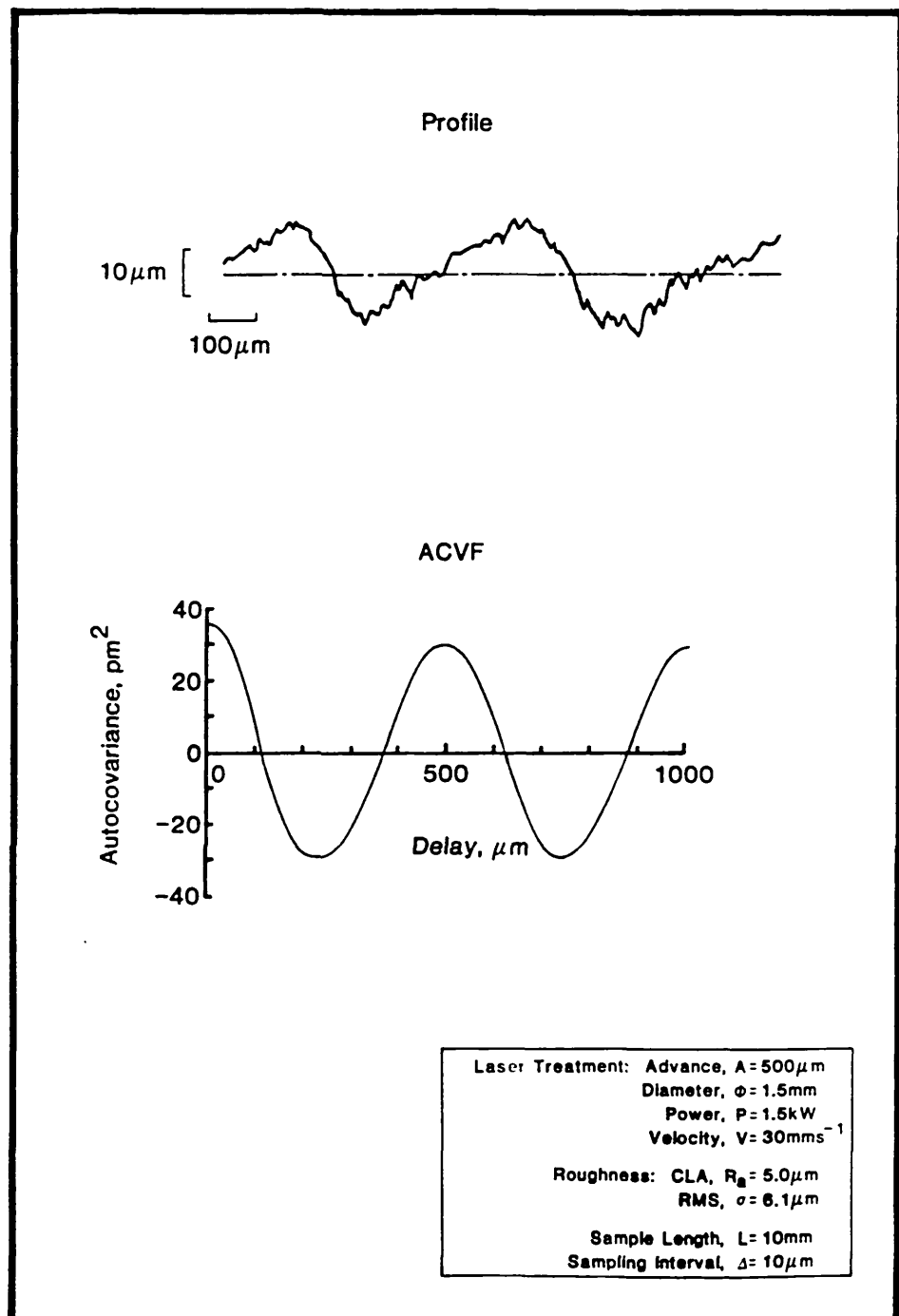


Figure 2.7

Surface Profile and its ACVF, along the
Centrelines of a Track in 316 Steel

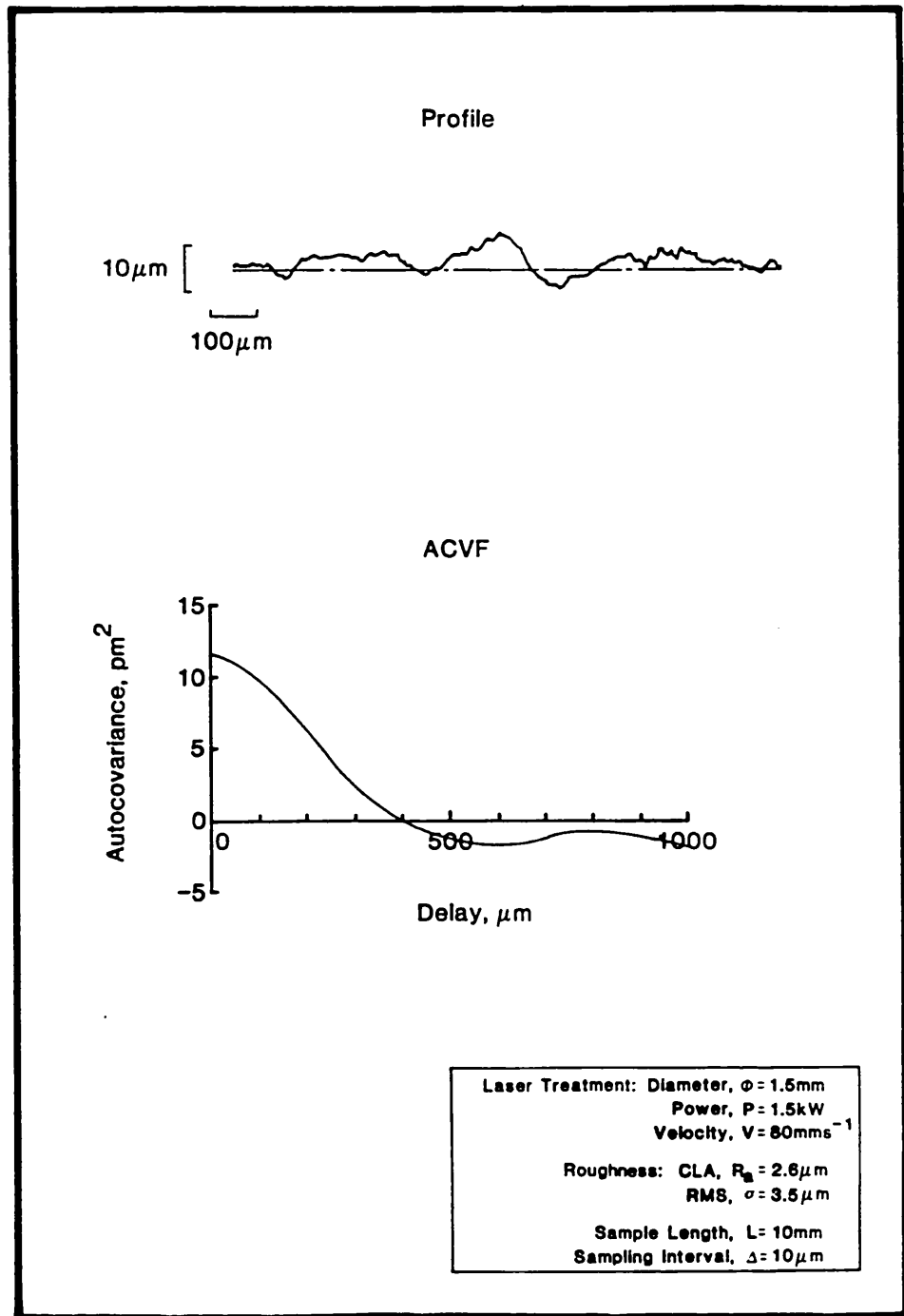
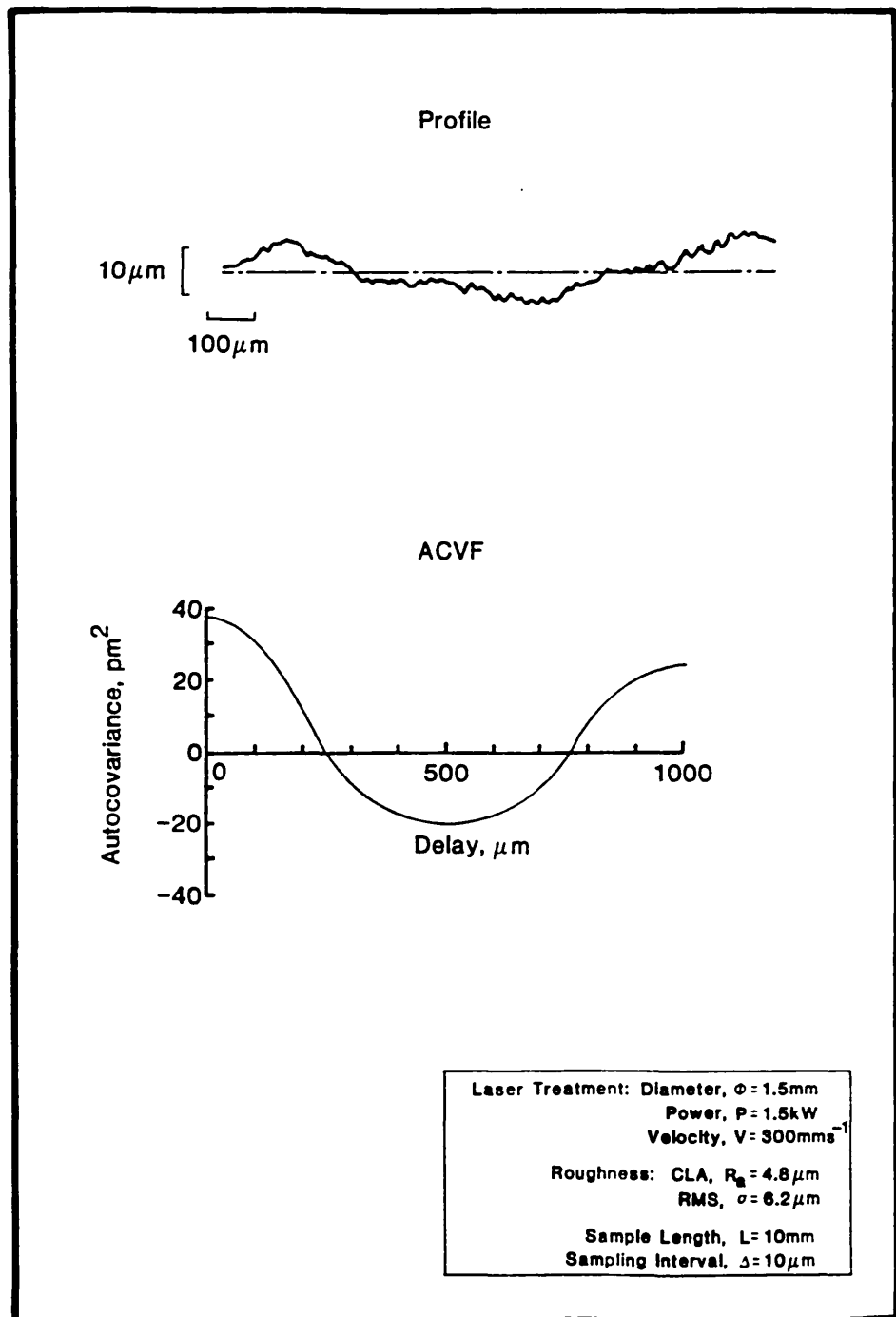


Figure 2.8

Surface Profile and its ACVF, along the
Centrelines of a Track in 420 Steel

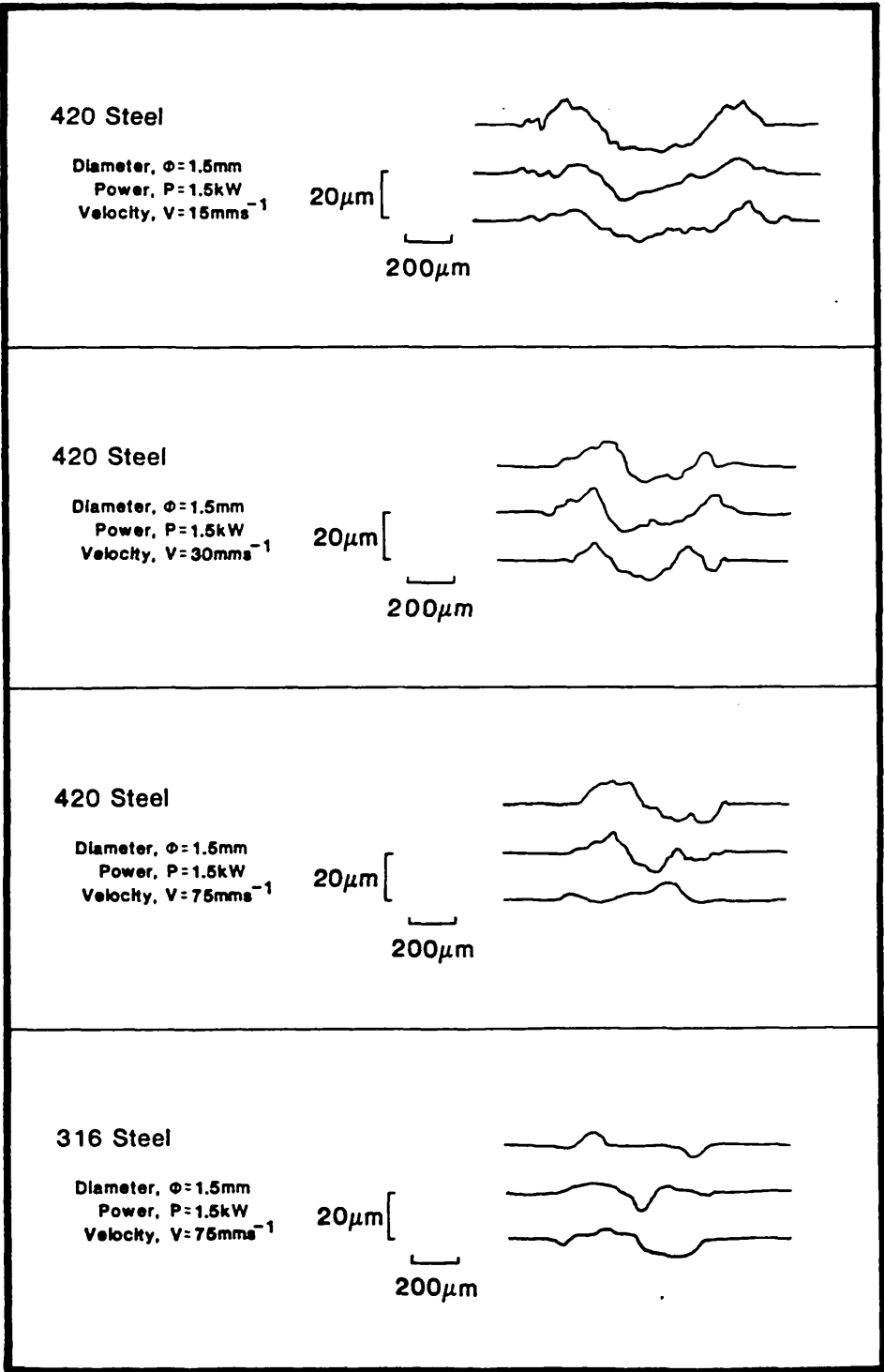


Profiles taken across single tracks show several kinds of crosssection, Figure 2.9. However, the profiles that were taken on the tracks that were produced at traverse speeds of 15 and 30 mms^{-1} all show a central depression. If several tracks with these profiles are spaced at regular intervals and overlap each other a periodic topography of the type seen in the profiles taken across the tracks will be produced.

There are two mechanisms that can give rise to rippling in the high speed tracks, namely, those where surface tension is the driving force and those where vapour pressure is the driving force. The effect of varying traverse speed on temperature gradients in the melt pool and therefore on surface tension gradient driven rippling has been studied by Kear et al (1979). They have found that the shallow melt pools that are produced at high traverse speeds are associated with relatively high temperature gradients. On the other hand the effects of vapour pressure will be most evident at low traverse speeds where there is more intense heating and metal vapourisation becomes more significant. Because unlike pressure gradients, surface tension gradients become more significant at high speeds it is assumed that the periodic rippling at high speeds is driven by surface tension gradients.

Figure 2.9

Profiles across Single Tracks



The melt pool size may also have an effect on the rippling. The larger melt pools associated with the low speed runs will allow more scope for the dissipation of the disruption set up by the power beam ripple. However, there is only a gradual change in the melt pool profile through the traverse velocity range associated with the transition from random to periodic rippling (see Figures 1.6 and 1.7), suggesting that this transition is not due to a change in the dimensions of the melt pool.

2.3.2 Height Distributions

The height distributions of the profiles that were produced over a range of treatment conditions have been characterised. Values of the roughnesses are given in Table 2.1 and Figures 2.10 to 2.12. Their skewnesses and kurtosises are given in Table 2.2. The profiles of the centrelines of the low speed tracks show skewnesses of about zero and kurtosises of about three. These are the values that would be expected for a Gaussian distribution. The ratio σ/R_a is about 1.25 through the treatment range, also suggesting a Gaussian height distribution. This distribution would be expected for a profile that was generated by a large number of independent events acting cumulatively (Sayles and Thomas 1978). As the treatment speed increases a change takes place. The height distributions become rougher, negatively skewed and leptokurtotic. It is difficult to explain these results in terms of the flow processes of laser surface melting. However, it is likely that these changes are associated with the surface tension driven flow that gives rise to a periodic structure at high speeds.

TABLE 2.1

STATISTICAL DESCRIPTORS OF PROFILES

Steel Code	Laser Treatment				Ordinate Separation / μm	Roughness		Decay Distance $\beta/\mu\text{m}$
	P /kW	V /mms ⁻¹	ϕ /mm	A /mm		σ / μm	Ra / μm	
420	1.5	15	1.5	—	10	2.12	1.7	660
"	"	30	"		"	2.3	1.8	300
"	"	40	"		"	2.8	2.1	360
"	"	60	"		"	2.2	1.6	420
"	"	80	"		"	1.8	1.6	400
"	"	120	"		"	2.0	1.6	550
"	"	200	"		"	3.2	2.5	280
"	"	300	"		"	6.2	4.8	—
"	"	400	"		"	4.9	3.4	—
"	"	15	"		3	1.5	1.2	300
"	"	30	"		"	1.2	1.0	300
"	"	40	"		"	2.6	1.7	190
"	"	60	"		"	1.5	1.2	230
"	"	80	"		"	1.5	1.3	220
"	"	120	"		"	1.3	1.0	250
316	"	40	"		10	2.6	2.1	1000
"	"	80	"		"	3.5	2.6	350
"	"	120	"		"	3.7	2.8	400
"	"	40	"		3	1.0	0.8	180
"	"	80	"		"	1.4	1.1	250
"	"	120	"		"	1.3	1.0	150
420	"	15	"	.6	10	3.0	2.6	—
"	"	30	"	.5	"	6.1	5.0	—
"	1.0	60	"	—	"	1.9	1.5	360
"	1.2	"	"		"	2.3	1.9	340
"	1.8	"	"		"	2.0	1.6	400
"	1.5	"	1.0		"	2.3	1.9	410
"	"	"	1.2		"	2.3	2.0	380
"	"	"	1.8		"	1.9	1.6	400
"	"	"	2.2		"	1.5	1.2	350
"	"	"	1.0		3	2.3	1.9	200
"	"	"	1.2		"	2.1	1.8	220
"	"	"	1.8		"	1.1	0.9	190
"	"	"	2.2		"	0.9	0.7	190

Figure 2.10

Treatment Speed against Roughness for
Profiles along the Centrelines of Tracks in
420 Steel

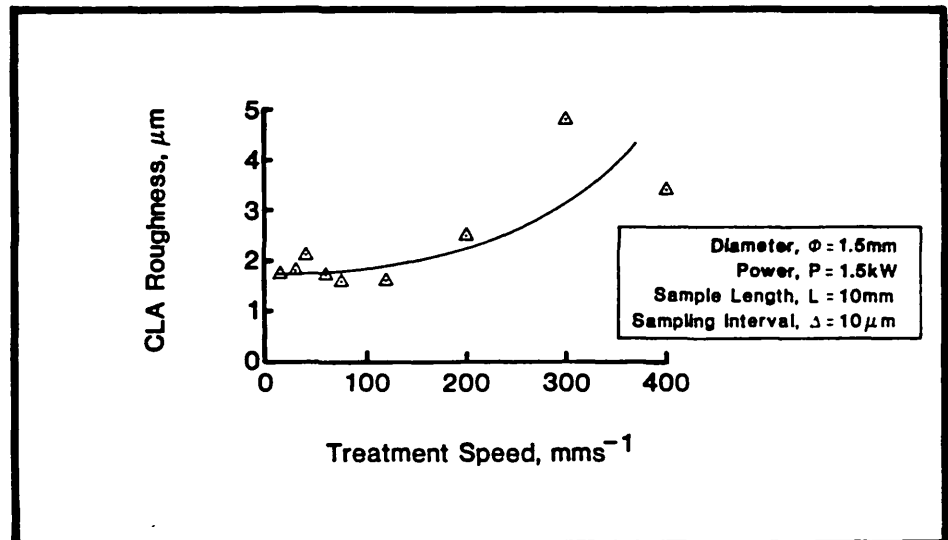


Figure 2.11

Beam Power against Roughness for Profiles
along the Centerlines of Tracks in 420 Steel

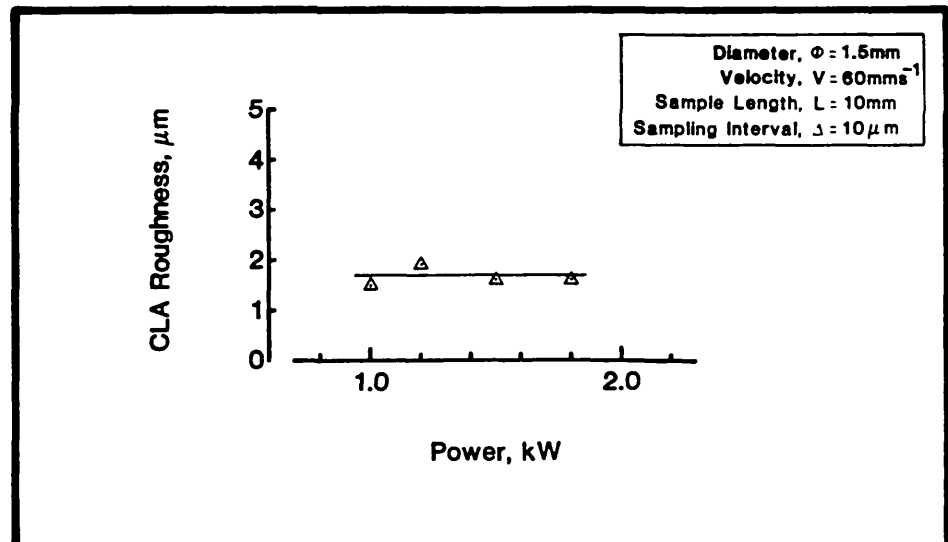


Figure 2.12

Incident Beam Diameter against Roughness for
Profiles along the Centrelines of Tracks in
420 Steel

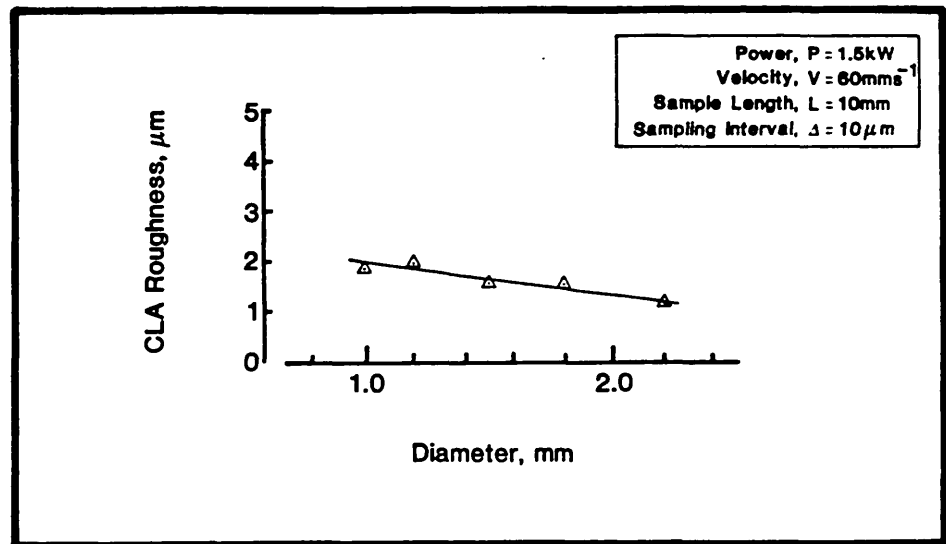


Table 2.2

Skewness and Kurtosis of Centreline Profiles

Traverse speed, V mms ⁻¹	Skewness	Kurtosis
15	.16	2.57
30	.13	2.9
40	.57	3.7
60	-.29	2.9
80	.22	3.1
120	-.21	3.2
200	-.18	4.3
300	-.44	3.2
400	-1.86	9.1

The tracks were produced at:

Power, P = 1.5kW
Diameter, ϕ = 1.5mm

The trend to high roughnesses at high speeds has been found elsewhere, Hawkes (1983). However, the opposite trend has been reported by Moore et al (1979). This difference may be explained in terms of the differences in the processing conditions. Moore et al used beam powers of up to 7.5kW at near focus conditions giving higher energy densities that were used in this work or the work of Hawkes et al (1983). Moore and his coworkers suggest that their surface disruption is due to vapour pressure gradients over the melt pool. This is reasonable in view of their high energy densities. If vapour pressure variations were the cause of the surface rippling then the heating and vapour pressure variations would produce more severe disruption at low speeds where convective cooling due to the movement of the substrate would be less significant and heating would be more intense.

The roughnesses of profiles that were perpendicular to the direction of the melt tracks were two to three times as high as the roughnesses of profiles taken along the centrelines of the tracks (see Table 2.1). Bearing this in mind it would be appropriate to carry out more work in this direction.

The effects of beam power and incident beam diameter were also considered (see Figures 2.11 and 2.12). The beam power has little effect over the range from 1.0 to 1.8kW. However, the work of Moore et al (1979) suggests this is not always the case; at higher beam powers increasing roughness is associated with increasing beam powers.

The beam diameter against roughness plot indicates that roughness can be minimised by maximising the beam diameter. Maximising the beam diameter will

affect the depth and width of the melt pool, the surface tension gradients and the vapour pressure gradients. All these factors will contribute to minimising the roughness at high incident beam diameters.

2.4 CONCLUSIONS

1. It is possible to produce macroscopically smooth surfaces by laser surface melting.
2. At low speeds (200mms^{-1} or less) the centreline profiles of conduction limited tracks produced at powers in the range 1.0 to 2.0kW are aperiodic over the bandwidth from $\sim 5\mu\text{m}$ to 2mm. They have centreline average roughnesses in the range 1.0 to $3.0\mu\text{m}$ over 10mm profiles.
3. The profiles measured across overlapping conduction limited tracks produced at 1.5kW are two to three times as rough as the corresponding centreline profiles. These profiles show periodic rippling with a wavelength equal to the intertrack advance.
4. Periodic rippling with a wavelength corresponding to the power ripple frequency on the laser beam occurs on the profiles of the centrelines of tracks produced at high speeds (300 and 400 mms^{-1}). These tracks are also rougher than those produced at low speeds having centreline average roughnesses of $\sim 4\mu\text{m}$ over 10mm profiles.
5. The roughnesses of the surfaces of conduction limited tracks show some variation with treatment conditions with high incident beam diameters (in the range 1 to 2mm) and low traverse velocities (in the range 15 to 400 mms^{-1}) minimising surface roughness.

3.1 INTRODUCTION

3.1.1 Effects of the Microstructures

3.1.1.1 420 Steel

Laser surface melting^t offers the possibility of forming a martensitic layer on a tempered substrate. This layer is interesting because of its high hardness and strength. High hardnesses are associated with good erosion resistance and if it is possible to develop the full hardness of the material (Vickers hardness ~510#) in a crack free layer that is well bonded to the substrate the erosion resistance of the steel should be substantially enhanced.

Although it is possible to raise the hardness of the steel by nitriding, this technique would deplete the chromium content of the matrix as chromium rich nitrides^{were} formed.

The martensite transformation itself is important not only for the hardness it generates but also for its influence on the materials residual stress. There is a ~3% volume increase during the transformation from austenite to martensite and as this transformation occurs close to room temperature, it will offset tensile residual stresses developed in tracks during cooling (Chapter 4).

If cracks are generated during cooling they would be expected to adversely affect both the corrosion and the fatigue behaviour of the material (Chapter 5 and 6).

3.1.1.2 316 Steel

It is known that it is possible to use laser surface melting to redistribute chromium in sensitized austenitic stainless steel so as to restore the intergranular corrosion resistance of the material (Anthony and Cline 1978).

However, in remelting and solidifying the material with a laser, solute gradients are introduced during the solidification process. This solute distribution is important in determining the corrosion behaviour of the steel (Chapter 6). If δ -ferrite is formed this will raise the possibility of brittle σ -phase forming on annealing at high temperatures (Pickering 1976).

The dislocation structure of the steel may enhance its stress corrosion cracking and hydrogen embrittlement resistance by providing innocuous traps for hydrogen or by resisting the formation of planar slip arrays. (Hanninen 1979).

As in the 420 steel cracks will reduce the corrosion and fatigue resistance of the material.

3.1.2 Solidification Front Morphologies

The conditions at a solidification front can be characterized in terms of G/R , the ratio of thermal gradient in the liquid to solidification front velocity. A planar solidification front will be stable when:

$$G/R > \frac{MC(1-k)}{kD}$$

where M = slope of the liquidus

C = initial solute concentration

k = Ratio of solute concentration in the solid
to solute concentration in the liquid

D = diffusivity of the solute in the liquid

At a lower value of G/R than the minimum for a stable planar solidification front, the solidification front will adopt a cellular morphology. At still lower G/R ratios constitutional supercooling just behind the cell tips will lead to the formation of branched dendrites.

The product $G.R$ is the cooling rate. High cooling rates are associated with:

- 1 Metastable crystal phases.
- 2 Small eutectic interphase spacings.
- 3 Extended solid solubilities.
- 4 Closely spaced cells, dendrites and dendrite branches.

Laser surface melting produces tracks containing material that has solidified at a range of G/R ratios, from extremely high values at the bottom

and sides of melt tracks where the rate of movement of the solidification front is low, to low values of G/R associated with the formation of branched dendrites at the tops and centres of the tracks (Kear, Breinan and Greenwald 1979 and David and Vitek 1981).

It is possible to produce high cooling rates after laser surface melting. Calculations by Kear, Breinan and Greenwald 1979 indicate cooling rates as high as 10^8°Cs^{-1} .

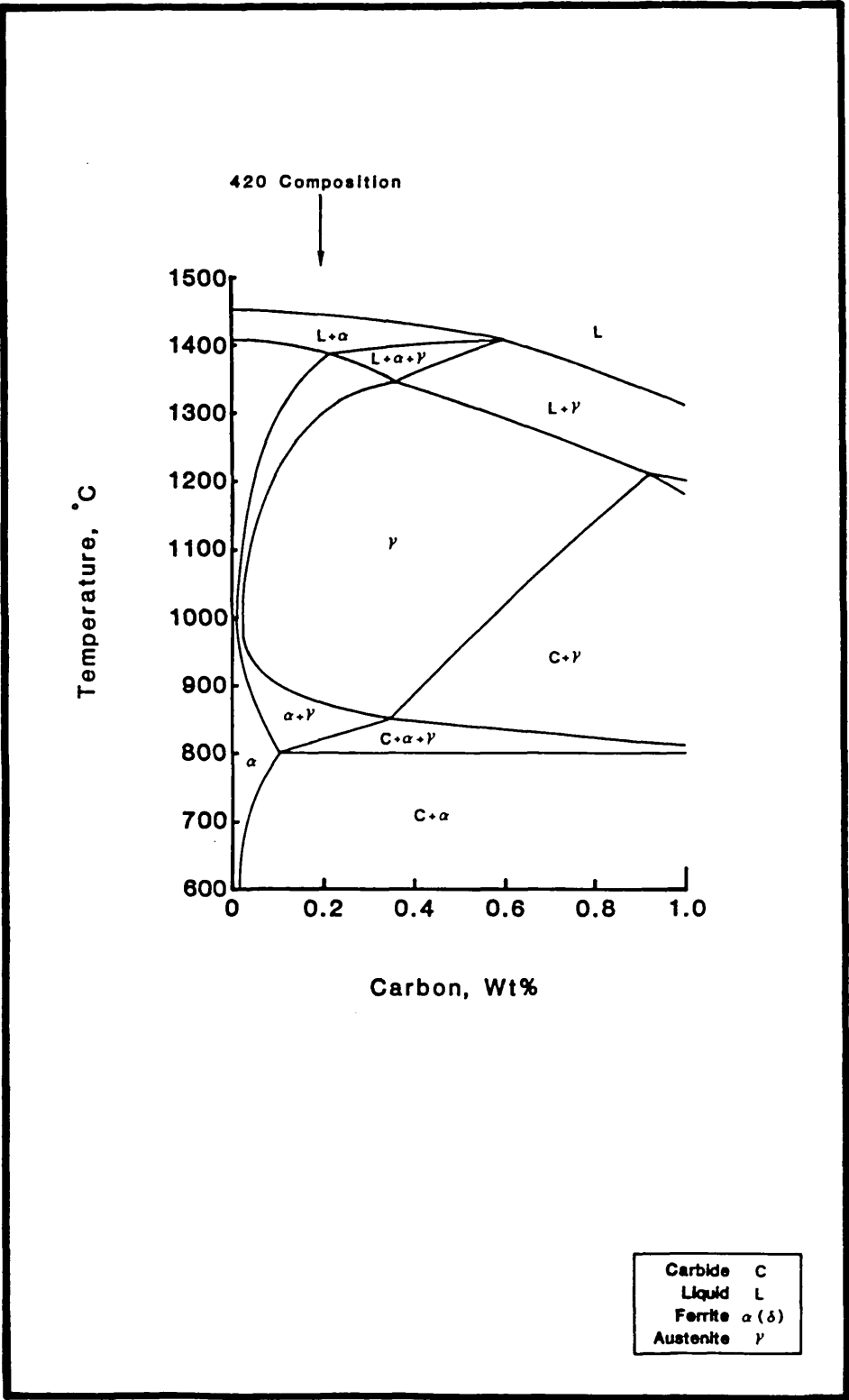
3.1.3 The Structure of Laser Surface Melted 420 Steel

The effect of carbon on the Fe-12%Cr equilibrium diagram is shown in Figure 3.1 (Irvine et al 1960). The M_S temperature of the 420 steel is $\sim 250^\circ\text{C}$ and the M_f temperature lies in the range $\sim 100^\circ\text{C}$ to $\sim 50^\circ\text{C}$ (Pickering 1976).

During the early stages of the tempering of 420, at temperatures of $\sim 500^\circ\text{C}$ and below, the precipitation of Cr_7C_3 and M_2X results in secondary hardening. This hardening competes with softening due to the removal of carbon from solution. The net result of these reactions is a retardation of softening in the early stages of tempering at $\sim 500^\circ\text{C}$ and below (Briggs and Parker 1965). In the overaged condition the Cr_7C_3 and M_2X are both replaced by M_{23}C_6 and there is softening.

Bee and Wood (1982) have examined the structures of rapidly quenched Fe-12%Cr-0.14%C steel. A fine wire and a thin ribbon produced by rapid quenching techniques were examined by x-ray diffraction and transmission electron microscopy respectively. In both cases a lath martensite structure was found without retained austenite. The cooling rates for the ribbon and the wire were in the range

Figure 3.1
Fe-12%Cr-C Phase Diagram



10^5 to 10^6 °C s⁻¹. This compares with the structures found by Molian (1984) in laser surface melted Fe-10%Cr-0.2%C steel. Here the lath martensite contained retained austenite at the interlath boundaries and the prior austenite grain boundaries. Both ϵ -carbide and cementite were found. These carbides were formed by the heating and tempering of tracks by subsequent overlapping tracks. The cooling rates involved in the laser treatment of these tracks were estimated from the solidification structures and from a heat transfer model (Kear et al 1979) and were found to lie in the range from 10^3 to 10^6 °C s⁻¹ depending on the melt depth.

The volume fraction retained austenite in steels is usually increased by rapid quenching (Ruhl and Cohen 1975, Donachie and Ansell 1975 and Bee and Wood 1981). This may be explained by considering the martensite transformation temperature range to be lowered by rapid quenching. However, direct measurements of M_s temperature during the rapid quenching of Fe-0.5%C and Fe-0.5%C-2.05Ni to produce lath type martensites, indicate that an increase of M_s temperature is associated with an increase in the cooling rate over the cooling rate range from 2.7×10^3 to 2.5×10^4 °C s⁻¹ (Messler, Ansell and Lizunov 1969). This increase was explained by considering the inability of carbon atoms to pin dislocations at high cooling rates when the time available to diffuse to dislocations was short. This reduces the shear strength of the ^{aus}martensite enabling the transformation to martensite to occur more readily, raising the M_s temperature.

Speich and Warlimont (1968) have pointed out that M_s may be lowered at high cooling rates because more carbon may be maintained in solution before the martensite transformation takes place. This stabilises the austenite and depresses the M_s temperature.

Sare (1981) has pointed out that when considering martensite morphology changes associated with rapid quenching it is important to consider the geometry of the specimen. For example thin films of Fe-C and Fe-N alloys form different microstructures from bulk materials. Also the M_s temperature in Fe-C and Fe-Ni alloys during electrochemical thinning is considerably higher than that of bulk material.

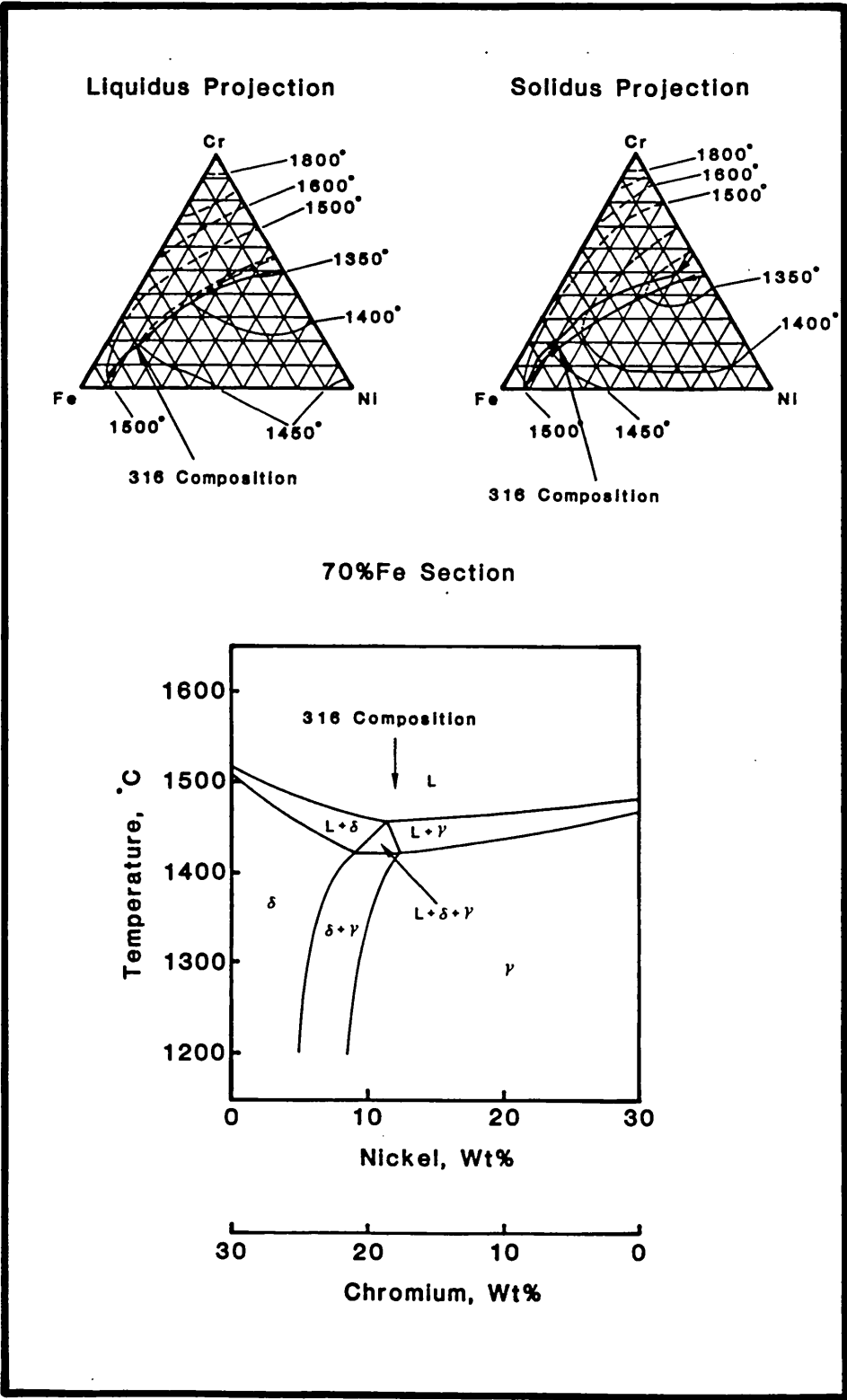
3.1.4 The Structure of Laser Surface Melted 316 Steel

The liquidus and the solidus surfaces of the Fe-Cr-Ni ternary equilibrium phase diagram are shown in Figure 3.2 as is the pseudobinary 70%Fe-Ni-Cr phase diagram (Rivlin and Raynor 1980). The 316 steel has a composition to the nickel rich side of the eutectic liquidus and will solidify as primary austenite. It will be rich in nickel and depleted in chromium in the first regions to solidify (Brooks et al 1983). As the composition of the steel is initially close to the eutectic liquidus this chromium enrichment may give rise to δ -ferrite in the last regions to solidify.

David and Vitek (1981) have studied the microstructure of 308 steel (Fe-20.5%Cr-10.5%Ni) after laser surface melting. A 9kW laser with an annular mode structure was used over a range of traverse speeds at near focus conditions.

At the higher traverse speeds of 25 and 65mm s^{-1} , associated with the higher cooling rates, the laser melt tracks formed an almost fully austenitic microstructure with less than 1% ferrite lying between the solidification cells, suggesting primary austenite solidification. At the lowest speed of 13mm s^{-1} there was a range of structures with fully

Figure 3.2
Cr-Fe-Ni System



austenitic material at the base of the track. The middle of the track showed a fine austenite and ferrite duplex structure, which became coarse towards the top of the track. These microstructures are associated with a range of cooling rates, with the cooling rates being highest towards the bottom of the track.

A third phase was noticed in all of the tracks consisting of manganese and silicon rich spheres of ~100 to ~200 nm diameter. No cracks were observed in any of the tracks.

Previous work by David, Goodwin and Braski (1979) showed that GTA welding produced a primary ferrite microstructure in the same steel (AISI 308). Thus, it would appear that the formation of δ -ferrite has been suppressed at the higher cooling rates associated with laser surface melting. As David and Vitek point out this may indicate undercooling below the δ -ferrite phase field. This agrees with the observations of Bee and Wood (1982) who found no δ -ferrite in rapidly cooled Fe-12%Cr-0.14%C steel and attributed this to an undercooling of at least 350°C and Kattamis and Flemmings (1966) who have reported undercooling of more than 300°C in Fe-25%Ni steel.

Anthony and Cline (1978) have laser surface melted sensitized 304 steel (Fe-18%Cr-8%Ni) to produce a structure of cellular austenite containing small needles of martensite. The formation of these needles was stress induced and indicates high residual stresses in the melted zone. The implications of these stresses are discussed in Chapter 4 and the intergranular corrosion behaviour of the treated steel is discussed in Chapter 6.

Wood and Honeycombe have examined the structure of rapidly cooled Fe-20%Cr-25%Ni austenitic steel splats. This technique produces samples that have gone through a wide range of cooling rates (10^5 to 10^7 °Cs⁻¹). A corresponding range of structures were found in various regions of the splats. As cooling rate increased the structures showed:-

- 1 Branched dendrites.
- 2 Low angle cells.
- 3 Grains containing parallel bands of dislocation loops.
- 4 Featureless homogeneous grains.

The possibility of segregation across a weld developing a solute difference between the centreline and the edges of the melt pool has been investigated by Kou and Le (1982). GTA welds were produced in 309 steel (Fe-22.5%Cr-14%Ni-2%Mn) and SEM-EDX analysis was carried out across the welds. A uniform compositional profile was found, apart from local variations associated with the dendritic solidification structure.

3.2 EXPERIMENTAL

3.2.1 The Specimens

Specimens covered by overlapping tracks and specimens with single melt tracks were produced in grit cleaned and degreased 420 and 316 steel. The steel compositions are given in Table 3.1.

Table 3.1

		Element, weight %										
		C	Cr	Cu	Fe	Mn	Mo	Ni	P	S	Si	V
420	12.7mm ϕ bar	0.28	12.4	0.09	bal.	0.5	0.03	0.22	0.022	0.024	0.5	0.06
	19.05mm ϕ bar	0.19	12.6	-	bal.	0.66	-	0.14	0.01	0.007	0.35	-
316	12.7mm ϕ bar	0.046	17.0	0.25	bal.	1.54	2.40	11.6	0.028	0.0005	0.28	0.04
	6.35mm plate	0.027	17.24	-	bal.	1.35	2.35	11.37	0.034	0.02	0.46	-

The 12.7mm ϕ bar stock was used for:-

- 1 The STEM microanalysis in this Chapter.
- 2 All the fatigue work (Chapter 5).
- 3 All the corrosion studies (Chapter 6).

The 19.05mm ϕ 420 steel bar and the 6.35mm 316 steel plate were used for:-

- 1 The initial processing studies (Chapter 1).
- 2 The topography studies (Chapter 2).
- 3 All of this Chapter except for the STEM microanalysis.

3.2.2 Optical Microscopy

Various routes were used to prepare the metal surfaces for the optical micrographs shown here, the most successful of which is given below. The specimens were washed in between steps.

- 1 Section the specimen with a laboratory cut off wheel (Struers "Discotom").
- 2 Polish the cut off surface with 36 μ m diamond paste on the ungrooved surface of a cast iron lapping plate.
- 3 Polish successively with 6 and 1 μ m diamond paste on the grooved surfaces of cast iron lapping plates.
- 4 Polish with 6 μ m diamond paste on a napless cloth.
- 5 Polish with 6 and 1 μ m diamond paste on napped cloths.
- 6 Etch.

Etching was by one of the following:-

- 1 Villelas Reagent

(5ml hydrochloric acid, 1g picric acid and 100ml ethanol or methanol). This was used to show the general structure of both steels. At 25°C a ~500s etch was suitable for the 420 steel and a ~1ks etch was suitable for the 316 steel.

- 2 Acid Chloride Etch

(10ml hydrochloric acid in 100ml ethanol). This was used to show the general structure of the 420 steel. The specimen was etched either by immersion in warm (25°C) etchant or electrolytically (6V for ~5s) to show the martensitic structure. A prolonged electrolytic etch (6V for ~50s) was used to show up the cellular solidification structure.

3 Oxalic Acid Etch

(10g oxalic acid and 100g of water). This was used to show the general structure and carbides of the 316 steel. The specimens were etched for a few seconds at 6V.

Microhardness traverses were carried out with an Akashi microhardness tester and a 100g load.

3.2.3 X-Ray Diffraction

Specimens consisting of overlapping tracks covering an area of at least 10mm x 10mm were rotated over the range of angle between the x-ray source and the specimen surface from 0.35rad through to 1.4rad. The specimens were spun during diffractometry to minimise texture effects. The work was carried out in a Philips "PW1710" diffractometer. The peaks were indexed and the various crystal structures were identified.

In the 420 steel retained austenite volume fractions were determined for the laser melted surfaces. This was carried out by comparing the integrated peak intensities due to the austenitic and the martensitic crystal structures. The background intensities were subtracted and the volume fractions of austenite and martensite evaluated from the equation:

$$V_{\gamma} = \frac{\frac{1}{n_{\gamma}} \sum_0^{n_{\gamma}} \left[\frac{I_{\gamma i}}{R_{\gamma i}} \right]}{\frac{1}{n_{\gamma}} \sum_0^{n_{\gamma}} \left[\frac{I_{\gamma i}}{R_{\gamma i}} \right] + \frac{1}{n_{\alpha}} \sum_0^{n_{\alpha'}} \left[\frac{I_{\alpha i}}{R_{\alpha i}} \right] + V_c}$$

where V_x = Volume fraction of phase x

n_x = No of peaks of phase x under
consideration

I_{xi} = Integrated intensity of ith peak of
phase x

R_{xi} = Relative intensity of ith peak of
phase x

and the subscripts γ , C and α' denote austenite,
carbide and martensite respectively.

Values of R were taken from the literature (Jatczak
1980).

3.2.4 Transmission Electron Microscopy

Thin foils suitable for this technique were prepared
as follows:-

- 1 A slice of material containing the laser treated region was cut off parallel to the specimen surface with a laboratory cut off wheel under flood cooling conditions to avoid heating.
- 2 The specimen was ground down to $\sim 100\mu\text{m}$ thickness on silicon carbide papers. Initial grinding was on 220 grade paper. The final $\sim 50\mu\text{m}$ were removed with finer 600 grade paper to minimise the thickness of the mechanically worked zone due to grinding. Material was removed from the underside of the treated zone.

- 3 3mm diameter discs were spark machined out using a Metals Research "Servomet" machine.
- 4 Electrochemical thinning was carried out in a Struers "Tenupol" machine.

This twin jet thinning device is designed to detect the formation of a hole in the disc by shining a light against one side of the disc and using a photocell in a dark chamber on the other side of the disc to indicate penetration. When a hole has been detected a buzzer sounds and the polarity of the cell is reversed to stop the thinning process.

The electrolyte was viscous perchloric acid (10 vol.% perchloric acid, 15 vol.% glycerol and 75 vol.% ethanol). This electrolyte is potentially explosive and must be kept below 30°C. Fortunately the small area of the specimen only generates a negligible temperature rise during thinning, which is carried out at room temperature. Thinning was at a potential of 18V for the 420 steel and 13V for the 316 steel.

- 5 Within a second or so of the buzzer sounding the specimen was removed from the cell and rinsed in acetone. It was then rinsed successively in two dishes of acetone and transferred to a final dish of acetone to soak.
- 6 The specimens were stored in a vacuum desiccator to prevent oxidation.

After preparation the foils were examined in a Philips "EM301" transmission electron microscope and a Jeol "120CX" scanning transmission electron microscope. STEM microanalysis was carried out with a 24.3aJ

resolution, energy dispersive x-ray spectrometer. During compositional analysis specimens were held in a carbon holder so as not to obscure the specimens' x-ray spectra with extraneous peaks.

When microanalysis was carried out on the thin intercellular δ -ferrite regions in the 316 steel there were practical difficulties associated with the alignment of these zones so that the regions being analysed were actually δ -ferrite. These difficulties stemmed from:

- 1 The fixed orientation of the specimen during analysis. It was tilted through 0.61rad off horizontal towards the detector in order to maximise the x-ray signal.
- 2 Movement of the specimen during analysis associated with heating and cooling of the specimen holder.

The problems were overcome by a process of ordered trial and error based on the observation of the contamination spots on the top and the bottom of the foils. It is possible, by moving round the δ -ferrite surrounding a cell, to find a region oriented parallel to the electron beam. This region was analysed, the contamination spots being checked after analysis to confirm that the analysis had been on the δ -ferrite. Where this was not the case data were rejected. Corrections were made for the relative intensities of the peaks of the various elements and for mass absorption. A fluorescence correction is also necessary for the chromium steels where the iron fluoresces onto the chromium to give an exaggerated chromium peak. This correction was by the method that has been discussed by Nockolds et al (1980). This method has the merit of predicting the significant

fluorescence effects that are observed in thin foils.

The thickness of foils must be known for the absorption and the fluorescence corrections. This was estimated from elementary trigonometry and measurements of the spacing of contamination spots after tilting the specimen back to the horizontal after analysis.

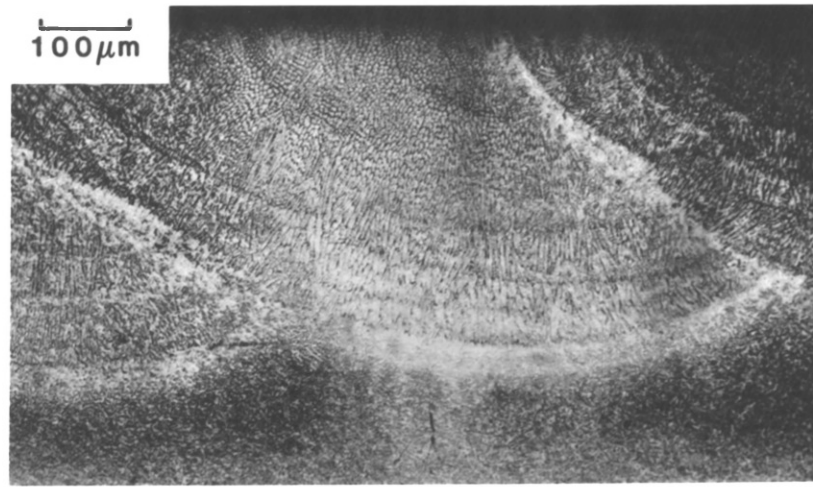
3.3 RESULTS

3.3.1 420 Steel

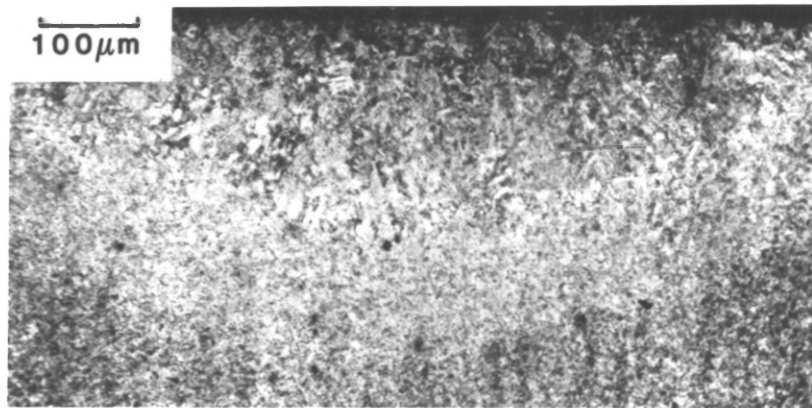
The structure of the laser melted tracks shows in Photographs 3.1, 3.2 and 3.3. Photograph 3.1 shows a series of overlapping tracks after prolonged electrolytic etching in dilute hydrochloric acid (6V for ~50s). This reveals the cellular solidification structure. Photograph 3.2 shows one of a series of overlapping tracks after etching by immersion in dilute hydrochloric acid for about 100s. It shows the martensitic structure of the melted zone as does Photograph 3.3.

A band of light etched material shows below the laser melted track in Photograph 3.2 and in the central track in Photograph 3.1, while a dark etching band shows below the laser melted region in Photograph 3.1.

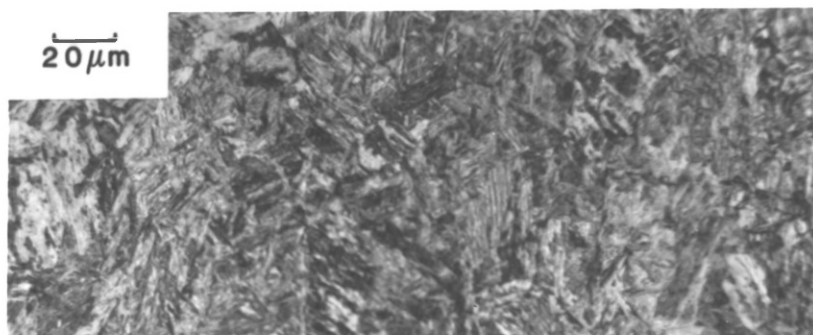
A microhardness traverse through a track produced at a speed of 60mm s^{-1} , a power of 1.5kW and an incident beam diameter of 1.5mm is shown in Figure 3.3. The Vickers hardness is ~510# throughout the melted zone, decreasing to ~220# through the ~60 μm of the underlying heat affected zone.



Photograph 3.1 Overlapping tracks in 420 steel
 ($A = 750\mu\text{m}$, $P = 1.8\text{ kW}$, $V = 25\text{mms}^{-1}$ and $\Phi = 400\mu\text{m}$)



Photograph 3.2 Melted zone in 420 steel ($A = 1.5\text{mm}$,
 $P = 1.8\text{ kW}$, $V = 10\text{mms}^{-1}$ and $\Phi = 1\text{mm}$)



Photograph 3.3 Martensite in a melted zone in 420
 steel ($A = 1.5\text{mm}$, $P = 1.8\text{ kW}$, $V = 10\text{mms}^{-1}$ and $\Phi =$
 $400\mu\text{m}$)

Figure 3.3
Hardness against Depth for Laser Surface
Melted 420 Steel

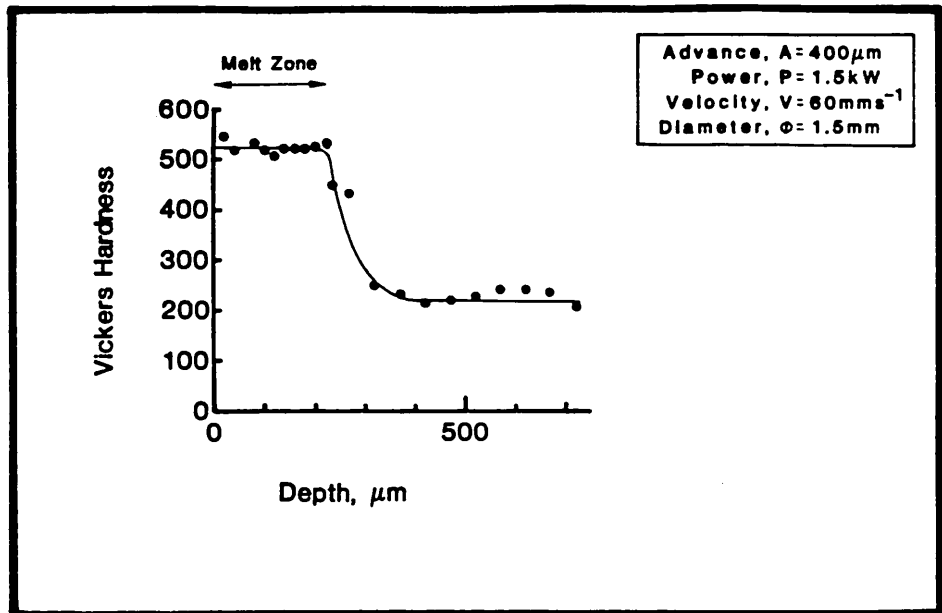
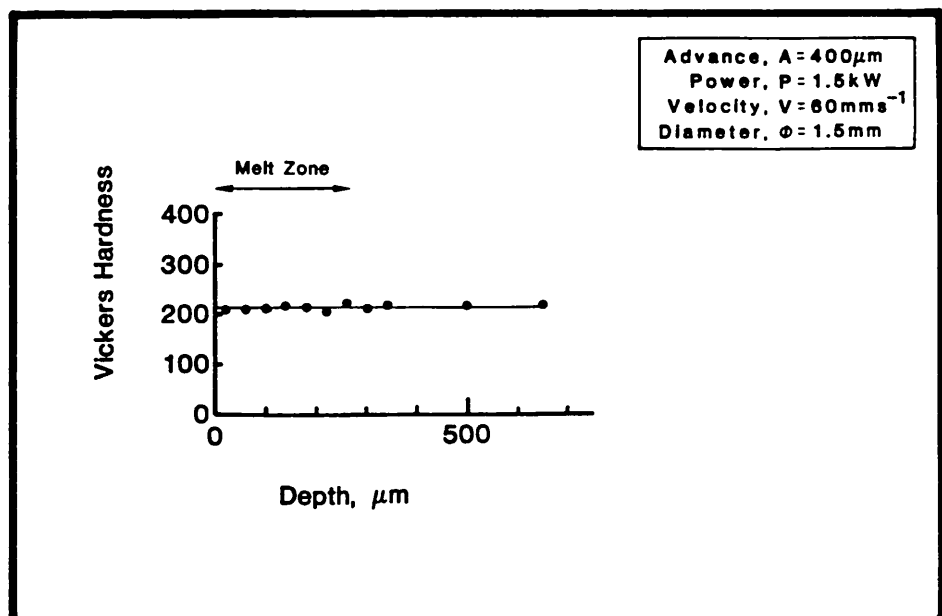


Figure 3.4
Hardness against Depth for Laser Surface
Melted 316 Steel



The fractions of retained austenite in the laser melt tracks were determined from the x-ray spectra for material hardened by quenching in oil after solution treatment at 960°C for 1 hour and for specimens that have been laser surface melted at traverse speeds in the range from 15 to 250mm s⁻¹, see Table 3.2. The lowest volume fraction of retained austenite shows in the oil-quenched specimen. Within the group of laser hardened specimens the lowest volume fractions of retained austenite show at the lowest traverse speeds, with a general trend towards higher volume fractions of retained austenite at the higher speeds rising to 13 vol.% at 100mm s⁻¹, although the volume fraction retained austenite falls off to 6 vol.% at 150mm s⁻¹ and 8 vol.% at 250mm s⁻¹.

STEM microanalysis was attempted on thin foils of 420 steel. This line of research was abandoned however when it indicated about 20% chromium. Photograph 3.4 shows a transmission electron micrograph of laser surface melted 420 steel. The solidification cells are revealed by the darkness of the intercell regions.

Photograph 3.5 shows a solid state transformation hardened track after etching in Vilellas' reagent; the Vickers hardness profile of the track falls from a maximum of ~350# at the surface to the ~220# of the base material within ~50µm of the bottom of the melt zone.

Cracks were not seen in the surface treated steel; however voids were found at the bases of keyholed tracks.

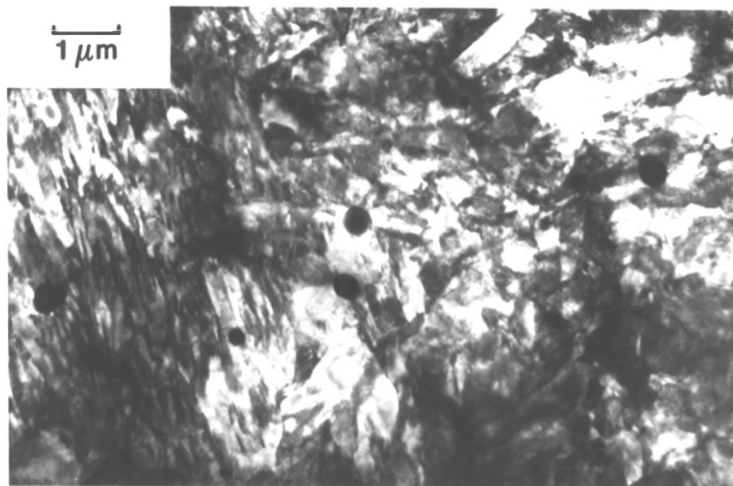
Table 3.2

Table 3.2

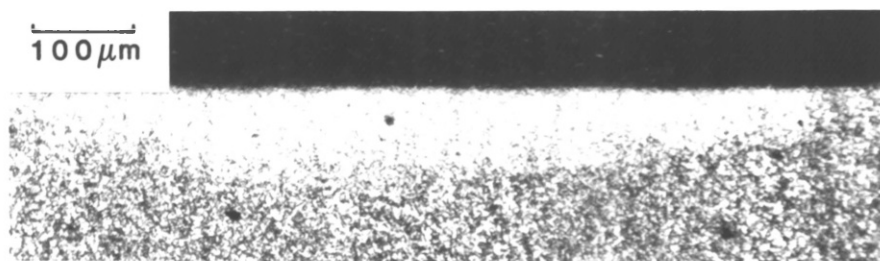
Integrated Peak Intensities and Volume Fractions Retained Austenite in 420 Steel

Cu Target: $\lambda = 154 \text{ pm}$

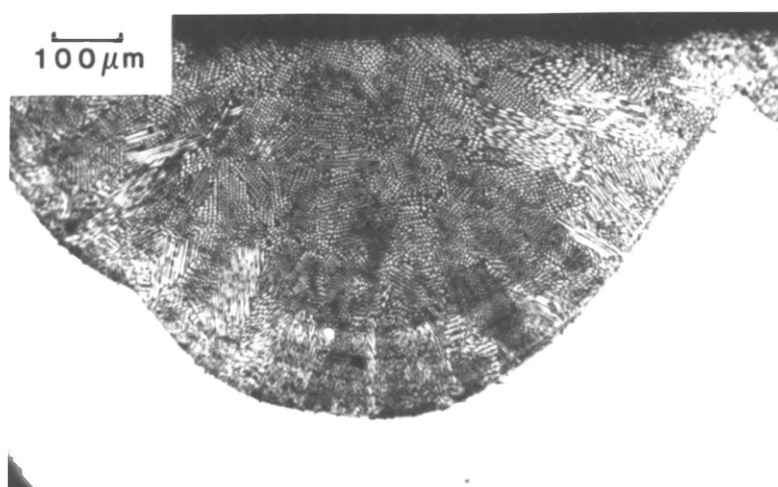
Miller Indices		2 θ rad	R	HEAT TREATMENT CONDITION															
				960°C 1 h % CO r		LASER SURFACE MELTED: ALL SPECIMENS AT P = 1.5kW, $\phi = 1.5\text{mm}$													
						V = 15mm ⁻¹ A = 600 μm		V = 30mm ⁻¹ A = 500 μm		V = 40mm ⁻¹ A = 400 μm		V = 60mm ⁻¹ A = 400 μm		V = 100mm ⁻¹ A = 300 μm		V = 150mm ⁻¹ A = 250 μm		V = 250mm ⁻¹ A = 200 m	
γ	α			γ	α	γ	α	γ	α	γ	α	γ	α	γ	α	γ	α		
200		0.886	81.6	-0.095		0.100		0.228		0.302		0.518		0.555		0.329		0.431	
	200	1.134	31.9		1.607		1.87		2.39		1.98		2.34		1.80		2.02		2.23
220		1.304	44.4	0.084		0.006		0.079		0.326		0.319		0.413		0.140		0.283	
	211	1.434	60.9		2.86		2.18		2.65		2.77		2.77		2.70		2.82		2.93
311		1.581	53.3	0.026		0.025		0.080		0.129		0.120		0.231		0.100		0.137	
	220	1.726	20.6		0.937		0.692		0.887		0.596		0.563		0.711		0.717		0.816
				4.11 E-4	4.76 E-2	1.06 E-3	4.27 E-2	2.04 E-3	5.38 E-2	4.52 E-3	4.55 E-2	5.29 E-3	4.87 E-2	6.87 E-3	4.51 E-2	3.04 E-3	4.81 E-2	4.77 E-3	5.26 E-2
Volume Fraction γ				1%		3%		4%		9%		10%		13%		6%		8%	



Photograph 3.4 TEI of melted zone in 420 steel ($A = 500\mu\text{m}$, $P = 1.5 \text{ kW}$, $V = 30\text{mms}^{-1}$ and $\Phi = 1.5\text{mm}$)



Photograph 3.5 Solid state transformed zone in 420 steel ($P = 1.8 \text{ kW}$, $V = 10\text{mms}^{-1}$ and $\Phi = 3.4\text{mm}$)



Photograph 3.6 Transverse section of a melt track in 316 steel ($A = 1.5\text{mm}$, $P = 1.5 \text{ kW}$, $V = 10\text{mms}^{-1}$ and $\Phi = 400\mu\text{m}$)

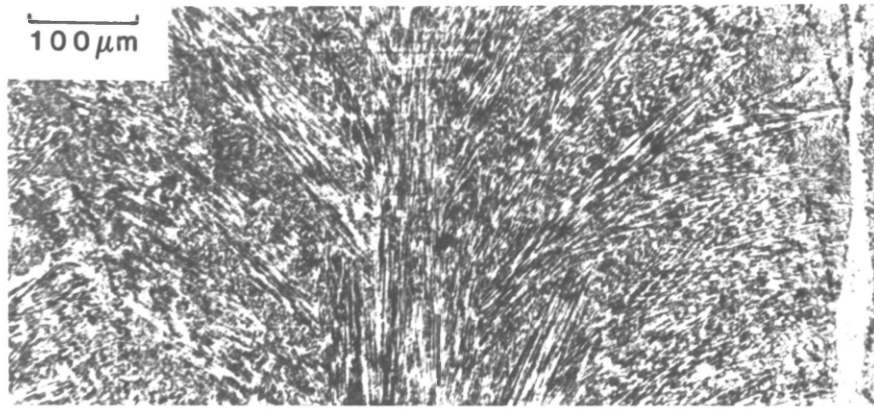
3.3.2 316 Steel

Photographs 3.6, 3.7 and 2.1 show sections through a laser melt track in 316 steel taken at three mutually perpendicular directions, orthogonal to the specimen surface. Photograph 3.6 shows a transverse section with the cells arranged in grains. The track solidification structure is predominantly cellular (see Photograph 3.8) although a few branched dendrites show at the extreme top centre of the track and a narrow band of planar solidified material shows around the edges of the melt track. This band is just discernable in Photograph 3.6. Photograph 3.9 shows the planar solidified zone at a higher magnification. Photograph 3.10 shows epitaxy between the grains underlying the melted track and the laser melted zone. The segregation banding that shows in Photograph 2.1 also shows towards the edges of the track in Photographs 3.6 and 3.7.

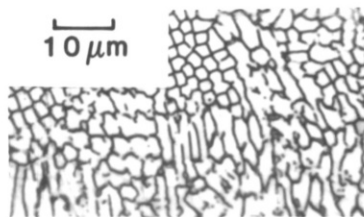
The solidification cells are oriented approximately normal to the segregation banding in Photographs 2.1, 3.6 and 3.7.

Vickers hardness traverses through tracks produced at traverse speeds of 15, 60 and 400mms^{-1} indicated very little difference between the hardness of the melt traces and the base material nor is there a change in the hardness the material near to the melt tracks, see Figure 3.4.

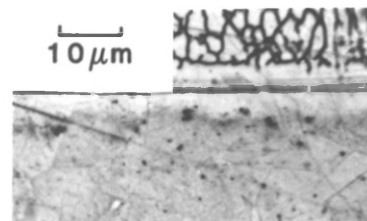
Both x-ray and electron diffraction indicate δ -ferrite in the steel after laser surface melting at velocities of less than $\sim 60\text{mms}^{-1}$. Transmission electron microscopy showed it to lie between the solidification cells, see Photograph 3.11. The volume fraction of δ -ferrite, estimated in TEM, decreased with increasing



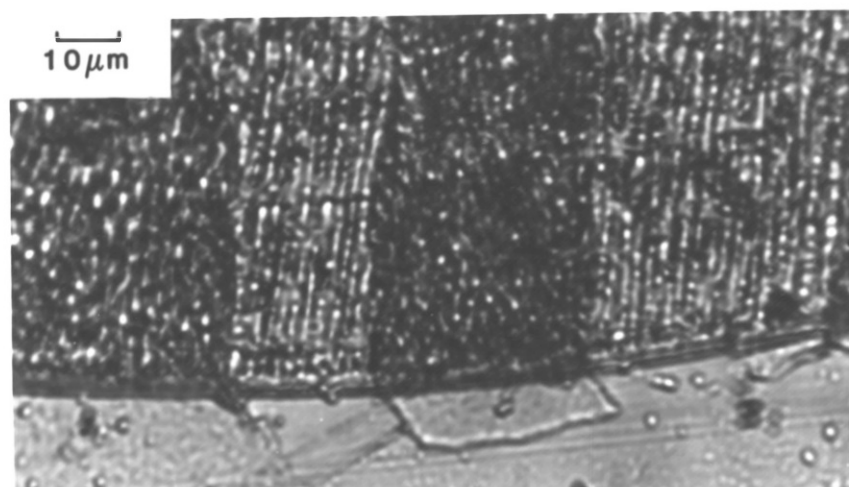
Photograph 3.7 Polished and etched top surface of a melt track in 316 steel ($A = 1.5\text{mm}$, $P = 1.6\text{ kW}$, $V = 10\text{mms}^{-1}$ and $\Phi = 400\mu\text{m}$)



Photograph 3.8
Cellular solidified zone in 316 steel
($P = 1.8\text{ kW}$, $V = 25\text{mms}^{-1}$ and $\Phi = 1\text{mm}$)

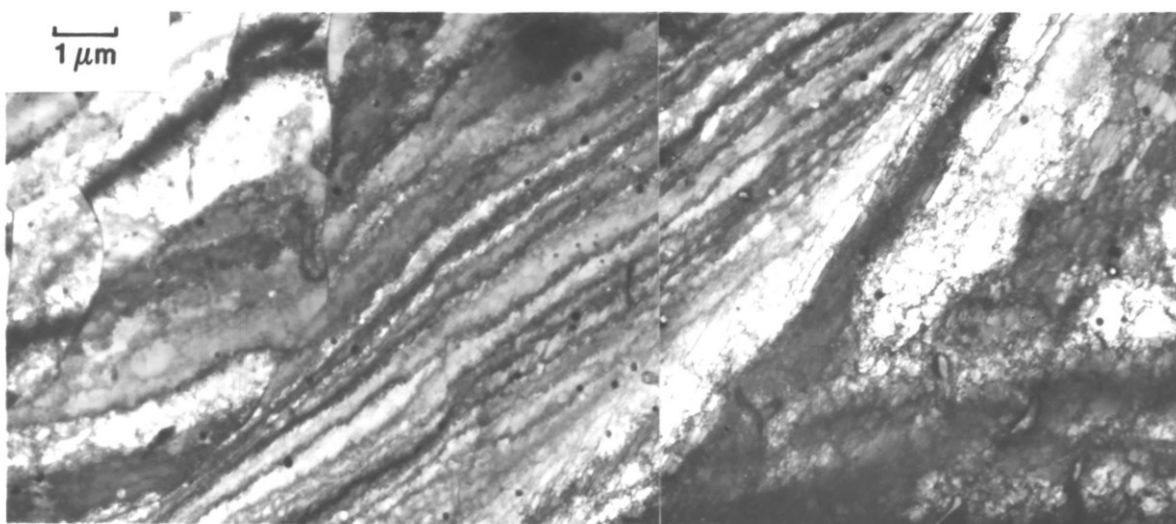
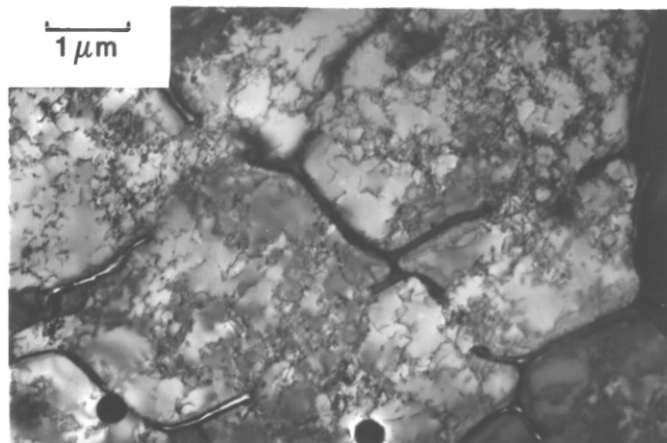


Photograph 3.9
Planar solidified zone in 316 steel ($P = 1.8\text{ kW}$, $V = 25\text{mms}^{-1}$ and $\Phi = 1\text{mm}$)



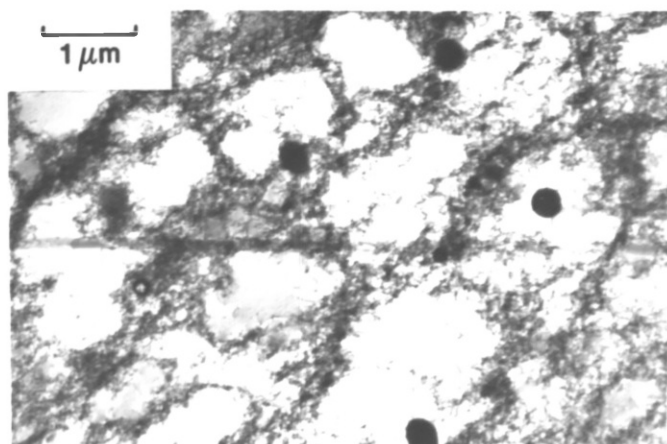
Photograph 3.10 Epitaxy at the base of a melt track in 316 steel ($P = 1.8\text{ kW}$, $V = 25\text{mms}^{-1}$ and $\Phi = 1\text{mm}$)

Photograph 3.11 TEI of
melt zone in 316 steel
($A = 600\mu\text{m}$, $P = 1.5\text{ kW}$,
 $V = 15\text{mm s}^{-1}$ and $\Phi = 1.5\text{mm}$)



Photograph 3.12 TEI of melt zone in 316 steel showing cellular and
planar solidified and back tempered material ($A = 150\mu\text{m}$, $P = 1.5\text{ kW}$,
 $V = 60\text{mm s}^{-1}$ and $\Phi = 1.5\text{mm}$)

Photograph 3.13 TEI of
melt zone in 316 steel
($A = 150\mu\text{m}$, $P = 1.5\text{ kW}$,
 $V = 60\text{mm s}^{-1}$ and $\Phi = 1.5\text{mm}$)



traverse speed and was ~1% in the specimen that was produced at 15mms^{-1} , the lowest speed at which the volume fraction of δ -ferrite was estimated. At traverse speeds of 100mms^{-1} and above no δ -ferrite showed.

STEM microanalysis was carried out across a solidification cell produced at a traverse velocity of 15mms^{-1} , see Figure 3.5. Regions were analysed from the δ -ferrite to the centre of the $1.5\mu\text{m}$ diameter cell. Chromium and molybdenum enrichment shows in the intercellular regions where the chromium and molybdenum contents are ~7% and ~1.5% higher than they are at the centres of the cells, where the nickel content is ~4% higher than at the intercellular regions.

STEM microanalysis was carried out at the centres of the cells that were produced at a range of traverse velocities between 15 and 250mms^{-1} . The chromium, nickel and molybdenum contents of these regions are given in Table 3.3.

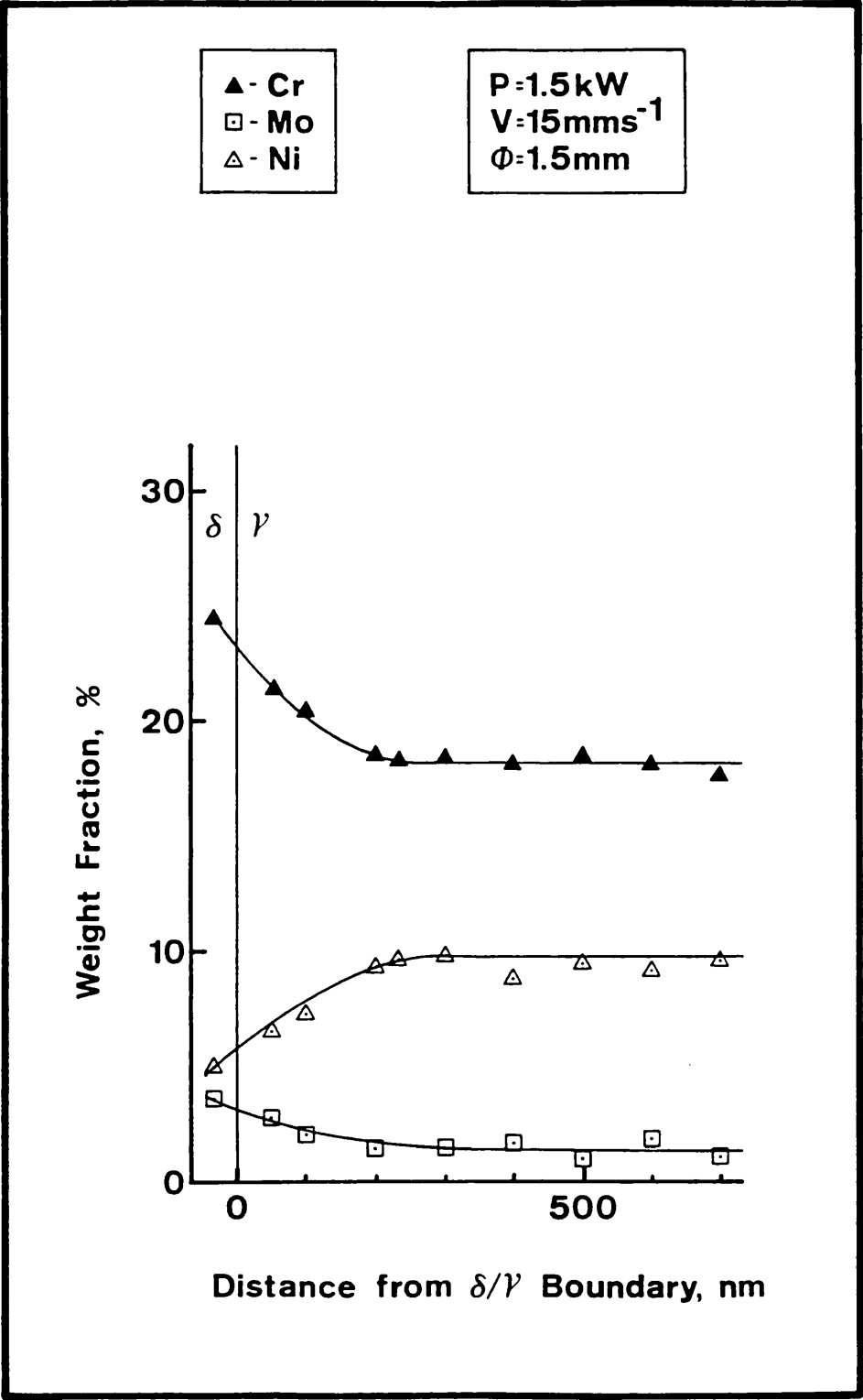
Table 3.3

The Compositions of the Centres of Solidification Cells Produced over a Range of Traverse Velocities

		Traverse Velocity mms^{-1}			
		15	30	60	250
Element, weight %	Cr	18.5	20	16.5	17.5
	Ni	10	8	12	11
	Mo	1.5	1.5	2	2

Figure 3.5

Compositional Profile through a Solidification Cell
in 316 Steel (Cell Diameter $\sim 1.5\mu\text{m}$)



No clear trend shows for any of the elements considered.

Photograph 3.12, the photocomposite shows two overlapping tracks. The cellular solidification structure with intercellular dislocation clusters shows in the later of the two tracks to be melted, to the right of Photograph 3.12 and in Photograph 3.13. A planar solidified zone shows along the centre of Photograph 3.12. To the left of Photograph 3.12 can be seen the subgrains that are formed in the back-heated region of the earlier of the two tracks.

Inclusions which show as black spots are evident in Photographs 3.11, 3.12 and 3.13. STEM microanalysis of one such inclusion showed it to be rich in manganese and silicon.

Macrocracking (crack size $\sim 500\mu\text{m}$) was not found in the steel after laser surface melting at traverse speeds of 60mms^{-1} and less, although occasional microfissures (surface length $\sim 50\mu\text{m}$ or less) did show at the lower speeds.

3.4 DISCUSSION

3.4.1 420 Steel

The cellular solidification structure that shows in the 420 steel indicates an intermediate value of the ratio, G/R at the solidification front.

The Vickers hardness of the laser melted tracks (510#) is the same as that of bulk specimen that has been hardened by conventional quenching after a soak at the solution treatment temperature (960°C). This hardness would be expected to substantially

enhance the erosion and wear resistance of the steel.

During the covering of a surface by a series of overlapping melt tracks there will be heating of tracks by succeeding neighbouring tracks and resultant tempering; however this does not show in the microhardness measurements where the hardness next to succeeding melt tracks does not differ from that elsewhere in the laser melted material. This uniform hardness can be partly understood in terms of the tempering behaviour of the steel, which does not soften in the early stages of tempering at temperatures below $\sim 500^{\circ}\text{C}$. However, the absence of a narrow softened zone in the regions in tracks that lie next to succeeding melt tracks does indicate very short thermal cycles as softening would be expected at temperatures above about 500°C .

The trend towards higher volume fractions of retained austenite at the higher treatment speeds, with their higher cooling rates (Kear et al 1977) follows behaviour that has been observed by other workers (eg Bee and Wood 1982, Donachie and Ansell 1975 and Ruhl and Cohen 1975). The increased volume fraction of retained austenite at high temperatures may be due to the maintenance of higher volume fractions of carbon in solution before the martensite transformation takes place (Speich and Warlimont 1968). The possibility of fine grain sizes produced by rapid cooling increasing the yield stress of the material and retarding the martensitic transformation does not apply to laser surface melting where crystal growth occurs epitaxially from the substrate and the grain size compares with that of the substrate. However it is possible that the cellular structure of the austenite may play a similar role to fine grains in retarding the martensitic transformation, although the low

angle intercell boundaries^d_L will exert a smaller influence.

STEM analysis was attempted in cells of 420 steel. However when a chromium content of ~20% was indicated it was clear that the chromium levels in the metal were being overestimated. This high chromium level may be attributed to chromium enrichment of the oxide film during electrothinning. Perhaps the most straightforward way to overcome this difficulty would be to prepare some foils by ion beam thinning.

The absence of cracking in the treated layers raises the possibility of the treated layers having useful fatigue and corrosion properties.

3.4.2 316 Steel

The transition from a planar to a cellular solidification structure that shows around the edges of the solidification tracks and the transition to a branched dendritic structure at the top centre of the low speed tracks can be understood in terms of the variation of the ratio, G/R with depth. Heat transfer calculations indicate that this ratio reaches a maximum at the bottom and sides of the solidification tracks and decreases moving through the tracks to reach its highest value at the centre of the track tops (Kear et al 1977). These solidification conditions are reflected in the range of structures that show through the melt profiles.

The orientation of the solidification cells, approximately normal to the segregation banding that marks the back of the, now solidified, melt pool indicates growth towards the direction of maximum

temperature gradient, although initially growth occurs epitaxially from the substrate.

The segregation of chromium and nickel can be explained by reference to the iron-chromium-nickel ternary equilibrium phase diagram, Figure 3.2. This suggests that nickel rich cell centres and chromium rich intercellular regions will be formed. The molybdenum appears to follow the chromium to the intercellular regions. A similar solidification pattern may be anticipated in the planar solidified zone, with regions near the unmelted substrate being nickel rich and chromium depleted and vice versa.

The suppression of δ -ferrite which occurs at high treatment speeds with their associated high cooling rates may be due to undercooling, see Figure 3.2. High undercoolings have been reported for rapidly cooled austenitic alloys eg Kattamis and Flemings 1966.

The cracking behaviour of the steel is in keeping with the observation that even very small volume fractions of δ -ferrite can prevent cracking (Borland and Younger 1960) in that only microfissures showed at the range of traverse speeds where δ -ferrite was produced. The cracking behaviour of the material is critically dependant on the effect of minor alloying elements which may affect the cracking process by suppressing δ -ferrite formation as is the case with nitrogen or by lowering the solidification temperature of boundaries as is the case with phosphorus and sulphur (Matsuda et al 1984).

The cellular dislocation tangles which show in the laser surface melted steel may enhance the materials stress corrosion cracking and hydrogen embrittlement resistance by offering harmless sites for hydrogen or by helping to prevent the formation of planar slip arrays (Hanninen 1979). However the high tensile residual stresses that are produced by laser surface melting might well offset any possible benefits, see Chapter 4.

The subgrains that are formed in the part of a track next to the succeeding track indicate a thermal relaxation process.

The inclusions that are observed are manganese and silicon rich, similarly to those observed in other weld microstructures (eg David and Vitek 1981).

3.5 CONCLUSIONS

1. The laser melt tracks in 420 steel develop the full hardness that is produced by quenching after a conventional solution treatment (960°C for 1 hour).
2. There is a trend towards increased retained austenite in the 420 steel at increased traverse velocities, with their increased cooling rates.
3. Planar, cellular and branched dendritic microstructures show in the predominantly austenitic laser melt tracks of 316 steel. The particular solidification microstructure is determined by the ratio, G/R .
4. The formation of intercellular δ -ferrite in laser surface melted 316 steel may be suppressed by melting at traverse speeds above $\sim 60\text{mms}^{-1}$, to produce high cooling rates.

5. Cracking becomes a problem in laser surface melted 316 steel where δ -ferrite is absent.
6. 316 steel shows chromium and molybdenum depletion and nickel enrichment at the centres of the solidification cells.

4.1 INTRODUCTION

4.1.1 Stresses in Laser Melted Surfaces

The thermal stresses associated with fusion welding can give rise to stresses of the order of the yield stresses of metals. Laser surface melting might be expected to give rise to similar stresses because the temperature gradients that lead to residual stresses in laser surface melting are higher than those associated with conventional welding processes, developing residual stresses as high as the yield stress. Such stresses will not only affect the mechanical properties such as the fatigue, creep and brittle fracture behaviour but also the shape and corrosion behaviour (Chastell et al 1979, Dwight 1981, Harrison and Leggatt 1981, Allen 1981 and Harrison 1981).

Gnanamuthu and his co-workers (1979) have used the x-ray diffraction method to measure the residual stresses in laser transformation hardened Fe-0.45%C plain carbon steel in the direction parallel to the laser hardened tracks. Measurements were taken down to 1.25mm below the surface (see Figure 4.1). There was a compressive stress through the region down to ~800 μ m below the surface. This stress reached a compressive maximum of 460 MPa, 250 μ m below the surface. The stress was tensile for depths of greater than ~800 μ m.

James, Gnanamuthu and Moores (1984) have measured the stresses on laser surface melted Fe-0.18%C plain carbon steel and Fe-0.4%C-0.25%Mo alloy steel. The x-ray beam was collimated to an incident beam

Figure 4.1
Residual Stress against Depth in
Transformation Hardened Fe-0.45%C Steel

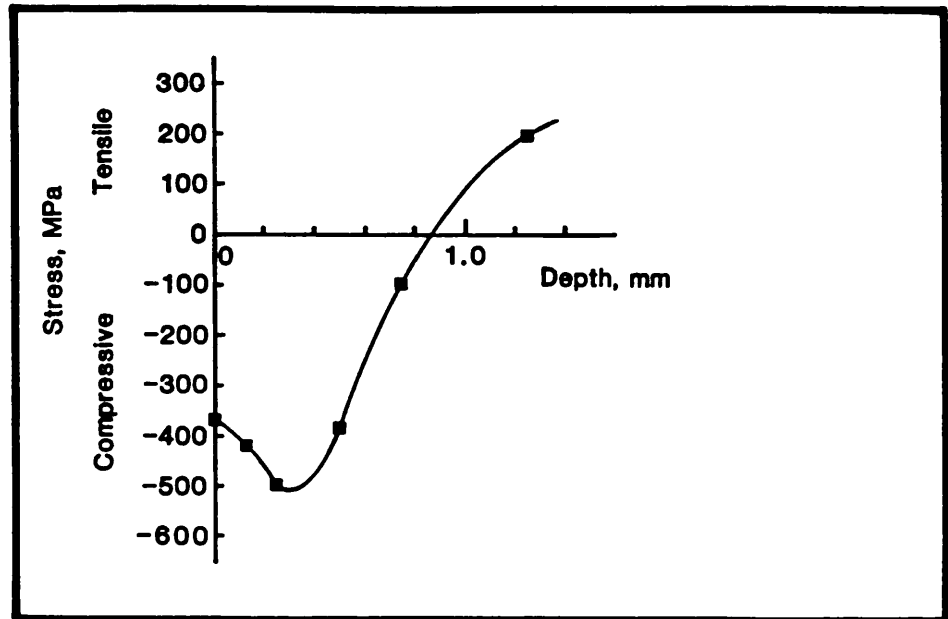
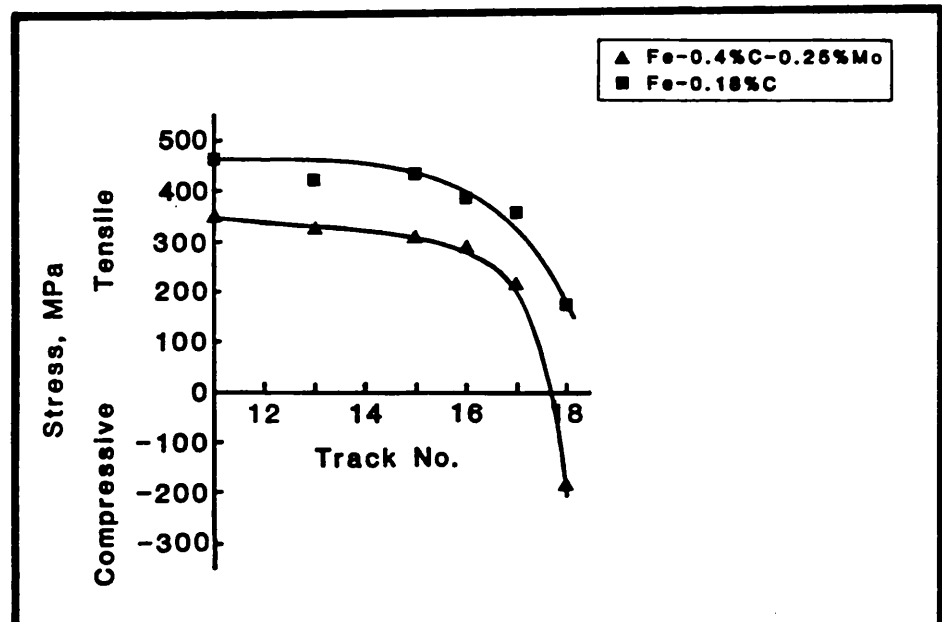


Figure 4.2
Residual Stress in a Series of
Overlapping Melt Tracks in Two Steels



diameter of ~0.75mm. This enabled the surface stresses in a series of individual tracks to be measured (see Figure 4.2). In both steels the stress was highest in the earlier tracks to be melted reaching its full tensile stress about five tracks behind the final track. The stress rose to 360 MPa, tensile in the alloy steel and 460 MPa, tensile in the low carbon steel.

The strain gauge/relaxation method has been used to measure the stress on the faces opposite laser treated surfaces on a series of grey cast iron plate samples (Langella and Tetti 1983). The samples were between 10 and 30mm thick and the measured stresses were between 28 and 52 MPa tensile. This approach gives a direct measure of the strain for a given cross-section and allows calculation of the bending moment, which is given by:

$$M = \int_A y \sigma_x dA$$

where A = area,

y = distance from the centroid, σ_x = stress at y in the x direction

This is useful when the effects of the bending moment, such as the deflection it gives rise to are of interest, but it does not contribute directly to an understanding of stress in the laser treated layer.

4.1.2 Sources of Residual Stress

Residual stress has been considered in the welding literature and the mechanisms that have been

identified as giving rise to residual stress have been identified as:-

4.1.2.1 Shrinkage

The laser surface melted regions are subjected to higher temperatures than the surrounding material and will therefore contract further on cooling. When this relative contraction is constrained by surrounding material residual stresses will be generated. Neglecting phase changes on cooling shrinkage will give rise to tensile stresses in steels that are equal to the yield stress (Parlane 1981 and Easterling 1983). These stresses can be reduced by preheating. This will prevent shrinkage stresses being developed between the preheat temperature and room temperature.

4.1.2.2 Plastic Deformation at High Temperature

When temperature gradients give rise to thermal stresses and plastic deformation at high temperatures internal stresses will be developed when the temperature becomes uniform after cooling (Macherauch and Wohlfahrt 1978). This is the mechanism that gives rise to stresses in metallic components that have been quenched after solution treatment. These stresses will be maximised in a material with a low flow stress in the temperature range in which the maximum thermal stress through the cross section occurs. They will also be maximised in treatment/material combinations giving rise to high thermal gradients. Laser

surface treatment gives rise to extremely high thermal gradients (Mazumder and Steen 1979 and Kear et al 1979).

4.1.2.3 Phase Transformation

The phase changes that metals undergo when they are cooled can result in volume changes. If these volume changes occur locally and are constrained by surrounding material residual stresses may develop. It is also possible for plastic flow to occur at stresses which are much lower than the yield stress during a phase change. This is termed transformation plasticity. For example transformation plasticity may occur during the phase transformation from austenite to ferrite in 2Cr Mo steel and 9Cr Mo steel. If the volume change associated with the phase change is assumed to off-load elastically, compressive stresses of 270 MPa and 390 MPa would be produced. However, the stresses that are measured experimentally are 30 MPa and 62 MPa (Jones and Alberly 1978).

Transformation plasticity is thought to result from the superposition of the low external stress field on the high local stress field associated with the transformation (Jong and Rathenau 1961 and Greenwood and Johnson 1965). Greenwood and Johnson have pointed out that for a rigid ideal plastic material there is a linear relationship between the strain during a transformation cycle, ϵ and the external stress, σ :

$$\frac{\delta \epsilon}{\delta \sigma} = \frac{5}{6} \frac{\Delta V}{V} \frac{1}{\sigma_y}$$

where $\Delta V/V$ is the relative volume difference between the two phases and σ_y is the yield stress of the weaker phase.

4.1.3 Scope of the Investigation

The experimental work studies residual stresses in 316 steel and 420 steel by x-ray diffractometry. The tests were designed to give an understanding of the mechanical and electro-chemical behaviour of laser melted surfaces, to allow optimisation of the laser melting process and to develop an understanding of the mechanisms giving rise to residual stresses in laser melted surfaces.

To these ends subsurface stresses were measured for both the steels. The process parameters of advance between tracks, traverse speed, incident beam diameter and beam power were varied and the residual stresses were measured over the various process conditions. As the tensile residual stresses were high the possibility of thermal stress relief was evaluated by a series of isochronal and a series of isothermal stress relieving heat treatments and subsequent residual stress measurements.

4.2 EXPERIMENTAL

4.2.1 Stress Measurements

4.2.1.1 The x-ray Diffraction Method

The residual stresses were measured by x-ray diffractometry. This technique is suitable

for any crystalline material where it is possible to measure a lattice spacing at a range of orientations to the surface of the specimen. It is surface selective, measuring the stress through a depth of $\sim 10\mu\text{m}$ for the combination of a chromium target and a steel specimen. This is an important advantage where stresses are to be measured in laser melted surface layers which are typically $\sim 250\mu\text{m}$ deep with residual stresses extending down to perhaps $500\mu\text{m}$. It is possible to measure stresses over small areas down to those limited by either the grain size or the excessive time necessary to acquire statistically acceptable data from a small area.

The x-ray technique measures stress indirectly by measuring the shift in the position of a diffracted peak, $\Delta\theta$ for crystal planes oriented at various angles to the surface of a specimen (Cullity 1956).

If an isotropic material is strained elastically then:

$$\frac{\Delta\theta}{(\sin\phi)^2} = \frac{\sigma (1 + \nu) \tan \theta}{E}$$

where σ = Stress

ν = Poisson's ratio

E = Young's modulus

θ = Bragg diffraction angle

ϕ = Angle between the normal to the specimen surface and the bisector of the incident and the diffracted beams.

This equation is derived in Appendix A.4.1. It follows that a plot of θ against $(\sin\phi)^2$

will follow a straight line with a slope of $\sigma (1 + \nu) \tan \theta / E$.

The accuracy of the technique is optimised if $\tan \theta$ is maximised. This is achieved by choosing a combination of x-ray wavelength and diffracting planes that give a value of θ close to $\pi/2$ rad (where $\tan \theta \rightarrow \infty$). On this basis monochromated chromium $K\alpha$ radiation was selected and the diffractometry was based on the (200) peaks of the austenitic steel and the (211) peaks of the martensitic steel. This gives diffraction angles of $\pi/1.73$ rad for the martensitic steel and $\pi/1.42$ rad for the austenitic steel.

4.2.1.2 Operation

The diffractometer was controlled by a computer based system (Lonsdale, Doig and Flewitt 1981). This system also logged and processed the test data.

Prior to a stress measurement the goniometer was positioned so that the specimen was at the centre of the circle. The distance from the centre of the goniometer circle to the specimen's surface was measured with a dial gauge and set to less than $50\mu\text{m}$ by adjustment screws.

The x-ray beam was mono-chromated, collimated by a Soller and passed through an aperture. Aperture sizes were selected so that when the stress was measured on specimens that had been covered with a series of overlapping tracks, the x-ray beam incident on the specimen surface was $\sim 10\text{mm} \times 3\text{mm}$. This allows a high x-ray count

rate and accurate stress measurements. When measurements were taken over small areas such as single melt tracks, the incident beam was collimated down to $\sim 500\mu\text{m}$ diameter.

In evaluating a stress level it is necessary to correct the peak positions for polarisation and absorption effects. The corrections were applied automatically by the computer based system (Doig, Lonsdale and Flewitt 1980).

Each residual stress measurement was evaluated from at least ten measurements of lattice spacing spread over a range of orientations to the surface of the specimen. The time taken for each stress measurement was typically ~ 20 minutes at the end of which the computer output a plot of $(\sin\phi)^2$ against $\Delta\theta$. A straight line was fitted to the data and the stress level was printed out.

4.2.1.3 Specimens

The specimens were parallel flat faced slabs of metal 6.35mm thick. The surfaces to be treated were grit cleaned prior to laser surface melting. One face of each slab was covered with overlapping tracks, except for the single track specimens where the tracks were spaced at least 2.5mm apart. In order to minimize oxidation, laser surface melting was carried out under a multiple-nozzle head as described in Chapter 1.

Where the effects of process conditions on residual stress were studied the processing parameters were varied, one at a time. The

conditions from which one of the processing parameters was varied are:-

Beam Power,	$P = 1.5\text{kW}$
Incident Beam Diameter,	$\phi = 1.5\text{mm}$
Traverse Speed,	$V = 60\text{mms}^{-1}$
Advance between Tracks,	$A = 400\mu\text{m}$

The conditions were chosen so that each of the parameters could be varied while still producing shallow conduction limited melt tracks. These conditions were used to produce the subsurface stress specimens. The stress relieving heat treatment specimens were produced at the same power and incident beam diameter but at a treatment speed of 100 mms^{-1} and an inter-track advance of $300\mu\text{m}$.

4.2.1.4 Effect of Surface Topography

The influence of surface profile on the measurement of stress by the x-ray diffraction method has been considered theoretically for the case of a sinusoidal surface profile (Doig and Flewitt 1981). This is a reasonable approximation to the surface profile across a series of laser surfaces melted tracks produced at similar conditions to those used in this work (see Chapter 2). This analysis characterises a surface of wavelength, λ and amplitude, a in terms of the ratio a/λ . For the more severe of the two cases that were evaluated in Chapter 2 ($\lambda = 500\mu\text{m}$ and $a = 5.0\pi/2$) the measured stress will be underestimated by $\sim 2.5\%$ for the 420 steel and by less for the 316 steel.

4.2.2 Effect of the Oxide Layer

It is known that in spite of efforts to shroud the specimens' surfaces during laser processing, some surface oxide is formed (Henry 1983). The possibility of this oxide layer introducing surface stresses was evaluated for laser surface melted samples. Residual stresses were measured parallel to and perpendicular to the direction of overlapping laser melt tracks both before and after the oxide had been stripped off. A solution of 6M hydrochloric acid inhibited with 2g/l hexamethyl tetramine was used to remove the oxide.

4.2.3 Electrolytic Thinning

Where subsurface stresses were to be measured material was removed from the surface of the specimens by electrolytic polishing. This method of thinning was chosen because it does not introduce its own residual stresses. Thinning was carried out in a solution of 15% perchloric acid and 10% glycerol in ethanol. This mixture is potentially explosive and must be kept below 30°C. The temperature of the solution was monitored during thinning and the current was turned off and the electrolyte was allowed to cool if the temperature approached 30°C. The beaker of thinning solution was kept in a dish of cold water, which acted as a heat sink. Thinning was at 18V for the 420 steel and 13V for the 316 steel. The specimens were covered with insulating lacquer apart from the surface to be polished; the exposed areas of the samples were 146 (mm)² for the 420 steel and 121 (mm)² for the 316 steel. The weight loss was ~480µm for each coulomb that passed through the specimen. A planar electrode was used as the cathode to give even polishing of the specimen, the anode. The depth of material removed was measured indirectly

by weighing the specimens to the nearest 100 μ g after drying with a hot air blower. The depth removed was calculated by dividing the weight loss by the density and the surface areas of the specimens. The densities are 7730 and 7930 Kg m^{-3} for the 420 and 316 steels respectively. Material was removed in increments of from 10 μ m to 60 μ m.

4.2.4 Stress Relieving Heat Treatments

Both the 420 and the 316 steel specimens were thermally stress relieved. Stress relief at less than $\sim 500^{\circ}\text{C}$ was carried out in air with the specimens wrapped in metal foil to minimise oxidation. Higher temperature stress relief was carried out in a vacuum furnace. After stress relief the specimens were quenched in oil.

In the 420 steel a series of isochronal stress relieving heat treatments were carried out for 5ks and isothermal tests were carried out at 750°C , 500°C , 450°C and 400°C for times of up to 20ks. In the 316 steel a series of isochronal heat treatments was carried out for 5ks and isothermal tests were carried out at 850°C and 750°C for times of up to 100ks.

4.3 RESULTS

4.3.1 The Effect of the Oxide Film on Residual Stress

Stresses in 316 and 420 steel measured parallel to and perpendicular to laser melted tracks before and after oxide stripping are given in Table 4.1. It would appear that the oxide film arising from laser surface melting does not significantly affect the residual stress.

The laser treatment for all the samples was:-

Power = 1.5kW
 Beam Diameter = 1.5mm
 Spacing between tracks = 300 μ m
 Treatment speed = 100mms⁻¹

Table 4.1

Steel Code	Oxide Layer on or off	Stress			
		Parallel to traces		At right angles to traces	
		σ MPa	Det Coeff r^2	σ MPa	Det Coeff r^2
316	On	557.5	.91	694	.91
	Off	580	.91	676	.88
420	On	269	.95	289	.96
	Off	289	.95	271	.98

4.3.2 Subsurface Stress

- 420 Steel

The stresses that were measured on the 420 steel and corrected for the effect of removing overlying stressed material during thinning are shown in Figure 4.3. The treatment conditions used to produce the subsurface stress specimen will produce a melt zone $\sim 120\mu$ m deep and a heat affected zone, as shown by a hardness traverse, down to $\sim 200\mu$ m subsurface (see Chapter 1).

Figure 4.3
Residual Stress against Depth in
420 Steel

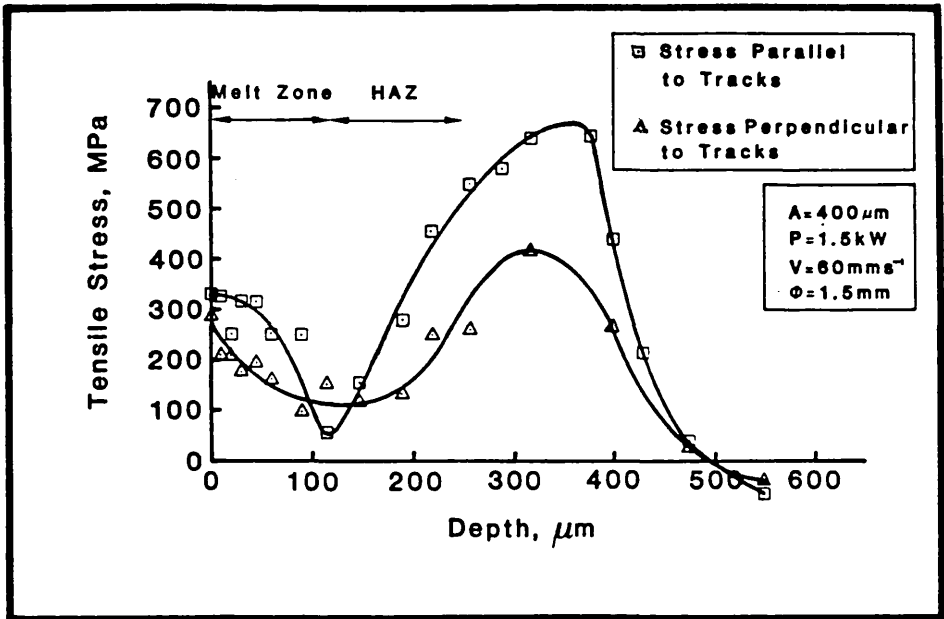
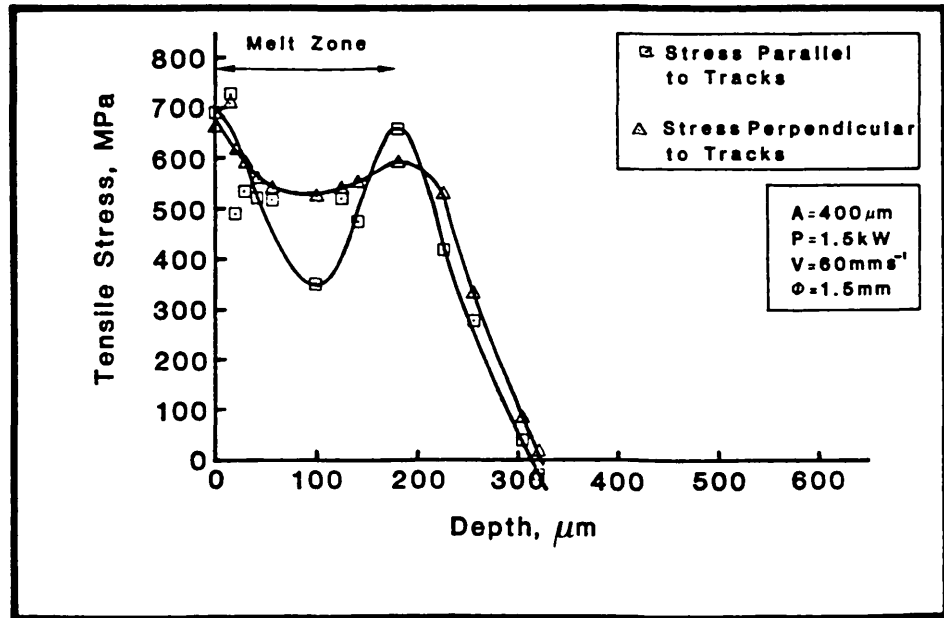


Figure 4.4
Residual Stress against Depth in
316 Steel



The residual stress decreases with depth through the melt zone reaching a minimum at the interface between the heat affected zone and the melted zone. Moving downwards through the heat affected zone the stress increases rapidly reaching a maximum at a depth of $\sim 350\mu\text{m}$. This is below the heat affected zone. Beyond this maximum the stress decreases to become $\sim 50\text{MPa}$ compressive in the matrix.

The stresses perpendicular to the tracks' direction are lower than those parallel to the tracks' direction. The stresses in both directions show the same general pattern of change with depth.

- 316 Steel

The stresses that were measured on the 316 steel and corrected for the effect of removing overlying stressed material are shown in Figure 4.4. The treatment conditions that were used to produce the subsurface stress specimen will produce a melt zone $\sim 180\mu\text{m}$ deep (see Chapter 1).

Both the stresses parallel to the melt tracks and the stresses perpendicular to the melt tracks reach a maximum immediately below the surface and then decrease to a minimum value in the melted zone. The stresses then increase to a maximum at a depth of $180\mu\text{m}$ corresponding to the bottom of the melt zone. After this the stresses decrease to zero in the matrix.

4.3.3 The Effect of Processing Parameters on Residual Stress

4.3.3.1 Advance between Tracks

- 420 Steel - Figure 4.5

The stresses that were measured at the surfaces of single tracks are shown to the right of Figure 4.5 for comparison.

Figure 4.5
Residual Stress against Advance between
Tracks for 420 Steel

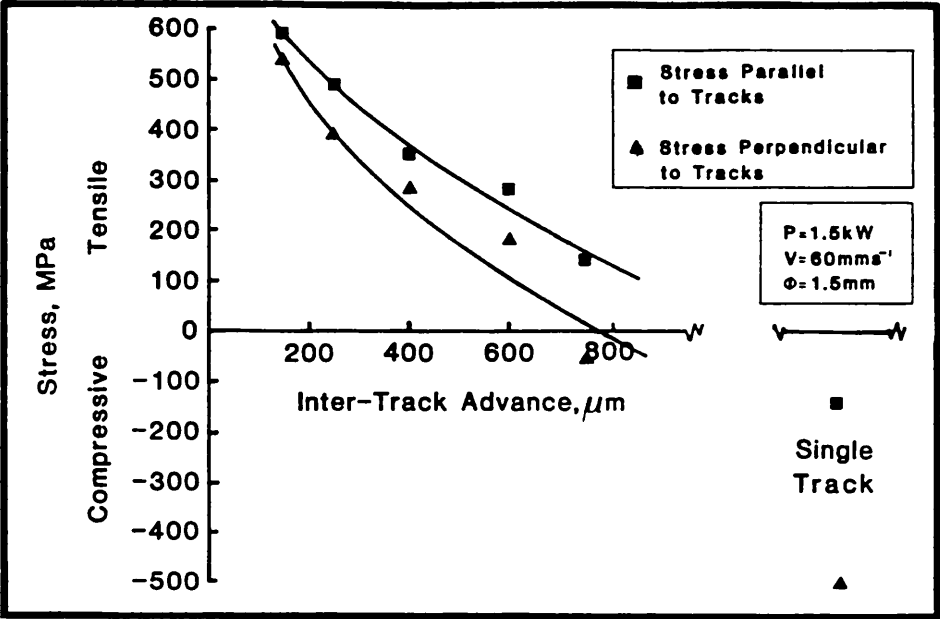
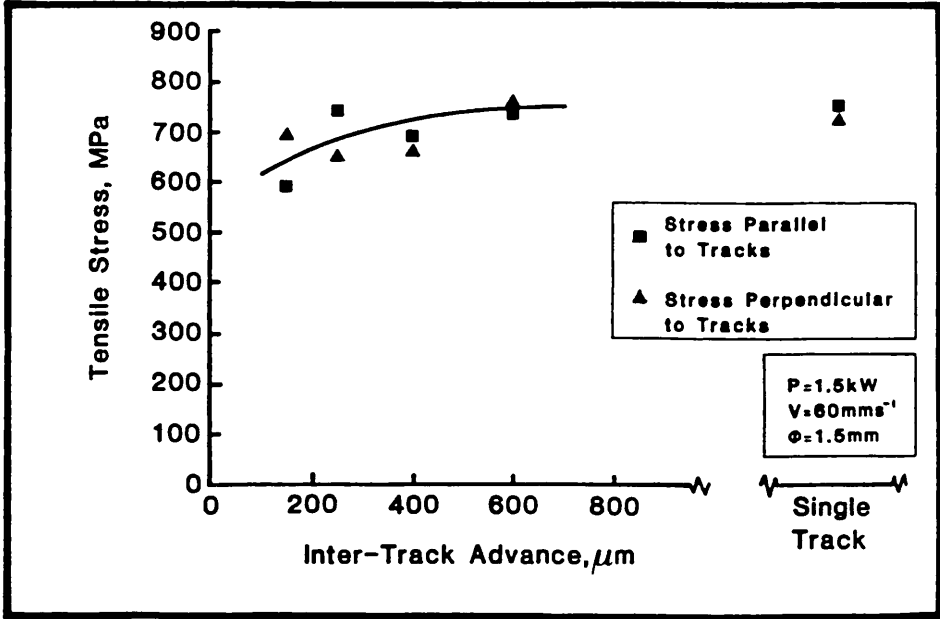


Figure 4.6
Residual Stress against Advance between
Tracks for 316 Steel



The width of the individual tracks was $800\mu\text{m}$ (see Chapter 1). The advances between tracks were varied from $150\mu\text{m}$ to $750\mu\text{m}$. The residual stresses are sensitive to changes in inter-track advance, decreasing as the advance increases throughout the range of advances. The stress parallel to the tracks reached 590MPa tensile at the smallest advance and went down to 140MPa tensile at the greatest advance, $750\mu\text{m}$. The stress perpendicular to the tracks showed similar behaviour but was less tensile throughout the range of advances falling from 530MPa at an advance of $150\mu\text{m}$ to -50MPa at an advance of $750\mu\text{m}$.

The stresses measured on a single track show even less tensile values than those measured at the maximum advance of $750\mu\text{m}$, being 140MPa compressive parallel to the track and 500MPa compressive perpendicular to the track.

- 316 Steel - Figure 4.6

The stresses that were measured on single tracks are shown to the right of Figure 4.6 for comparison.

The width of the individual tracks was $\sim 800\mu\text{m}$ (As it was for the 420 steel - See Chapter 1).

There is not a consistent difference between the stresses measured parallel to the tracks and those measured perpendicular to the tracks. The effect of overlap is less marked than it is in the 420 steel. However, there is a trend towards higher residual stresses as

the advance between tracks increases. The residual stress increases by ~100MPa over the range from 150 μ m to 600 μ m advance. This maximum value is also shown by the single track.

4.3.3.2 Treatment Speed

- 420 Steel - Figure 4.7

The residual stresses increase with treatment speed over the range of speeds from 30mms⁻¹. There is an increase of ~250MPa over the full range of speeds to a highest value of ~500MPa at 100mms⁻¹. The stresses parallel to the tracks are 25 to 50MPa higher than those perpendicular to the tracks.

- 316 Steel - Figure 4.8

The residual stresses measured perpendicular to the tracks show a slight increase (~100Mpa) with increasing treatment speed. The residual stress measured parallel to the tracks reaches a maximum at 60mms⁻¹. There is no consistent difference between the stresses measured parallel to the tracks and those measured perpendicular to the tracks.

Overall there is no clear variation of stress with speed.

4.3.3.3 Incident Beam Diameter

- 420 Steel - Figure 4.9

The residual stresses decrease by ~150MPa as the diameter increases from 1.0mm to 2.2mm. The stresses parallel to the tracks are consistently higher than those perpendicular to the tracks.

Figure 4.7
Residual Stress against Treatment Speed
for 420 Steel

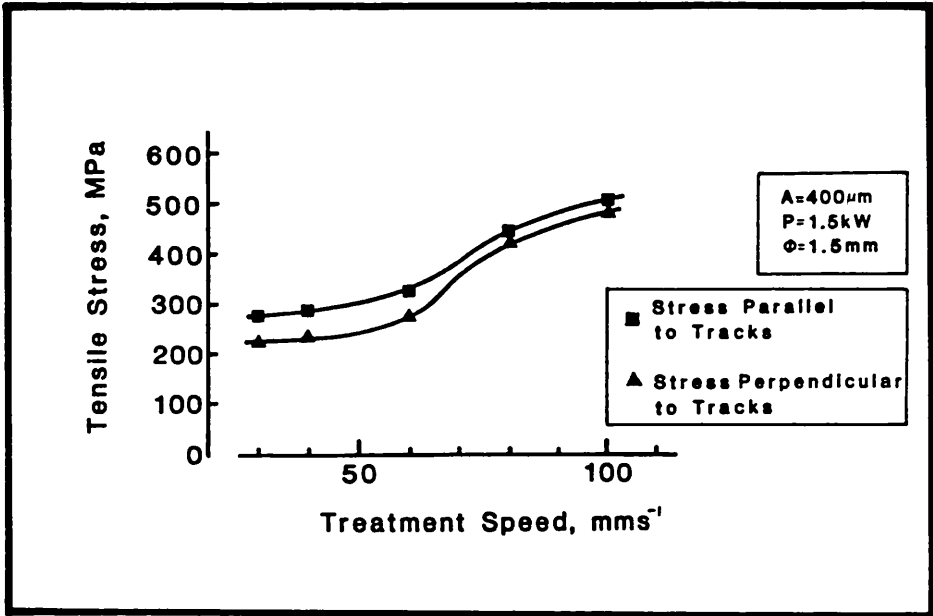


Figure 4.8
Residual Stress against Treatment Speed
for 316 Steel

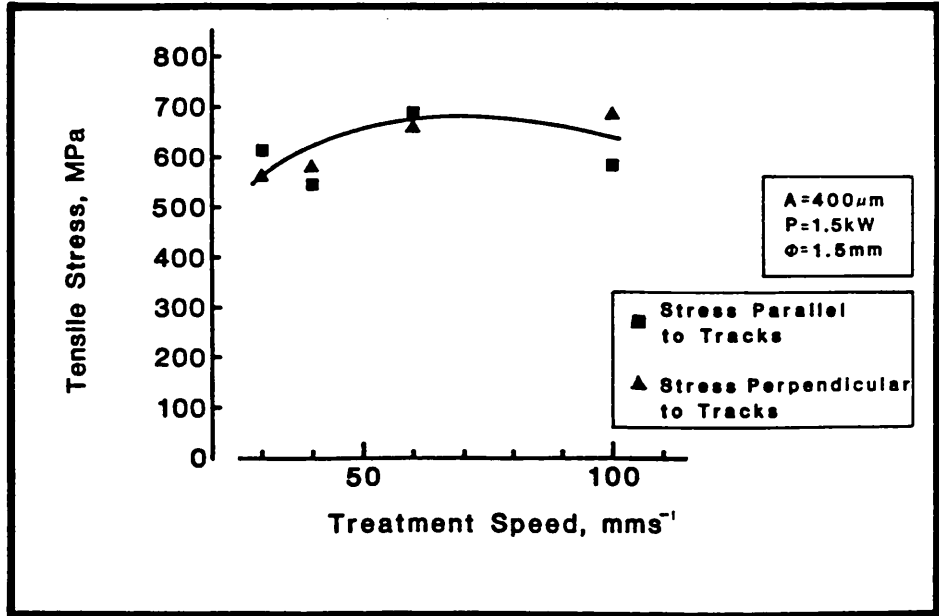


Figure 4.9
Residual Stress against Incident Beam Diameter for 420 Steel

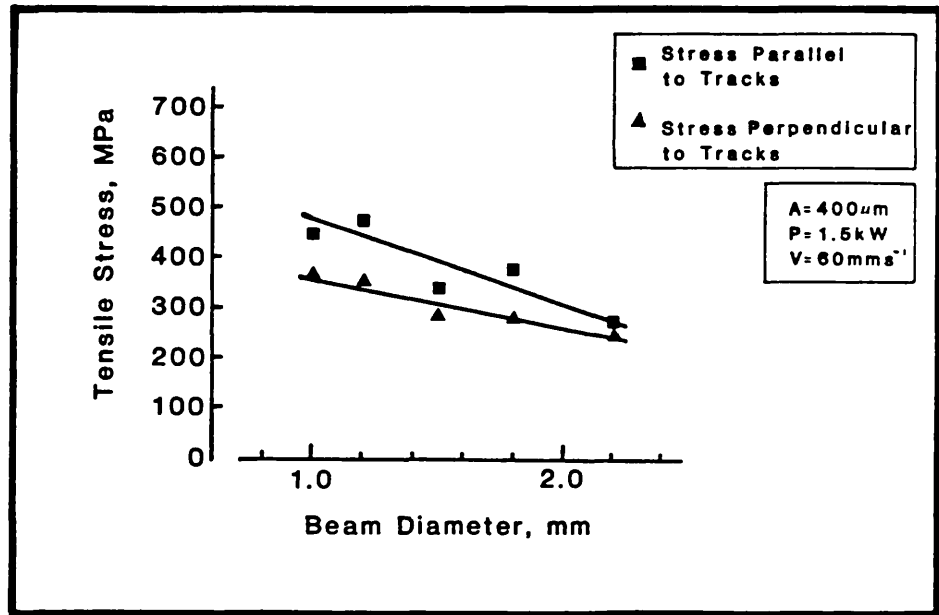
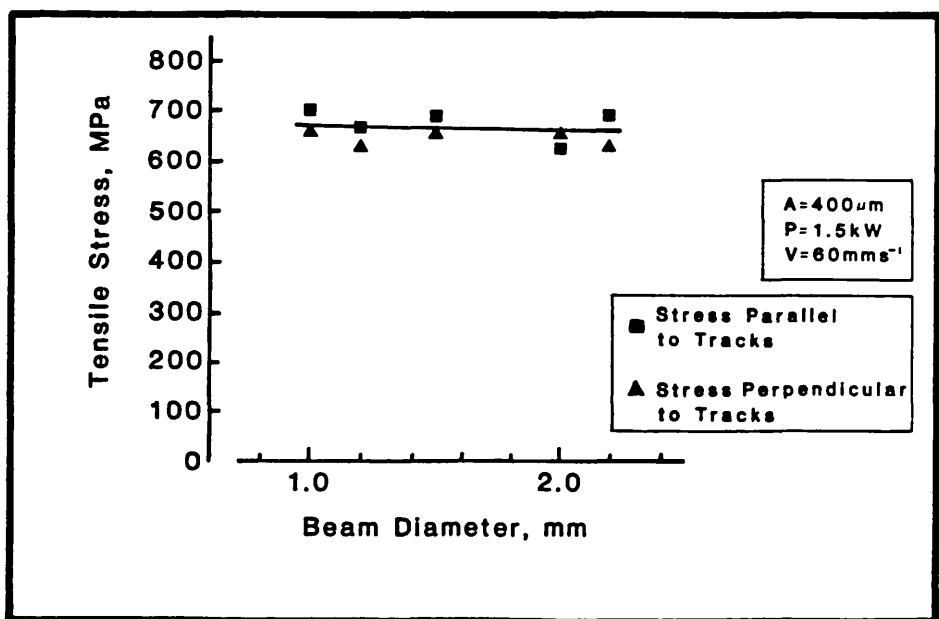


Figure 4.10
Residual Stress against Incident Beam Diameter for 316 Steel



- 316 Steel - Figure 4.10

The residual stress is independent of beam diameter between 1.0mm and 2.2mm. The stresses measured parallel to the tracks and those measured perpendicular to the tracks are not distinct.

4.3.3.4 Beam Power

- 420 Steel - Figure 4.11

The residual stress increases by ~100MPa over the range of beam power from 1.0kW to 2.0kW. The stresses parallel to the tracks are higher than those perpendicular to the tracks throughout the range of beam power.

- 316 Steel - Figure 4.12

The residual stress is independent of beam power in the range 1.0kW to 1.5kW but decreases with increasing power by 100MPa over the range from 1.5kW to 2.0kW. The stresses perpendicular to and parallel to the tracks do not show distinct behaviour.

4.3.4 Thermal Stress Relief

- 420 Steel

Figure 4.13 shows the variation of stress with time for 420 steel that had been laser surface melted and subsequently stress relieved at 340, 400, 450, 500 and 750°C.

Figure 4.11
Residual Stress against Beam Power for
420 Steel

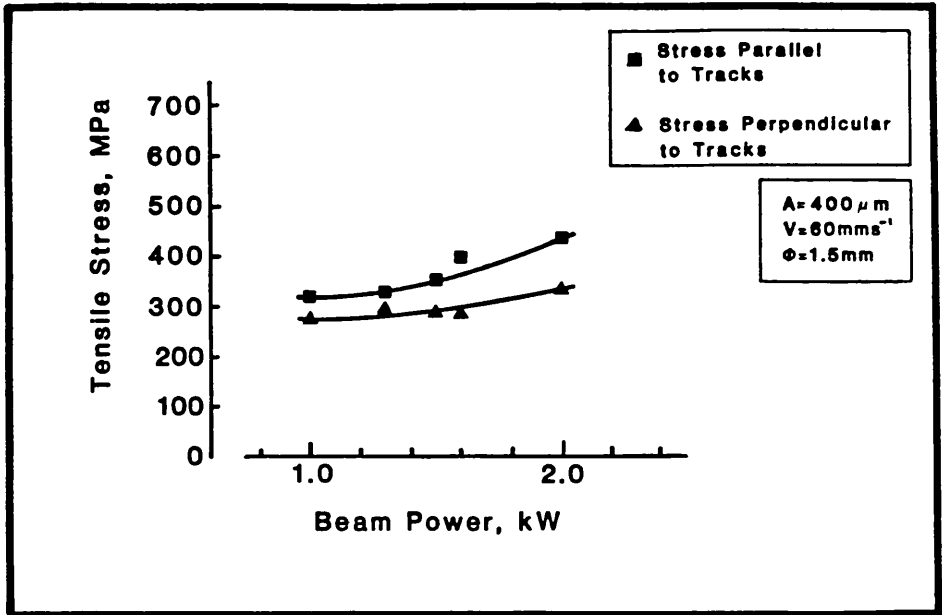


Figure 4.12
Residual Stress against Beam Power for
316 Steel

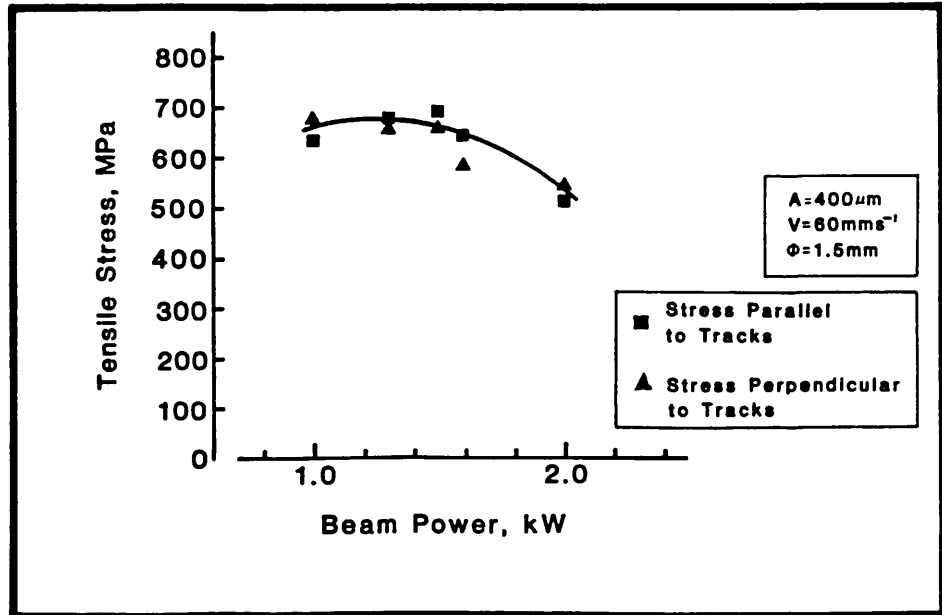


Figure 4.13

Thermal Stress Relief of 420 Steel

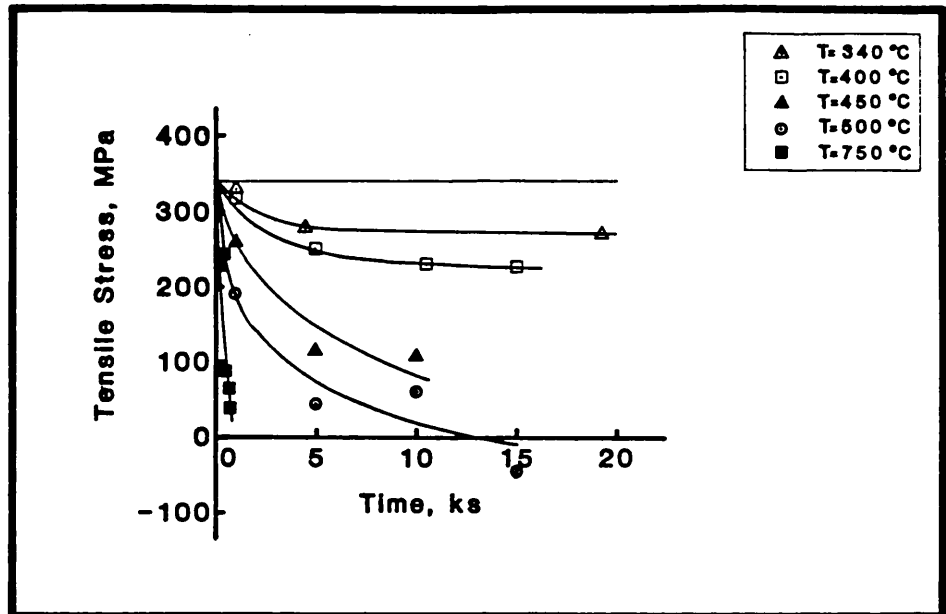


Figure 4.14

Residual Stress after 5ks in 420 Steel

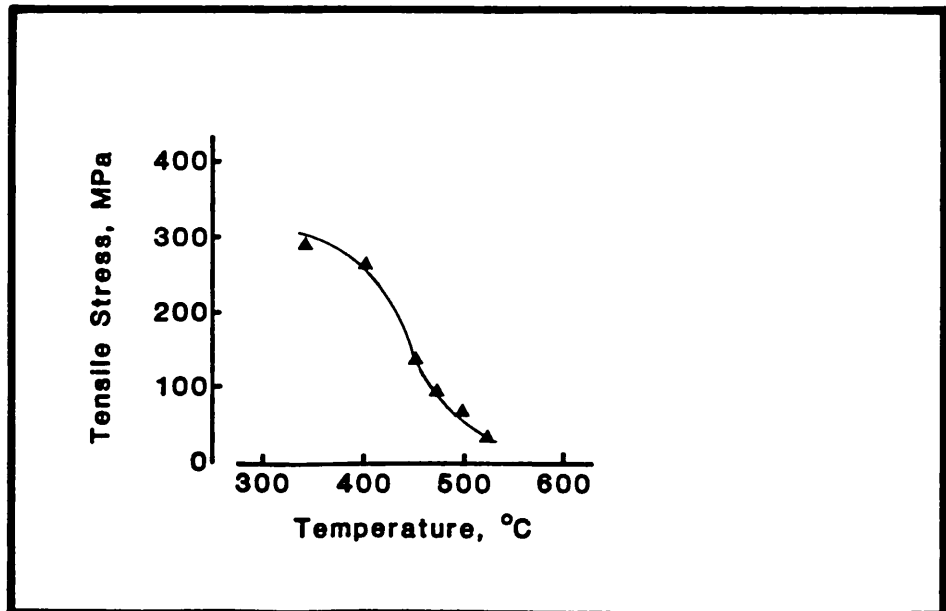


Figure 4.14 shows the variation of residual stress with temperature after 5ks.

Some stress relief takes place at temperatures as low as 340°C. Both the 340°C and the 400°C isotherms show stress relaxation at short heat treatment times after which the stress remains at a constant tensile level. At 500°C the residual stress is fully relieved after 15ks. More rapid stress relief is evident at 750°C.

- 316 Steel

Figure 4.15 shows the variation of stress with time for 316 steel that had been laser surface melted and subsequently stress relieved at 750°C and 850°C.

Figure 4.16 shows the variation of residual stress with temperature after 5ks.

There is negligible stress relief after 5ks at 340°C. At temperatures in the range from 550°C to 950°C there is appreciable stress relief. The degree of stress relief increases with increasing temperature until all but 30MPa has been relieved after 5ks at 950°C.

The two isothermal plots show rapid stress relief for the short heat treatment times after which the stress decreases more slowly. Full stress relief is not achieved at 850°C even after 100ks.

4.4 DISCUSSION

4.4.1 Subsurface Stress

The subsurface stresses are important not only because they determine the mechanical behaviour below the surface but also because they allow evaluation of the bending moment and distortion resulting from these

Figure 4.15

Thermal Stress Relief of 316 Steel

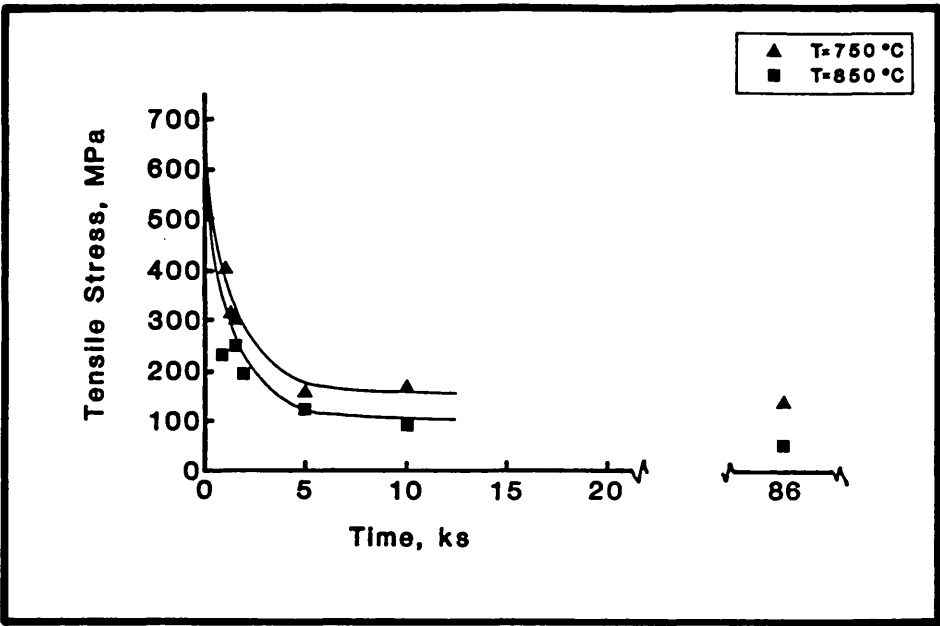
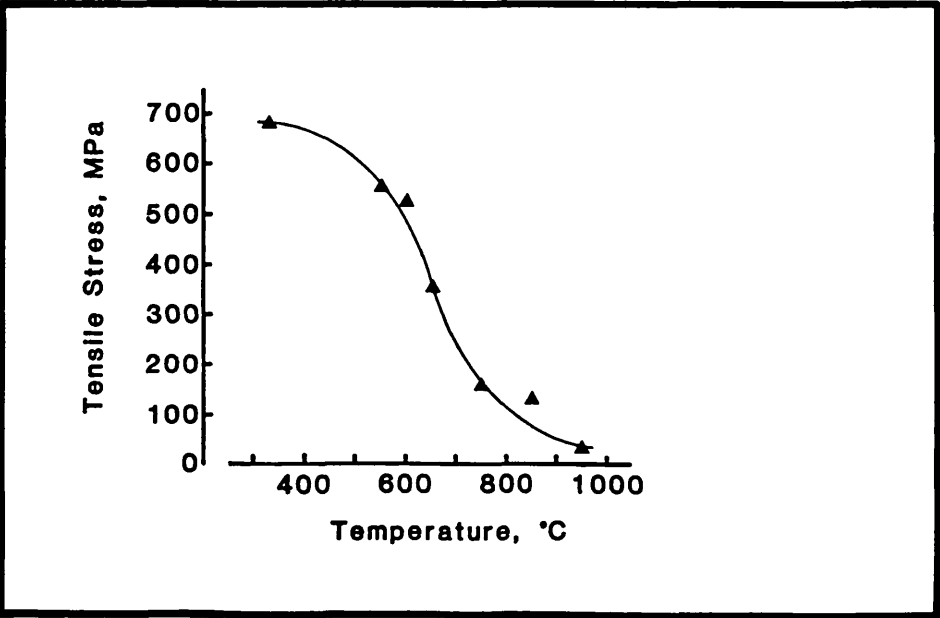


Figure 4.16

Residual Stress after 5ks in 316 Steel



stresses (Dwight 1981, Harrison and Leggatt 1981, Allen 1981 and Harrison 1981).

The region immediately below the surface is critically important in determining the mechanical and particularly the fatigue behaviour of the material, because it is not possible to detect cracks here either ultrasonically or by the techniques that reveal surface cracks. During the fatigue tests that were carried out in this investigation it was found that in the laser surface melted 420 steel all the cracks initiated in the region below the heat affected zone where the maximum residual stresses were developed (see Chapter 5)

4.4.1.1 Correction for the Effect of Overlying Stressed Material

For compliant specimens, such as the 6.35mm thick plates that were used in this work, the stresses^{that} are measured after removing some depth of material from the surface will not be the same as the stresses that exist at the same depth below the surface on the unthinned specimen. This is because as stressed material is removed from the surface of the specimen the remaining material relaxes and its internal stresses are redistributed. The stresses that were measured after electrolytic thinning have therefore been corrected for the effect of overlying material to give the stresses in the unthinned material.

The corrections for overlying material indicate that the measured stresses over estimate the subsurface residual stresses by as much as 60MPa. The method of correction is described in detail in Appendix A.4.2

Figures 4.3 and 4.4 indicate the corrected stresses.

4.4.1.2 The Stresses

- 420 Steel

The melted zone of the 420 steel subsurface stress samples extends $\sim 120\mu\text{m}$ below the surface. In this zone shrinkage stresses are offset by the expansion that takes place due to the martensitic phase transformation. Stresses are also developed by the plastic deformation that takes place due to thermal stresses.

The decrease of tensile residual stress with increasing depth which takes place through the melted zone can be interpreted in terms of the effects of the heating of a track by a successive track. As a track is made the preceding track, and possibly earlier tracks, will be heated by both the conduction of heat from the melted zone and at the surface, by the "wings" of the laser beam. It will be cooled predominantly by the conduction of heat into the matrix although significant heat losses will also occur by radiation from the surface (Mazumder and Steen 1979). This heating/cooling pattern holds the surface at relatively high temperatures during cooling, giving rise to plastic deformation in compression at high temperatures near the surface. This heating will also melt and austenitize parts of the preceding track. Martensite will form again on cooling, but the combined action of these effects is an increasingly tensile stress towards the surface of the track. As successive tracks

are made this stress pattern will apply to all but the last tracks of the treated region to be melted.

The increase in the tensile residual stress with increasing depth through the heat affected zone can be attributed to the effect of the thermal cycle on the volume fraction of material undergoing the martensite phase transformation. The material in the heat affected zone that lies towards the surface is heated to higher temperatures and subjected to longer thermal cycles than the underlying material. This results in more complete dissolution of carbides and a higher volume fraction of material undergoing the austenite to martensite phase transformation towards the surface, as is evidenced by the hardness profile (see Chapter 1). This will give rise to greater stress relief towards the top of the heat affected zone in both the single tracks and the multiple overlapping tracks. The highest tensile residual stress approaches the yield stress of the tempered material, 680MPa (En Steels Data Book 1969). It occurs parallel to the tracks in the region below the heat affected zone. Here there is plastic deformation in compression due to thermal stresses during the laser surface melting leaving tensile stresses after cooling, but no transformation to martensite to offset the tensile stresses.

The compressive stresses that occur at a depth of 500 μ m oppose the bending moment due to the tensile stress in the laser treated region. When the overlying region of tensile residual stress was removed by electrolytic polishing

the measured stresses in this region were close to zero (see Appendix A.4.2).

- 316 Steel

Stresses will be developed by constrained shrinkage during cooling and by plastic deformation at high temperatures as in the 420 steel. However, unlike the 420 steel there is no austenite to martensite phase transformation to offset tensile residual stresses. As well as differences in the residual stress pattern due to the absence of the austenite to martensite phase change differences will occur due to the different mechanical properties of the two materials. The 316 steel is more creep resistant than the 420 steel requiring temperatures $\sim 100^\circ\text{C}$ higher to produce a given strain rate at a given stress (Metals Handbook 1979). The thermal conductivity of the 316 steel, $19\text{Wm}^{-1}\text{K}^{-1}$, is lower than that of the 420 steel, $28\text{Wm}^{-1}\text{K}^{-1}$ (En Steels Data Book 1969).

The maximum residual stress of 725MPa which occurs close to the surface exceeds the yield stress measured on a tensile specimen, 660MPa, indicating the importance of specimen size in determining the yield stress as well as the differences between the structures of laser surface melted and the cold worked steel. The cold worked steel was chosen as a basis for comparison because of the high dislocation densities of both the cold worked and the laser surface melted steels.

The melted zone of the 316 steel extends about $180\mu\text{m}$ below the surface. The decrease in the stresses perpendicular to the tracks and

parallel to the tracks through the top 100 μm of the melted zone can, similarly to the corresponding variation in the 420 steel, be attributed to the plastic deformation that takes place when the region close to the surface is in compression at high temperatures.

The increase in the residual stress with increasing depth that occurs both parallel to and perpendicular to the tracks can not readily be explained in terms of the mechanisms giving rise to residual stress. The stresses that balance the bending moment that is set up by the tensile stresses at the surface will become more tensile with increasing depth. However, the stress gradient that is set up by the tensile stresses at the surface will only be 21 MPa/mm perpendicular to the tracks and 13 MPa/mm parallel to the tracks (see Appendix A.4.2). These stress gradients are more than an order of magnitude smaller than the observed stress gradients and the observed increase of stress with depth can not readily be explained in terms of the mechanisms giving rise to residual stresses.

The residual stress profile below the melted zone in the 316 steel is shallower than the corresponding profile in the 420 steel. This difference can be accounted for by the greater creep resistance of the 316 steel and its lower thermal conductivity. The higher creep resistance will reduce the deformation that takes place at a given temperature and the lower thermal conductivity will reduce the depth of the region that is heated into the temperature range where plastic deformation occurs.

4.4.1.3 Equivalent Surface Force

The residual stress against depth profiles also indicate the bending that laser surface melting will produce. For a cross-section that is thick relative to the 500 μ m deep layer of residual stress this can be treated in terms of the equivalent surface force per unit length perpendicular to the direction of the force. That is the force that at the surface, acting parallel to the surface produces the same bending of a thick section as the residual stress associated with laser surface treatment.

The equivalent surface force per unit length can be calculated from the total bending moment, M resulting from the treated material. This is given (divided by the moment of inertia, I) in Tables A.4.2 (1) to A.4.2 (4).

We have:-

$$I = \frac{bh^3}{12} \quad -(1)$$

For a rectangular cross-section of height, h and breadth, b :-

$$M = F.y \quad -(2)$$

From the definition of moment, where F is the force acting at distance y from the centroid.

$$y = \frac{h}{2} \quad -(3)$$

For a force acting at the surface of a rectangular cross-section.

$$\Rightarrow \frac{F}{b} = \frac{1}{6} \frac{h^2 M}{I} \quad \text{-(4) Combining (1), (2) + (3)}$$

Giving the equivalent force per unit length.

Substituting appropriate values into (4) gives the equivalent surface forces per unit length that are summarised in Table 4.2.

TABLE 4.2

Steel	Orientation Relative to Tracks	Surface Force per Unit Length /kNm ⁻¹
420	Parallel	142
	Perpendicular	110
316	Parallel	92 130
	Perpendicular	145

4.4.2 The Variation of Residual Stress with Processing Conditions

This work investigates the possibility of minimising the tensile residual stresses in the steels or possibly producing, generally desirable, compressive stresses by controlling the laser processing conditions. The measured stresses are discussed in terms of the mechanisms by which they are developed.

4.4.2.1 Inter-Track Advance

- 420 Steel

A reduction of the advance between tracks will increase the tempering of tracks by successive tracks as the tracks come closer. This will lead to an increase of thermal stress relief associated with tempering as the tracks are moved closer together. Reducing the inter-track advance will also bring the regions that are heated by successive tracks closer together and will subject a greater volume fraction of the treated material to plastic flow in compression at high temperatures. This will be accompanied by the formation of austenite and subsequent martensite formation on cooling. These interactions lead to the formation of tensile residual stresses, similarly to the formation of tensile residual stresses in the heat affected zone of the subsurface stress specimens. As the advance between the tracks is reduced and a greater and greater volume fraction of the treated zone is affected by heating from succeeding melt tracks the interactions between tracks become more significant. This develops an increasingly tensile residual stress as the inter-track advance is reduced.

In the single melt tracks the martensite transformation is sufficient to offset the tensile residual stresses and generate highly compressive stresses. It is the plastic deformation associated with the compressive thermal stresses of succeeding tracks that develops the tensile surface residual stresses that are observed on all but the single or the most slightly overlapping laser melted tracks.

James, Gnanamuthu and Moores (1984) have made measurements of residual stress on each of a series of overlapping melted tracks in a plain carbon steel and a low alloy steel and found relatively compressive stresses in the last tracks to be melted and increasingly tensile stresses on the earlier tracks. This increase of tensile residual stress with distance from the final tracks is analogous to the increase of residual tensile stress with decreasing inter-track advance here, in that in both cases the increase in surface tensile residual stress is associated with increased inter-action of tracks with succeeding tracks and increasing plastic deformation due to thermal stresses.

The high residual compressive stresses in the single tracks indicate the minor role played by transformation plasticity in relieving these stresses. High compressive residual stresses set up by the martensite phase change have also been reported in the welding literature, Jubb (1970) and Luxmoore, Kan and Egan (1970). As the compressive stresses were generated when the austenite to martensite phase change was taking place the conditions for transformation plasticity were fulfilled. Transformation plasticity is known to be a time dependent process where the sensitivity of flow stress σ_f to strain rate, $\dot{E}$ may be described by:

$$\sigma_f = K \dot{E}^m$$

where K is a constant and m is stress dependent (Kot and Weiss 1970). The lack of transformation plasticity in the single tracks may be attributed to the short interaction times associated with laser surface melting.

The low stresses that were found at the maximum inter-track advance to ensure overlap, 750 μ m for the 800 μ m wide tracks, indicate the possibility of minimising the tensile residual stresses by maximising the inter-track advance.

- 316 Steel

A reduction in the inter-track advance will increase the thermal cycling that material is subject to after solidifying. This introduces the possibility of sensitizing material. It may give rise to thermal stress relief. As in the 420 steel it is possible that the plastic deformation that takes place around melt tracks at high temperatures will introduce tensile residual stresses. Unlike the 420 steel the residual stresses in the 316 steel are almost independent of changes in the overlap between tracks. This difference should not be surprising. When the 316 steel cools the stresses in the laser melted tracks are tensile and equal to the flow stress throughout the cooling cycle. Overlapping the 420 steel brought the compressive stress, due to the martensite phase change, up towards the tensile yield stress. The 316 steel, undergoing no phase change on cooling in the solid state has a residual stress equal to the tensile yield stress and cannot sustain additional stress. Any plastic deformation at high temperatures will therefore not increase the residual tensile stress. This view is confirmed by the stresses in the single track specimens which fell within the scatter band for the overlapping track specimens indicating the absence of additional stresses due to

plastic deformation at high temperatures.

4.4.2.2 Beam Diameter and Traverse Speed

These parameters may be grouped together in that they determine the interaction time, ϕ/V . An increase in the interaction time will increase the surface area that is treated. This widespread heating will result in material being subject to more reheating and cooling cycles after solidification. Such increasingly repeated cycling will have effects similar to those of decreasing the inter-track advance. Thus there will be more cycles of plastic deformation at high temperatures, increased thermal stress relief and any metallurgical effects associated with cycling such as the tempering of 420 steel or the sensitization of 316 steel will be more severe. The slower heating and cooling associated with long interaction times will tend to produce lower thermal gradients parallel to the surface. This will reduce the compressive stresses which produce plastic deformation at high temperatures and tensile residual stresses after cooling.

It is not possible to treat traverse speed and beam diameter solely in terms of interaction time as is evident when the total incident energy per unit specimen area is considered. The total incident energy per unit area will be independent of beam diameter but will increase with decreasing traverse velocity giving rise to increased overall heating of the specimen.

This behaviour is complicated by the temperature dependence of reflectivity which results in enhanced absorption at high temperatures (see Chapter 1).

- 420 Steel

The residual tensile stresses are sensitive to interaction time, decreasing with decreasing interaction time. This is due to the increased stress relief associated with long interaction times and the reduced residual stresses developed by plastic deformation due to thermal stresses at high temperatures. In view of the importance of plastic deformation stresses in controlling the residual stresses when inter-track spacing is varied it would be expected that plastic deformation stresses would play a major role in determining the residual stresses.

- 316 Steel

Like advance between tracks, interaction time has little influence on the residual stress in 316 steel. Here again the residual stresses are close to the tensile yield stress and are not raised by plastic deformation at high temperatures.

4.4.2.3 Incident Beam Power

The reflectivities of metals are sensitive to surface contamination, oxide formation and temperature. A change in surface reflectivity will change the absorbed beam power as will a change in the incident beam power.

Investigating the effect of incident beam

power on residual stress will therefore give an indication of the importance of surface reflectivity in determining the residual stress.

- 420 Steel

The increase of $\sim 100\text{MPa}$ over the power increase from 1.0 to 2.0 kW can, like the other effects of processing conditions on residual stress, be interpreted in terms of the plastic deformation that takes place at high temperatures. As the power increases the rate at which the irradiated area is heated will also increase, raising the thermal stresses. This will result in more severe plastic deformation at high temperatures and higher residual stresses after cooling.

- 316 Steel

The decrease of tensile residual stress with increased power may be due to the extra heating at high powers giving rise to thermal stress relief.

4.4.3 Thermal Stress Relief

The thermal stress relief of residual stresses takes place as a component is heated during which time the stress falls to the yield stress of the metal at the elevated temperature. During and after this, creep processes give rise to time dependent stress relief (Poli and Spedaletti 1981). Both these forms of stress relief take place in the tests carried out in this investigation.

- 420 Steel

Stress corrosion tests on Fe-12.5%Cr-0.1%C martensitic stainless steel in a chloride ion environment indicate that tempering in the range 350°C to 500°C reduces the stress corrosion resistance of the alloy, limiting the usefulness of stress relief in this temperature range (Metals Handbook 1979). The other constraint on the thermal stress relief of the 420 steel is the tempering of the hardened outer layer. It is possible to avoid resoftening the material by tempering at 450°C or below for times as long as 100 hours. At 500°C it is possible to maintain the full hardness by heat treating for less than 2 hours. Rapid softening takes place at 500°C if the material is held at temperature for more than 5 hours. At 550°C softening takes place from the onset of tempering (Irvine 1960).

Considerations of stress corrosion cracking and re-tempering leave two windows of acceptable heat treatments, those below 350°C and treatments at 500°C for less than 2 hours. It is possible to reduce the residual tensile stresses by ~60MPa to ~270MPa by heating to 340°C. More complete stress relief can be achieved by heating to 500°C for 5ks, this bringing this stress down to ~50MPa. Such a treatment appears to offer the optimum stress relief.

- 316 Steel

The thermal stress relief of 316 steel is limited by the possibilities of sensitisation and sigma phase formation. The precipitation of $M_{23}C_6$ carbide and the associated depletion of chromium in grain boundaries will occur after exposure between ~425°C and ~825°C (Metals Handbook 1979). Sigma phase will form at high temperatures and result in embrittlement. The rate of its formation and the maximum temperature of

its formation are determined by the Cr and Mo contents. These contents are raised locally in the regions between the solidification cells, accelerating the formation of sigma phase and raising the temperature at which it will form. At the Fe-25%Cr-9%Ni-3.5%Mo composition that has been found in the inter-cellular delta-ferrite, sigma phase will form at temperatures as high as 1100°C (Columbier 1967).

The 316 steel is more creep resistant than the 420 steel and this shows in the higher temperatures that are necessary for stress relief. It is possible to achieve stress relief by heating to 850°C for a day. This treatment gives a relieved stress of ~50MPa. Such a treatment would not risk sensitisation provided the material was cooled through the sensitisation range sufficiently quickly, although there is the possibility of sigma phase formation - especially in the surface layers produced at low treatment speeds where delta-ferrite would be present (see Chapter 3). Although higher temperatures give more rapid stress relief as they approach the solution treatment of 1050°C they raise the question: "Why laser melt the material as a means of solution treatment and subsequently thermally relieve the residual stresses when it is possible to solution treat the material in the solid state at a temperature similar to the stress relieving heat treatment temperature that is necessary after laser surface melting?"

As it appears that thermal stress relief is not appropriate for 316 steel it would be interesting to investigate alternative methods of stress relief such as peening.

4.5 CONCLUSIONS

1. The high residual stresses that are developed during laser surface treatment will be a major factor in determining the mechanical and electro-chemical behaviour of laser surface melted 316 and 420 steel.
2. The residual stresses at the surfaces of single tracks of 420 steel are compressive. This compressive stress is developed by the volume increase associated with the transformation from austenite to martensite which counteracts the tensile stresses developed during cooling. However, plastic deformation at high temperatures gives rise to tensile residual stresses at the surface of 420 steel specimens that are covered with overlapping tracks at all but the slightest overlaps.
3. The maximum residual tensile stresses in laser surface melted 420 steel is developed below the region that transforms to martensite for the experimental conditions that were evaluated. However, it is possible that at smaller inter-track advances plastic deformation towards the surface would become more significant and the maximum tensile residual stress would be developed there.
4. The surface residual stress in the 420 steel may be minimised by maximising the advance between tracks and to a lesser extent be minimised by maximising the interaction time.
5. The surface residual stress in the 316 steel is tensile and of the order of the yield stress. It is essentially independent of processing conditions.

6. The maximum tensile residual stress in the laser surface melted 316 steel is developed at the surface of the treated layer.
7. Thermal stress relief of laser surface melted 420 steel for one hour at 500°C offers the possibility of reducing the residual tensile stress to ~50MPa without adverse metallurgical effects.
8. It is possible to stress relieve laser surface melted 316 steel without sensitization by heating to 850°C for one day. However, such a heat treatment may result in the formation of sigma phase.

5.1 INTRODUCTION

Both the residual stresses and the metallurgical structures that are produced by laser surface treatment would be expected to modify the fatigue life of components.

The aim of this investigation was not to generate extensive fatigue data but rather to allow a comparison of the fatigue behaviour over a range of treatment conditions. Material was tested after it had been conventionally heat treated, laser surface melted, and laser surface melted and subsequently stress relieved. Conventionally heat treated samples were electrolytically polished and tested to give an indication of the influence of the surface damage due to machining on fatigue life.

Bending fatigue tests are particularly suitable for assessing surface conditions because the maximum stresses are generated at or near the surface of the specimens. The rotating bend test developed by Wohler (1870) was selected for this work because of the simplicity of machining the specimens.

Previous work has been carried out on laser surface treated material in both the solid state hardened and the surface melted conditions (Gnanamuthu et al 1979 and Singh et al 1981). These investigations were both carried out on SAE4340 (Fe-1.8%Ni-0.85%Cr-0.45%C low alloy steel). Gnanamuthu et al carried out strain controlled tests on flat faced specimens. These specimens were tested in simple fully reversed bending at maximum strains of ± 0.0090 and ± 0.0026 . Laser solid state hardening

produced a 15% increase in life over untreated tempered material at the lower strain and a decrease at the high strain amplitude. This decrease was possibly due to the inability of the hardened layer to accommodate plastic deformation at high strains. Residual stress measurements showed compressive stresses immediately below the surface which became tensile below a depth of 800 μ m, see Figure 4.1.

Singh and his co-workers (1981) have tested laser surface melted material under stress control. Laser surface treatment increased the fatigue life 15 fold and the fatigue limit stress by 30% over untreated material.

5.2 EXPERIMENTAL

5.2.1 The Specimens

The rotating beam specimens were cut from 12.7mm diameter bar on a profile lathe to the form shown in Figure 5.1. The surface conditions of the various test specimens are summarized in Tables 5.1 and 5.2. The martensitic steel was supplied in the fully tempered condition and the austenitic steel was supplied in the solution treated condition. The specimens to be tested in these two conditions were therefore ready for testing after machining. The remaining specimens were produced as described below.

5.2.2 Hardening 420 Steel

The 420 steel was austenitized at 960°C for 1 hour in a vacuum furnace and hardened by oil quenching. The material was not subsequently tempered.

Figure 5.1

Rotating Bend Specimen

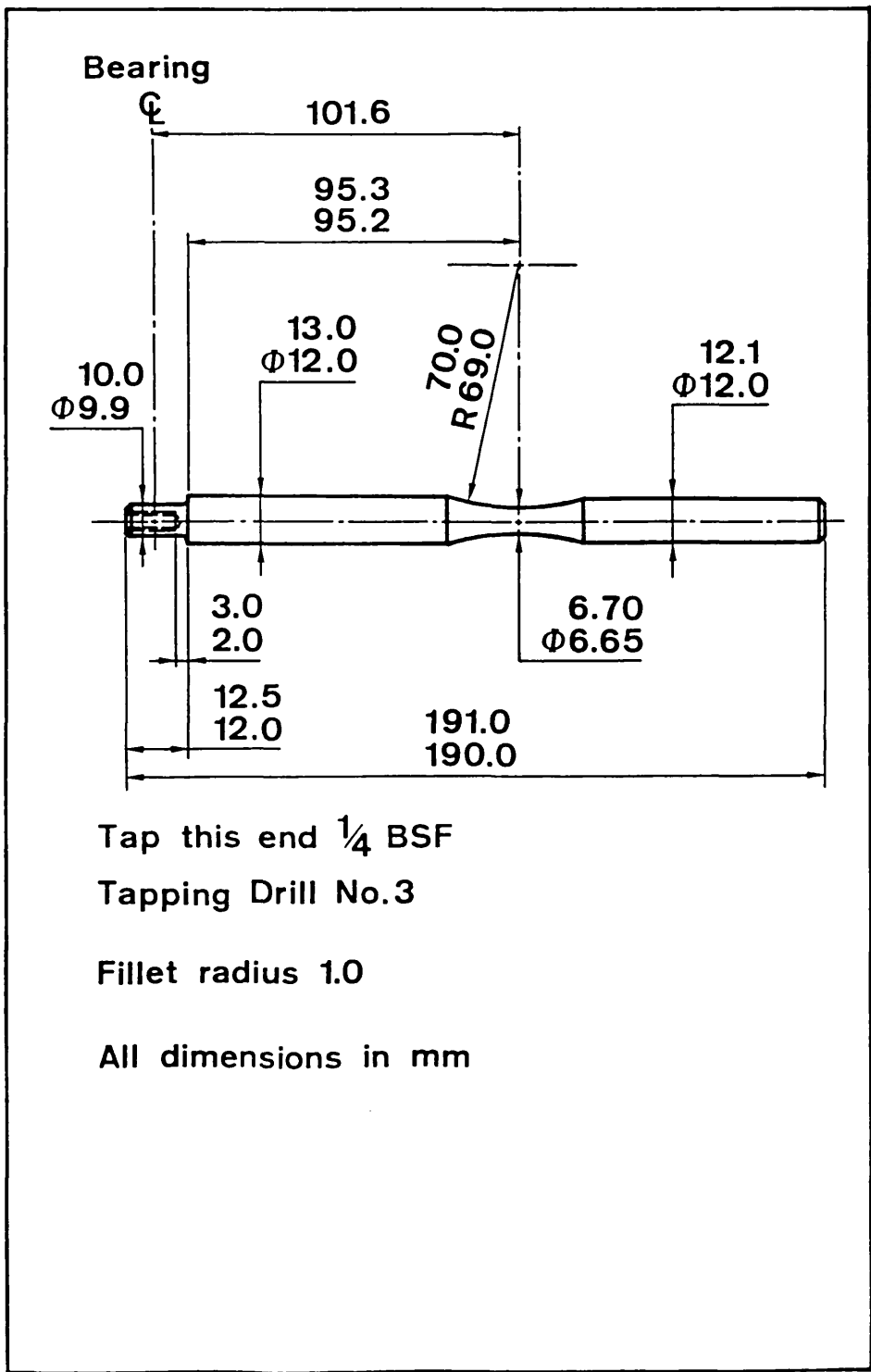


Table 5.1

420 Steel Rotating Bending Specimens

[illegible]

Table 5.2

316 Steel Rotating Bending Specimens

[illegible]

5.2.3 Electropolishing

Electropolishing was carried out in an electrolyte of 10% perchloric acid and 15% glycerol in ethanol. The specimens were clamped vertically in the centre of a cylindrical electrode for even thinning. Polishing was at 18V for the martensitic steel and 13V for the austenitic steel. Material outside the gauge length was covered with laquer. For safety it is important to ensure that the electrolyte does not become heated above 30°C. The temperature of the solution was therefore monitored throughout the thinning process and the current switched off when the temperature reached 30°C. A dish of iced water surrounded the electrode to act as a heat sink.

After about 500 μ m had been removed from the surface, thinning was discontinued. The diameter of the gauge length was measured, after thinning, with vernier callipers. Allowance was made for the reduced cross sections of the thinned specimens when loading the fatigue testing machine.

5.2.4 Laser Surface Treatment of Specimens

The residual stresses that are developed by laser surface melting can lead to eccentric samples. This problem has been encountered in both the Laser Group and industrially where banana shaped shafts have been reported (Lipscombe 1982, Man 1983, Morris 1983). One way of avoiding this problem is to cover the gauge length of a specimen with a single helical track. When a specimen is produced in this way any uneven stresses produced during processing are "wrapped" evenly around the

specimen and are balanced so that concentricity is maintained. This method was adopted by Singh et al (1981). However this technique suffers from the drawback that the continuous irradiation of a specimen can result in overall heating (Man 1982) while if a series of longitudinal (axial) tracks are used to cover a surface the specimen has time to cool down in between the production of individual tracks. The overall heating of a specimen can lead to wide range of metallurgical consequences.

A system has been developed in this investigation which overcomes the problems of eccentricity and specimen heating by applying successive longitudinal tracks nearly opposite each other so that any variation of residual stress during treatment is balanced and any shape change is cancelled out. The 15s time interval between which successive tracks are laid down allows specimen cooling. The sequence in which successive tracks are produced is shown in Figure 5.2. The apparatus that was used to achieve accurate positioning is shown in Figure 5.3 and Photographs 5.1 and 5.2. The specimen is held by a Jacob's chuck and rotated by a stepping motor. The stepping motor goes through two hundred steps in a complete revolution. The angle through which the specimen is turned is controlled by a Research Machines "380Z" mini-computer. A short program developed in the Laser Group to control stepping motors was modified to facilitate interactive control. The modified program is listed in Appendix A.5.1. As the gauge length of the sample is moved under the beam the distance from the lens to the irradiated area on the sample will vary and the incident beam diameter will also vary. This variation was minimised by using a long focal length lens ($f.l = 150\text{mm}$). The incident beam diameter that is referred to in this

Figure 5.2

Section through the Gauge Length of a Partially Laser Surface Melted Specimen

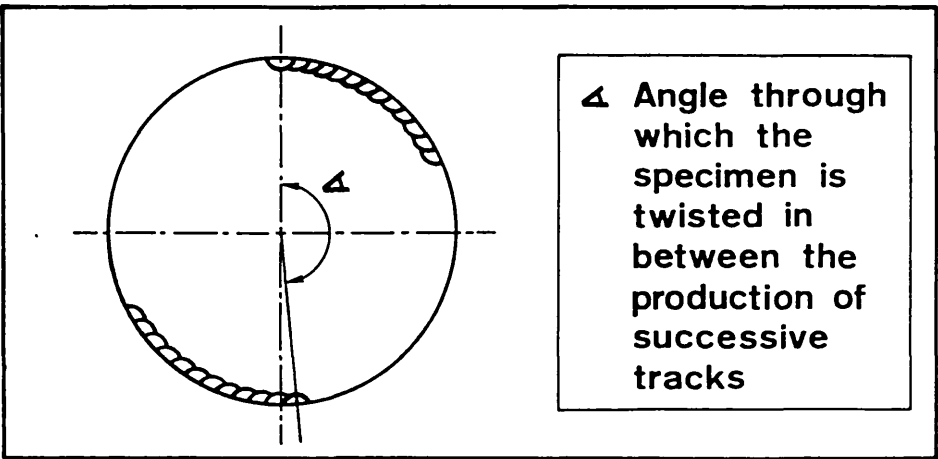
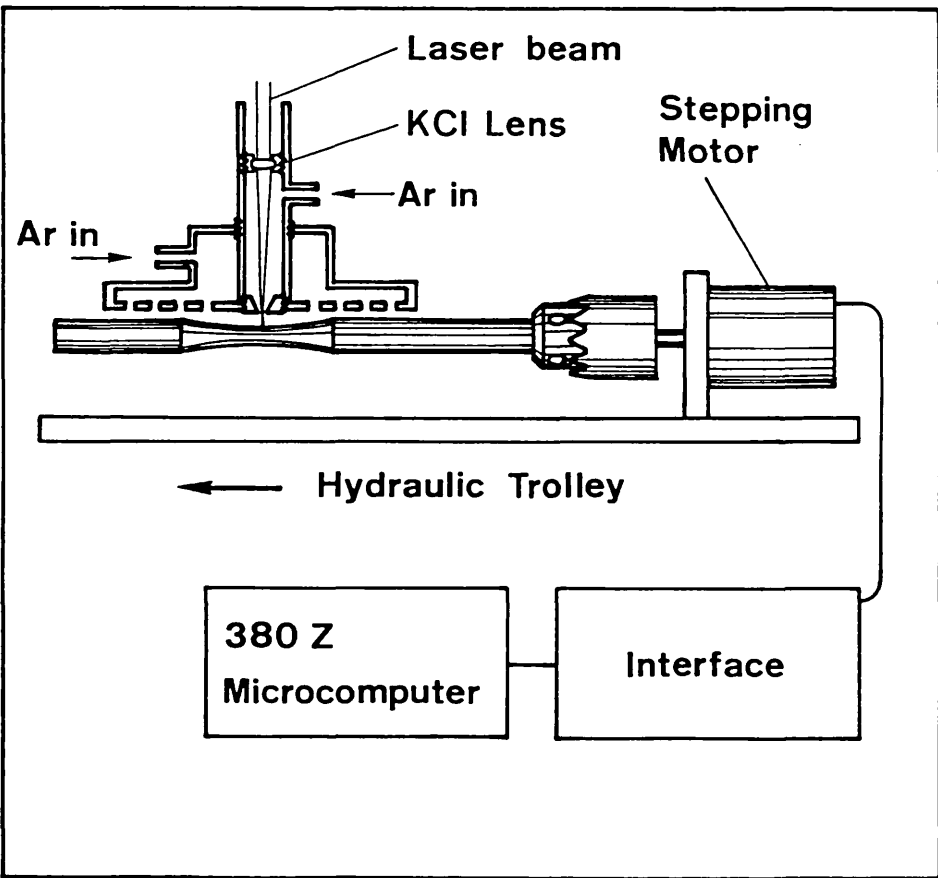


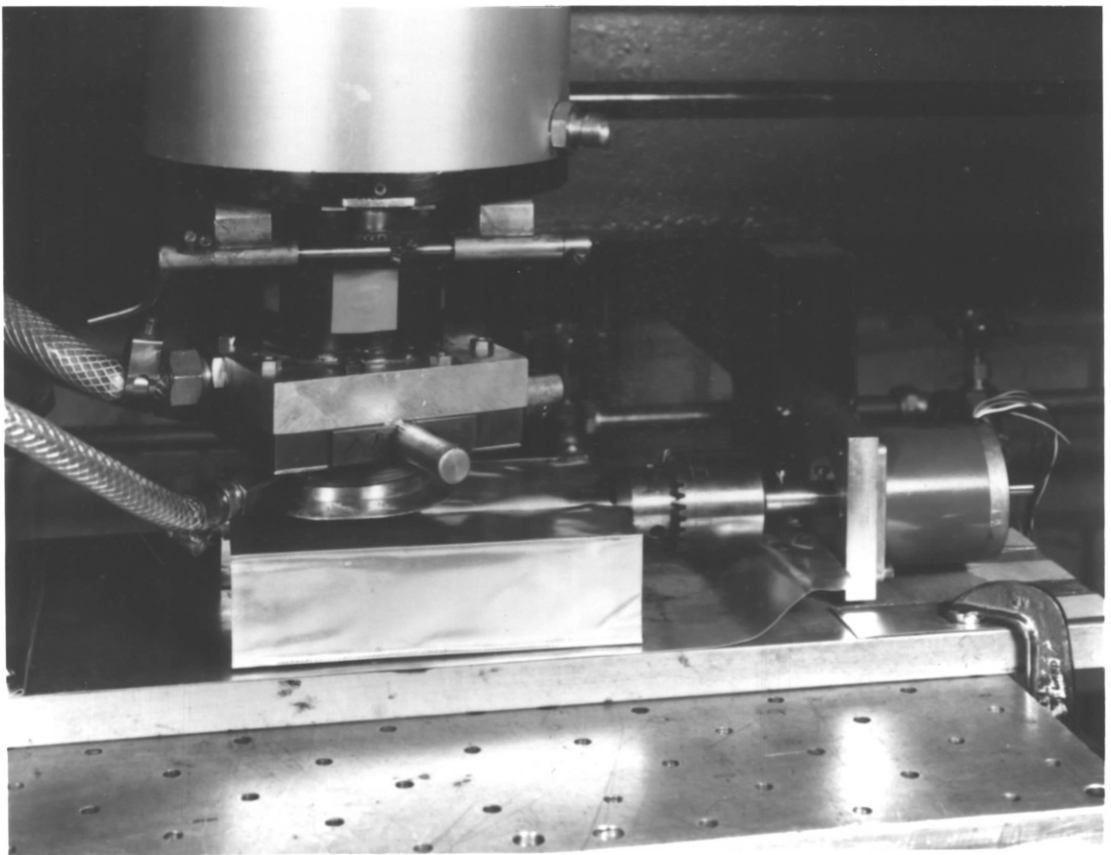
Figure 5.3

System for Making Specimens





Photograph 5.1 System for laser surface melting fatigue specimens



Photograph 5.2 Arrangement of shrouding head and stepping motor

chapter is the diameter at the centre of the gauge length. The focal point of the lens was positioned below the irradiated surface so that the beam was defocussed beyond the nominal incident beam diameter over the treated surface away from the middle of the gauge length. This arrangement was adopted so that the tracks away from the middle of the gauge length would err towards being wide and shallow rather than being keyholed.

A flow of argon was maintained through the nozzle to assist the effect of the shrouding gas and to help protect the lens. Shrouding gas was provided by a series of argon jets above the specimen. A plate immediately above the specimen assisted the shrouding by restricting the flow of gas away from the specimen. It also restricted the heated area to the gauge length of the specimen. Linear movement was provided by a hydraulic table. The treatment conditions that were adopted for the 420 steel are summarized in Table 5.1 and those for the 316 steel are summarized in Table 5.2.

5.2.5 Stress Relief

- 420 Steel

A stress relieving heat treatment of 4 hours at 450°C in vacuum was adopted. This treatment was chosen because it would be expected to reduce the tensile residual stress to less than 100 MPa (see Figure 4.13) while maintaining the hardness developed by laser surface treatment.

- 316 Steel

Two stress relieving heat treatments were applied, partial stress relief, 4 hours at 750°C and a more

severe treatment, 24 hours at 850°C in a vacuum furnace in both cases. These treatments would be expected to reduce the tensile stresses to ~ 200MPa and ~ 100MPa respectively.

5.2.6 Measurement of Residual Stress

The residual stresses at the surfaces of laser surface treated rotating bending specimens were measured in the axial and the hoop directions using an x-ray diffractometer operating with two degrees of freedom as described in Chapter 4. Residual stresses were measured at the centres of the gauge lengths of the specimens. In order to minimize errors due to the curvature of the specimens' surfaces the incident beam was collimated so that the stress was measured over an area of about a square millimetre.

5.2.7 Mechanical Testing

Fatigue testing was carried out with a Lancashire Dynamo "A5G2" rotating bending testing machine. The experimental arrangement is shown in Figure 5.4. This test subjects the gauge length of the specimen to a sinusoidally varying stress with a mean stress of zero. The specimens rotate at 50 cycles per second. The maximum stresses at the gauge lengths were controlled by varying the loads on the pans. Switches below the pans turned the motor off when a specimen failed. The fatigue lives were recorded on dial gauges.

5.2.8 Fractography

The failure surfaces were examined using a Vickers "M41" binocular microscope and a JEOL "T200" scanning electron microscope. Where fatigue crack

Figure 5.4
Fatigue Testing Arrangement

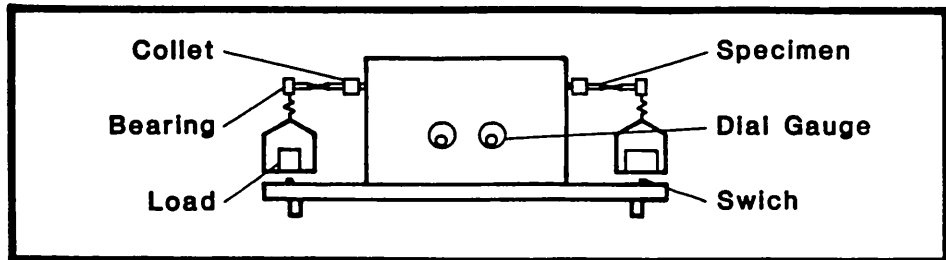


Figure 5.5
Fatigue Behaviour of 420 Steel

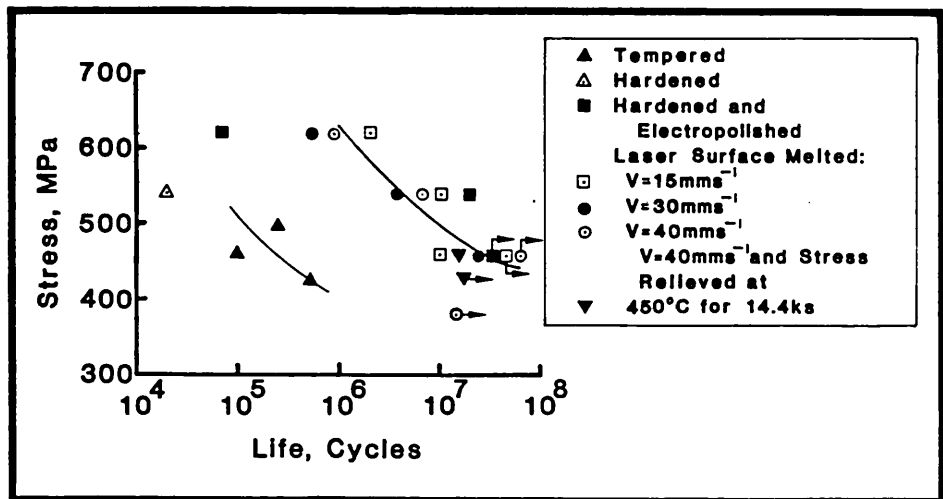
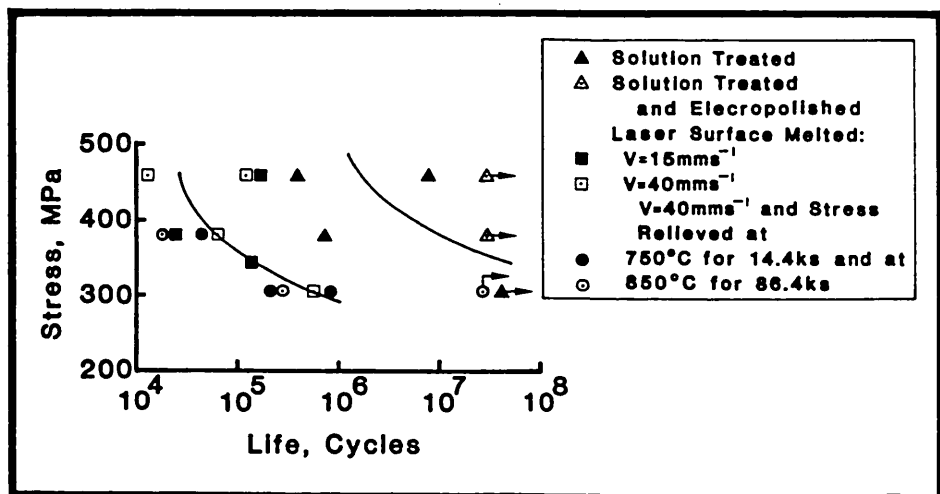


Figure 5.6
Fatigue Behaviour of 316 Steel



origins could be identified an energy dispersive x-ray analysis system was used to identify their chemical composition. The dimensions and positions of inclusions at crack origins were noted.

5.3 RESULTS

5.3.1 Outline of Fatigue Test Results

- 420 Steel

The maximum stresses that were reached in the rotating bending specimens during fatigue testing are plotted against cyclic life for 420 steel in Figure 5.5. The test results fall broadly into two groups: high life and low life. The high life group contains all the specimens that were laser surface melted, while the low life group contains the conventionally heat treated samples in either the hardened or the tempered condition, that were not electrolytically polished. The hardened and electrolytically polished samples straddle the two groups showing highly stress sensitive behaviour.

- 316 Steel

Maximum stresses are plotted against cyclic lives for 316 steel in Figure 5.6. All the samples that were laser surface treated and not subsequently stress relieved show low lives. Two of the specimens that were laser surface treated and stress relieved at 850°C showed low lives; the remaining specimen in this group remained unbroken after 30×10^6 cycles at 309MPa maximum stress. The specimens that were partially stress relieved at 750°C show low lives. The untreated samples all show longer lives than the laser surface melted samples that were tested at the same stresses. The longest lives were those of the conventionally heat

treated, machined and electrolytically polished samples.

5.3.2 Optical Examination of Fracture Surfaces

- 420 Steel

Optical examination of the fracture surfaces of laser surface treated samples revealed clearly identifiable crack origins (see Photograph 5.3). These origins were surrounded by bright elliptical zones of fatigue crack propagation reaching to the surfaces of the specimens. The major axes of the ellipses were oriented parallel to the surfaces of the specimens. These zones in turn were surrounded by dull oxidised zones of crack propagation. The regions of final failure are characterised by ductile failure dimples in a rough surface. The effect of the laser treated zone can be seen round the edge of the specimen. This zone shows fast fracture rather than ductile tearing.

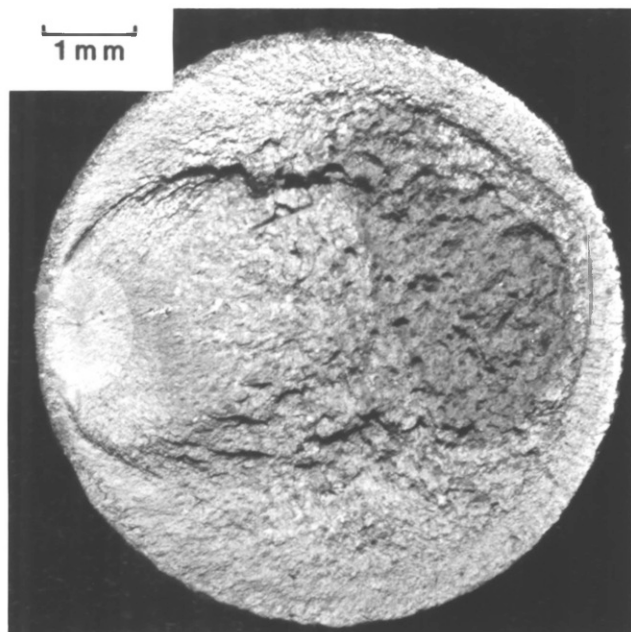
The conventionally hardened specimens all show a uniform topography over their fracture surfaces (see Photograph 5.4). No crack initiating defects were identified in these specimens.

The tempered specimens show regions of fatigue growth and regions of ductile failure, Photograph 5.5. No fatigue initiating defects were positively identified.

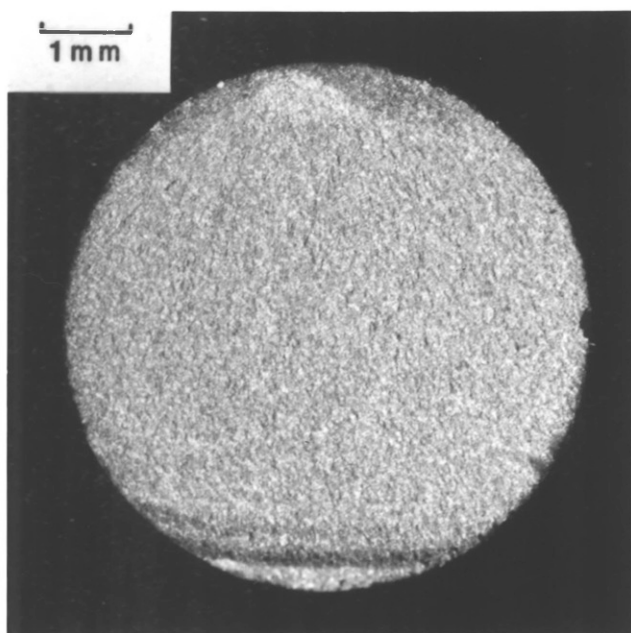
- 316 Steel

In contrast to the 420 steel laser surface melting made little difference to the appearance of the fracture surfaces of the 316 steel specimens. No crack initiating inclusions were positively

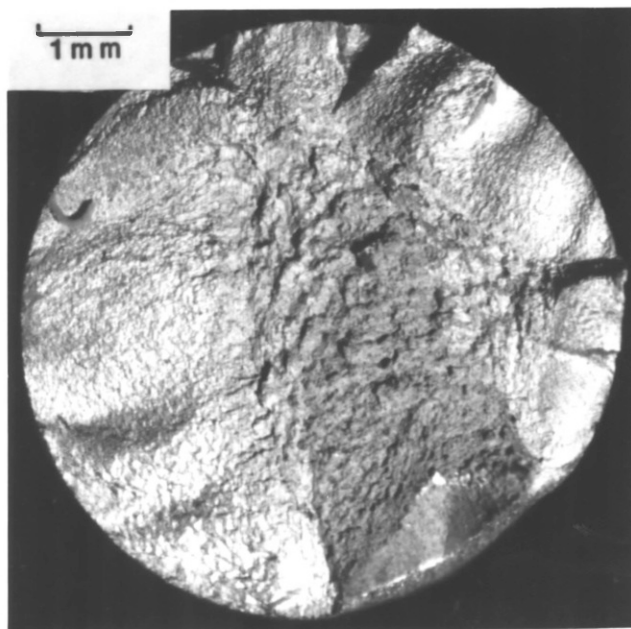
Photograph 5.3 Fracture
surface - laser surface
melted 420 steel



Photograph 5.4 Fracture
surface - hardened and
electropolished 420 steel



Photograph 5.5 Fracture
surface - tempered 420
steel



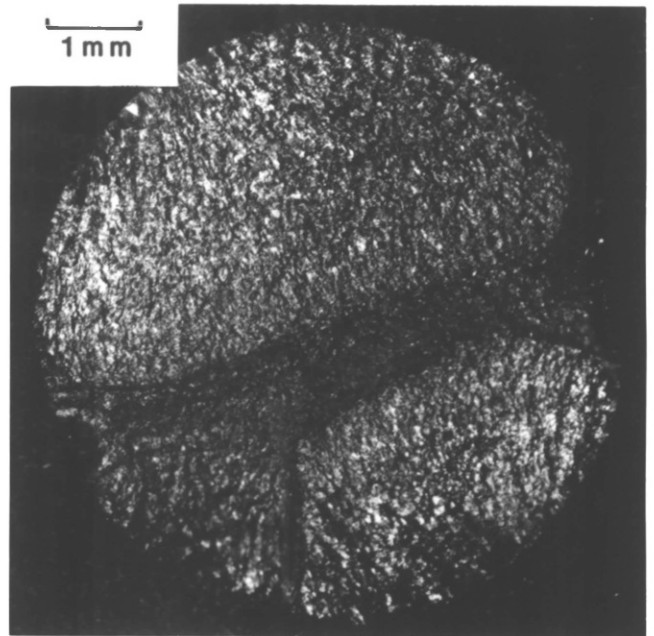
identified. Regions of fatigue crack growth and regions of ductile failure were identified. Photographs of the fracture surfaces of treated and untreated specimens are shown, Photographs 5.6 and 5.7.

5.3.3 Scanning Electron Imaging and Analysis

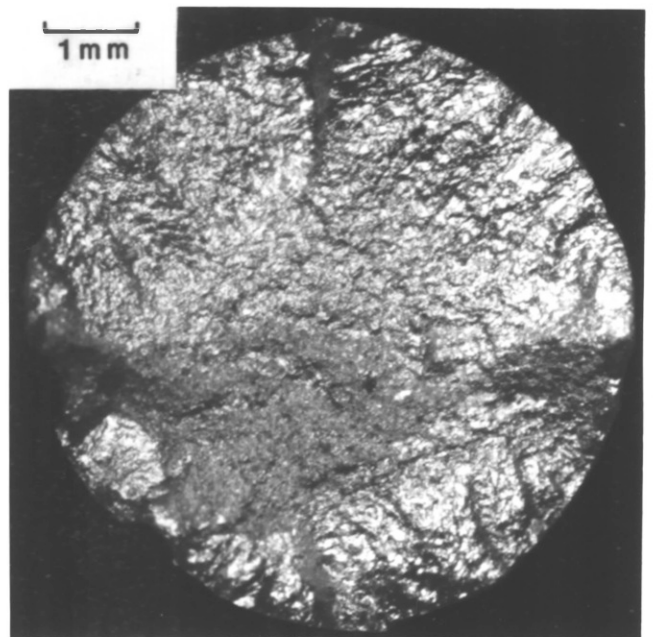
Photographs 5.8 to 5.18 show scanning electron images of the various failure regions that are described in the optical examination section. The laser surface melted zone can be seen to have a similar fracture morphology to the conventionally hardened material, in the 420 steel, Photographs 5.12 and 5.13. Scanning electron microscopy also showed areas of fatigue striations in parts of the fatigue crack in the 316 steel, Photograph 5.15. No fatigue striations were observed in the fracture surfaces of the 420 steel.

The defects that initiated fatigue cracks in the laser surface melted 420 steel specimens were chemically analysed using the x-ray analysis system on the scanning electron microscope. The defect cross sections are approximately elliptical with major axes of about $25\mu\text{m}$. This is large enough to allow spot analysis of the inclusions without an unwanted contribution from the matrix. Plots of x-ray energy against frequency are shown for an inclusion excited by the electron beam in Figure 5.7 and for base material excited by the electron beam in Figure 5.8. Figure 5.7 shows silicon and little else indicating a silicate inclusion, in contrast to Figure 5.8 where iron and chromium peaks predominate. All the fatigue crack initiating inclusions showed spectra similar to Figure 5.7. The lengths of the major and minor

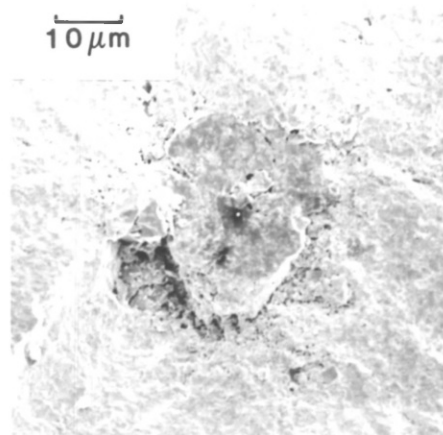
Photograph 5.6 Fracture
surface - laser surface melted
316 steel



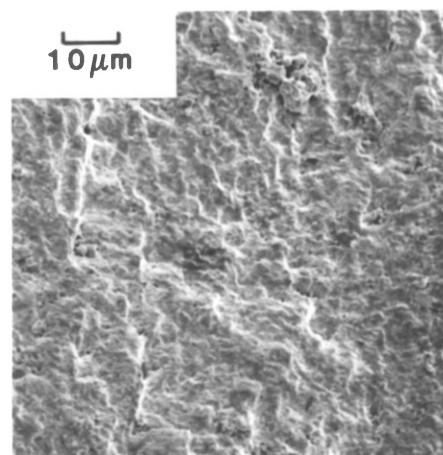
Photograph 5.7 Fracture
surface - solution treated
316 steel



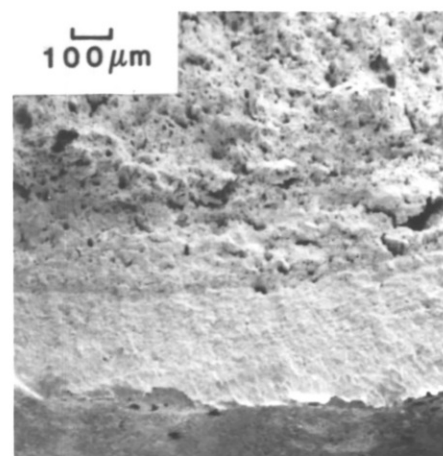
Photograph 5.8 Fatigue crack initiation site in 420 steel



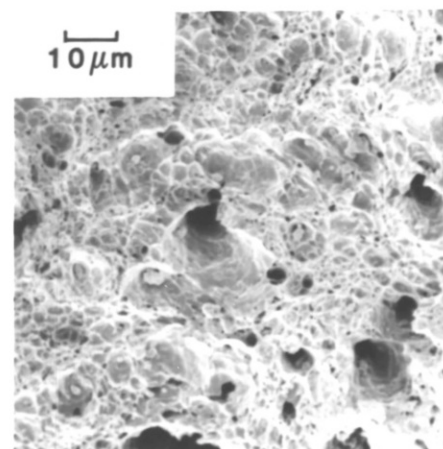
Photograph 5.9 Fatigue crack in laser surface melted 420 steel



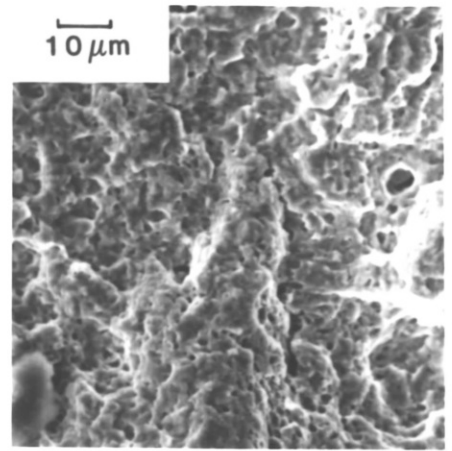
Photograph 5.10 Transition from laser melted to tempered fracture surface in 420 steel



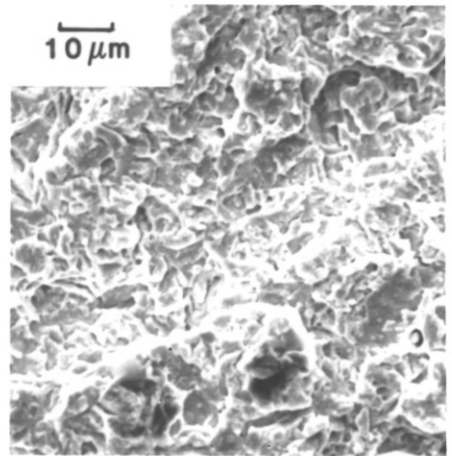
Photograph 5.11 Ductile fracture surface in 420 steel



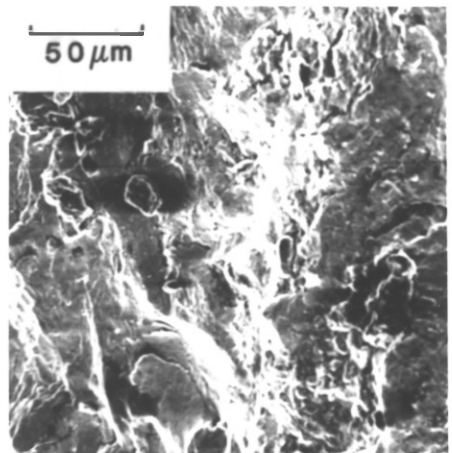
Photograph 5.12 Fracture surface in laser melted zone in 420 steel



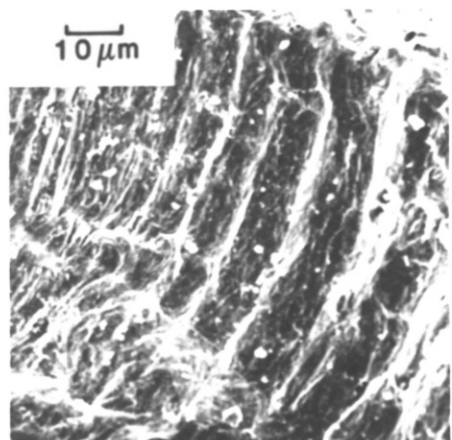
Photograph 5.13 Fracture surface of hardened 420 steel



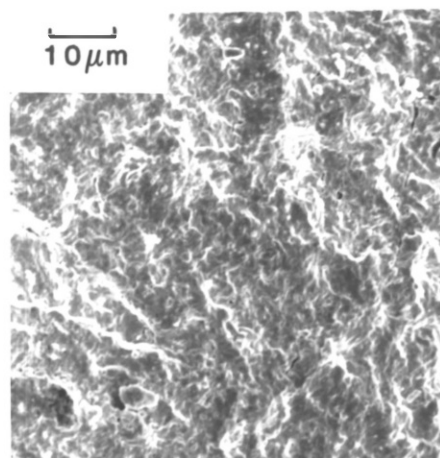
Photograph 5.14 Neighbourhood of fatigue crack initiation site in solution treated 316 steel



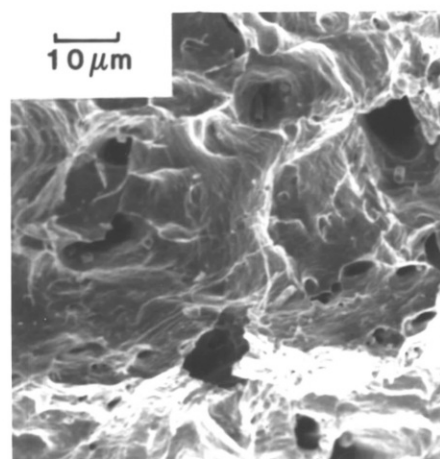
Photograph 5.15 Fatigue striations in solution treated 316 steel



Photograph 5.16 Fatigue crack in laser
surface melted 316 steel



Photograph 5.17 Ductile fracture surface
in 316 steel



Photograph 5.18 Ductile fracture surface
in laser surface melted 316 steel

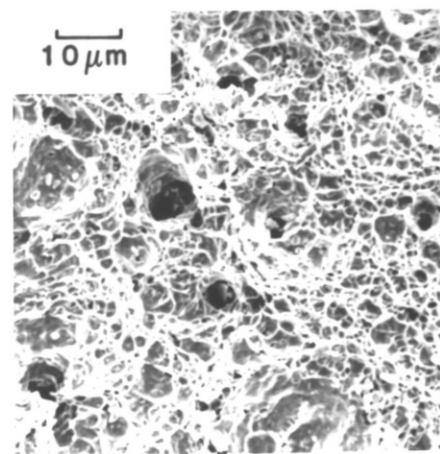


Figure 5.7

Fatigue Crack Initiating Inclusion in 420 Steel - x-Ray Spectrum

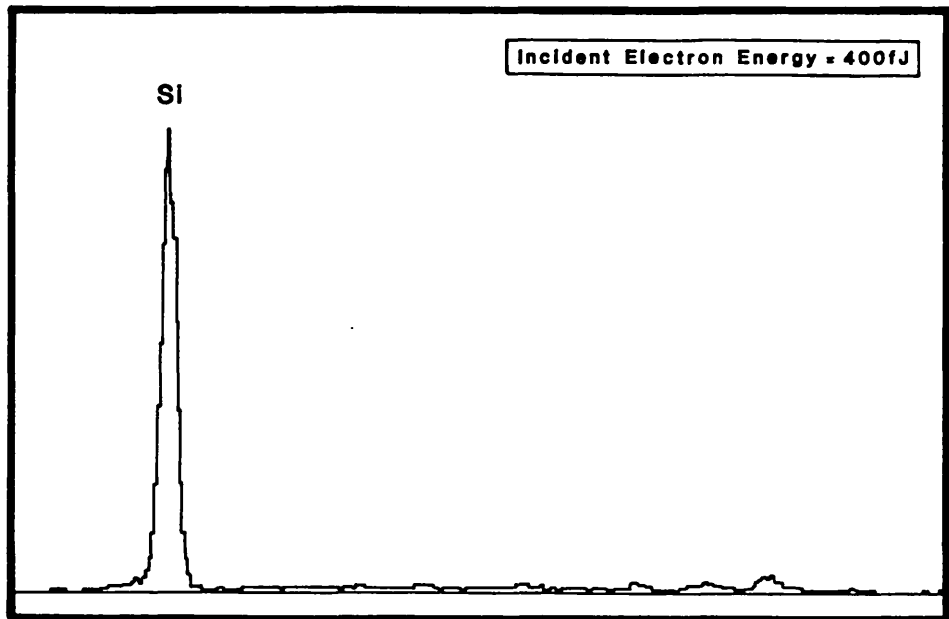
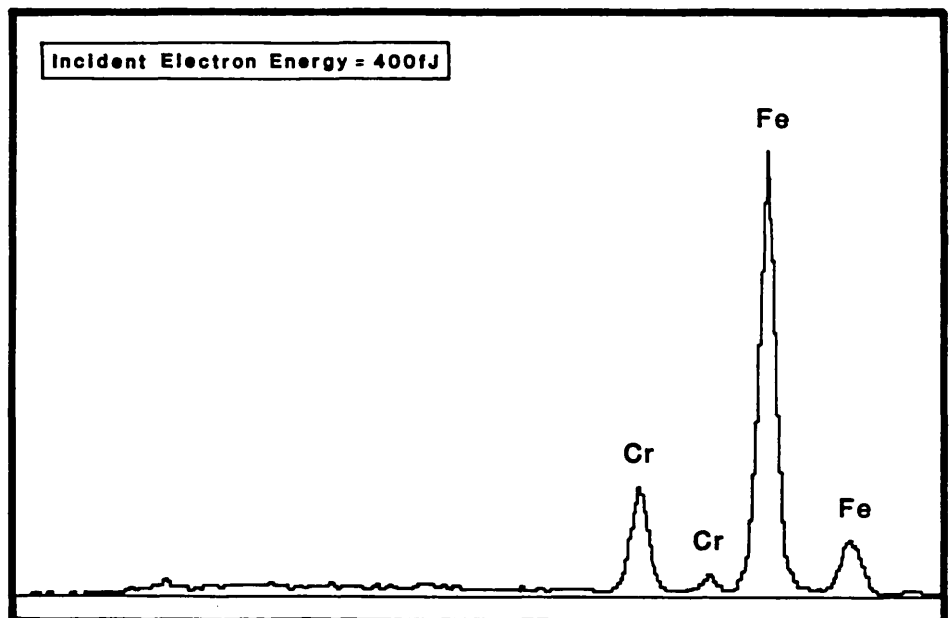


Figure 5.8

Fracture Surface of 420 Steel Fatigue Specimen - x-Ray Spectrum



axes of the defects and their depths are given in Table 5.3.

Stress relief appears to have little effect on the depth of the crack origin below the specimen surface in 420 steel.

Generally the depth of the crack origins increased as the speed at which the specimens were laser surface melted decreased.

5.3.4 Residual Stress in the Fatigue Test Samples

The heights of the diffracted peaks varied depending on orientation. This effect was attributed to the crystallographic texture of the materials and was particularly evident in the austenitic steel. This variation is exaggerated by the small specimen area that was sampled, one square millimetre. The difference between the two materials can be understood by considering the number of diffracting planes that are available. Stress measurements are based on the (200) planes in the austenitic steel and the (211) planes in the martensitic steel. Thus there are twice as many diffracting planes available in the martensitic steel which is less texture sensitive. The measured stresses are summarised in Table 5.4.

5.4 DISCUSSION

5.4.1 Subsurface Stresses

The subsurface mechanical stresses for 6.8mm diameter gauge length specimens that are predicted by elastic solid mechanics (Timoshenko and Young 1968) are shown in Figures 5.9 and 5.10 as are the measured subsurface residual stresses for flat specimens.

Table 5.3

Position and Dimensions of Fatigue Crack Initiating Inclusions in
Laser Surface Melted 420 Steel Specimens

Laser Treatment	Power, Velocity, Diameter, Angle,	P/kW V/mm ^s ⁻¹ ϕ /mm Δ/π rad	1.5 1.5 1.5 0.97	1.5 30 1.5 0.98	1.5 40 1.5 0.98	1.5 40 1.5 0.98
Thermal Stress Relief	Temperature Time	T/°C t /ks	- -	- -	- -	450 32.4
Fatigue Testing	Stress Life	σ /MPa N/cycles $\times 10^6$	463 540 618 10.5 11.6 1.8	463 540 618 20.0 3.8 0.6	540 618 4.1 0.8	463 14.7
Defect Dimensions	Major Axis, Minor Axis,	a/ μ m c/ μ m	31 23 29 30 21 23	23 28 24 17 23 20	30 33 18 33	8.3 8.0
Defect Depth		D/ μ m	860 890 760	530 480 425	540 480	413

Table 5.4

Residual Stresses in Laser Surface Melted Rotating Bend Specimens

Steel	Residual Stress, MPa	
	Parallel to Tracks	Perpendicular to Tracks
420	215	180
316	610	520

Both the specimens were produced with the following processing conditions:

Power, $P = 1.5\text{kW}$
Diameter, $\phi = 1.5\text{mm}$
Velocity, $V = 40\text{mms}^{-1}$
Angle, $\angle = 0.98\pi \text{ rad}$

Figure 5.9
 Axial Stresses in a 420 Steel Rotating Bend Specimen

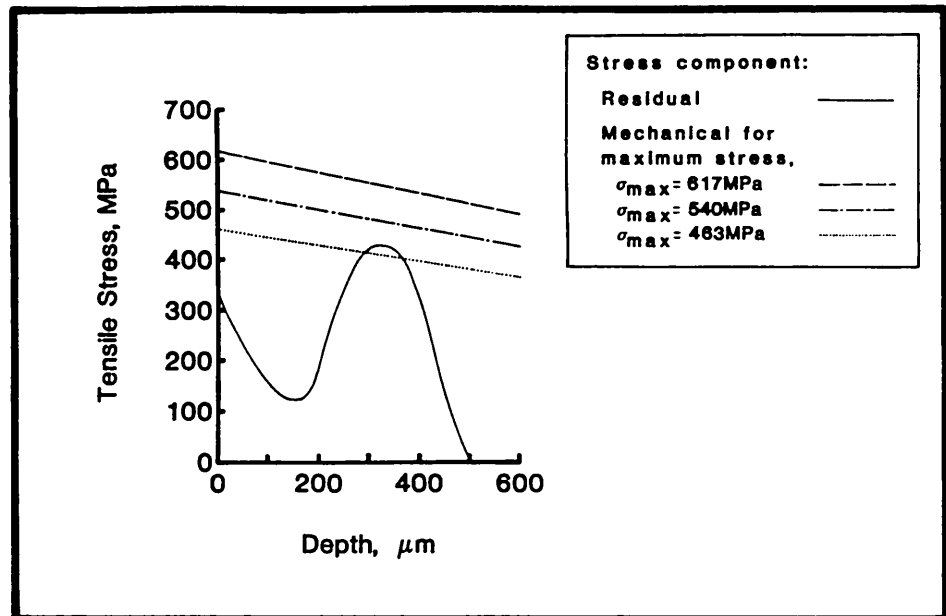
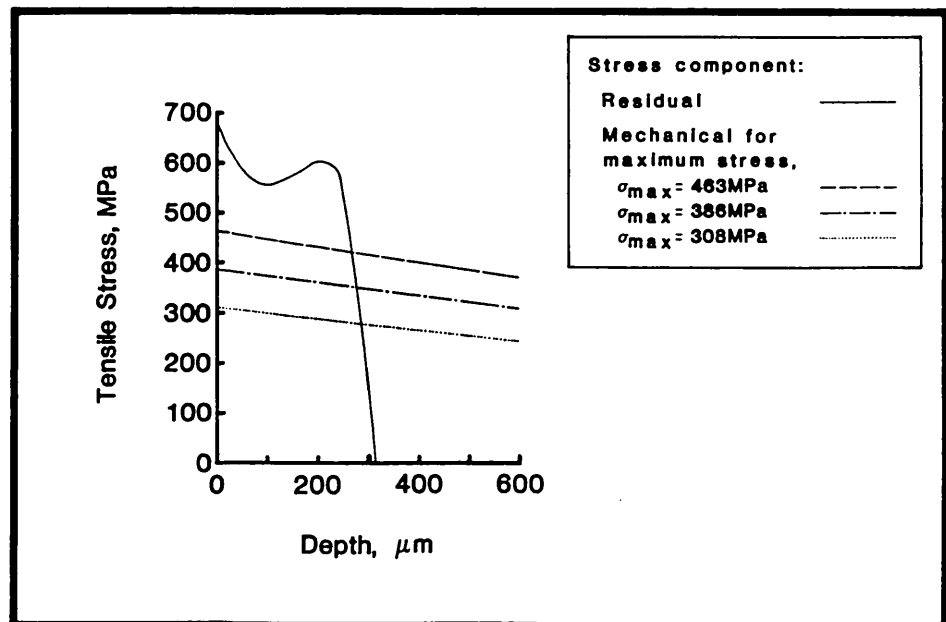


Figure 5.10
 Axial Stresses in a 316 Steel Rotating Bend Specimen



There will be some differences between these residual stresses and those for rotating bending specimens due to differences in the laser treatment speeds, the inter-track spacings and the different geometries. Figures 4.5, 4.6, 4.7 and 4.8 give an indication of the differences at the surface due to the different laser treatment conditions and suggest a maximum difference between the subsurface stress samples and the rotating bending specimens of 35% in the 420 steel and little difference in the 316 steel, where the residual stress is less sensitive to variations in processing conditions. This use of subsurface stresses measured on flat samples to explain the behaviour of rotating beam specimens is supported by the measured surface residual stresses of the rotating bending specimens which fall within the range that would be expected from the results for flat samples.

5.4.2 316 Steel

During the fatigue loading of ductile materials slip bands may be formed along planes oriented close to the maximum shear stress. Where these planes reach the surface of a material ridges and grooves are formed. These surface irregularities can initiate fatigue cracks (Mott 1958 and Backofen 1959). Once a micro-crack is formed it may grow. This growth will initially be along the slip bands. When the crack length is sufficient for the crack tip stress field to become significant with respect to the body in which it is set the crack will turn to grow perpendicular to the direction of the maximum principle stress. Finally the crack becomes unstable and failure occurs by either ductile tearing or brittle fracture.

Laser surface melting does not harden 316 steel but does introduce tensile residual stresses. In view of the ductility of the material and the fact that

no inclusions were positively identified it was assumed that the fatigue cracks were initiated from slip bands.

Laser surface melting will remove any irregular topography and residual stresses that are developed during machining and subsequently introduce its own topography and residual stresses.

Where the combination of residual and mechanical stress results in plastic deformation the residual stress will be reduced. Any remaining tensile residual stress will impose a mean stress and where this stress is tensile reduce the stress below which fatigue failure does not occur, the fatigue limit. This reduction may be described by an empirical relationship such as that due to Gerber (1874), Soderburg (1930) or Goodman (1899). These may be expressed mathematically:-

$$\text{Gerber} \quad \pm \sigma_L = \pm \sigma_o \left[1 - \left(\frac{\sigma_m}{\sigma_t} \right)^2 \right]$$

$$\text{Soderburg} \quad \pm \sigma_L = \pm \sigma_o \left(1 - \frac{\sigma_m}{\sigma_y} \right)$$

$$\text{Goodman} \quad \pm \sigma_L = \pm \sigma_o \left(1 - \frac{\sigma_m}{\sigma_t} \right)$$

where σ_y = Yield stress
 σ_t = Ultimate tensile stress
 $\pm \sigma_o$ = Fatigue limit when $\sigma_m = 0$
 $\pm \sigma_L$ = Fatigue limit
 σ_m = Mean stress

If the residual stress were the only factor leading to a decrease of fatigue life, thermal stress relief would offer a way of restoring the fatigue life of the specimens. That one of the the laser surface melted and stress relieved components showed a high life of 30×10^6 cycles, unbroken, at 309MPa suggests that the stress relieving heat treatment at 850°C can increase the fatigue life. However the remainder of the laser surface treated and stress relieved specimens showed low lives which are similar to those of the samples that were not stress relieved. This indicates that some form of damage associated with laser surface melting remains after stress relief, probably subsurface solidification cracking.

The as machined specimens showed longer lives than the laser surface melted specimens and the electrolytically polished specimens showed the longest lives of all, remaining intact after 30×10^6 cycles at 386 and 463 MPa. These long lives reflect the relatively undamaged surface condition of the machined samples and the removal of machining damage from the electrolytically polished samples.

5.4.3 420 Steel

Laser surface hardening will modify the fatigue behaviour of 420 steel by hardening both the laser surface melted and the heat affected zone, by introducing residual stresses and by modifying the surface topography.

Fatigue cracks can initiate from inclusions in the metal matrix. This has been shown to be the case for wrought high strength steels (Ranson and Mehl

1952). Smooth steel specimens with ultimate tensile strengths of 900MPa or more have been shown to initiate fatigue cracks at inclusions (Frith 1956). Fatigue crack initiating inclusions were identified at the crack origins of the fracture surfaces of all the 420 steel specimens that had been laser surface melted. In both steels it is possible that inclusions will be broken up and separated in the melted zone by the stirring and high thermal gradients associated with laser surface melting.

Tomkins (1973) has proposed a criterion for the fatigue limit of steel components based on the onset of plasticity. He points out that micro-yielding occurs in all fatigue tests. The von Mises criterion for yielding predicts yielding when $\bar{\sigma} = \text{constant}$, where σ is the equivalent stress and is given by

$$\bar{\sigma} = 2^{-\frac{1}{2}} [(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]^{\frac{1}{2}}$$

where σ_1 , σ_2 and σ_3 are the principle stresses (R. von Mises 1913). Tomkins shows that the equivalent stress below which fatigue cracks do not grow is the same for push/pull, reversed torsion and thick cylinder fatigue tests. Hardening a material will raise the equivalent stress level above which yielding will occur, raising the fatigue limit.

If yielding does occur and a fatigue crack is formed a higher hardness level will reduce the size of the plastic zone that is formed ahead of the crack tip. This will reduce the strain energy necessary for crack growth and the crack tip stress necessary for ^{final} fracture.

The laser surface melted zone at the outside of the specimen will have the yield point and ultimate tensile strength of fully hardened material (1.45 and 1.6 GPa respectively). The tensile stress due to the superimposed action of the residual and the mechanical stress will reach a maximum of about 1.0GPa in the laser surface melted layer on the most severely loaded specimens (see Figure 5.9). This will result in elastic deformation of the surface melted layer during testing.

The hardnesses of the heat affected zones will be somewhat above those of the fully tempered material (Chapter 3) and correspondingly high yield stresses would be anticipated in this region. These yield stresses will decrease as the hardness does with increasing depth below the surface.

The residual stress reaches a maximum immediately below the heat affected zone ~~where at 800MPa it exceeds the yield stress of 680MPa, as measured on a tensile specimen.~~ When mechanical stresses are applied during the fatigue testing this region will deform plastically and the tensile residual stress will be partially relieved. Although the mechanical stresses at this depth are below the yield stress, for all the tests local plastic deformation will take place, especially near stress concentrating inclusions, possibly initiating fatigue cracks. The crack initiating inclusions that were found were all identified as silicates. These inclusions could have been introduced by the oxidation of de-oxidising additions during the steel making process or from pieces of broken off refractory lining (Kiessling 1979). The crack initiating inclusions were all found in the region immediately below the heat affected zone. This would be anticipated from a consideration of the

variation of both stress and hardness with depth in that this region develops the highest tensile stresses and is not hardened.

That the stress relieving heat treatment did not alter the position of the crack origin suggests that the residual stress, which will have been reduced to about 100 MPa has less effect on the position of the crack origin than the hardness profile which is essentially unchanged.

The hardness profile of a laser surface hardened component is similar to the hardness profile of a component that has been hardened by a conventional process, such as carburising. When surface hardened components are loaded so that the hardened layer behaves elastically and the core is stressed beyond its flow stress a tri-axial tensile stress state similar to that at a notch, is generated at the interface between the hardened layer and the core (Ebert, Krotine and Troiano 1965). Ebert, Krotine and Troiano (1966) point to experimental confirmation of this in that the impact transition temperature changes due to carburising are similar to those due to notches. These "metallurgical notches" in laser surface melted specimens would be expected to reduce the specimens fatigue life in a similar way to mechanical notches.

The low lives of the machined specimens of tempered steel that were not subsequently laser treated may reflect machining damage. Unfortunately no tests were carried out on tempered, machined and electrolytically polished specimens in this investigation. However rotating bending fatigue data is available in the literature to cover this deficiency (Metals Handbook 1984). This data is for AISI 410 steel which has the same chemical

composition as AISI 420 steel, apart from its carbon content which is 0.15% maximum as against 0.15% to 0.20% for 420 steel. The "Metals Handbook" results for tempered machined and polished specimens fall between the high and the low life groups found in this investigation.

The material that was hardened by quenching from 960°C and subsequently electrolytically polished shows highly stress sensitive behaviour with the longest life of any of the specimens at stresses of 463 and 540 MPa but failure after only 80 000 cycles at 618 MPa. This can be understood in terms of the hardening treatment's effect on fatigue crack initiation and propagation. The hard material is resistant to crack initiation by plastic deformation near inclusions. However there will be little plastic strain at the crack tip and little strain energy associated with fracture and fast fracture will occur at a lower stress intensity than in tempered material. This is in agreement with the fracture topography which is predominantly one of fast fracture. The low life of the conventionally hardened specimen that was not electrolytically polished can also be understood in these terms if it is assumed that crack initiation takes place from areas that have suffered machining damage.

5.5 Conclusions

- 1 Laser surface melting can increase the fatigue life of 420 steel. The life increase is associated with hardening of the treated layer.
- 2 Stress relief does not offer the possibility of increasing the fatigue life of laser surface melted 420 steel.
- 3 Fatigue cracks in laser surface melted 420 steel originate from silicate inclusions in the region below the heat affected zone of the laser treated layer.
- 4 Laser surface melting severely reduces the fatigue life of 316 steel. This loss of life is due to both residual stresses in the treated layer and other damage associated with laser surface melting, possibly solidification cracking.
- 5 Stress relief does not reliably increase the fatigue life of 316 steel, but may do so.

6.1 INTRODUCTION

6.1.1 Laser Surface Melting and Corrosion Resistance

Laser surface treatment offers the possibility of modifying the corrosion properties of metals by melting, alloying or cladding. Melting may be used to redissolve carbides and redistribute alloying elements. Alloying can be carried out by applying a surface layer of the alloying elements by electroplating or by sputtering, subsequently the alloying elements and part of the substrate are laser melted to produce an alloy enriched surface layer. Alternatively a stream of alloying powder may be fed into the melt pool. It is also possible to clad corrosion resistant material onto a substrate using a laser to melt a layer of cladding which solidifies onto the substrate (Gnanamuthu 1979).

The possibility of enhancing the corrosion properties of steels by melting in alloying metal has been investigated by Moore and McCafferty (1981). Chromium was either electroplated or sputtered onto the surface of Fe-0.18%C-0.8%Mn steel and subsequently melted into the steel by a scanning laser beam to produce laser alloyed surface layers with average chromium contents of 5, 20 and 80%. Anodic polarization curves were determined for the three alloys in 0.1M sodium sulphate solution. Increasing the chromium content was seen to decrease both the critical current density for passivation and the passivation current density. It was also noted that the passivation current densities were higher than those for conventionally produced alloys with the same compositions.

6.1.2 Pitting Corrosion

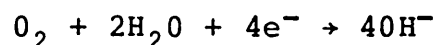
6.1.2.1 The Pitting Process

The importance of pitting corrosion stems from the way pits can locally penetrate components quickly. Corrosion pits are initiated at inclusions and in particular at manganese sulphide inclusions in stainless steels (Sedriks 1982). Once formed they propagate by the dissolution of metal at the pit bottoms. The high acidity that forms here results in rapid metal dissolution.

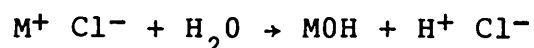
Figure 6.1 shows the processes occurring in a pit in stainless steel in an aerated sodium chloride environment. The anodic metal dissolution which takes place at the bottom of the pit,



is balanced by the cathodic oxygen reduction which takes place on the adjacent metal surface,



The increased metal ion concentration in the pit gives rise to the migration of chloride ions to maintain electroneutrality. The metal chloride that is formed in the pit is hydrolysed to form the hydroxide and the free acid,



This develops a high concentration of hydrogen ions in the pit lowering the pH

Figure 6.1
Processes Occurring in a Corrosion Pit

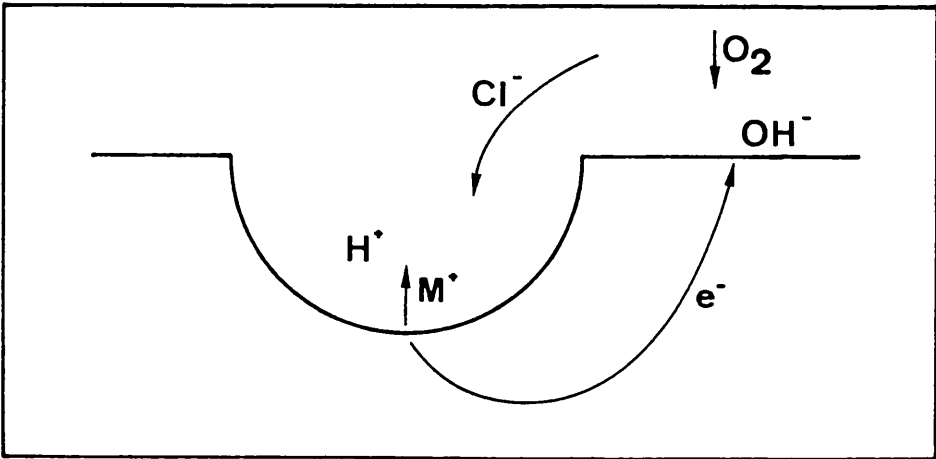
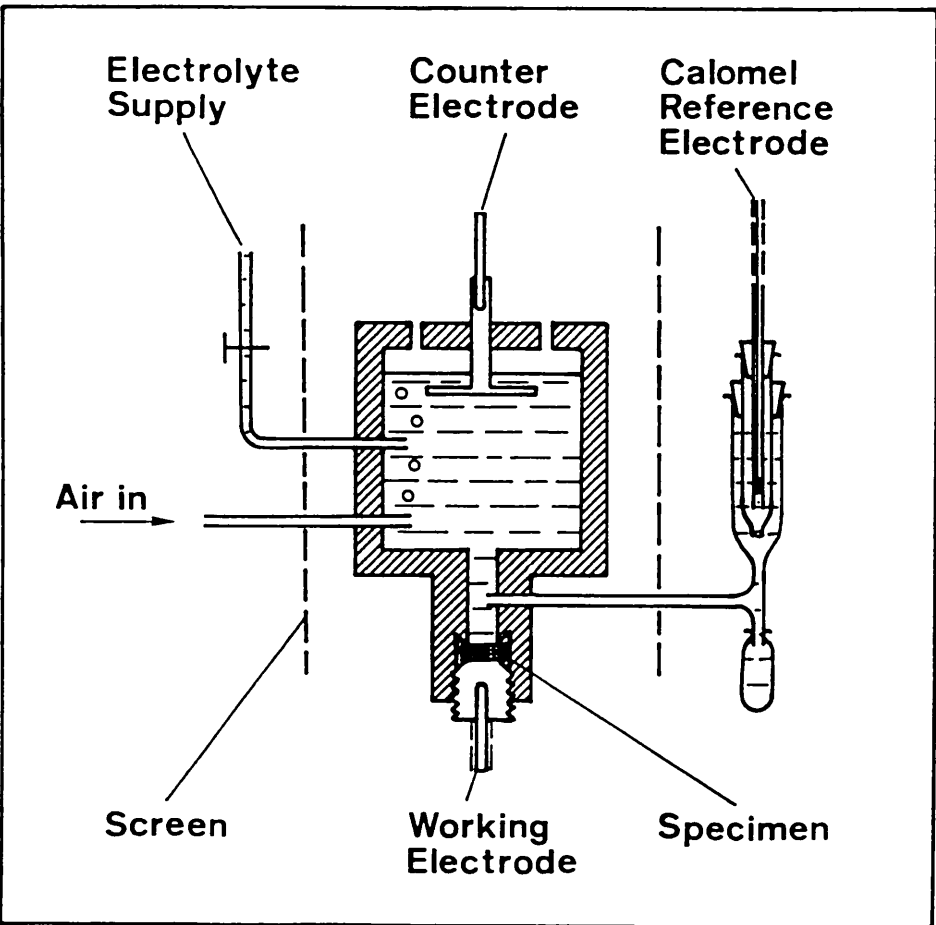


Figure 6.2
Electrochemical Cell



to 1.3 to 1.5 (Smialowska 1974). The high concentration of hydrogen and chloride ions at the bottom of the pit accelerates the dissolution of metal there giving rise to a self-sustaining process.

6.1.2.2 The Quantification of Pitting Resistance

It is possible to quantify the resistance of an alloy to pitting in a given environment by measuring the difference between the pitting potential and the corrosion potential. The separation of these two values gives a measure of the resistance of the alloy to pitting. Where these two potentials are close any slight environmental change that shifts the corrosion potential up to the pitting potential will cause pitting. Conversely where the potentials are well separated a more severe environmental change is necessary to cause pitting. The corrosion potential of stainless steels in chloride solutions may not change significantly from alloy to alloy or from condition to condition. So in this case the pitting resistance may be quantified in terms of just the pitting potential, the higher the pitting potential, the more pitting resistant the alloy.

The pitting and corrosion potentials can be measured using the slow potential sweep technique, the method used in this study. This technique has the merits of having been extensively used and developed (eg Man and Gabe 1981). However, there are alternative techniques which give

sometimes different and arguably more applicable data. Such techniques include measuring the potentials at which scratches repassivate (Pessau and Lau 1971) fast potential sweeps (Morris and Scarberry 1972) and immersion in aggressive solutions.

6.1.2.3 Laser Surface Treatment and Pitting Corrosion

It is established that tempering reduces the pitting corrosion resistance of the 12% chromium stainless steels (Kraxner and Zitter 1964 and Truman 1976). It has been suggested that this loss of pitting corrosion resistance is due to chromium depletion associated with the formation of chromium rich carbides during tempering (Truman 1976). However it is necessary to temper these steels for applications where brittle fracture is a potential risk. Laser surface treatment offers the possibility of redistributing chromium to produce corrosion resistant surfaces, while leaving the bulk of the treated component unaffected because of the highly selective nature of the heating. In this investigation the potential sweep method has been used to assess the pitting resistance of laser surface melted 420 steel. These results are compared with results for solution treated 420 steel and tempered 420 steel.

Although the austenitic steel is generally more corrosion resistant than the martensitic steel, pitting corrosion can lead to local damage of, and rapid failure of austenitic steel components

(Henthorne 1972 and Sedriks 1982). The pitting behaviour of the 316 steel has been evaluated by an analogous method to that adopted for the 420 steel. That is laser surface melted, sensitized and solution treated specimens were investigated by the slow potential sweep method.

The electrochemical behaviour of laser surface melted Fe-19%Cr steel has been investigated by Cottrell and his co-workers (1983). The surfaces of "untreated" material and laser surface melted material were investigated by determining anodic polarization curves as the surfaces were swept from the passive to the active regions in 1M sulphuric acid. The laser surface melted material showed premature breakdown of the passive film indicating degraded corrosion resistance. This was associated with the formation of corrosion pits from chromia inclusion rich regions of the specimen surface.

6.1.3 Intergranular Corrosion

Intergranular corrosion is the rapid local corrosive attack of grain boundaries. In certain environments the austenitic steels are sensitive to intergranular corrosion associated with chromium depletion at the grain boundaries of the steel. This depletion is due to the formation of chromium rich carbides at grain boundaries when the steels are held in, or cooled slowly through the sensitization temperature range, from ~480 to ~815°C (Metals Handbook 1979).

Sedriks (1979) has summarized methods of avoiding sensitization to intergranular corrosion:-

1. The use of titanium or niobium additions to precipitate out the carbon as titanium or niobium carbides. These carbides are formed in the temperature range, 870 to 1150°C so that little carbon is left to deplete the grain boundaries of chromium as the material is cooled through the sensitization temperature range.
2. Post weld heat treatment to rediffuse chromium to the grain boundaries.
3. The use of low carbon alloys containing less than 0.03% carbon to prevent the formation of carbides.

However, these measures have certain drawbacks.

The titanium and niobium carbides may be dissolved by heating to above 1150°C after which if the steel is cooled through the range of formation of titanium and niobium carbides sufficiently quickly carbon will remain in solution and be available to sensitize the steel. When the now carbon rich steel is sensitized intergranular cracking may occur subsequently. During welding the thermal sequence that gives rise to such sensitization in niobium and titanium stabilized grades occurs in a narrow zone and the corrosion associated with this condition is known as knifeline attack.

A Welding Research Council study (1969) has assessed the effects of various heat treatments on the intergranular corrosion of 316 steel, 317 steel and the low carbon version of 316 steel, 316L steel. Although the 316L steel did not show

intergranular corrosion after heating into the temperature range associated with carbide formation and subsequent intergranular corrosion, it did show intergranular corrosion after heating into the temperature range of σ -phase formation. This is 565 to 925°C for austenitic steels containing less than 32% nickel and more than 16% chromium, Nicholson, Samans and Shortsleeve (1952).

Although post weld heat treatments can redissolve carbides and redistribute chromium to prevent intergranular cracking they are not always suitable for large welded structures where widespread heating is both costly and can give rise to a wide range of metallurgical consequences.

It is possible to sidestep this problem by taking advantage of the highly local nature of laser heating. Anthony and Cline (1978) have used a laser to melt and normalize the surface of sensitized 304 steel. The laser melted material was evaluated by a test consisting of boiling the specimens in acid and subsequently examining them for cracking, as specified in ASTM-A262-E. This indicated that laser surface melting restored the intergranular corrosion resistance of the material.

In this work the effect of laser surface melting sensitized 316 steel was assessed by two standard tests. Firstly an electrolytic etch in oxalic acid (as specified in ASTM-A262-A) was used to screen out intergranular corrosion resistant material. Material failing this test is not necessarily susceptible to intergranular corrosion. Such material was evaluated by testing according to ASTM-A262-E, similarly to Anthony and Cline's specimens.

Lula and Davies (1978) have investigated the possibility of testing the 12% chromium steels for intergranular corrosion. The test specified in ASTM-A262-E which is designed to evaluate austenitic stainless steels, produces rapid general corrosion of the 12% chromium stainless steels and is too severe to produce intergranular corrosion. A modified less severe version of ASTM-A262-E does permit testing of 409 and 405 ferritic steels, however this test did not produce cracking in fully martensitic 12% chromium stainless steel.

In this work no attempt has been made to investigate the intergranular corrosion resistance of the 420 steel, because the 12% chromium martensitic steels do not readily show this behaviour.

6.2 EXPERIMENTAL

6.2.1 Chronopotentiometry

6.2.1.1 The Specimens

The specimens in the form of 5mm thick discs were cut from 12.7mm diameter bars of 316 and 420 steel. The faces of the discs were ground flat and grit cleaned prior to laser surface treatment. Two laser processing parameters were varied, the treatment speed and the intertrack advance. The laser treatment conditions that were tested are summarised in Table 6.1.

Table 6.1

Laser Surface Treatment of Potential Sweep
Specimens

Steel	Power P/kW	Diameter ϕ /mm	Velocity V/mm s^{-1}	Advance A/ μm
316+420	1.5	1.5	15	600
316+420	"	"	30	500
420	"	"	"	150
316+420	"	"	100	300

Discs were also prepared from both steels in the solution treated and segregated conditions. The solution treated 316 steel was commercially supplied bar which had been annealed at 1050°C. The segregated 316 steel was sensitized for one day at 650°C in a vacuum furnace. The martensitic steel was supplied in the tempered condition, produced by heat treatment for one hour at 700°C. This produces a dispersion of the equilibrium carbide in a matrix of tempered martensite. The solution treated martensitic samples were produced by treating the tempered material at 960°C in a vacuum furnace and subsequently quenching in oil.

6.2.1.2 The Apparatus

The electrochemical cell that was used for the tests is shown in Figure 6.2. The electrolyte was 0.05M sodium chloride adjusted to pH10 by 6.7mM sodium hydroxide. A dummy cell was used during the development of the test technique both to save the time spent washing out, filling and fitting specimens in the electrochemical cell and to give

an indication of the behaviour of the circuit in the absence of any electrical noise developed by the electrochemical cell. This dummy cell consists of a 470 Ohm resistor in series with a 100 Ohm resistor. The resistors and various sockets corresponding to the cell connections were fitted in a metal box (see Figure 6.3).

The electrical circuit that was used in the earlier work is shown in Figure 6.4. The electrometer indicates the potential difference between the working electrode, the specimen and the standard calomel reference electrode, SCE. A high impedance is necessary here to minimize the leakage current between the reference electrode and the working electrode. The impedance of the electrometer, $>100T\Omega$, is sufficient for this application. The current through the working electrode is measured by a Wenking "ML81" null input resistance current sink which converts the input signal, i to an output voltage, $k \log |i|$, where k is a constant. This provides signal compression for input currents in the range from 100nA to 200mA. The output signal from the instrument controls the y-pen of the x-y recorder while the x-pen is controlled by the signal from the electrometer. Potential control for the cell is provided by a Wenking "ST72" potentiostat, which supplies a cell potential which is controlled by the signal across its "voltage input" terminals. This signal was supplied by a scanning potentiometer. A reverse switch on the potentiometer permitted scanning up and down.

Figure 6.3

Dummy Cell

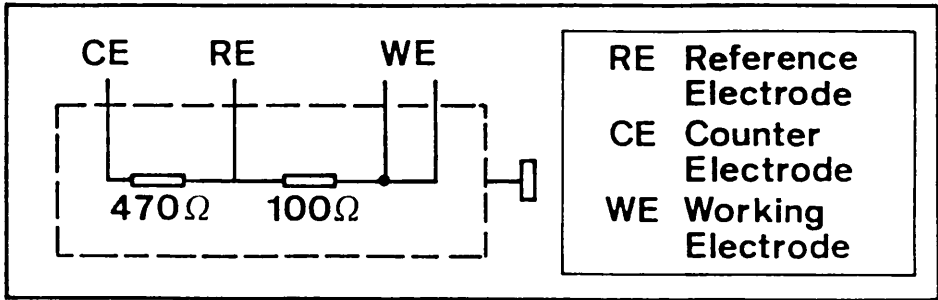
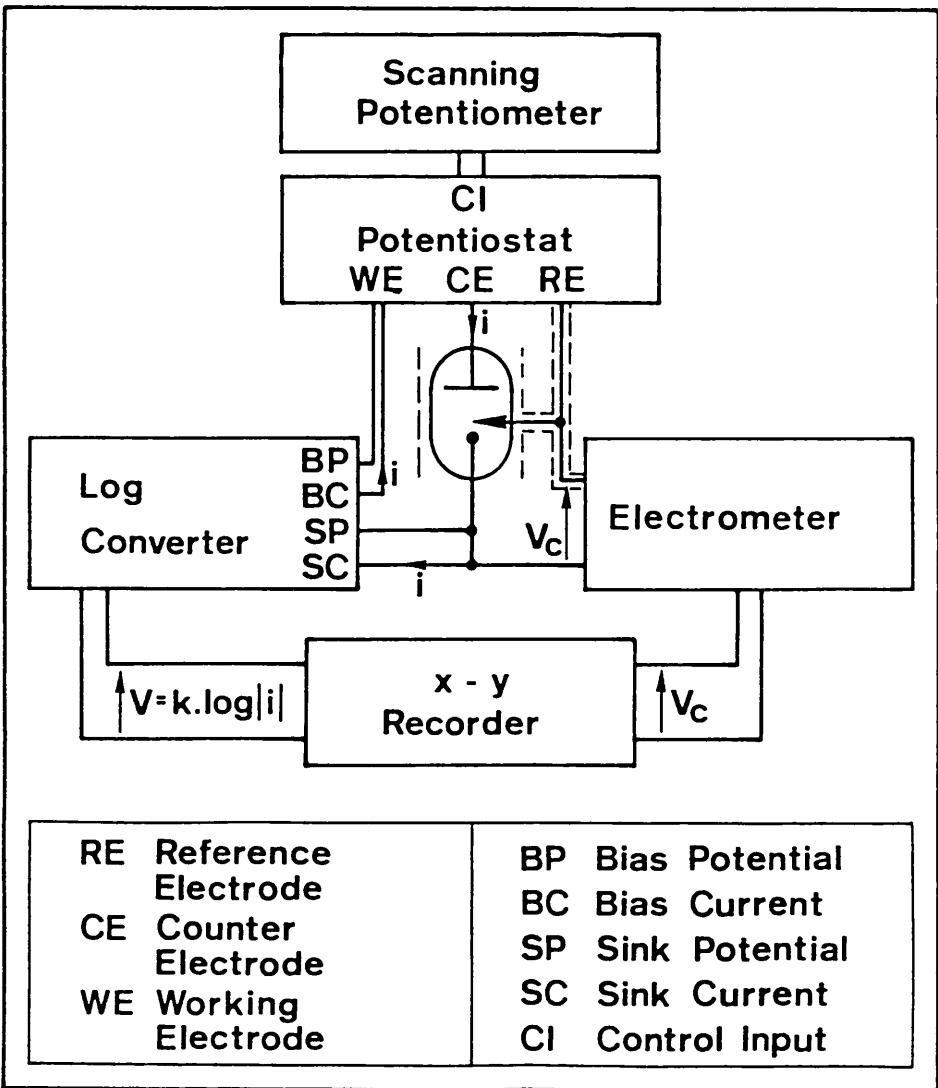


Figure 6.4

Chronopotentiometric Apparatus



6.2.1.3 The Testing

Before testing the cell was rinsed out twice with distilled water. The specimens were degreased with acetone and fitted in the cell which was filled with electrolyte. A potential of -1200 mV relative to the standard calomel electrode, was applied to the specimen for $\sim 1.5\text{ks}$ to strip off its oxide film. The potential was then ramped upwards at a rate of 10, 20, 50 or 200 mV/min when either the measured potential reached 600mV vs SCE or the cell current reached 100mA the ramp direction was reversed and the potential was swept downwards. This was continued till the specimen was cathodically polarized when the test was concluded.

The pitting potentials usually showed as sharply defined changes of gradient on the anodic polarization curves with a rapid increase of current showing at the pitting potential, E_p , see Figures 6.7 to 6.12. Where there was no sharply defined pitting potential, but where there was still a rapid rise in the cell current beyond a transitional potential range, the pitting potential was taken as the intercept of the extrapolations of the sections of the polarization curve above and below the transitional potential range.

The corrosion potential was taken as the potential at the intercept of the anodic and cathodic linear sections of the polarization curve to either side of the zero crossing (The so called Tafel or blackboard method of estimation).

6.2.1.4 The Minimisation of Electrical Noise

Early on in the investigation it became clear that electrical noise was obscuring measurements of cell currents of less than $\sim 50\mu\text{A}$. This prevented the determination of the corrosion potential, the corrosion current density and the pitting potential.

The following measures were taken to reduce the noise:-

1. A metal screen was used to shield the cell from electrical fields.
2. The electrode and ground connections were arranged so as not to form rings, to prevent the pick up of magnetic fields.
3. Connections were made with the minimum lengths of cable that were practical.

A low pass filter was used to increase the response time of the log converter from $\sim 1\text{ms}$ to $\sim 50\text{ms}$.

The log converter raises the threshold for d.c. measurement by the RMS average of each ripple current passing through. So in an attempt to extract extra information from the cell, the current was monitored by measuring the potential difference across a 100Ω , 4W resistor in series with the counter electrode. The x-y recorder was changed for an x-y-y recorder and the potential across the load resistor plotted on the second y-pen, the other two signals being monitored as before.

6.2.1.5 Crevice Corrosion

A ring of local corrosion damage was found in some of the tested specimens. This was due to crevice corrosion in the part of the specimen in contact with the PTFE cell. This damage occurs because the gap between the specimen and its holder can ~~from~~^{be} a ready made pit. Although care was taken to prepare flat specimens and fit them carefully in place this problem was not overcome. Where there was evidence of crevice corrosion, tests were repeated. An attempt to seal off the edges of samples with lacquer was entirely unsuccessful. A crevice formed under the lacquer.

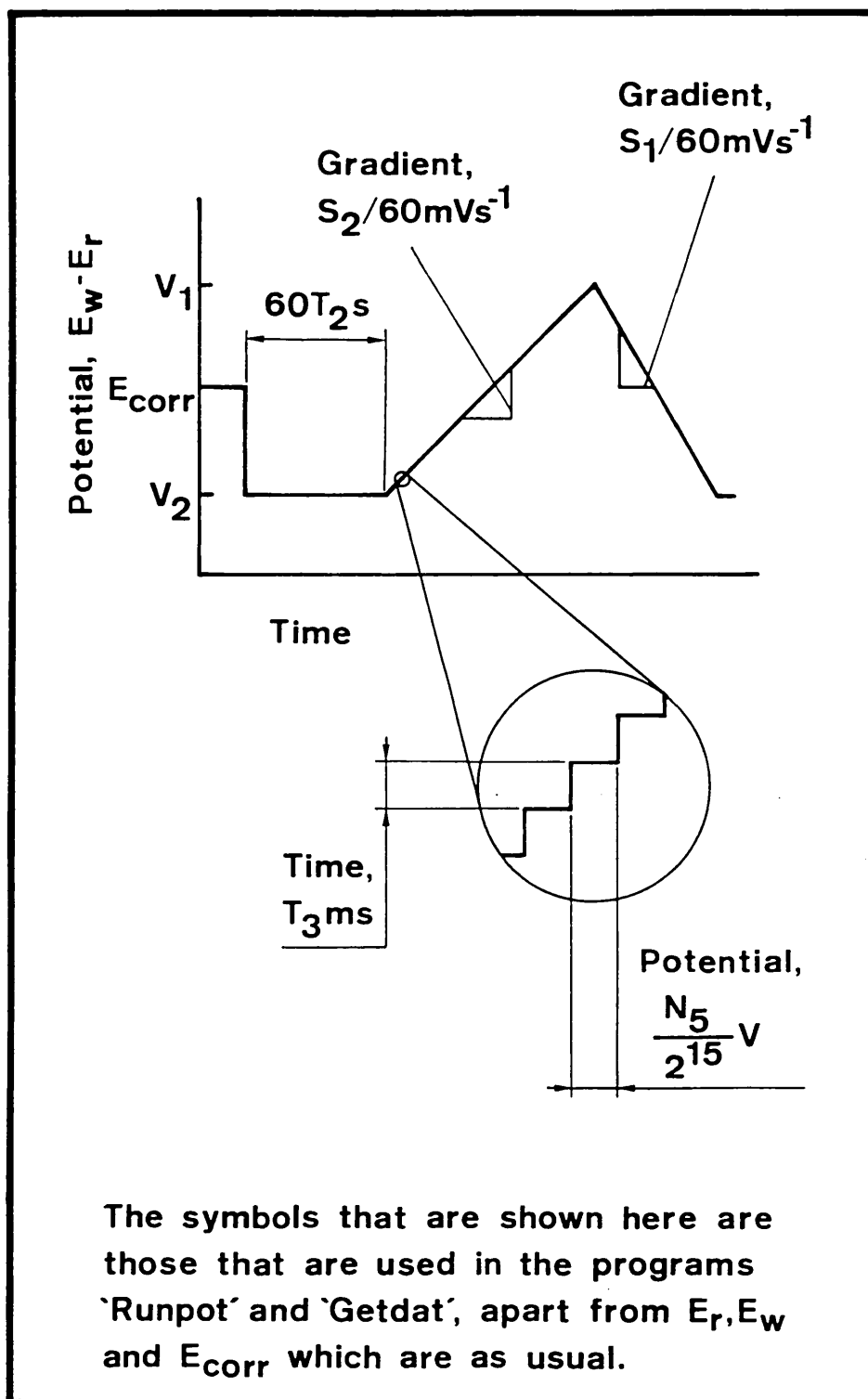
6.2.1.6 Computer Controlled Testing

A Hewlett Packard "HP85" micro-computer has been interfaced with a potentiostat and programmed to control and monitor an electrochemical cell through a potential scanning test. This system allows fully automated chronopotentiometric corrosion testing. A test follows the standard sequence of cathodic oxide stripping followed by a potential sweep upwards to either a predetermined maximum cell current or potential, after which the cell potential is ramped downwards eventually into the cathodic region where the cell is finally held. The progress of these changes is shown in Figure 6.5.

During a test the data gathered is displayed on the micro-computer's screen

Figure 6.5

The Potential History of a Potential Sweep Test



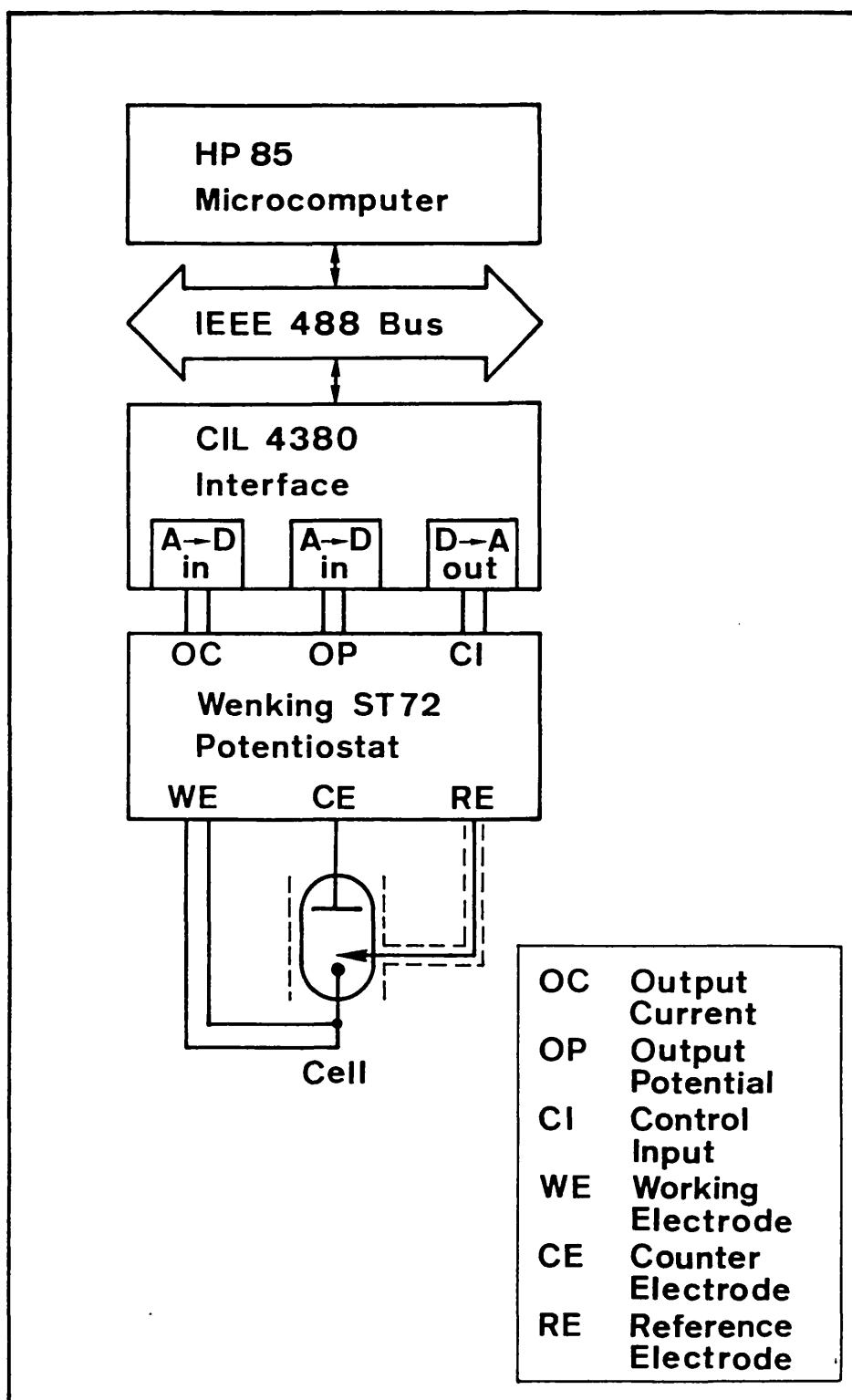
as a plot of potential against $\log|\text{current}|$. This graph is printed after a test. It is possible to selectively enlarge part of the plot, to allow for example, for the accurate determination of pitting potential. The data from a test is stored on magnetic tape. A program written to carry out the various functions that are described here is listed and annotated in Appendix A.6.1. Another program was written to retrieve test data from magnetic tape after which the data can be plotted and selectively enlarged. This program is listed and annotated in Appendix A.6.2. The electrical circuit that was used is shown in Figure 6.6.

6.2.1.7 Interfacing the Micro-Computer and the Potentiostat

The micro-computer is interfaced with the potentiostat by a commercially available interface the CIL Electronics "PCI 6380". The micro-computer is linked to the interface by an IEEE 488 bus. The micro-computer is programmed to output a voltage in the form of an ASCII. This digital signal is converted to an analogue signal in the range from -10V to 10V and output across the "voltage input" terminals of the potentiostat. This voltage is increased stepwise, a step being taken for each measurement of current and voltage.

Two readings are taken from the cell, the cell current and the potential difference between the working electrode and the reference electrode. The interface

Figure 6.6
Microcomputer Controlled Chronopotentiometric
Apparatus



measures these signals from the "recorder output" terminals of the potentiostat. These terminals provide buffered voltages relative to virtual ground corresponding to the cell current and the cell potential. These signals are converted to ASCII and set to the micro-computer. Digital filtering is carried out by the interface by averaging each sixteen signal readings. The cell potential is measured over the range from -10V to 10V and sent to the micro-computer by way of the interface. The ± 15 bit resolution of the interface provides an accuracy of $\pm 150^{300} \mu\text{V}$, more than adequate for voltage measurement. Autoranging is necessary to allow accurate measurement of $\log|\text{current}|$ over the five decades from $1\mu\text{A}$ to 100mA . This is accomplished by using the variable gain facility of the interface. The cell current is initially read over the range from -100mA to +100mA. A gain appropriate to a current range of -100mA to 100mA, -10mA to 10mA or -1mA to 1mA is then selected and the current is measured again. Further digital filtering of both the measured signals is accomplished by repeating cell current and potential readings as often as time permits during each voltage step. At a ramp rate of 20mV/min this allows for about thirty readings to be averaged for each measurement, effectively filtering out noise even at the bottom end of the current range.

6.2.1.8 Observation of Pits

Scanning electron images of the surfaces of treated material were photographed

before and after potential scanning. The morphology of the pits and the location of the pits with respect to the microstructure of the tracks were observed.

The cross-sections of pitted material were also examined with a view to characterising the pit morphologies and locations.

6.2.2 Intergranular Corrosion Testing

The oxalic etch test as specified in ASTM-A262-A has been used to assess the intergranular corrosion susceptibility of laser surface melted 316 steel. The test allows the rapid identification of material that is resistant to intergranular attack. Samples of material that had been laser surface melted under the conditions given in Table 6.2 were ground and polished. Etching was in a solution of 100g oxalic acid in 900ml water at a current density of $100\mu\text{Am}^{-2}$ for 90s. The etched surfaces were characterised as "step" or "ditch" depending on the appearance of the grain boundaries. If the grain boundaries are preferentially attacked ditches are formed and the possibility of intergranular attack remains. Steps result from the different attack rates of variously oriented grains and indicate a metallurgical structure that is resistant to intergranular attack.

Material showing etch ditches was tested in boiling acid to determine its intergranular cracking susceptibility. The test that was adopted was the copper sulphate - copper - sulphuric acid test as specified in ASTM-A262-E. This test has the merits of only taking a day and not using hydrofluoric acid. It detects intergranular attack associated with the formation of chromium rich carbides.

Samples in the form of 3 x 10 x 100mm rectangular slabs were laser melted under the conditions summarised in Table 6.2. These samples were boiled in reflux alongside solution treated material that was tested for comparison. The samples were examined under a binocular microscope and by the dye penetrant method to ensure that they were crack free before testing. The test solution was made up of 200g of hydrated copper sulphate and 200ml of sulphuric acid diluted to 2l with distilled water. Copper pellets were added to accelerate intergranular attack. The solutions, pellets and specimens were boiled in reflux for a day, after which the samples were removed.

After testing the samples were examined for cracks under a binocular microscope and by the dye penetrant method. Where no cracks were found the samples were subjected to the Π rad bend test to reveal undetected cracks. This was carried out by clamping the specimens against a rod in a vice and using a hammer. Final bending was carried out by closing the specimens around the rod in the vice.

6.3 RESULTS

6.3.1 Chronopotentiometry

The potentials which were measured against the standard calomel electrode are reported relative to the standard hydrogen electrode, the SHE according to convention. The results fall into three sections:

1. Those concerned with the development of the experimental technique. This work was carried out on 316 steel - Section 6.3.1.1.

TABLE 6.2

TREATMENT CONDITIONS OF, AND PRESENCE OF CRACKING IN 316 STEEL

Condition	Cracks before Testing ?	Cracks after Testing ?	
	Dye Penetrant	Dye Penetrant	π rad Bend
Solution Treated at 1050°C	No	No	No
Sensitized at 650°C for 24 hours.	No	Yes	Yes
Sensitized as above then laser surface melted at: V = 30mms ⁻¹ ϕ = 1.5mm P = 1.5kW A = 500 μ m	No	No	No

2. Those concerned with the behaviour of tempered, hardened and laser surface melted 420 steel. This work was carried out at a scan rate of 20mV/min - Section 6.3.1.2.
3. Those concerned with the behaviour of sensitized, solution treated and laser surface melted 316 steel. This work was carried out at a scan rate of 20mV/min - Section 6.3.1.3.

6.3.1.1 Experimental Technique

- The Reduction of Noise and the Effect of Digital Filtering

The analogue system modified to minimise noise, allowed for the measurement of current densities down to $\sim 0.02 \text{ Am}^{-2}$. However some runs still had to be repeated so that the information at low current densities could be obtained. The circuit with the dummy cell did not produce noise hiding the signal at current densities of more than $\sim 0.1 \text{ Am}^{-2}$ when it was used with the various noise reducing measures.

When the computer based system was used with only the filtering available from the interface, noise prevented the extraction of information at current densities of less than $\sim 1 \text{ Am}^{-2}$. However resolution down to 0.01 Am^{-2} is possible with the extra filtering that is gained by averaging the maximum possible number of the already filtered measurements from the interface. At 20mV/min this allows thirty measurements from the interface to be averaged to give each final measurement.

- Polarization Curves at Four Scan Rates -
Figure 6.7

The corrosion potential of the system is independent of scan rate being -100mV vs. SHE for all the curves. There is little difference between the polarization curves for scan rates of 10 and 20 mV/min which both show pitting potentials of ~600 mV vs SHE and these two are shown as one. At the higher scan rates of 50 and 200 mV/min the pitting potential is higher, the higher the scan rate. The polarization curve for a sweep rate of 50mV/min does not show a clearly defined pitting potential. This may be due to crevice corrosion. A ring of crevice corrosion attack was seen on the specimen after testing. At 200 mV/min the features that show on the polarization curve are modified before the onset of pitting at ~980mV vs. SHE.

- Repeatability of the Pitting Potential Measurements

Five polarization curves were taken at a scan rate of 20mV/min to evaluate the repeatability of the pitting potential measurements. This gave pitting potentials of 568, 588, 593, 613 and 633 mV vs. SHE. These data have a mean value of 599 mV and a standard deviation of 25 mV.

Figure 6.7
Effect of Varying Scan Rate on the
Polarisation Curve of Solution Treated
316 Steel

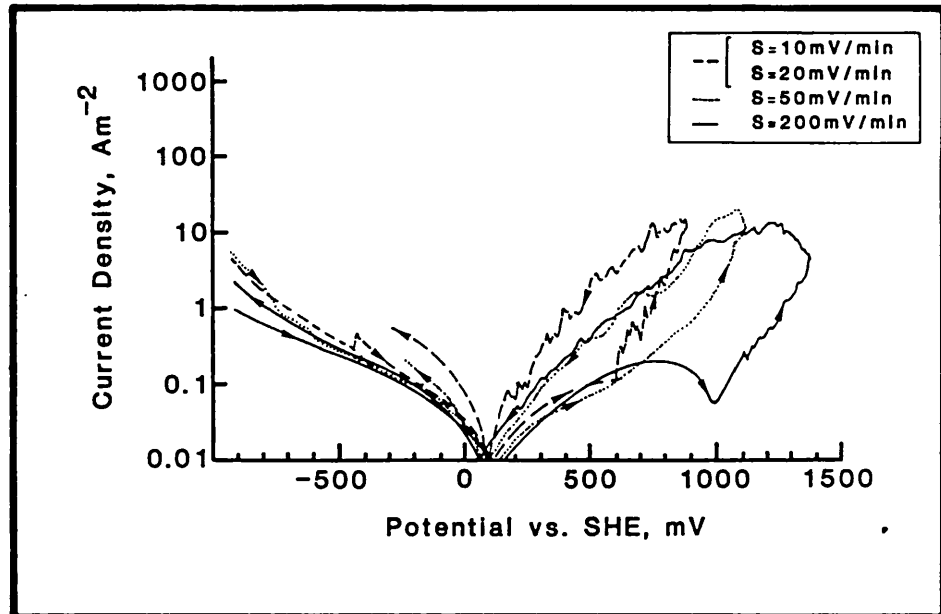
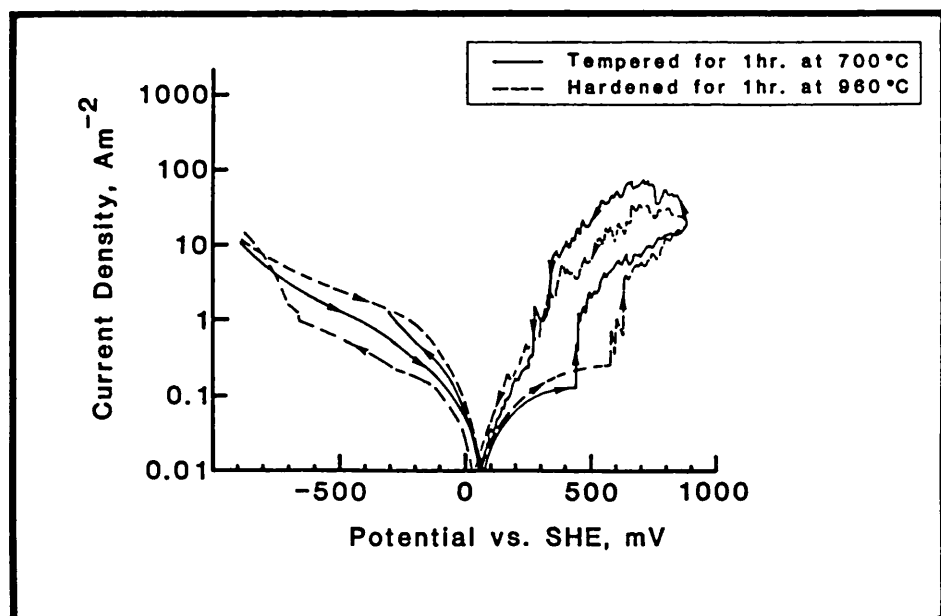


Figure 6.8
Polarization Curves for Fully Tempered
420 Steel and Hardened 420 Steel



6.3.1.2 Polarization Studies on 420 Steel

- Behaviour of the Tempered Steel and the Hardened Steel - Figure 6.8

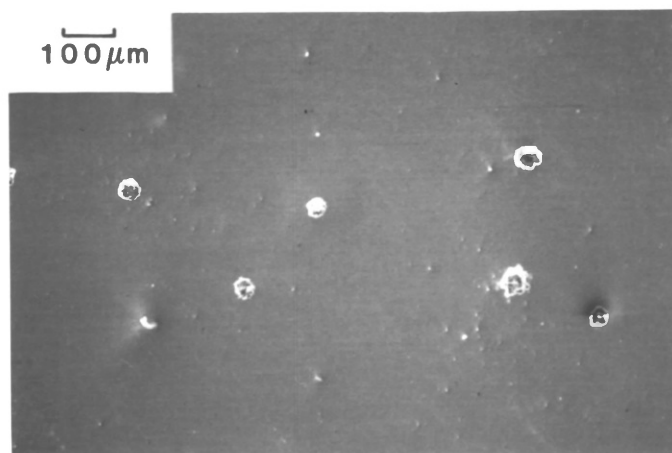
The two polarization curves, show similar features with regions of passivation followed by a sharply defined breakdown potential on the ramp upwards. The passivation current density is slightly higher for the hardened material than it is for the tempered material. The breakdown potential in the hardened condition, ~580mV vs. SHE is higher than the breakdown potential in the tempered condition where it is ~440mV vs. SHE. The corrosion potential is ~60mV vs. SHE for both conditions. No repassivation shows on the reverse sweep of the material in either condition.

The pit distributions and shapes are shown in Photographs 6.1 and 6.2 for the hardened material and Photographs 6.3 and 6.4 for the tempered material. Both conditions show rounded pits with unclustered distributions, although the pits are smaller and more closely spaced in the hardened condition.

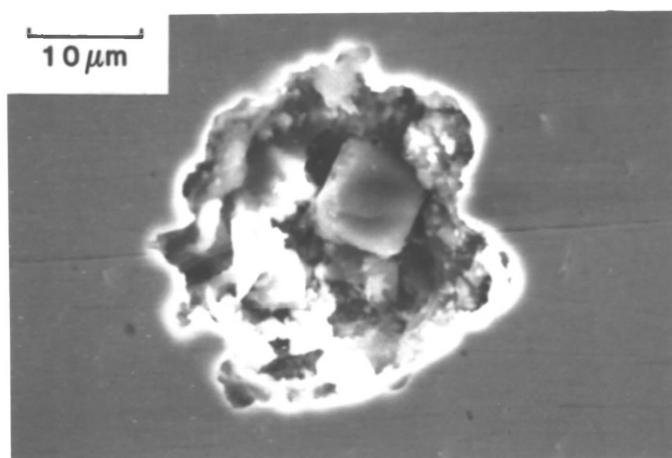
- Behaviour of the Steel after Laser Surface Melting at Three Traverse Speeds - Figure 6.9

The specimens that were melted at traverse speeds of 15 and 30 mms^{-1} show similar curves to those for the hardened steel and the tempered steel. However, the

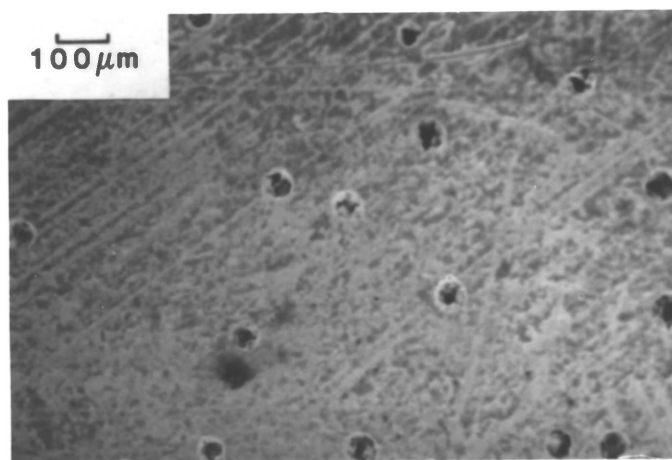
Photograph 6.1 Pit distribution in hardened 420 steel



Photograph 6.2 Pit shape in hardened 420 steel



Photograph 6.3 Pit distribution in tempered 420 steel



Photograph 6.4 Pit shape in tempered 420 steel

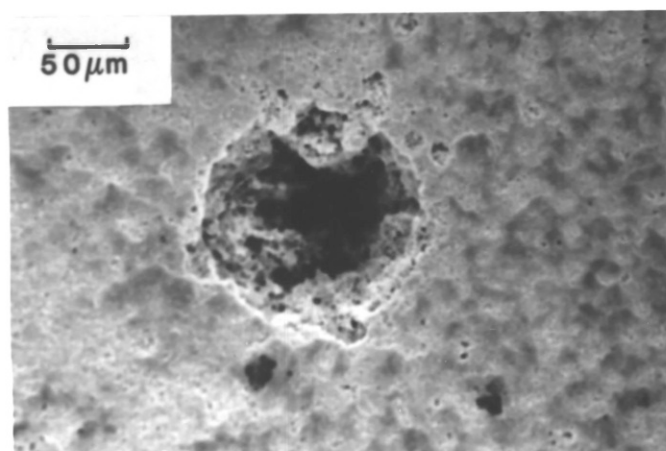


Figure 6.9
Polarisation Curves for 420 Steel Laser
Surface Melted at Various Traverse
Speeds

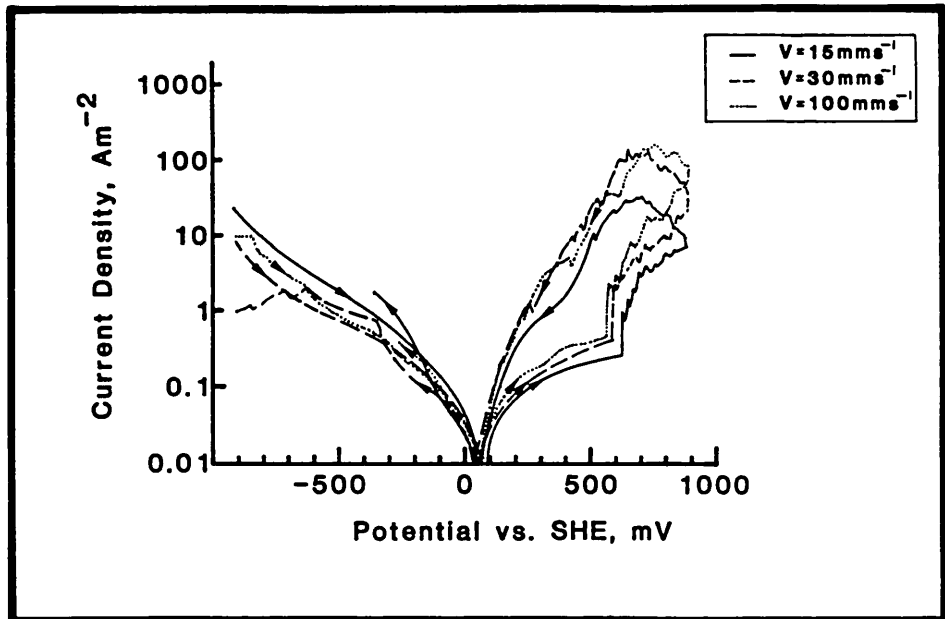
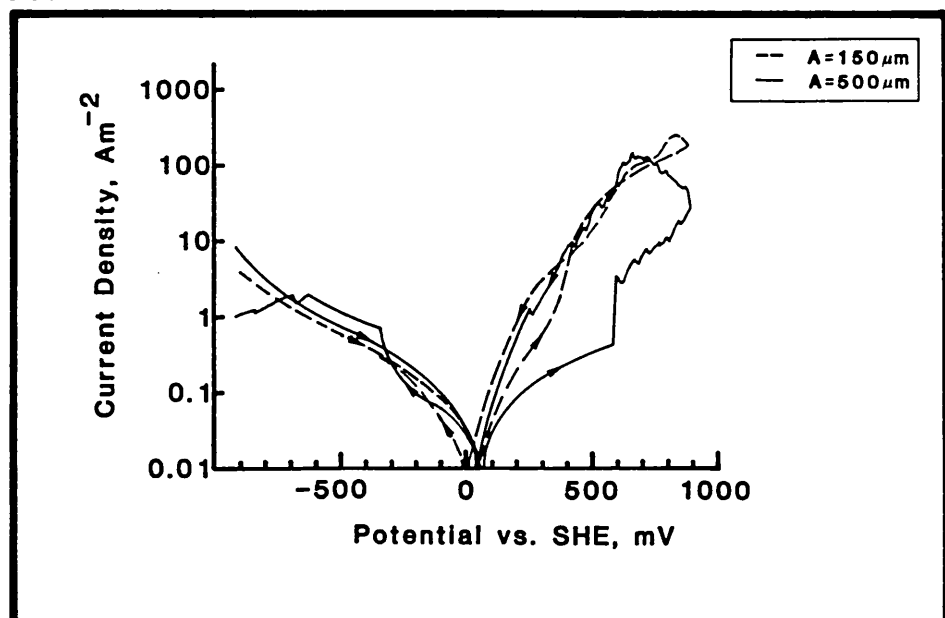


Figure 6.10
Polarization Curves for 420 Steel Laser
Surface Melted at Two Inter-Track
Advances



passivation current densities of the laser treated specimens are higher than those of the tempered and the hardened specimens. The pitting potential of the specimen that was melted at a traverse velocity of 15 mms^{-1} , at 630mV vs. SHE, is higher than that of either of the conventionally treated specimens. The pitting potential of the specimen that was melted at a traverse velocity of 30 mms^{-1} , 570 mV vs. SHE, lies between the values for the conventionally heat treated specimens. The specimen that was treated at a traverse velocity of 100 mms^{-1} shows a somewhat lower pitting potential of $\sim 550 \text{ mV}$ vs. SHE.

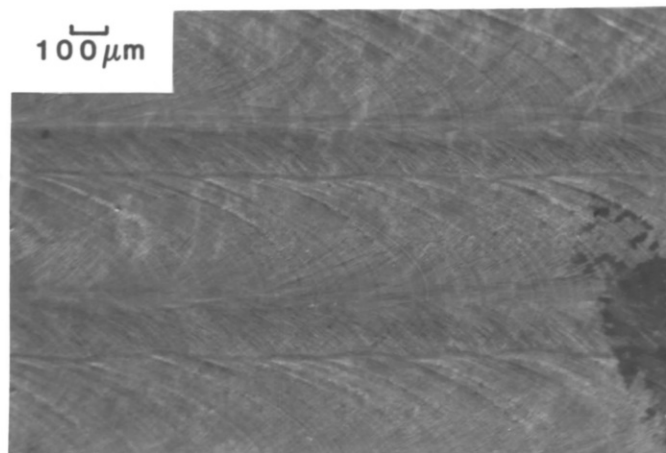
Photograph 6.5 shows a scanning electron image of the specimen that was laser surface melted at a traverse speed of 30 mms^{-1} before the potential sweep test and indicates the surface topography before pitting. Photograph 6.6 shows a scanning electron image of the same specimen after testing and indicates the pit distribution. The pits lie along the centrelines of the individual melt tracks. The pit shapes are irregular and

stretched out in the direction of the centrelines of the melt tracks (see Photographs 6.6 and 6.7).

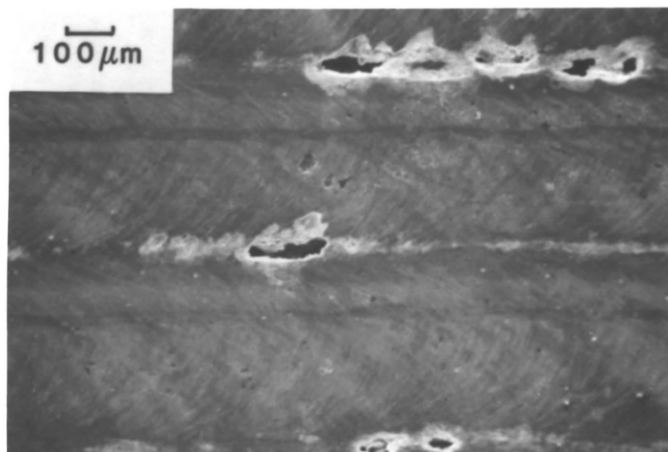
- Behaviour of the Steel after Laser Surface Melting at Two Inter-Track Advances - Figure 6.10

The curve for the inter-track advance of $5400 \mu\text{m}$ is as described before for the

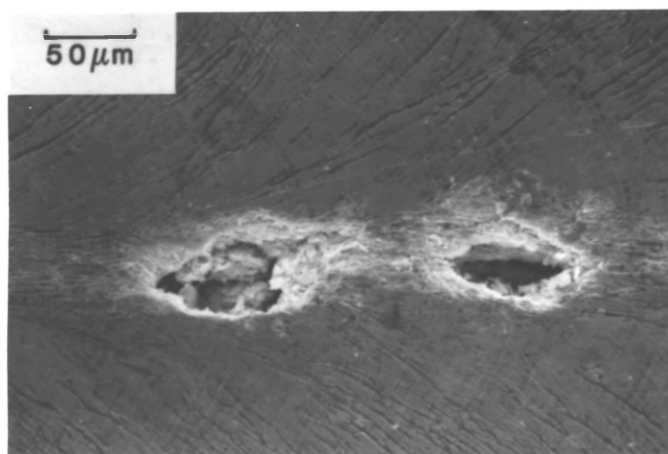
Photograph 6.5 Laser melted tracks in 420 steel ($A = 500\mu\text{m}$, $P = 1.5\text{ kW}$, $V = 30\text{mmms}^{-1}$ and $\Phi = 1.5\text{mm}$)



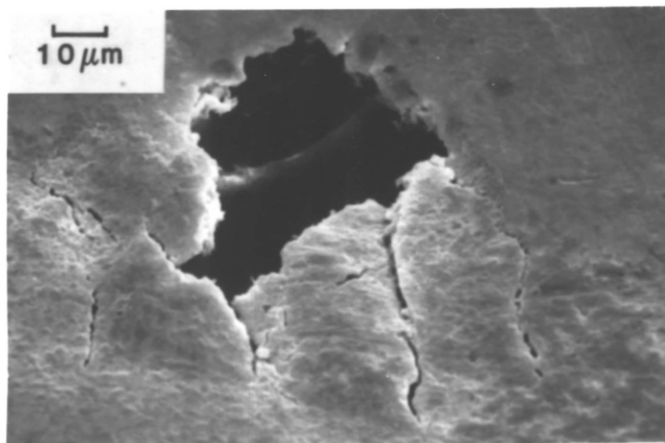
Photograph 6.6 Pit distribution in laser melted tracks in 420 steel ($A = 500\mu\text{m}$, $P = 1.5\text{ kW}$, $V = 30\text{mmms}^{-1}$ and $\Phi = 1.5\text{mm}$)



Photograph 6.7 Pit shape in laser melted tracks in 420 steel ($A = 500\mu\text{m}$, $P = 1.5\text{ kW}$, $V = 30\text{mmms}^{-1}$ and $\Phi = 1.5\text{mm}$)



Photograph 6.8 Pit shape in laser melted tracks in 420 steel ($A = 150\mu\text{m}$, $P = 1.5\text{ kW}$, $V = 30\text{mmms}^{-1}$ and $\Phi = 1.5\text{mm}$)



specimen produced at a traverse velocity of 30mm s^{-1} . The specimen that was produced at an inter-track advance of $150\mu\text{m}$ shows no passivation plateau. It also shows a higher anodic current density on the ramp upwards through the anodic potential range than any of the other 420 steel specimens tested here.

Photograph 6.8 shows the cracked irregular morphology of a pit in the sample produced at an inter-track advance of $150\mu\text{m}$.

6.3.1.3 Polarization Studies on 316 Steel

- Behaviour of the Sensitized Steel and the Solution Treated Steel - Figure 6.11

The solution treated steel shows a passivation current density of $\sim 0.12\text{A m}^{-2}$ before film breakdown at a potential of $\sim 600\text{mV}$ vs. SHE. The sensitized material shows a passivation current density about five times higher than that of the solution treated material but the same breakdown potential.

Photograph 6.9 shows the even distribution of the round etch pits in the solution treated material. Photograph 6.10 shows the random distribution of pits in the sensitized material. The pits are faceted with preferential attack showing at the grain boundaries (see Photographs 6.10 to 6.12). Small crystallographically oriented faceted etch pits are also evident in Photograph 6.12.

Figure 6.11
Polarization Curves for Solution Treated 316 Steel and Sensitized 316 Steel

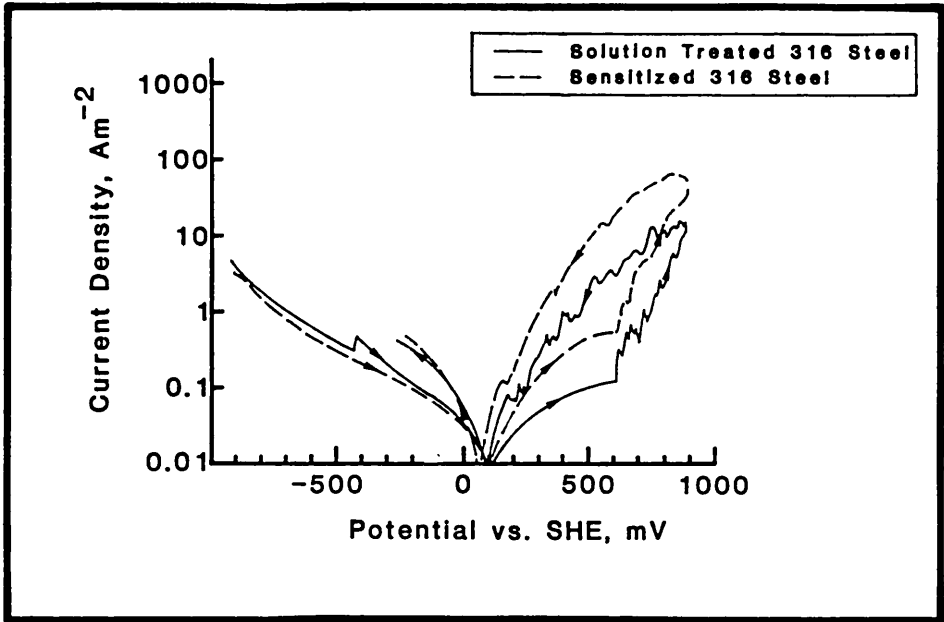
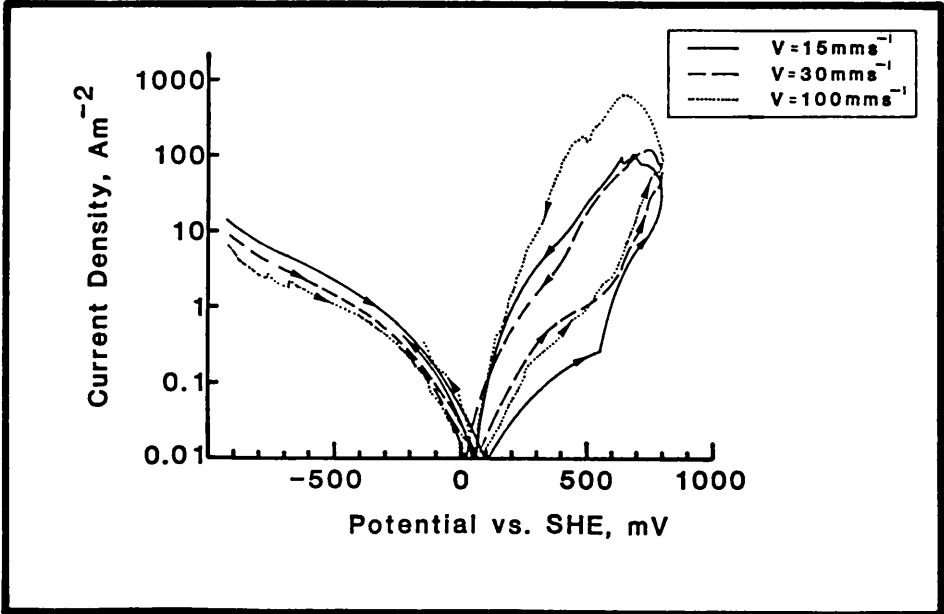
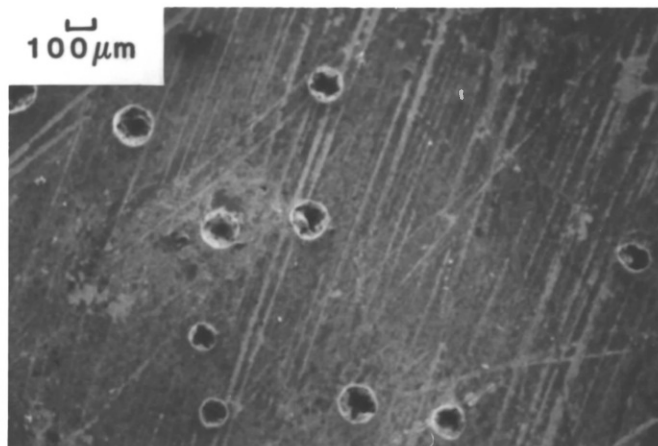


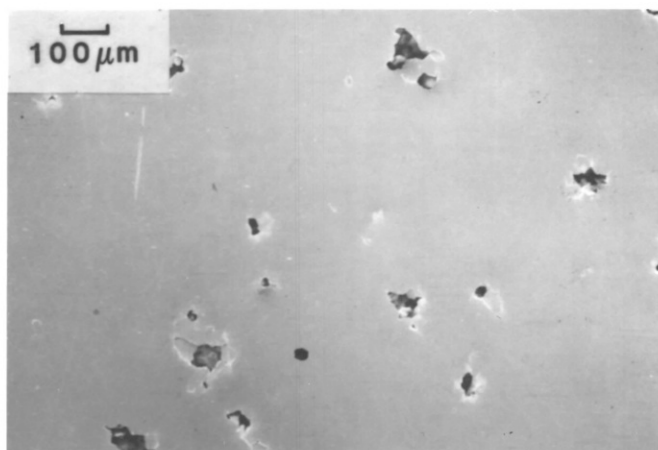
Figure 6.12
Polarisation Curves for 316 Steel Laser Surface Melted at Various Traverse Speeds



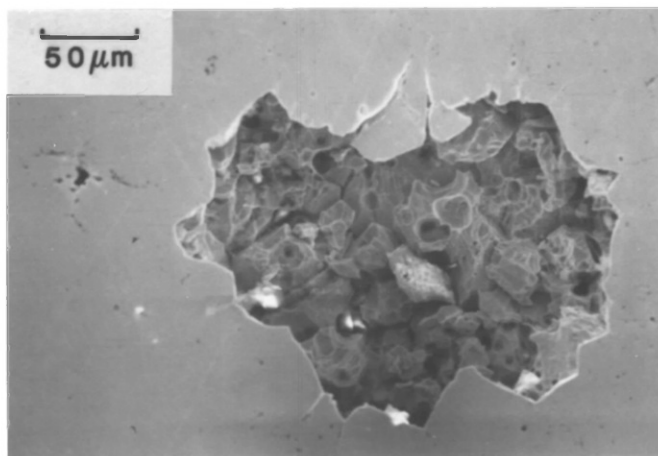
Photograph 6.9 Pits in
solution treated 316 steel



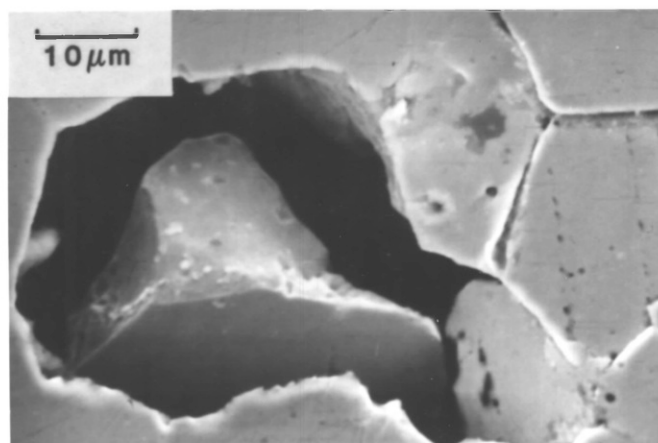
Photograph 6.10 Pit
distribution in sensitised
316 steel



Photograph 6.11 Pit shape
in sensitised 316 steel



Photograph 6.12 Pit shape
in sensitised 316 steel



- The Behaviour of the Steel after Melting at Three Traverse Speeds - Figure 6.12

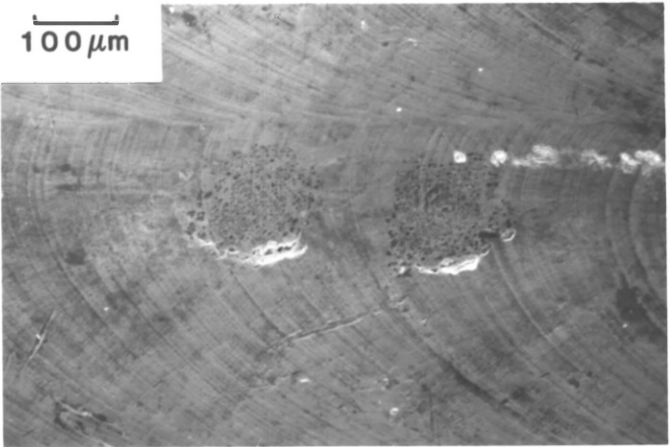
Laser surface melting at a traverse speed of 15mms^{-1} raises the current density through the anodic polarization regime over that for the solution treated steel and lowers the pitting potential to $\sim 540\text{mV}$ vs. SHE. These changes show to a greater extent on the polarization curve for a specimen melted at 30mms^{-1} . Still higher anodic current densities show on the polarization curve for the specimen melted at 100mms^{-1} .

Scanning electron microscopy showed that the pits lie towards the middle of the individual laser melted tracks, Photograph 6.13. It also showed the cracked irregular morphology of the larger pits, Photograph 6.14. Preferential attack^k was seen at the centres of the solidification cells with tentacle like strings of small ($\sim 2\mu\text{m}$ diameter) pits running together in bunches, Photographs 6.15 and 6.16.

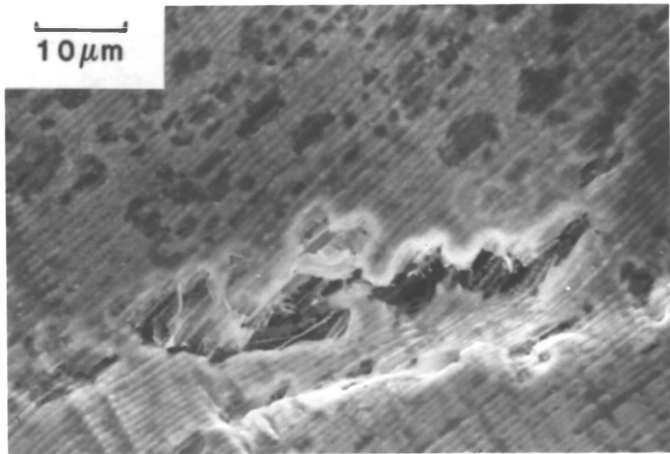
6.3.2 Intergranular Corrosion Testing

Before intergranular corrosion testing the specimens were checked by the dye penetrant method to find if they were crack free, and no cracking was found. After boil-in-acid testing both the laser surface melted and the solution treated specimens showed no cracking unlike the sensitized specimen which showed cracking after testing. The results are summarized in Table 6.2.

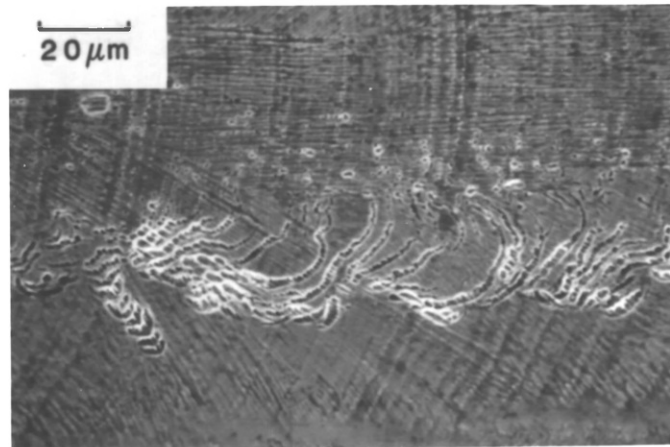
Photograph 6.13 Pit distribution in laser melted tracks in 316 steel ($A = 500\mu\text{m}$, $P = 1.5\text{ kW}$, $V = 30\text{mmms}^{-1}$ and $\Phi = 1.5\text{mm}$)



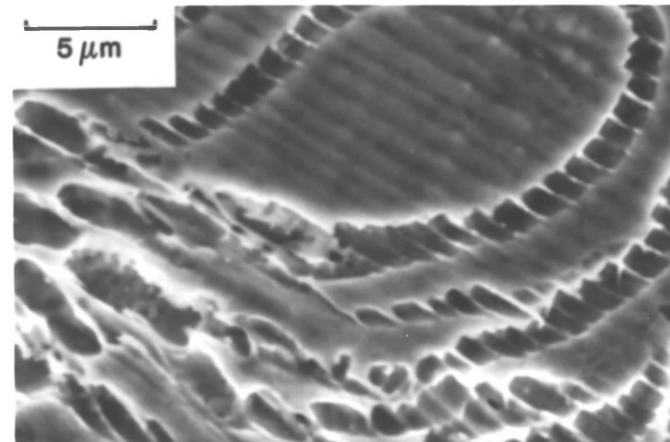
Photograph 6.14 Pit shape in laser melted tracks in 316 steel ($A = 500\mu\text{m}$, $P = 1.5\text{ kW}$, $V = 30\text{mmms}^{-1}$ and $\Phi = 1.5\text{mm}$)



Photograph 6.15 Pit distribution in laser melted tracks in 316 steel ($A = 500\mu\text{m}$, $P = 1.5\text{ kW}$, $V = 30\text{mmms}^{-1}$ and $\Phi = 1.5\text{mm}$)



Photograph 6.16 Pits in laser melted tracks in 316 steel ($A = 500\mu\text{m}$, $P = 1.5\text{ kW}$, $V = 30\text{mmms}^{-1}$ and $\Phi = 1.5\text{mm}$)



6.4 DISCUSSION

6.4.1 Chronopotentiometry

6.4.1.1 The Experimental Technique

- The Reduction of Noise and the Effect of Digital Filtering

Both the analogue system with the precautions taken to minimise noise on all but the noisiest runs and the fully digitally filtered system allow for the accurate measurement of corrosion and pitting potentials. The low level of noise on the polarization curves obtained with the dummy cell indicates that the noise is partially due to instabilities in the cell itself. In the region of passivation and subsequent film breakdown these instabilities are associated with the degradation and subsequent reformation of the passive film.

- The Effect of Scan Rate

Subsequent testing was carried out at 20mV/min on both alloys. This is twice the scan rate specified in the standardised test, ASTM G5-72. This scan rate was chosen because it was seen to give the same polarization curve as the 10mV/min scan, while permitting quicker testing. In all other respects the requirements of ASTM G5-72 were met.

By varying the scan rate it was possible not only to shift the measured breakdown potential but also to modify the features that are observed. It is known that there is an induction time associated with the formation of corrosion pits. Schwenk (1964) has pointed out that the cell current does not increase at once when the pitting potential is applied but only after an induction time which may be several hours long. This indicates that pitting potential measurements based on chronopotentiometric techniques may be too low. This would appear to be the case for the 200mV/min scan reported here. Because of this indication of an induction time dependance the slow scan technique was adopted here.

The tendency reported above is not always the case. Morris and Scarberry (1972) have measured the potentials of austenitic stainless steels after rapid potential scanning ($\sim 1\text{V/min}$) and observed lower values of pitting potential after slow scanning. Bond and Lizlovs (1968) have reported similar behaviour for Fe-13.5%Cr-2.9%Mo steel in 1M NaCl. Other later work by Lizlovs and Bond (1975) on ferritic Fe-Cr-Mo alloys in an ambient temperature chloride solution compared fast and slow scanning. This showed similar pitting potentials (within 75mV) from the two techniques. This work did not show consistently higher potentials from either technique. Where there was a decrease in measured pitting potential with increasing scan rate this trend was

explained by considering the build up of a passive film during a potential scan test. At high scan rates there was less time available for the build up of a passive film, producing a thinner passive film that would breakdown at a lower potential.

- Repeatability of the Pitting Potential Measurements

The standard deviation in the measured values of pitting potential of 25mV while adequate for the purposes of this study compares unfavourably with reproducibilities claimed in the literature. Wilde and Williams (1971) have reported clearly defined pitting potentials with a reproducibility between replicate experiments of less than 10mV for austenitic steels in 1M NaCl.

6.4.1.2 Polarization Studies of 420 Steel

- Behaviour of the Tempered Steel and the Hardened Steel

The slightly higher passivation current density of the hardened material cannot readily be explained in terms of the behaviour of the passive film, because the more uniform distribution of chromium in the fully hardened material would be expected to enhance the resistance of the passive film to electrochemical attack and reduce the passivation current density. The higher pitting potential and the smaller pits in the hardened material can however be explained in terms of the

even chromium distribution associated with this condition before the formation of chromium rich carbides during tempering (Truman 1976).

- The Effect of Traverse Speed

Laser surface melting can modify the corrosion behaviour of the material by redistributing solute, by vapourising non-metallic inclusion and by introducing residual stress.

Laser surface melting will dissolve up the carbide particles and redistribute their chromium and other alloying elements. The as solidified structure will be modified by back-tempering by neighbouring successive tracks. An increase in the treatment speed will tend to minimize any such tempering although this possible benefit will be partly undone by the increased interaction between successive tracks as tracks are moved closer together in order to cover the surface at the higher traverse speeds.

That the pits follow the centrelines of the tracks suggests that the effect of backtempering is not as strong as the other microstructural, segregation and stress effects that vary across the individual tracks.

The residual stress measurements reported in Chapter 4 indicate that the higher traverse speeds will introduce higher residual stresses into the 420 steel. The smaller inter-track advances that were

adopted at the higher speeds, will also tend to increase the residual stress. Residual stresses have been reported for the conditions used here (Lamb et al 1983). These measurements show an increase of residual stress of $\sim 250\text{MPa}$ over the traverse velocity range from 15 to 100mms^{-1} . Tensile stresses have been shown to adversely affect the pitting resistance of a 12CrMoV steel (Chastell et al 1979) and the increasing residual tensile stresses at high speeds may account for the poor corrosion behaviour of the 420 steel at these speeds.

It is not likely that the vapourisation of manganese sulphide inclusions will play a role in enhancing the pitting resistance of the laser treated steel as the manganese and sulphur contents of the steel should not give rise to such inclusions.

- Effect of Inter-Track Advance

By reducing the inter-track advance it is possible to increase the overlap between tracks to more than half a track width and remelt the centreline of the tracks, the region that is most vulnerable to pitting attack, potentially enhancing the pitting corrosion resistance of the material.

A specimen was produced with an inter-track advance of $150\mu\text{m}$ giving an overlap of $\sim 80\%$. The anodic polarisation curve of this specimen showed high anodic current densities and no passivation plateau. These indications of poor

corrosion resistance may be interpreted in terms of the increased back tempering and tensile residual stresses that are developed at this small advance (see Figure 4.5). The tempering shows over a distance of $\sim 500\mu\text{m}$ after etching, indicating modified electrochemical behaviour. If the carbides that are formed during back-tempering are chromium rich the associated chromium depletion of the matrix would be expected to reduce the stability of the passive film and reduce the corrosion resistance of the treated layer.

6.4.1.3 Polarization Studies on 316 Steel

- Behaviour of the Sensitized Steel and the Solution Treated Steel

The higher passivation current density in the sensitized material can be interpreted in terms of the local chromium depletion at the grain boundaries of the sensitized material. Such depletion reduces the stability of the passive film at the grain boundaries allowing local electrochemical attack and an increase in the passivation current density. The morphology of the etch pits indicates local attack at the grain boundaries supporting this view.

Similar results have been obtained by other investigators, Henthorne (1972) and Osazawa Bohnenkamp and Engell (1966) have also found an increase in the passivation current density of about one decade after sensitization.

- Effect of Laser Surface Melting at a Range of Traverse Speeds

Laser surface melting will affect the 316 steel similarly to the way it affects the 420 steel, by redistributing solute, by introducing residual stresses and by vapourizing non-metallic inclusions. When the tempered 420 steel is melted the chromium carbides are dissolved and their chromium is redistributed enhancing the stability of the passive film. Melting the 316 steel will also dissolve up any carbides in sensitized material and redistribute their chromium, but as the carbon content of the 316 steel is lower this will only release a correspondingly low volume fraction of chromium.

As in the 420 steel there is a trend towards impaired pitting resistance at the higher treatment speeds; unlike the 420 steel the manganese and sulphur contents are sufficient for pit initiating manganese sulphide inclusions to form. This raises the possibility of the laser having vapourised these inclusions and enhanced the corrosion resistance of the steel (Sedriks 1984); it is possible that the more severe heating at low traverse speeds could lead to more efficient vapourising of these inclusions, giving rise to less impaired pitting corrosion resistance at low speeds.

The pits lie on or near the centre lines of the individual tracks. The effect of chromium and molybdenum depletion at the centres of the cells shows as preferential

attack there. Similar behaviour has been observed in corrosion pits in welded austenitic stainless steels (Garner 1979). It is possible that the tentacle like pit distribution follows the bands of solute segregation which show on etching (see Photograph 2.1).

Increasing traverse speed will suppress the formation of delta-ferrite and reduce the cell size, while the composition of the centres of the cells is independent of traverse speed in the range of speeds that were used for the pitting studies. In as much as the composition and crystal structure of the centres of the cells are not affected by traverse speed and pitting occurs preferentially at the cell centres the variation of pitting resistance with traverse speed must be due to other effects, possibly residual stress effects, although the residual stress only increases slightly over the treatment range from 15 to 100mms⁻¹ (Lamb et al 1983).

6.4.2 Intergranular Corrosion Testing

The observed cracking in the sensitized material and the absence of cracking in the annealed material after the boil in acid test serve to confirm the effectiveness of the test. The absence of cracking in the laser surface melted material indicates the effectiveness of laser surface melting as a means of restoring the intergranular corrosion resistance of the sensitized steel. This restoration is achieved by the stirring and rapid diffusion in the melt pool during laser surface melting which removes the thin regions of chromium depletion at the grain boundaries.

This observation confirms the work of Anthony and Cline (1978) who achieved a similar restoration of the intergranular corrosion resistance of sensitized material.

It also indicates that during resolidification and any subsequent heating and cooling cycles associated with back tempering, chromium depletion associated with chromium rich carbide formation does not occur at the newly formed grain boundaries.

6.5 CONCLUSIONS

A system has been developed which permits the automated chronopotentiometric testing of materials. Data from a test is logged, displayed as a graph and stored on magnetic tape.

A series of chronopotentiometric tests in 0.05M NaCl adjusted to pH10 by the addition of NaOH on conventionally heat treated specimens and specimens that were covered with overlapping laser melted tracks indicates the following:

1. The polarization curve of 316 steel in the solution treated condition is sensitive to scan rate at high scan rates (50 and 200 mV/min) while little difference shows between polarization curves determined at low scan rates (10 and 20 mV/min). This behaviour may be explained in terms of an induction time for film breakdown.
2. The polarization curve of 420 steel is sensitive to heat treatment with the polarization curve of the hardened material indicating a greater pitting resistance than the polarization curve of the tempered material (Pitting potentials of ~580mV and ~440mV vs. SHE show for the hardened and the tempered material).

3. The polarization curves for laser surface melted 420 steel are similar to the curve for the hardened steel for certain laser treatment conditions. At these conditions pitting occurs preferentially along the centre-lines of the melt tracks.
4. The polarization curve of laser surface melted 420 steel is sensitive to the laser processing conditions and indicates an absence of passivation for certain conditions ($P=1.5\text{kW}$, $A=150\mu\text{m}$, $V=60\text{mm}^{-1}$ and $\phi=1.5\text{mm}$).
5. The polarization curves of laser surface melted 316 steel show higher passivation current densities and lower pitting potentials than the solution treated material, indicating a degraded corrosion resistance associated with laser surface treatment. In the laser surface melted specimens the pits are distributed in tentacle like strings close to the centres of the melt tracks. The pits form by preferential attack of the chromium and molybdenum depleted centres of the solidification cells.

Laser surface treatment can restore the intergranular corrosion resistance of sensitized 316 steel, as indicated by a standardized boil-in-acid test (as specified in ASTM-A262-E).

CONCLUSIONS

420 Steel

Laser surface melting can produce surfaces that are macroscopically smooth and which are suitable for all but the most topography sensitive applications, such as bearing surfaces which would require subsequent grinding. A surface preparation of grit cleaning prior to laser surface treatment allows the melting of tracks with reproducible dimensions without introducing contamination. Treatment conditions were identified that produced conduction limited tracks on these surfaces over a range of traverse speeds from 10 to 400mm s⁻¹. This gives cooling rates in the range from $\sim 10^3$ to $\sim 10^6$ °C s⁻¹ with the higher cooling rates being associated with the higher traverse speeds.

The highly selective heat treatment achieved by laser surface melting produces hard layers on the steel (Vickers hardness ~ 510 H_V). The structure of the laser melt tracks is predominantly martensitic with a small volume fraction of retained austenite (the highest volume fraction of retained austenite that was indicated by x-ray diffraction was $\sim 13\%$). The high cooling rates that are associated with laser surface melting produce a higher volume fraction of retained austenite than conventional quenching and there is a trend towards an increased volume fraction of retained austenite at increased traverse speeds, with their increased cooling rates. These surface layers are crack free for all the conditions that were evaluated.

The residual stresses that are developed during laser surface melting may be high (600MPa) and tensile, such stresses will be an important factor in determining the mechanical and electrochemical behaviour of the treated regions. The surface residual stresses in single melt tracks are compressive, but when a surface is covered by a series of overlapping tracks the interaction between the

tracks produces tensile surface residual stresses at all but the slightest intertrack overlaps. The surface residual stress is process sensitive and may be minimized by maximizing the intertrack advances and to a lesser extent by maximizing the interaction time. The maximum residual tensile stress in laser surface melted 420 steel is developed below the region that transforms to martensite for the experimental conditions that were evaluated, although it is possible that at smaller intertrack advances plastic deformation towards the surface would become more significant and the maximum tensile stress would be developed there. If it is not possible to adequately control residual stress by controlling the processing conditions a stress relieving heat treatment of 500°C for one hour will reduce the stresses to ~50MPa, without adverse metallurgical effects.

Laser surface treatment can increase the fatigue life of the steel. This life increase is associated with hardening of the treated layer. Fatigue cracks in the laser melted steel originate from silicate inclusions. These crack initiating inclusions lie in the region below the heat affected zone as indicated by a microhardness traverse. The pitting corrosion resistance of the steel shows an improvement providing suitable treatment conditions are chosen.

In summary laser surface melting can produce smooth, hard, crack free tracks. Although laser surface melting can produce high tensile residual stresses these stresses are controllable by controlling the processing conditions and, if necessary, by means of a stress relieving heat treatment. Laser surface melting can enhance the fatigue life and pitting corrosion resistance of the steel. This combination of properties and the selective nature of the treatment offers a useful surface treatment technique.

316 Steel

As in 420 steel it is possible to produce smooth melt tracks in 316 steel by laser surface melting. Likewise the optimum surface preparation prior to laser surface melting is grit cleaning and it is possible to produce conduction limited tracks over treatment speeds in the range 10 to 400mm^s⁻¹, which cool at from $\sim 10^3$ to $\sim 10^6$ °C^s⁻¹.

The laser surface melted steel shows planar, cellular and branched dendritic microstructures depending on the ratio of thermal gradient in the liquid to the velocity of the solidification front. The microstructure of the laser surface melted steel is predominantly austenitic with some intercellular δ -ferrite at low traverse velocities. At high traverse velocities ($>100\text{mm s}^{-1}$) the formation of δ -ferrite is suppressed. However when this is so solidification cracking becomes a problem. The centres of the solidification cells show chromium and molybdenum depletion and nickel enrichment.

Laser surface melting produces tensile residual stresses of the order of the yield stress of cold worked material ($\sim 660\text{MPa}$). These stresses are essentially independent of treatment conditions and are high enough to severely degrade many of the mechanical and electrochemical properties of the steel. The maximum residual stress was developed at the surface of the treated layer for the conditions studied. When the stress relieving heat treatment of the steel is considered the potential user of the laser surface melted steel is faced with two choices, neither of them good. It is necessary either to accept the high stresses and the associated degradation of properties or to heat the steel to 750°C or above for a long time (for example a heat treatment at 850°C for one day will reduce the stress to $\sim 50\text{MPa}$). Apart from the risk of σ -phase formation the difficulties of laser surface melting and subsequently stress relieving are likely to compare unfavourably with

the difficulties of solution treating the steel by heating at 1050°C.

It is possible to restore the intergranular corrosion resistance of the steel by laser surface melting; however this benefit must be considered as an alternative to using a low carbon grade of steel which would not show intergranular cracking. Both the fatigue life and the pitting corrosion resistance of the steel are degraded by laser surface melting. In the case of the fatigue behaviour this degradation is associated with the high residual tensile stresses, but it is not possible to reliably restore the fatigue life by using a stress relieving heat treatment - suggesting some other form of damage associated with laser surface treatment. The pitting corrosion resistance of laser melted material will be reduced by the segregation of chromium and molybdenum to intercell regions and the tensile residual stresses.

In view of the various damaging effects of laser surface melting it is unlikely that laser surface melting without the introduction of additional alloying elements to the melted layer, is a useful treatment for 316 steel or other related austenitic alloys.

FUTURE WORK

1. The properties of the laser surface melted 420 steel are promising enough that the author hopes to see the process being widely adopted industrially. One such application would be the hardening of the power generating turbine component mentioned in the introduction, where the next steps forward could be an economic assessment of the process and testing of treated components in service.
2. While the laser surface melting of the 316 steel has little to offer the potential user the possibility of depositing a thin layer of alloying material on the surface of 316 steel and melting this material into the substrate with a laser has the potential to show an improvement of properties, for example by alloying chromium into the steel to enhance its corrosion behaviour. This raises the possibility of effectively using expensive and/or strategic materials for surface applications, where previously they were unsuitable for economic reasons. This line of research is also a possibility for the 420 steel and is being investigated by the author's successor to this project.
3. The possibility of peening laser surface melted 316 steel to relieve its residual stresses might be investigated as an alternative to thermal stress relief.
4. Spaced laser melted tracks on 420 steel or other hardenable steels might produce useful wear properties as the hardened regions would resist wear while the softer unhardened regions would act as a sink for wear debris. This offers the potential benefit that the wear debris that accelerates wear could be removed from a locally hard surface.

5. The results of the pitting corrosion testing reported here do not positively point to a mechanism leading to the degradation of the steel for certain treatment conditions. This is because varying one of the laser processing parameters will affect several aspects of the microstructure of the laser melted tracks. It would be possible to isolate the effect of the residual stress by cutting off thin slices of material close to the surface so as to relieve their stress and testing them chronopotentiometrically. The polarization curves from these tests would be compared with the corresponding curves for unrelaxed material.
6. If the solute distributions across the planar solidified zones were studied by STEM-EDX analysis, this would yield compositional data that could be more readily interpreted in terms of solidification theory than the complex solute distributions of the cellular solidified regions that have been studied.
7. Any future investigation measuring the solute distribution across solidification cells in the 420 steel could avoid the problems of solute enrichment of the surface film during electrolytic thinning by preparing specimens by ion beam thinning.

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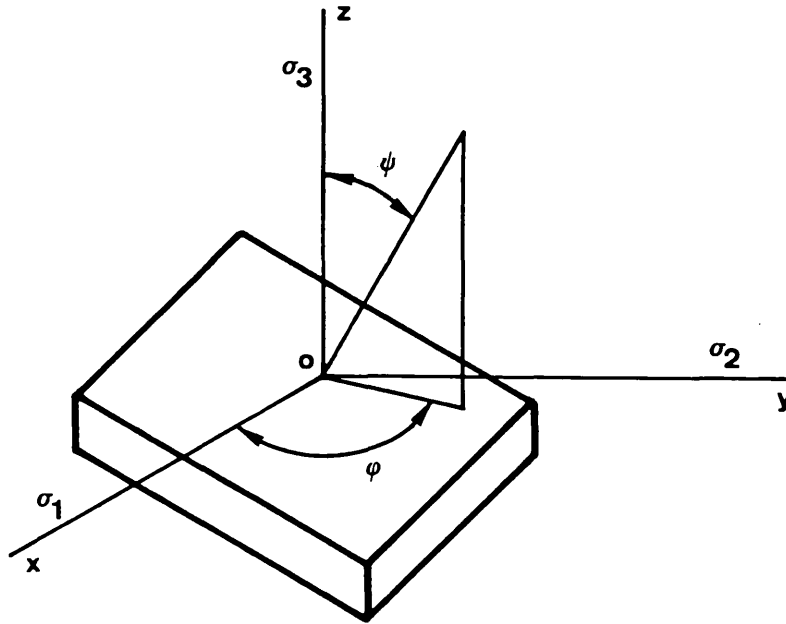
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Appendix A.4.1

Relationship Between X-Ray Peak Shift with Orientation and Stress

If a sphere of an isotropic material is stressed an ellipsoid is formed.



For the arrangement above

$$\sigma = \sigma_1 \alpha_1^2 + \sigma_2 \alpha_2^2 + \sigma_3 \alpha_3^2 \quad - (1)$$

where α_1 , α_2 and α_3 are the x, y and z direction cosines of stress σ .

Similarly for the strain ellipsoid

$$\epsilon = \epsilon_1 \alpha_1^2 + \epsilon_2 \alpha_2^2 + \epsilon_3 \alpha_3^2 \quad - (2)$$

The principal stresses σ_1 , σ_2 and σ_3 are taken parallel to the x, y and z axes and α_1 , α_2 and α_3 are the direction cosines relative to these axes.

$$\begin{aligned}\text{Now } \alpha_1 &= \sin\phi \cos\phi \\ \alpha_2 &= \sin\phi \sin\phi \\ \alpha_3 &= \cos\phi\end{aligned}\quad - (3)$$

Combining (1) and (3) gives

$$\sigma_\phi = \sigma_1(\sin\phi)^2 (\cos\phi)^2 + \sigma_2(\sin\phi)^2 (\sin\phi)^2 + \sigma_3(\cos\phi)^2 \quad - (4)$$

For stresses at the surface and parallel to the surface $\phi = 0.5\pi$ rad and (4) simplifies to:

$$\sigma_\phi = \sigma_1(\cos\phi)^2 + \sigma_2(\sin\phi)^2 \quad - (5)$$

$$\text{now } \epsilon = \frac{\sigma}{E} \text{ and } -\epsilon_x = \epsilon_y = \nu\epsilon_z = \frac{\nu\sigma_2}{E}$$

for a uniaxial stress in the z direction, by definition of E and ν

$$\epsilon_x = \frac{1}{E} (\sigma_x - \nu [\sigma_y + \sigma_z])$$

$$\epsilon_Y = \frac{1}{E} (\sigma_Y - \nu[\sigma_X + \sigma_Z])$$

$$\epsilon_Z = \frac{1}{E} (\sigma_Z - \nu[\sigma_X + \sigma_Y]) \quad - (6)$$

$$\begin{aligned} \text{We have } \epsilon_\phi &= \epsilon_1 (\sin \phi \cos \phi)^2 + \\ &\quad \epsilon_2 (\sin \phi \sin \phi)^2 + \\ &\quad \epsilon_3 \cos \phi \end{aligned} \quad - (7)$$

combining (2) + (3)

Combining (6) and (7) gives

$$\begin{aligned} \epsilon_\phi &= \frac{1}{E} [(\sigma_1 - \nu\sigma_2) (\sin \phi \cos \phi)^2 + \\ &\quad (\sigma_2 - \nu\sigma_1) (\sin \phi \sin \phi)^2] \\ &\quad + \epsilon_3 (\cos \phi)^2 \end{aligned}$$

Re-arranging using $\sigma_3 = 0$, putting in $(\cos \phi)^2 = 1 - (\sin \phi)^2$ and $\epsilon_3 = -\nu\sigma_1 - \nu\sigma_2$ gives:

$$\epsilon_{\phi} = \frac{1+\nu}{E} (\sigma_1 (\cos \phi)^2 + \sigma_2 (\sin \phi)^2) (\sin \phi)^2 + \epsilon_3 \quad - (8)$$

Combining with (5) gives

$$\sigma_{\phi} = (\epsilon_{\phi} - \epsilon_3) \frac{E}{(1+\nu)(\sin \phi)^2} \quad - (9)$$

Now $\epsilon_3 = \frac{dz - d_0}{d_0}$ and $\epsilon_{\phi} = \frac{d\phi - d_0}{d_0}$ from the definition of ϵ , where

d_0 = relaxed interplanar spacing

dz = interplanar spacing in z direction

d_{ϕ} = interplanar spacing in ϕ direction

Taking ϵ_3 from ϵ_{ϕ} gives

$$\epsilon_{\phi} - \epsilon_3 = \frac{d\phi - dz}{d_0}$$

Although it is necessary to measure d_{ϕ} and dz accurately because they are nearly equal it is not necessary to measure d_0 with similar accuracy and d_0 may be replaced with dz .

$$\therefore \epsilon_{\phi} - \epsilon_3 = \frac{d\phi - dz}{dz} \quad - (13)$$

$$\therefore \sigma_{\phi} = \frac{d\phi - dz}{dz} \frac{E}{(1+\nu)(\sin \phi)^2} \quad - (14)$$

by combining (13) and (9).

Braggs law gives: $2d \sin \theta = n\lambda$

$$\therefore \frac{d\theta}{dd} = \frac{-1}{d} \tan \theta \text{ differentiating}$$

$$\therefore \epsilon = \frac{dd}{d} = \frac{d\theta}{\tan \theta} \quad - (15)$$

$$\therefore \sigma_{\phi} = \frac{E}{1+\nu} \frac{1}{(\sin \phi)^2} \frac{\Delta \theta}{\tan \theta} \quad - (16)$$

for small $\Delta \theta$, combining (14) and (15).

$$\therefore \frac{\sigma (1+\nu) \tan \theta}{E} = \frac{\Delta \theta}{(\sin \phi)^2}$$

So over the small range of $\Delta \theta$ that will be generated by a residual stress a plot of $\Delta \theta$ and $(\sin \phi)^2$ will give a straight line of slope $\sigma(1+\nu) \tan \theta / E$.

(16) may also be expressed as:

$$\sigma = \frac{\Delta \theta}{(\sin \phi)^2} \frac{1}{K}$$

$$\text{where } K = \frac{E}{\sigma (1+\nu) \tan \theta} \quad - (17)$$

(17) holds for an isotropic elastic material. In practice however the anisotropy of the mechanical properties of individual grains leads to K varying from the value predicted by the bulk elastic properties (Macherauch 1966). In this work the values of K that were used were found by measuring the peak shift on loaded tensile specimens (Lonsdale, Doig and Flewitt 1981).

Appendix A.4.2

Correction of Subsurface Stresses

The laser treated specimens are treated as a number of thin layers parallel to the surface of the specimen. Corrected stresses were calculated working downwards from the surface layer by layer.

The following simplifications were made:-

- 1 The stress is assumed to be measured at the surface. This is not in fact the case. The stress is sampled through a depth of $\sim 10\mu\text{m}$. There is a case therefore for adding $\sim 5\mu\text{m}$ to the measured depths. However the residual stresses extend through a depth of $\sim 500\mu\text{m}$ and it was not possible to control the track depths to better than $\sim \pm 50\mu\text{m}$ over the $\sim 250\mu\text{m}$. The sampling depth is therefore not considered in the correction procedure.
- 2 The corrections are based on elastic solid mechanics. The measured stresses are higher than the corrected stresses and in view of the magnitude of the residual stresses some plastic deformation would be anticipated during the electrolytic thinning process. It is not difficult to envisage an elastic/plastic stress correction procedure based on the yield behaviour. However any such correction to the stress correction is felt to be beyond the scope of this work.
- 3 The values of bending moment due to material overlying a measured stress should include a contribution for the final half-layer above the depth corresponding to a stress measurement. This consideration is most significant where corrections are being made to deep highly stressed layers. In practice it is never more

than 1.5% of the residual stress in this work and is not considered, in order to simplify the correction procedure.

Procedure

The procedure that was used to give corrected stresses in Tables A.4.2.(1) to A.4.2.(4) is described below:-

1. D - Depth

This is the depth corresponding to a stress measurement.

2. σ_m - Measured Stress

This is the stress that was measured by x-ray diffractometry.

3. y_i - Distance from Centroid

The centroid lies half-way down the rectangular cross-section of the specimen, so y_i is given by

$$y_i = \frac{1}{2}h - D_i \text{ where } h = \text{height of specimen}$$

4. Δh - Strip Height

The boundary between two successive layers is considered to lie half-way between the depths of two successive stress measurements. This results in layers with heights given by:-

$$\Delta h = \frac{1}{2} (D_{i+1} - D_{i-1})$$

5. $\Delta M/b$ - Bending Moment/Distance

Each stressed layer develops a bending moment. The value of this bending moment is given by:-

$$\Delta M = \int_A y \sigma dA = y \cdot \sigma_c \cdot \Delta h \cdot b$$

where σ_c is the stress in the layer after a correction has been made for the effects of any overlying material. The values in Tables 4.2(1) to 4.2(4) are bending moment per unit specimen width.

6. $\Delta M/I$ - Bending Moment/Moment of Inertia

The moment of inertia of a rectangular cross-section of width, b and height, h is given by:

$$I = \frac{bh^3}{12} \text{ where } I \text{ is the moment of inertia}$$

It follows that

$$\Delta M/I = (\Delta M/b) (12/h^3)$$

substituting for I .

7. M/I - Total Bending Moment/Moment of Inertia

The total value of M/I is found by summing $\Delta M/I$ for the overlying material.

8. $\Delta \sigma$ - Stress Correction

The correction to the measured stress is found from:

$$\Delta\sigma = \frac{M}{I} \cdot y$$

9 σ_c - Corrected Stress

The stress in the unrelaxed specimen is found by subtracting the stress correction from the measured stress.

Table A.4.2(1)

420 - Stress Parallel to Tracks

i	Depth	Dist from Centroid	Strip Height	Measured Stress	Correction to Stress	Corrected Stress	Moment of Strip/b	$\Delta M/I$	M/I
	mm	mm	mm	MPa	MPa	MPa	N	MPa/mm	MPa/mm
1	0.000	3.175	0.0045	330	0.00	330	4.71	.221	.221
2	.009	3.166	.0095	327	0.70	326	9.81	.460	.681
3	.019	3.156	.011	252	2.15	250	8.67	.406	1.087
4	.031	3.144	.0115	317	3.42	314	11.34	.531	1.618
5	.042	3.133	.015	313	5.07	308	14.47	.678	2.296
6	.061	3.114	.0235	258	7.15	251	18.36	.860	3.156
7	.089	3.086	.027	259	9.74	249	20.77	.973	4.129
8	.115	3.060	.029	66	12.64	53	4.74	.222	4.351
9	.147	3.028	.033	167	13.17	154	15.37	.720	5.071
10	.181	2.994	.0355	294	15.18	279	29.63	1.388	6.460
11	.218	2.957	.0385	485	19.10	466	52.91	2.480	8.940
12	.258	2.917	.0355	572	26.08	546	56.53	2.650	11.589
13	.289	2.886	.030	615	33.45	581	50.35	2.360	13.949
14	.318	2.857	.050	680	39.85	640	91.44	4.286	18.234
15	.389	2.768	.041	694	50.47	643	73.03	3.423	21.657
16	.400	2.775	.0205	500	60.10	440	25.02	1.173	19.830
17	.430	2.745	.0375	270	54.43	215	22.19	1.040	20.870
18	.475	2.700	.060	87	56.35	31	4.96	.233	21.103
19	.550	2.625		-10	55.39	-65			

Table A.4.2(2)

420 - Stress Perpendicular to Tracks

i	Depth	Dist from Centroid	Strip Height	Measured Stress	Correction to Stress	Corrected Stress	Moment of Strip/b	$\Delta M/I$	M/I
	mm	mm	mm	MPa	MPa	MPa	N	MPa/mm	MPa/mm
1	0.000	3.175	0.0045	290	0.00	290	4.14	0.194	0.194
2	.009	3.166	.0095	207	0.62	206	6.21	.291	.484
3	.019	3.156	.011	205	1.53	203	7.06	.331	.815
4	.031	3.144	.0115	184	2.56	181	6.56	.307	1.122
5	.042	3.133	.015	198	3.52	194	9.14	.428	1.550
6	.061	3.114	.0235	164	4.83	159	11.65	.546	2.096
7	.089	3.086	.027	103	6.47	97	8.04	.377	2.473
8	.115	3.060	.029	160	7.57	152	13.53	.634	3.377
9	.147	3.028	.033	126	10.22	116	11.57	.542	3.919
10	.181	2.994	.0355	145	11.73	133	14.16	.664	4.583
11	.218	2.957	.0385	287	13.55	273	31.13	1.459	6.042
12	.258	2.917	.050	366	17.62	348	50.81	2.381	8.423
13	.318	2.857	.071	442	24.06	417	84.77	3.973	12.396
14	.400	2.775	.0785	300	34.40	266	57.86	2.711	16.108
15	.475	2.700	.075	68	43.49	24	4.96	.232	16.340
16	.550	2.625		5	42.89	-38			

Table A.4.2(3)

316 - Stress Parallel to Tracks

i	Depth	Dist from Centroid	Strip Height	Measured Stress	Correction to Stress	Corrected Stress	Moment of Strip/b	$\Delta M/I$	M/I
	mm	mm	mm	MPa	MPa	MPa	N	MPa/mm	MPa/mm
1	0.000	3.175	0.005	690	0.00	690	10.95	0.51	0.513
2	.010	3.165	.0105	721	1.62	719	23.91	1.12	1.633
3	.021	3.154	.0105	499	5.15	494	16.35	.77	2.399
4	.031	3.144	.011	546	7.54	538	18.62	.87	3.272
5	.043	3.132	.016	530	10.25	520	26.04	1.22	2.051
6	.063	3.112	.0285	540	6.38	534	47.33	2.22	4.269
7	.100	3.075	.032	360	13.13	347	34.13	1.60	2.669
8	.127	3.048	.0205	525	8.14	517	32.30	1.51	4.183
9	.141	3.034	.028	488	12.68	475	40.38	1.89	6.078
10	.183	2.992	.0435	679	18.18	661	86.01	4.03	10.106
11	.228	2.947	.0345	445	29.78	415	42.22	1.99	12.084
12	.252	2.923	.039	310	35.32	275	31.31	1.47	13.551
13	.306	2.869	.034	80	38.88	41	4.01	.19	13.739
14	.320	2.855		12	39.22	-27			

Table A.4.2(4)

316 - Stress Perpendicular to Tracks

i	Depth	Dist from Centroid	Strip Height	Measured Stress	Correction to Stress	Corrected Stress	Moment of Strip/b	$\Delta M/I$	M/I
	mm	mm	mm	MPa	MPa	MPa	N	MPa/mm	MPa/mm
1	0.000	3.175	0.005	660	0.00	660	10.48	.49	.491
2	.010	3.165	.0105	709	1.55	707	23.51	1.01	1.593
3	.021	3.154	.0105	620	5.02	615	20.4	.95	2.547
4	.031	3.144	.011	598	8.01	590	20.4	.96	3.503
5	.043	3.132	.016	569	10.97	558	27.9	1.31	4.814
6	.063	3.112	.0285	554	14.98	539	47.8	2.24	2.054
7	.100	3.075	.032	547	21.69	525	51.7	2.42	9.476
8	.127	3.048	.0205	569	28.88	540	33.7	1.58	11.058
9	.141	3.034	.028	586	33.55	552	46.9	2.20	13.257
10	.183	2.992	.0435	630	39.7	590	76.8	3.60	16.858
11	.228	2.947	.0345	580	49.68	530	53.9	2.53	19.385
12	.252	2.923	.039	390	56.7	333	38.0	1.78	21.166
13	.306	2.869	.034	150	60.7	89	8.7	.41	21.6
14	.320	2.855		82	61.6	20			

Appendix A.5.1

Listing of the Program "BANBAN"

```
10 REM Stepping motor control ML
20 DATA &C1,&E1,&3E,0,&BD,&CA,&19,&6D
30 DATA &24,&B9,&CA,&1E,&6D,4,&D1
40 DATA &22,&OE,&6D,&7B,&E6,&FF
50 DATA &32,&FF,&FB,&2D,&C2,&28,&6D
60 DATA &25,&C2,&28,&6D,&E6,&3F
70 DATA &32,&FF,&FB,&3E,&32,&3D
80 DATA &C2,&37,&6D,&2A,&OE,&6D
90 DATA &0D,&C2,&22,&6D,5
100 DATA &C2,&22,&6D,&C9
110 DATA 1
120 I=&6D10:A=I
130 READ V
140 IF V=1 THEN 180
150 POKE I,V
160 I=I+1
170 GOTO 130
180 REM
190 F1=&80:R1=&A0:F2=&40:R2=&50
200 FF=&C0:FR=&D0:RF=&E0:RR=&F0
210 ?:?:?
220 INPUT "Give track separation ",N
230 A$=GET$(0)
240 IF A$="H"ORA$="h"THEN CALL A,F1,500,100
250 IF A$="A"ORA$="a"THEN CALL A,F1,500,100-N
260 IF A$="P"ORA$="p"THEN CALL A,F1,500,1
270 IF A$="M"ORA$="m"THEN CALL A,R1,500,1
280 IF A$="E"ORA$="e"THEN END
290 GOTO 230
```

Appendix A.6.1

Annotation and Listing of the Programm, "Runpot"

This programm controls a potentiostat during a potential sweep test and logs, processes, stores and plots the data that is acquired.

Lines 1010 and 1020 declare the dimensions of the data storage matrices. The operator is asked to set the potentiostat to "Standby". Lines 1080 to 1380 control the execution of the various subroutines that follow. The test conditions are typed in by the operator (line 1080 going to subroutine 3500). The ASCII codes corresponding to the maximum and minimum cell potentials are evaluated (line 1090 going to subroutine 5500). Before the upward sweep is commenced the program evaluates and stores both the upward and the downward step times and voltage increments (lines 1100 to 1150). This sequence is used so that there is no delay at the maximum anodic voltage during a test. This could occur if the downward ramp conditions were calculated during a test, before the ramp direction was reversed. After the upward sweep (line 1220) the ramp limits and conditions are set for the downward sweep (lines 1230 to 1260) and the downward sweep is commenced. On completion of the test the data that has been acquired is stored on magnetic tape (line 1300 going to subroutine 2000). Finally the operator is asked to turn the potentiostat off and the task is completed.

Subroutines

The program operates through a number of subroutines on lines 1500 to 8510. The functions of these subroutines are indicated below:-

- Subroutine 1500 "Potential Control"

This outputs an appropriate potential difference across the cell via the interface and the potentiostat. It measures the cell current and asks the operator to turn the potentiostat on.

- Subroutine 2000 "File Data"

This assigns buffer No 1 for the numerical data and buffer No 2 for the data header. Files with names in stores F\$ and G\$ are created and filled with information from buffers No 1 and 2 respectively.

- Subroutine 2500 "Ramp"

This outputs a cell potential, which increases stepwise from V1 to V3 via subroutine 7000. Each step lasts for a time interval, T3. If the current is anodic and greater than I9 or cathodic and exceeds I8 the subroutine is exited. During each step the cell p.d. and cell current are measured via subroutine 6500. The current measurement incorporates autoranging. The cell p.d and current measurements are repeated as often as possible till the time remaining till the next step is twice the time required for the current and p.d measurements. When this time is reached the mean measurements are calculated, plotted and stored.

- Subroutine 3500 "Data Input"

This interactive routine invites the operator to type in the experimental conditions.

- Subroutine 4500 "Evaluate Step Length and Timer Delay"

This sets an initial value of N5, an ASCII code corresponding to the voltage step, according to the limited data storage capacity of the microcomputer. This

allows for 1000 measurements to be stored for each potential sweep test. The time interval per step, T3 is then calculated and if this is too brief to allow both a voltage reading and a current reading (with autoranging) the voltage step size is increased and the step time is recalculated. This process is repeated till the time interval is sufficient for the measurements. These measurements were timed and found to take ~600ms so one second is allowed.

- Subroutine 5000 "Evaluate Zero Offset"

This evaluates the systematic additive error in the measured current arising from analogue to digital conversion. This is found by measuring the cell current signal from the ADC before the potentiostat is switched on. This value is subtracted from the current measurements.

- Subroutine 5500 "Evaluate ASCII Limits"

This evaluates the ASCII codes corresponding to the maximum and the minimum cell potentials.

- Subroutine 6000 "Plot Expansion"

This enables the operator to select and expand a particularly interesting part of the plot, for example to accurately measure the pitting potential.

- Subroutine 6500 "Read Signal" and 7000 "Output Signal"

These subroutines contain the commands necessary to retrieve or send the relevant ASCII information via the IEEE 488 bus.

- Subroutines 7500 "Print Header" and 8000 "Draw Graph"

The printed header includes the time, date, the scan rates upwards and downwards and the data and header filenames.

The graph is a plot of $\log|i|$ against p.d. Descriptions of the specimen and the electrolyte are printed on the graph. Appropriate axis limits are selected and the axes are labelled and numbered.

```

1000 CLEAR
1010 DIM U(1000)
1020 DIM C(1000)
1030 DISP "SET POTENTIOSTAT"
1040 DISP "TO STANDBY. THEN"
1050 DISP "ENTER A CHARACTER"
1060 DISP "TO CONTINUE"
1070 INPUT Q$
1080 GOSUB 3500 : INPUT DATA
1090 GOSUB 5500 : RAMP LIMITS
1100 S3=S1
1110 GOSUB 4500 : SET N5 AND T3
1120 N3=N5
1130 T1=T3
1140 S3=S2
1150 GOSUB 4500 : SET N5 AND T3
1160 GOSUB 5000 : SET 0 OFFSET
1170 SETTIME 0.0
1180 GOSUB 1500 : POT CONTROL
1190 GOSUB 8000 : DRAW GRAPH
1200 IF TIME<T2*0 THEN 1200
1210 Z=0
1220 GOSUB 2500 : RAMP UP
1230 N2=N1
1240 N1=N0-N3
1250 N3=-N5
1260 T1=T3
1270 GOSUB 2500 : RAMP DOWN
1280 GOSUB 7500 : PRINT HEADER
1290 COPY
1300 GOSUB 2000 : FILE DATA
1310 GOSUB 6000 : EXPAND PLOT
1320 CLEAR
1330 DISP "TURN THE POT'STAT OFF
      THEN ENTER A CHARACTER"
1340 INPUT Q$
1350 A$="A.00,0.1"
1360 GOSUB 7000 : OUTPUT SIGNAL
1370 DISP "TEST OVER"
1380 END
1500 :
1510 : *** POT CONTROL ***
1520 :
1530 N0=N1
1540 A$="A.00"&VAL$(N0)&".1"
1550 GOSUB 7000 : OUTPUT P.D
1560 B$="A.F1,G0,I5,IC2"
1570 GOSUB 6500 : READ CURRENT
1580 C=A/32768*10*B-A1
1590 I=C*2/AS
1600 I=ABS(I)
1610 IF I<11 THEN 1640
1620 N1=N1+N3
1630 GOTO 1530
1640 DISP "SET THE POT'STAT TO"
1650 DISP "CONTROL THE CELL."
1660 DISP "AND THEN ENTER A "
1670 DISP "CHARACTER TO CONT "
1680 INPUT Q$
1690 RETURN
2000 :
2010 : *** FILE DATA ***
2020 :
2030 CREATE F$.4048.8
2040 ASSIGN# 1 TO F$
2050 CREATE G$.16.16
2060 ASSIGN# 2 TO G$
2070 FOR K=1 TO 2
2080 PRINT# 1 : V(K),C(K)
2090 NEXT K
2100 ASSIGN# 1 TO *
2110 PRINT# 2 : L$,M$,N$,O$,S1.5
      2,V1,V2,I1,I0,A1,Z
2120 ASSIGN# 2 TO *
2130 RETURN
2500 :
2510 : *** RUN RAMP ***
2520 :
2530 FOR N0=N1 TO N2 STEP N3
2540 SETTIME 0.0
2550 I=0 @ T5=0
2560 M=0
2570 E=0
2580 A$="A.00"&VAL$(N0)&".1"
2590 GOSUB 7000 : OUTPUT SIGNAL
2600 T6=TIME
2610 SETTIME 0.0
2620 M=M+1
2630 B$="A.F1,G0,I4,IC2"
2640 GOSUB 6500 : MEASURE P.D
2650 P=-(A/32768*10)
2660 B$="A.F1,G0,I5,IC2"
2670 GOSUB 6500 : MEASURE I
2680 IF ABS(A)<200 THEN 2710
2690 IF ABS(A)<3000 THEN 2740
2700 GOTO 2760
2710 B$="A.F1,G2,I5,IC2" @ B=-1
2720 GOSUB 6500 : MEASURE I
2730 GOTO 2760
2740 B$="A.F1,G1,I5,IC2" @ B=0
2750 GOSUB 6500 : MEASURE I
2760 C=A/32768*10*B-A1
2770 I=I+C*I1/.2
2780 IF M>1 THEN 2840
2790 IF N3<0 THEN 2830
2800 IF I<-ABS(I0) THEN 2980
2810 IF I>19 THEN 2990
2820 GOTO 2840
2830 IF I<-ABS(I0) THEN 2990
2840 E=E+P
2850 T5=T5+TIME
2860 IF 2*TIME+T5+T6<T1+1000 THE
      N 2610
2870 SETTIME 0.0
2880 I=I/M/AS
2890 Z=Z+1
2900 C(Z)=I
2910 E=E/M
2920 V(Z)=E
2930 I=ABS(I)
2940 IF I< 0.000001 THEN I=.000001
2950 PLOT LGT(I)*E*1000
2960 T7=T5+T6
2970 IF TIME+T5+T6<T1+1000 THEN
      2970
2980 NEXT N0
2990 PENUP
3000 RETURN
3500 :
3510 : *** INPUT DATA ***
3520 :
3530 DISP "START POTENTIAL; mV"
3540 INPUT V1
3550 DISP "MAX POTENTIAL; mV"
3560 INPUT V2
3570 DISP "SPECIMEN AREA; cm^2"
3580 INPUT AS
3590 DISP "SETTLING TIME; mins"
3600 INPUT T2
3610 DISP "CURRENT RANGE; mA"
3620 INPUT I1
3630 I1=I1/1000
3640 I0=.000001
3650 DISP "MAX. ANODIC CURRENT;
      mA"
3660 INPUT I9
3670 I9=I9/1000
3680 DISP "MAX. CATHODIC CURRENT
      : mA"
3690 INPUT I8
3700 I8=I8/1000
3710 DISP "SCAN RATE UPWARDS; mV
      /min"
3720 INPUT S1
3730 DISP "SCAN RATE DOWNWARDS;
      mV/min"
3740 INPUT S2
3750 S2=ABS(S2)
3760 : IF I1>10/R1 THEN I1=10/R1
3770 DISP "ENTER THE NAME OF"
3780 DISP "THE FILE IN WHICH"
3790 DISP "THE TEST DATA WILL"
3800 DISP "BE STORED"
3810 INPUT F$
3820 DISP "ENTER THE HEADERS"
3830 DISP "FILE NAME"
3840 INPUT G$
3850 DISP "ENTER THE TIME"
3860 INPUT L$
3870 DISP "ENTER THE DATE"

```

```

3890 INPUT M$
3890 DISP "ENTER THE METAL"
3900 INPUT N$
3910 DISP "ENTER THE ELECTROLYTE"
"
3920 INPUT O$
3930 RETURN
4500 !
4510 ! *** EVALUATE STEP LENGTH
AND TIME DELAY ***
4520 !
4530 N5=INT(ABS(N2-N1)/.500+1)
4540 T3=INT(N5*10*1000000/2^15/3
3*60)
4550 IF T3>1000 THEN 4580
4560 N5=N5+1
4570 GOTO 4540
4580 RETURN
5000 !
5010 ! *** EVALUATE ZERO OFFSET
***
5020 !
5030 A1=0
5040 B$="A.F1.G2.I5.I02" @ B=-1
5050 FOR I=1 TO 30
5060 GOSUB 6500 ! MEASURE 1
5070 A1=A1+A/2^15*10^8
5080 NEXT I
5090 A1=A1/30
5100 RETURN
5500 !
5510 ! *** EVALUATE ASCII RAMP
LIMITS ***
5520 !
5530 N1=INT(2^15*V1/10000)
5540 N2=INT(2^15*V2/10000)
5550 RETURN
6000 !
6010 ! *** PLOT EXPANSION ***
6020 !
6030 DISP "ENTER 1 TO EXPAND THE
PLOT OTHERWISE ENTER 0"
6040 INPUT Q
6050 IF Q=0 THEN 6330
6060 DISP "MINIMUM POTENTIAL, mV"
"
6070 INPUT V1
6080 DISP "MAXIMUM POTENTIAL, mV"
"
6090 INPUT V2
6100 IF V2<=V1 THEN 6060
6110 DISP "MINIMUM CURRENT, A"
6120 INPUT I0
6130 DISP "MAXIMUM CURRENT, A"
6140 INPUT I1
6150 IF I1<=I0 THEN 6110
6160 GCLEAR
6170 GOSUB 8000 ! DRAW GRAPH
6180 FOR J=1 TO 2
6190 X=C(I)
6200 X=ABS(X)
6210 IF X< 0000001 THEN X= 0000001
6220 Y=V(I)*1000
6230 IF X>I1 THEN 6290
6240 IF X<I0 THEN 6290
6250 IF Y>V1 THEN 6290
6260 IF Y>V2 THEN 6290
6270 PLOT LGT(X),Y
6280 GOTO 6300
6290 PENUP
6300 NEXT J
6310 COPY
6320 GOTO 6000
6330 RETURN
6500 !
6510 ! *** READ SIGNAL ***
6520 !
6530 OUTPUT 710 :B$
6540 SEND 7 : UNL
6550 RESUME 7
6560 ENTER 710 : A
6570 SEND 7 : UNT
6580 RESUME 7
6590 RETURN
7000 !

```

```

7010 ! *** OUTPUT SIGNAL ***
7020 !
7030 ! THE SIGNAL IS AN ASCII
7040 ! CODE IN THE RANGE -2^15
7050 ! TO 2^15, CORRESPONDING
7060 ! TO AN OUTPUT VOLTAGE IN
7070 ! THE RANGE -10 TO 10V.
7080 ! A DEVICE SELECTOR OF 710
7090 ! SPECIFIES DEVICE 10 ON
7100 ! INTERFACE 7
7110 !
7120 OUTPUT 710 :A$
7130 SEND 7 : UNL
7140 RESUME 7
7150 RETURN
7500 !
7510 ! *** PRINT HEADER ***
7520 !
7530 PRINT "TIME OF TEST",L$
7540 PRINT "DATE OF TEST",M$,""
7550 PRINT "SCAN RATE UP" =":S1
":mV/min"
7560 PRINT "SCAN RATE DOWN" =":S2
":mV/min",""
7570 PRINT "DATA FILENAME:" :F$
7580 PRINT "HEADER FILENAME:" :G$
""
7590 RETURN
8000 !
8010 ! *** DRAW GRAPH ***
8020 !
8030 GCLEAR
8040 V3=V2-V1
8050 V4=500
8060 IF V3<2500 THEN V4=250
8070 IF V3<1000 THEN V4=100
8080 IF V3<500 THEN V4=50
8090 IF V3<100 THEN V4=10
8100 IF V3<50 THEN V4=5
8110 X1=INT(LGT(10))
8120 X8=INT(LGT(I1))
8130 Y1=V1-V4
8140 Y8=V2+V4
8150 Y2=Y8-Y1
8160 X2=X8-X1
8170 X0=X1-X2/3.5
8180 X9=X8+X2/10
8190 Y0=Y1-Y2/5
8200 Y9=Y8+Y2/5
8210 SCALE X0,X9,Y0,Y9
8220 XAXIS Y1,1000000,X1,X8
8230 YAXIS X1,1000000,Y1,Y8
8240 FOR I=X1 TO X8
8250 MOVE I,Y1
8260 IDRAW 0,Y2/30
8270 MOVE I-X2/30,Y1-Y2/15
8280 LABEL VAL$(I)
8290 IF I=X8 THEN 8340
8300 FOR J=2 TO 10
8310 MOVE I+LGT(J),Y1
8320 IDRAW 0,Y2/40
8330 NEXT J
8340 NEXT I
8350 FOR I=Y1 TO Y8 STEP V4*2
8360 MOVE X1,I
8370 IDRAW X2/50,0
8380 MOVE X1-X2/4.5,I
8390 LABEL VAL$(I)
8400 NEXT I
8410 MOVE X1+X2/20,Y8+(Y9-Y8)*.5
8420 LABEL "Specimen:"&N$
8430 MOVE X1+X2/20,Y8+(Y9-Y8)*.1
8440 LABEL "Electrolyte:"&O$
8450 MOVE X1-X2/4,Y1+Y2/10
8460 LDIR 90
8470 LABEL "Potential: mV"
8480 LDIR 0
8490 MOVE X1,Y1-Y2/6
8500 LABEL "log(abs(1/area)), Ac
m^-2"
8510 RETURN

```

Appendix A.6.2

Annotation and Listing of the Program "GETDAT"

The subroutine 4000 acquires data from magnetic tape. The operator is asked to type in the data file and header names in lines 4030 to 4060. Buffers are assigned for the transfer of data in lines 4070 and 4080. The remainder of the subroutine reads in the data.

Once data has been acquired via subroutine 4000 subroutines are entered to display the data and to expand the display, if the user requests this, at lines 1030 to 1070. These subroutines are exactly the same as the subroutines with corresponding line numbers in the program "RUNPOT" (See Appendix A.6.1) and are not described in detail here.

```

1000 DIM V(1000)
1010 DIM C(1000)
1020 GOSUB 4000 ! READ DATA
1030 GOSUB 7500 ! PRINT HEADER
1040 GOSUB 8000 ! DRAW GRAPH
1050 GOSUB 5000 ! PLOT DATA
1060 COPY
1070 GOSUB 6000 ! EXPAND PLOT
1080 ASSIGN# 1 TO *
1090 ASSIGN# 2 TO *
1100 CLEAR
1110 END
4000 !
4010 ! *** READS IN DATA ***
4020 !
4030 DISP "ENTER DATA FILE NAME"
4040 INPUT F$
4050 DISP "ENTER HEADER NAME"
4060 INPUT G$
4070 ASSIGN# 1 TO F$
4080 ASSIGN# 2 TO G$
4090 READ# 2 ; L$,M$,N$,O$,S1,S2
      ,V1,V2,I1,I0,A1,Z
4100 FOR K=1 TO Z
4110 READ# 1 ; V(K),C(K)
4120 NEXT K
4130 RETURN
5000 !
5010 ! *** PLOTS DATA ***
5020 !
5030 FOR K=1 TO Z
5040 Y=V(K)*1000
5050 I=C(K)
5060 I=ABS(I)
5070 IF I<.000001 THEN I=.000001
5080 PLOT LGT(I),Y
5090 NEXT K
5100 RETURN
6000 !
6010 ! *** PLOT EXPANSION ***
6020 !
6030 DISP "ENTER 1 TO EXPAND THE
      PLOT OTHERWISE ENTER 0"
6040 INPUT Q
6050 IF Q=0 THEN 6340
6060 DISP "MINIMUM POTENTIAL; mV"
      "
6070 INPUT V1
6080 DISP "MAXIMUM POTENTIAL; mV"
      "
6090 INPUT V2
6100 IF V2<=V1 THEN 6060
6110 DISP "MINIMUM CURRENT; A"
6120 INPUT I0
6130 DISP "MAXIMUM CURRENT; A"
6140 INPUT I1
6150 IF I1<=I0 THEN 6110
6160 GCLEAR
6170 GOSUB 8000 ! DRAW GRAPH
6180 FOR I=1 TO Z
6190 X=C(I)
6200 X=ABS(X)
6210 IF X<.000001 THEN X=.000001
6220 A=V(I)
6230 Y=A*1000
6240 IF X>I1 THEN 6300
6250 IF X<I0 THEN 6300
6260 IF Y<V1 THEN 6300
6270 IF Y>V2 THEN 6300
6280 PLOT LGT(X),Y
6290 GOTO 6310
6300 PENUP
6310 NEXT I
6320 COPY
6330 GOTO 6000
6340 RETURN
7500 !
7510 ! *** PRINT HEADER ***
7520 !
7530 PRINT "TIME OF TEST",L$
7540 PRINT "DATE OF TEST",M$,"

```

```

7550 PRINT "SCAN RATE UP  =" ;S1
      ;"mV/min"
7560 PRINT "SCAN RATE DOWN =" ;S2
      ;"mV/min",""
7570 PRINT "DATA FILENAME  ;" ;F$
7580 PRINT "HEADER FILENAME;" ;G$
      ;""
7590 RETURN
8000 !
8010 ! *** DRAW GRAPH ***
8020 !
8030 GCLEAR
8040 V3=V2-V1
8050 V4=500
8060 IF V3<2000 THEN V4=250
8070 IF V3<1000 THEN V4=100
8080 IF V3<500 THEN V4=50
8090 IF V3<100 THEN V4=10
8100 IF V3<50 THEN V4=5
8110 X1=INT(LGT(I0))
8120 X8=INT(LGT(I1))
8130 Y1=V1-V4
8140 Y8=V2-V4
8150 Y2=Y8-Y1
8160 X2=X8-X1
8170 X0=X1-X2/3.5
8180 X9=X8+X2/10
8190 Y0=Y1-Y2/5
8200 Y9=Y8+Y2/5
8210 SCALE X0,X9,Y0,Y9
8220 XAXIS Y1,1000000,X1,X8
8230 YAXIS X1,1000000,Y1,Y8
8240 FOR I=X1 TO X8
8250 MOVE I,Y1
8260 IDRAW 0,Y2/30
8270 MOVE I-X2/30,Y1-Y2/15
8280 LABEL VAL$(I)
8290 IF I=X8 THEN 8340
8300 FOR J=2 TO 10
8310 MOVE I+LGT(J),Y1
8320 IDRAW 0,Y2/40
8330 NEXT J
8340 NEXT I
8350 FOR I=Y1 TO Y8 STEP V4*2
8360 MOVE X1,I
8370 IDRAW X2/50,0
8380 MOVE X1-X2/4.5,I
8390 LABEL VAL$(I)
8400 NEXT I
8410 MOVE X1+X2/20,Y8+(Y9-Y8)*.6
8420 LABEL "Specimen; "&N$
8430 MOVE X1+X2/20,Y8+(Y9-Y8)*.1
8440 LABEL "Electrolyte; "&O$
8450 MOVE X1-X2/4,Y1+Y2/10
8460 LDIR 90
8470 LABEL "Potential; mV"
8480 LDIR 0
8490 MOVE X1,Y1-Y2/6
8500 LABEL "log(abs(i/area)); Ac
      m^-2"
8510 RETURN

```

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