

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF A WEAR
RESISTANT NICKEL ALLOY

Thesis submitted for the degree of
Doctor of Philosophy

by

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September 1985

TO MY SON DANIEL, without whom this work would have been
very much easier, but not nearly so worthwhile.

ABSTRACT

The microstructure and mechanical properties of a nickel base wear resistant alloy known as Tribaloy T-700 (composition: 50% Ni, 32% Mo, 3% Si, 15% Cr) have been investigated.

The fracture toughness and modulus of rupture values were found to be $20.1 \text{ MN/m}^{3/2}$ and 537 MN/m^2 respectively, and the alloy was found to be stable up to 900°C , which confirmed the manufacturer's claim of alloy stability.

The intermetallic Laves phase present in this alloy was found to be composed of two different primary Laves phase structure types, namely the hexagonal and dihexagonal structures.

The effect of compositional modifications to the microstructure and mechanical properties of T-700 were also investigated, and it was found that the addition of iron to the alloy was not generally detrimental, although there was a slight decrease in the macrohardness in the as-cast condition.

Even after heat treatment at 700°C for 24h, there was no change in the above noted mechanical properties, and no

deterioration in the wear resistance was found on the addition of 5wt% iron to T-700.

Silicon, however, was found to be a necessary addition to the alloy, primarily in the formation of the hexagonal type Laves phase structure, since it appeared that this Laves phase structure type shows increased wear resistance properties to that without silicon. However, the presence of silicon inhibited the formation of a lamellar eutectic, which is the condition more favourable for an increase in the fracture toughness and modulus of rupture of the alloy.

The modifications made to the original material lead to the identification of the phase previously term P in the Ni-Cr-Mo phase diagram as being a cubic Laves structure type.

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1. INTRODUCTION

Nickel-based alloys have been used widely for a number of years and the main development has been in the superalloys so called because of their high temperature and corrosion resistance properties. The development of the superalloys for gas turbines began with the attempt to strengthen the heat resistant 80-20 Ni-Cr alloy by precipitation hardening and this work led to the discovery of the nimonic alloys. Nickel has proved to be a remarkable matrix metal for high temperature alloys and it maintains good strength at temperatures up to about $0.7T_m$.

Because nickel-based alloys have heat, corrosion and abrasion resistance they are particularly suitable for situations where resistance to wear is important. The industrial process of hardfacing, which consists of applying the wear resistant material as a surface coating by a fusion welding process, is a good application of the nickel-base alloy. Most commercially available hardfacing alloys gain their wear resistance from a dispersion of carbides.

A group of intermetallic materials has been developed by the Du Pont Company which is covered by the tradename of Tribaloy and includes both nickel- and cobalt-based materials. These metals contain a hard intermetallic phase dispersed in a matrix of eutectic or solid solution. Thus

the wear resistance of these alloys is not associated with carbides, but with the intermetallic compound. However, the brittle nature of the intermetallic phase restricts their range of application.

Some work has already been carried out on the wear and corrosion resistance of the nickel- and cobalt-based alloys (Cameron & Ferris, 1974; Schmidt & Ferris, 1975; Allnatt & Bell, 1980) and recently the microstructure and mechanical properties of the cobalt-based alloys have been extensively investigated (Halstead, 1980). But, there is very little information available about the microstructure and mechanical properties of the nickel-based Tribaloy, and the aim of this work is to investigate its mechanical properties and relate these to its microstructure.

1.1 The Alloy

The manufacturers claim that Triballoys possess a unique combination of wear-, friction- and corrosion-resistant properties (Du Pont, 1973) which can be attributed to the hard intermetallic phase in a softer matrix. When used as antiwear surfaces and for bearing materials, they exhibit

- good resistance to galling and wear
- low friction
- high corrosion resistance
- good high temperature properties

Although several Triballoys have been produced, the principal

ones which have found practical uses are T-400, T-700 and T-800 (Cabot Corp., 1979), where T-400 and T-800 are cobalt-based and T-700 is nickel-based. Table 1 shows the basic compositions of the three Tribaloys (Du Pont, 1973), as given by the manufacturers.

T-700 contains a higher chromium content than alloy T-400 for improved oxidation and corrosion resistance, and since it does not contain cobalt, it has been considered as a prime candidate for nuclear applications replacing Co-Cr-W because it is not susceptible to radiation activation.

The alloy is available as a fine, near-spherical powder (for plasma-spraying, plasma transferred arc surfacing or powder metallurgy parts), or as hardfacing rods, castings, conventional P/M powder or a hot isostatically pressed alloy. Thus components may be fabricated by a number of different methods and items currently in use include bearings, seals, valves, pistons and piston rings.

1.2 Microstructure

In the Cobalt-based Tribaloys, the intermetallic phase is a Laves phase $(\text{MgZn})_2$ type, a close packed hexagonal compound of cobalt, molybdenum and silicon which can exist between the stoichiometric limits of $\text{Co}_3\text{Mo}_2\text{Si}$ and CoMoSi (Cameron & Ferris, 1974; Du Pont, 1973; Halstead, 1980). According to Cameron & Ferris (1974), the intermetallic compound in

the nickel-based Triballoys is also the hexagonal type Laves phase, and it is possible for nickel to replace the cobalt in the $\text{Co}_3\text{Mo}_2\text{Si}$ and CoMoSi compounds and chromium can also be substituted in the lattices. In the cobalt-based Triballoy, the Vickers hardness of the Laves phase is between 1000 and 1200 HV (Kg mm^{-2}) depending on the composition, and the matrix hardness is between 200 and 800 HV . Although values of the hardness of the two different phases for T-700 are not quoted in the literature, the macrohardness values quoted are less than for the cobalt-base Triballoy (Cabot Corpn., 1979). Table 2 shows a comparison of hardness values for the three Triballoys.

T-700 contains between 40 and 60% primary Laves phase (Cabot Corpn.) the balance being fcc solid solution. Standard X-ray diffraction techniques have been used to determine these phase compositions. Table 1 shows the composition of the Triballoys calculated from the peak heights of the X-ray diffraction patterns (Table 3).

1.3 Wear and Corrosion Resistance

The wear resistance of the Triballoys is attributed to the hard primary Laves phase which is harder than the bulk hardness of the hardest tool steel, but is much softer than more common wear resistant materials such as tungsten carbide and alumina. These materials tend to wear away their mating surfaces unless the surface finish is very fine

and the mating geometry has to be prepared very carefully at a high cost. In a matrix of the much softer solid solution alloy, the hard Laves phase particles resist adhesive wear. A number of wear tests have been reported by Schmidt and Ferris (1975) to demonstrate the qualities of Tribaloy in air and 5% hydrochloric acid. The wear tests are performed in acid to simulate and accelerate the effects of lubricants and their byproducts.

1.4 Mechanical Properties

Table 4 shows the typical properties of Triballoys. They are all strong in compression, but because of the presence of the intermetallic phase they show little plastic deformation in tension or compression and fail abruptly by brittle crack propagation.

The resistance of a material to crack propagation is measured by its fracture toughness, and this can be used to determine the largest acceptable defect size at a known operating stress. Table 5 shows a comparison of the fracture toughness values of various materials. It can be seen that the fracture toughness of Triballoys lies below that of metals such as steel and Titanium, but above that of the brittle ceramics and glasses.

1.5 Research Programme

Bearing in mind the components which are likely to be

constructed from Tribaloy T-700, it will be subjected to a variety of temperatures and stresses during its fabrication and operation. It is thus important to investigate i) the stability of the microstructure at elevated temperatures, as one of the outstanding features claimed by the manufacturers is that once the component has been fabricated, the material cannot be hardened or softened by heat treatment, and ii) the mechanical properties at room and elevated temperatures.

The aim of the project is to study:-

1. Mechanical properties and microstructure of the cast alloys i.e. T-700 and related alloys.
2. Effect of heat treatment to the mechanical properties and microstructure.
3. The role of the microstructure in controlling crack initiation and propagation.
4. Alloy variations to achieve the best properties.

TABLE 1:

Basic compositions of Triballoys (Cabot Corpn., 1979)

	Co	Ni	Mo	Si	Cr	Laves phase vol %
T-400	62	-	28	2	8	50
T-700	-	50	32	3	15	40-60
T-800	52	-	28	3	17	60

(Figures quoted are in weight percent)

TABLE 2:

Comparison of hardness values (Cabot Corpn., 1979)

	<u>T-400</u>	<u>T-700</u>	<u>T-800</u>
Hardness Rockwell C	51-48	42-48	54-62
(Vickers Kg/mm ²	572-710	410-500	600-790)
(The figures quoted are for as cast material tested at room temperature).			

TABLE 3:

Determination of phase percent in T-700 (Cabot Corpn.)

Phase	(hkl) of peak	d spacing/A
FCC	(200)	1.78 to 1.81
Laves	(103)	2.14 to 2.17
Sigma	(411)	1.92
R (or other)	As appropriate	

TABLE 4:

Comparison of mechanical properties of Triballoys (Cabot Corp., 1979)

<u>Property</u>	<u>Tribaloy Alloy</u>		
	<u>T-400</u>	<u>T-700</u>	<u>T-800</u>
Hardness Rockwell C (H_V Kg/mm ²)	51-58 (572-710)	42-48 (410-500)	54-62 (600-790)
Tensile Strength MN/m ²	620		
Compressive strength MN/m ²	1896	1450	1780
Modulus of Elasticity GN/m ²	266	215	243
Charpy Impact Strength (un-notched) J	4.1	1.4	1.4
Transverse Rupture Strength (MN/m ²)	1379	660	725

TABLE 5:

Typical values of plane strain fracture toughness (Halstead, 1980; Cabot Corp., 1979; R.A. Smith, 1979)

<u>Material</u>	<u>Young's Modulus</u> $E \text{ (GN/m}^2\text{)}$	<u>Fracture Toughness</u> $K_{Ic} \text{ (MNm}^{-3/2}\text{)}$	<u>Strain Energy Release Rate</u> $G_{Ic} \text{ (J/m}^2\text{)}$
Steels:			
Medium carbon	210	54	257
High strength alloy		98	466
Maraging steel		76	362
AFC 77 Stainless		83	395
Aluminium alloys	72	23-30	375
Titanium alloys	110	38-73	345-664
WC-Co composites	100	13	130
PMMA	3	1.5	50
Concrete	40	0.2-1.4	20
Glass	70	0.3-0.6	6
Alumina	350	4	11
T-400	266	21-24	85
T-700	215	15-17	74
T-800	243	19-22	84

2. THE ALLOY SYSTEM

Topographically close packed phases (TCP) have been known to exist in binary and ternary systems for some considerable time. The TCP phases consist of A_2B type, θ , σ , χ and Laves phases, and these structures are characterized by the presence of hexagonal or pseudohexagonal nets (also called Kagome nets) which are superimposed in one or more of the planes of the reciprocal lattice (Laves, 1956; Hume-Rothery et al., 1969). In nickel alloys the matrix is fcc and both σ and Laves phases form in this matrix. These phases appear as thin plates often nucleating on the grain boundaries, where refractory elements, such as chromium and molybdenum which are constituents of the Laves and σ phase, concentrate (Schmidt & Ferris, 1975).

Investigation of phases in the ternary systems, Cr-Co-Ni, Cr-Co-Fe, Cr-Co-Mo and Cr-Ni-Mo found that the σ phase appeared to be an electron compound. In the Ni-Cr-Mo system, which is basically T-700, it was noted that no σ phase existed in the Ni-Cr binary but did exist in the ternary, where molybdenum replaced the chromium in forming the σ phase. This can be explained in terms of electron valency concentrations (Laves, 1956). The effect of molybdenum replacing chromium was also later observed to occur in the Laves phase within the ternary system.

Under normal circumstances, in nickel-based superalloys, the presence of Laves or σ phases is detrimental because of increased brittleness, and consequently the formation of these phases is generally avoided (Sims & Hagel, 1972). However, the uniqueness of the combined properties of the Triballoys does in fact depend on the formation of the Laves phase.

2.1 Theory of Laves phases

In a system where the atomic diameters of the components are too large to form interstitial phases and too small to form an electron-compound, it is possible to form an alloy structure called a Laves phase.

Laves phases are compounds which have the general form AB_2 , whose atomic diameters (d_A and d_B) are approximately in the ratio 1.2:1. In practice the ratio $d_A:d_B$ can differ greatly from this ideal packing value, (the A component is always larger). The particular Laves phase formed has a closely related close-packed structure which is either Cubic ($MgCu_2$), Hexagonal ($MgZn_2$) or Dihexagonal ($MgNi_2$); all being closely related structures differing only in the stacking of the similarly built close-packed layers. Certain Laves phases have a structure which changes with temperature, whilst others depend on composition (Allen, Delavignette & Amelinckx, 1972).

All three structures can be described in terms of the hexagonal lattice with axial ratios in the proportions 3:2:4 respectively (Berry & Raynor, 1953). Figure 1 shows the arrangement of the atoms in the three different types of Laves phase. The B atoms occupy the corners of the tetrahedra which are joined alternately point to point and base to base in ^{the} hexagonal structure and point to point throughout the cubic structure. The dihexagonal structure contains both types of arrangement (Berry & Raynor, 1953), but the A and B atoms never touch, there are only A-A and B-B contacts.

Laves phases are essentially determined by "size" effects. However, work has been carried out which confirms that the ratio of atomic diameters is not the only important contributing factor in the formation of Laves phases. Laves and Witte (1935) recognized long ago that the electron concentration is significant in determining which type of Laves phase is formed, and work by Bardos Gupta and Beck (1961) indicates that the average electron concentration (average number of electrons per atom outside the closed shell of the component atoms) may also be an important factor in determining whether or not a Laves phase can occur at all in a given system. Their work showed that with certain transition elements, Laves phases are absent at electron concentrations of 8 or larger, and these absences could not be accounted for on atomic size considerations

alone.

Although the ideal ratio of atomic diameters for efficient sphere packing is given by $d_A/d_B = 1.222$, (Allen, Delavignette & Amelinckx, 1972; Laves, 1956; Duwes, 1956; Bilski, 1969), in systems with a coordination number of 12 and which do have Laves phases the ratio ranged from 1.10 to 1.46, and Laves phases were absent when d_A/d_B was less than 1.10.

So the chemical composition of many intermetallic compounds is determined by the average electron concentration as well as the atomic arrangements that are formed to achieve the lowest possible energy of the total alloy system (Laves, 1956). So providing the "size" considerations are met the actual stoichiometric formula of the compound is variable. For example, in T-700 the formula of the Laves phase varies from MoNiSi to $\text{Mo}_2\text{Ni}_3\text{Si}$.

However, Laves phases were also absent in some alloys with a diameter ratio between 1.10 and 1.46, showing that size is not a sufficient criterion for the formation of Laves phases.

As mentioned previously the average electron concentration is also a contributory factor in the formation of Laves phases. Hume-Rothery et al. (1969) found that for certain

pseudobinary alloys of the form $Mg(B^I, B^{II})_2$, where B^I and B^{II} are taken from the elements Cu, Ag, Zn or Si, the value of e/a determined which of the three structures was formed. With increasing electron concentration one or more of the Laves phases were formed in the successive order cubic, dihexagonal and then hexagonal structures. Following this work many more combinations of elements have been discovered which have similar effects.

When the binary Laves phase is formed with titanium, niobium, tantalum or zirconium as the A element, and a transitional metal of the first long period as the B element, structural variations have been observed that are indicative of electronic effects. It is interesting to note the absence of any Laves phase structure containing nickel as the B atom. It appears that although a value of approximately 1.2 for the ratio of atomic diameters is a necessary condition for the formation of Laves phases, it is not a sufficient condition for predicting their existence. Another electronic effect was also observed in ternary phases containing silicon, where the silicon appears to act as an electron acceptor in a similar manner to that seen in the σ phases. So tantalum-nickel, niobium-nickel and titanium-nickel phases for example, which are not formed in the binary systems are stabilized by the addition of silicon to give the compound A_2B_3Si . This suggests that the third element reduces the effective electron concentration in

these phases, thereby lowering the Fermi energy and the free energy of the alloy (Hume-Rothery et al., 1969).

Considering the binary and ternary systems related to the T-400 and T-800 cobalt-based Triballoys, Gladyshevskii and Kuzma (1960) discovered a ternary phase $\text{Mo}(\text{CoSi})_2$ which existed at a composition between MoCoSi and $\text{Mo}_2\text{Co}_3\text{Si}$ but was no longer seen as the composition approached that of the binaries Mo-Co and Mo-Si. Their X-ray study enabled them to establish that it was a Laves phase with an hexagonal structure. Thus a Laves phase exists in the ternary MoCoSi alloy, but not in the constituent binaries which have d_A/d_B ratios of 1.11 and 1.045 for Mo-Co and Mo-Si respectively.

The nickel-based Tribaloy consists of approximately 40-60% by volume of intermetallic phase, primarily Laves phase. If nickel replaces cobalt in the Mo-Co-Si ternary alloy, it might be expected that a Laves phase would form with a similar structure and composition i.e. $\text{Mo}(\text{Ni,Si})_2$, between the limits MoNiSi and $\text{Mo}_2\text{Ni}_3\text{Si}$: but a Laves phase does not form with nickel atoms in the B position ($d_{\text{Mo}} > d_{\text{Ni}}$). The atomic radius ratio $d_{\text{Mo}}:d_{\text{Ni}}$ is 1.13, which is almost sufficient to form a Laves phase on size considerations, but the average electron concentration has a value of eight, so no Laves phase forms. Since it forms on the addition of silicon, it appears that the silicon acts to adjust the average electron concentration enabling the Laves phase to

form.

2.1.1 Effect of Silicon

Numerous investigations have been carried out on the influence of silicon additions to various alloys which contain TCP phases, and more specifically Laves phases. The stabilising effects of silicon have been observed in Cr-Nb-Si alloys (Goldschmidt & Brand, 1961), Mn-Cu-Si (Mukerjee & Gupta, 1973), V-Co-Si, V-Ni-Si, Mn-Co-Si (Bardos et al., 1961; Bardos & Beck, 1966), and in Nb-Fe-Si and Nb-Co-Si alloys (Singh & Gupta, 1972). They all confirm the stabilising effect of silicon first put forward by Hume-Rothery et al. (1969).

Gupta, Rajan and Beck (1960) also concluded that in alloys containing transition element and forming σ phases, silicon may act as an acceptor of electrons, thus stabilizing the σ phase at electron concentrations higher than those at which it would normally occur.

A phase recognized as related to the hexagonal Laves phase was found by Westbrook et al. and they investigated whether Laves phases, which did not occur in binary nickel and cobalt systems, were able to form in the ternary system by adding silicon. They concentrated on alloys of the type $A_2(B_3Si)$, where silicon substitutes for 25% of the

B-component in which the binary AB_2 Laves phase does not form. X-ray diffraction and metallographic examination revealed that all the alloys chosen contained the hexagonal type Laves phase. In particular, they found Laves phases present in ternary systems for which the d_A/d_B ratios are 1.08 and 1.10. However, in these cases a larger amount of silicon had to be added. They hypothesised that if the silicon with a coordination number of 12 and an atomic radius of 0.134nm, occupies B-positions in the structure, then the average d_B becomes larger on alloying with silicon.

It follows that the d_A/d_B ratio is even further removed from the ideal value of 1.222, which suggested that the absence of the corresponding binary Laves phases is not a result of atomic size conditions, but a consequence of the electron concentration. The effect of the silicon appeared to decrease the effective electron concentration.

Bardos et al., investigated the effective atomic radius of the silicon in ternary Laves phases, ^{and} similarly concluded that the silicon decreased the effective electron concentration in stabilising the Laves phase. However, they also noted that the calculated value of the silicon radius varied according to what other elements were present in the Laves phase. From this it was concluded that the concept of atomic radii as defined in terms of touching spheres has a limited significance in this case (Bardos et al., 1963). In an observation on the two papers (Bardos et al., 1961;

Bardos et al., 1963) Hume-Rothery noted that the silicon radius in the Laves phases has values between 0.116 and 0.121nm and is almost very similar to that for the covalent element silicon at 0.117nm. The acceptance of electrons by the silicon is not so much an accumulation of negative charge on the silicon ion as suggested by Bardos et al., as the formation of covalent bonds in using up the electrons ((Hume-Rothery, 1965).

The quantity of silicon needed to stabilise the Laves phase varies from one alloy system to another, which may be due to the presence of other phases at or near the alloy composition in question (Mittal et al., 1978). The Laves phases are also stable over a wide range of silicon content (Bardos et al., 1963).

All the Laves phases investigated that are stabilised by silicon additions are of the hexagonal type, with one exception. In the Mn-Ni-Si system a cubic structure is stable at low silicon concentrations but a hexagonal type is stable at higher silicon concentrations (Mittal et al., 1978). The hexagonal structure is the most stable from a geometrical point of view (Laves, 1956) and so this is the preferred form adopted when the Laves phase is stabilised.

As previously seen an addition of silicon to a system can stabilise a Laves phase in the ternary system where it did

not exist in the binary. Also in a few cases, if a Laves phase does exist in a binary system then the addition of silicon extends it into the ternary (Mittal et al., 1978).

In summary the average number of electrons ^{per atom} / for nickel and molybdenum is 8, and as already stated formation of the primary Laves phase is unlikely, but the addition of silicon to form a compound between NiMoSi and Ni₃Mo₂Si acts as an electron acceptor and reduces the e/a thus Laves phases are able to form.

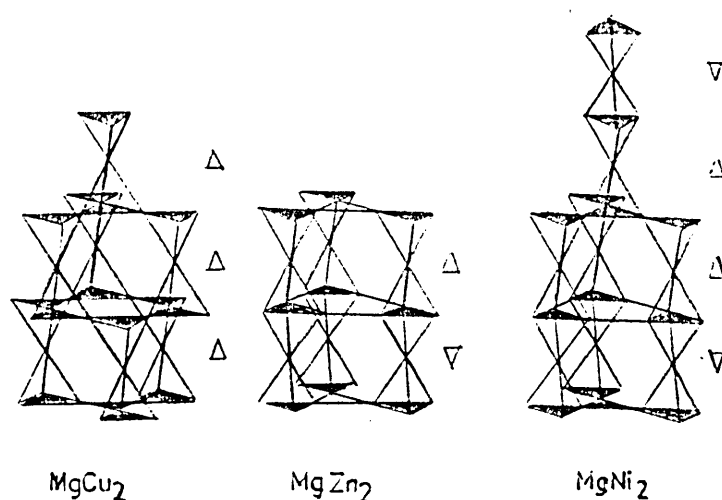


FIGURE 1: Arrangement of tetrahedra of B atoms in the three Laves phases. The symbols identify the type of stacking; Δ indicates the case in which an upper layer is stacked above three atoms in orientation Δ , and vice versa for the symbol ∇ . (Berry & Raynor, 1953)

2.2 The Matrix

The hard intermetallic primary phase is dispersed in a matrix α , which consists of a relatively soft nickel solid solution. Various methods, including microscopy and X-ray diffraction patterns, may be used to determine the proportion of phases present within the compound.

Although pure nickel alone does not have a particularly high modulus of elasticity or low diffusivity (two factors that promote rupture and creep resistance) the basic reasons for using a nickel-base alloy for high temperature and strength requirements are firstly its high tolerance for alloying without phase instability owing to its nearly filled third electron shell and secondly, its tendency, when chromium is added, to form Cr_2O_3 -rich protective scales, which have a low cation vacancy content, thereby restricting the diffusion rate of metallic elements outward and oxygen, nitrogen and sulphur and other aggressive atmospheric elements inwards. (Sims & Hagel, 1972).

Since Tribaloy T-700 consists mainly of nickel, molybdenum and chromium it is worth considering the alloying effects of these elements in turn. (Silicon having previously been discussed when considering Laves phase stability).

Nickel itself has a face centred cubic (fcc) crystal

structure with a melting point of 1728K and atomic radius of 0.124nm. Both molybdenum and chromium have body centred cubic (bcc) structures and their atomic radii are greater than nickel (0.136nm = Mo; 0.125nm = Cr). These values are corrected for CN = 12). (Laves, 1956; Tennent, 1971).

2.2.1 Ni-Mo

Figure 2 shows the Ni-Mo equilibrium diagram. Since the atomic radius of molybdenum is somewhat greater than that of nickel, molybdenum atoms on the addition to nickel must go into solution by substitution which leads to a distortion of the lattice, because molybdenum is thereby replacing nickel and large amounts of molybdenum can be accommodated, and molybdenum is thus considered a solid solution strengthener.

Casselton & Hume-Rothery (1964) carried out a detailed examination of the Ni-Mo phase diagram. The β -phase, which lies on the Mo-rich side, was thought to have a tetragonal cell, and this was used as the basis for indexing powder photographs. Although the complete structure was not determined, it was suggested that it probably related to the σ -structure.

The alloy also contains an intermediate γ -phase whose composition limits include the value corresponding to MoNi_3 . This γ -phase has been found to have an orthorhombic structure.

The δ -phase was found to have a restricted composition range, and does not include the exact ratio MoNi_4 . They also found that the tetragonal cell obtained could be regarded as a superlattice of the fcc solid solution of molybdenum in nickel.

The authors found a number of similarities between the Ni-Mo and Co-Mo phase diagrams, the main difference being that, in spite of their similar size, the solubility of nickel (atomic radius 0.124nm) in molybdenum is very much less than that of cobalt (atomic radius 0.125nm). This is in agreement with the Hume-Rothery electrochemical rule, where cobalt is higher in the electrochemical series than nickel (i.e. more negative potential). In the cobalt-rich and nickel-rich ends of their phase diagrams, both show a phase with the composition MoX_3 . The structure of MoNi_3 is orthorhombic, which is only a slightly distorted modification of an ordered close packed hexagonal (cph) structure, whilst MoCo_3 possesses an ordered cph structure.

2.2.2 Ni-Cr

Chromium also has a very similar atomic radius to that of nickel (Cr atomic radius = 0.125nm) and it would be expected that there would be very little distortion of the lattice by the addition of chromium to nickel, (Figure 3). Like molybdenum, chromium is a solid solution strengthener

and also forms carbides, but the main reason for the addition of chromium to any nickel alloy is because it forms an oxide (Sims & Hagel, 1972).

2.2.3 Ni-Cr-Mo

Figure 4 shows the ternary phase diagram of Ni-Cr-Mo at 1250°C, proposed by Bloom and Grant (1954). The phases that appear in the isothermal section are

- (Cr) A solid solution of chromium containing nickel and molybdenum and having a body-centred cubic structure. The solubility shown for nickel in the (Cr) phase may be slightly too high in the Mo-Rich region.
- (Ni) A solid solution of nickel containing chromium and molybdenum, and having a face centred cubic structure.
- MoNi An intermetallic compound denoted as the β -phase in the Ni-Mo diagram (Figure 1).
- σ A hard, brittle intermetallic phase with a tetragonal structure. It is isomorphous with the σ -phase in other systems, such as Fe-Cr.

P A ternary intermetallic phase of unknown crystal structure.

Rideout et al. (1951) give an isothermal section at 1200°C. It is reasonably close to the isothermal section at 1250°C shown in Figure 4, except that the compositional range of the P-phase appears to extend further toward the Ni-Mo side.

Molybdenum is a slow diffusing element and its presence lowers the diffusivity of chromium. (Sims & Hagel, 1972). The P-phase identified in the ternary diagram could possibly be the Laves phase.

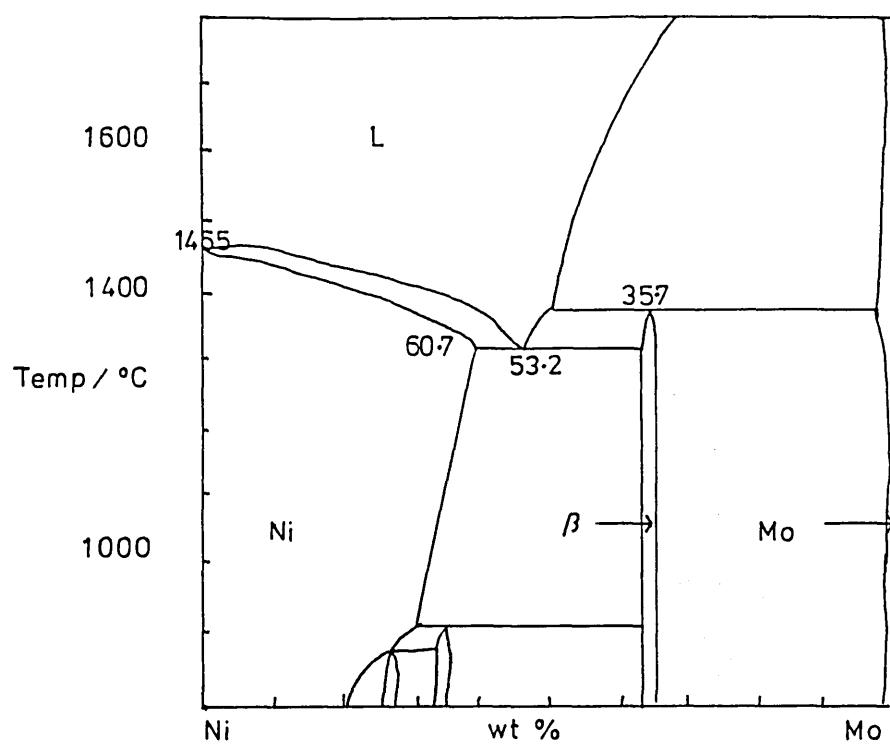


FIGURE 2: Ni-Mo binary phase diagram (Am. Soc. Met.).

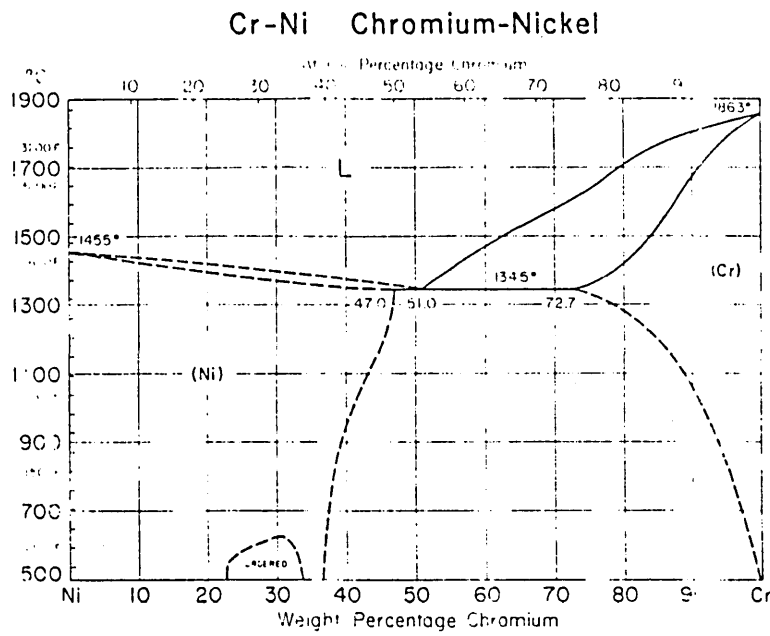


FIGURE 3: Ni-Cr binary phase diagram (Am. Soc. Met.)

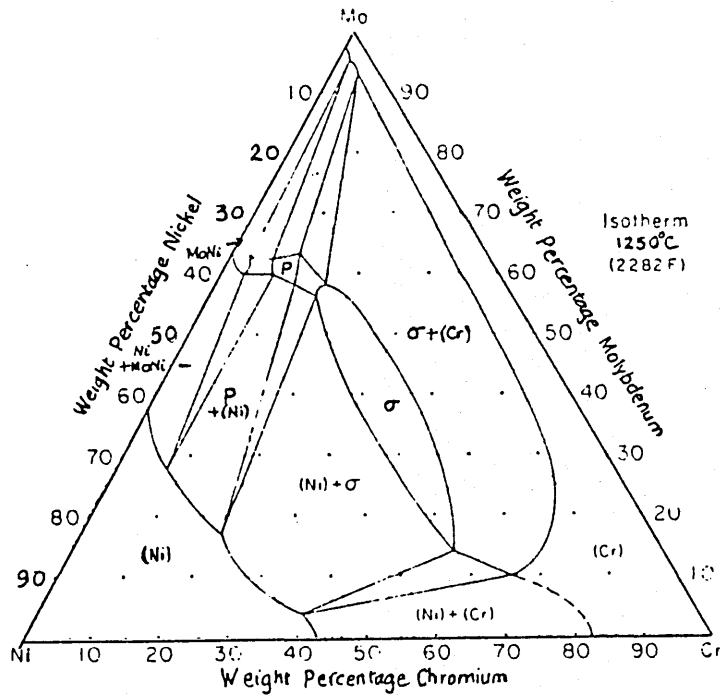


FIGURE 4: Ni-Cr-Mo ternary phase diagram (Am. Soc. Met.)

2.3 Iron Additions

As mentioned previously, T-700 is not used extensively due its brittleness, and thus it is necessary to consider adding various metals to improve its overall mechanical properties.

A principal candidate for alloying with T-700 is Iron, the two main reasons are as follows:

i) if it could be introduced without significantly affecting the properties, then the amount of nickel in the alloy is reduced which would reduce its cost (nickel being more expensive than iron). As Ni-Fe superalloys are prone to the formation of minor phases such as the Laves phase (Sims & Hagel, 1972), it might be that small additions of iron would vary the amount of Laves phase formed.

ii) Since the Tribaloy would be generally used on steels as a hardfacing material, there is inevitably some diffusion of iron into the alloy coating which will cause dilution. Thus it is necessary to determine the effect this has on the mechanical properties. If the good wear

resistant properties are retained, thinner layers of the alloy may be employed when used as a hardfacing material, which leads to a saving in the cost of materials.

Some preliminary work on the addition of iron to the cobalt-based Triballoys (T-400 and T-800) was carried out by Halstead (1980), the results of which are shown in Table 6. She found that the effect of adding iron was to stabilise the fcc form of the cobalt solid solution. She also found that there was a decrease in the hardness and in the percentage of primary Laves phase for both Triballoys as the amounts of iron added were increased.

Although no change in the fracture toughness was found, the modulus of rupture did increase with increasing iron content, which was very encouraging from the point of view of wear resistance.

Information regarding the quaternary phase diagram of Ni-Mo-Cr-Fe could not be found, thus the ternary phase diagrams for Cr-Fe-Ni and Fe-Mo-Ni must briefly be considered together with that for Ni-Mo-Cr (Figure 4).

Figures 5, 6 and 7 show the phase diagrams for Fe-Ni, Fe-Mo-Ni and Cr-Fe-Ni respectively.

From the Fe-Ni binary phase diagram it appears that γ is the predominant phase even for small concentrations of iron. However, it should be noted that γ' is the ordered phase, based on the stoichiometric composition of FeNi_3 . For temperatures above about 320°C the alloy will start to disorder.

This γ phase is also present in both the ternaries.

Figure 6 is the ternary phase diagram for Fe-Mo-Ni for the isothermal section at 1200°C . (Das et al., 1952).

The phases appearing are

(Fe,Mo) A solid solution of iron and molybdenum containing nickel and having a bcc structure.

(Fe,Ni) A solid solution of iron and nickel
or γ containing molybdenum and having an fcc structure.

- MoNi An intermetallic compound.
- or β Iron can be dissolved in this phase to some extent.
- P A hard, brittle intermetallic phase. The crystal structure is unknown, but the phase is isomorphous with the phase of the same designation in the Cr-Mo-Ni system.
- (Fe,Ni)Mo₂ An intermetallic phase with a composition close to Fe₃Mo₂ in the Fe-Mo binary system.

Most of the studies of the Cr-Fe-Ni system have been restricted to the iron-rich and nickel-rich regions because most stainless steels and the high temperature nickel-based alloys containing chromium are associated with these regions. The principal features of the Cr-Fe-Ni system include the phase equilibria resulting from the high temperature fcc structure of γ -Fe (Austenite) and of nickel which are completely miscible with each other; the low temperature bcc structure of α -Fe (ferrite) and chromium, which are completely miscible above 821°C; and the formation of the σ -phase at higher

chromium contents, at temperatures below 821°C, as seen in figures 7, 8 and 9.

The ferrite-stabilizing influence of chromium is predominant at high and low temperatures, whereas the austenite-stabilizing influence of nickel is predominant at intermediate temperatures (Figure 6). The outstanding feature, however, is the pronounced reluctance of metastable austenite to transform when once established at high temperatures. Aborn and Bain (1930) and Schafmeister and Ergant (1939) showed that the temperature range in which the stable γ -region is broadest lies between 900°C and 1300°C, but the range for a particular phase is often considerably narrower and depends on composition.

TABLE 6: Effect of iron additions on microstructure and mechanical properties of Tribaloy (Halstead, 1980).

Test and Units	T-400 arc melt	T-400 5% Fe	T-400 10%Fe	T-400 15%Fe
V.H.N. as cast	658 $\pm$ 25	646 $\pm$ 15	611 $\pm$ 10	597 $\pm$ 13
V.H.N. after 20 hours 800°C	729 $\pm$ 9	686 $\pm$ 8	619 $\pm$ 12	597 $\pm$ 13
Microhardness Laves 100g	1068 $\pm$ 90	1018 $\pm$ 100	1013 $\pm$ 90	1018 $\pm$ 70
Microhardness Eutectic 50g	598 $\pm$ 41	588 $\pm$ 70	590 $\pm$ 60	575 $\pm$ 50
Quantitative % Vol. Fraction Laves	42 $\pm$ 8	35 $\pm$ 7	25 $\pm$ 3	17 $\pm$ 7
Size Laves μ m	6 $\pm$ 7	8 $\pm$ 6	5 $\pm$ 10	5 $\pm$ 12
K _{IC} (MNm ^{-3/2})	22.3 $\pm$ 2	20.8 $\pm$ 2	24.8 $\pm$ 1.2	22.9 $\pm$ 1.5
MOR σ_f (MNm ⁻²)	917 $\pm$ 54	965 $\pm$ 55	1280 $\pm$ 90	1279 $\pm$ 115
Flaw size mm ²	0.17	0.11	0.07	0.05
Test and units	T-800 arc melt	T-800 5%Fe	T-800 10%Fe	T-800 15%Fe
V.H.N. 50kg as cast	728 $\pm$ 15	668 $\pm$ 10	654 $\pm$ 20	629 $\pm$ 12
V.H.N. after 20 hours 800°C	809 $\pm$ 8	748 $\pm$ 20	676 $\pm$ 21	661 $\pm$ 16
Microhardness Laves 100g	1081 $\pm$ 70	1017 $\pm$ 50	1027 $\pm$ 70	1020 $\pm$ 90
Microhardness Eutectic 50g	-	610 $\pm$ 60	589 $\pm$ 50	590 $\pm$ 40
Quantitative % Vol. Fraction Laves	70 $\pm$ 12	57 $\pm$ 7	43 $\pm$ 8	26 $\pm$ 6
Size Laves μ m	9 $\pm$ 7	8 $\pm$ 10	8 $\pm$ 12	4 $\pm$ 20
K _{IC} (MNm ^{-3/2})	19.2 $\pm$ 1.8	20.9 $\pm$ 2.3	19.1 $\pm$ 2.8	19.8 $\pm$ 1.4
MOR σ_f (MNm ⁻²)	752 $\pm$ 35	746 $\pm$ 60	809 $\pm$ 55	871 $\pm$ 82
Flaw size mm ²	0.21	0.31	0.15	0.13

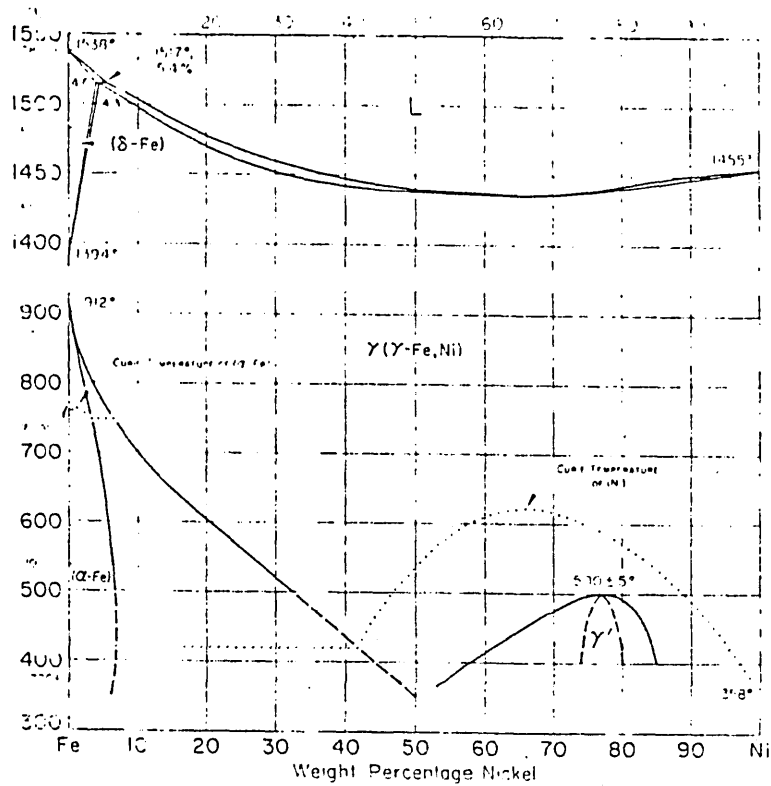


FIGURE 5: Fe-Ni binary phase diagram (Am. Soc. Met.)

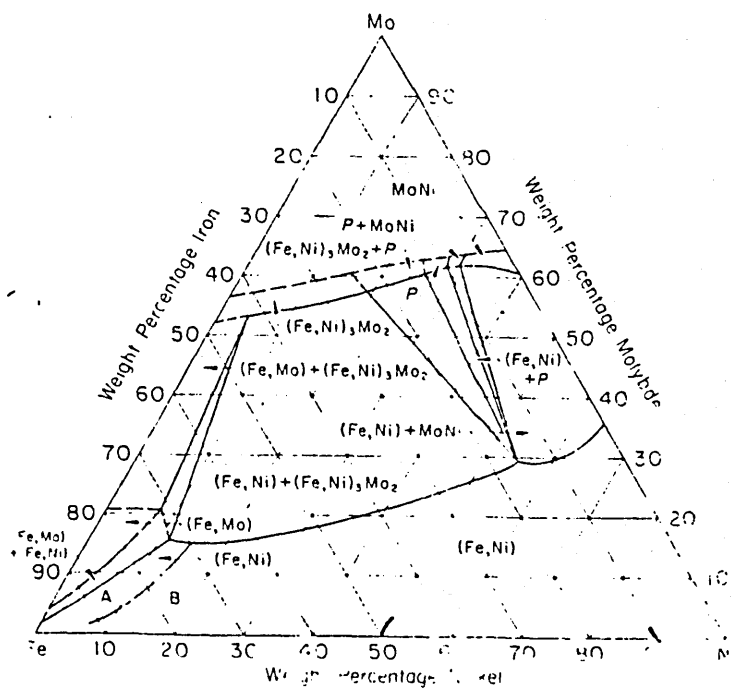


FIGURE 6: Fe-Mo-Ni ternary phase diagram. Isothermal section at 1200°C. (Am. Soc. Met.; Das, Rideout & Beck, 1952).

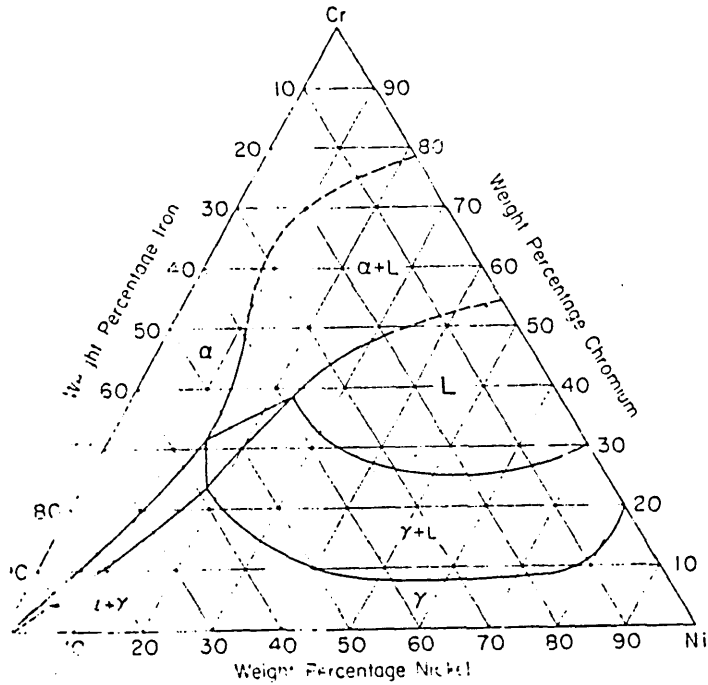


FIGURE 7: Cr-Fe-Ni ternary phase diagram. Isothermal section at 1400°C. (Am. Soc. Met.; Aborn & Bain, 1930; Schafmeister & Ergang, 1939).

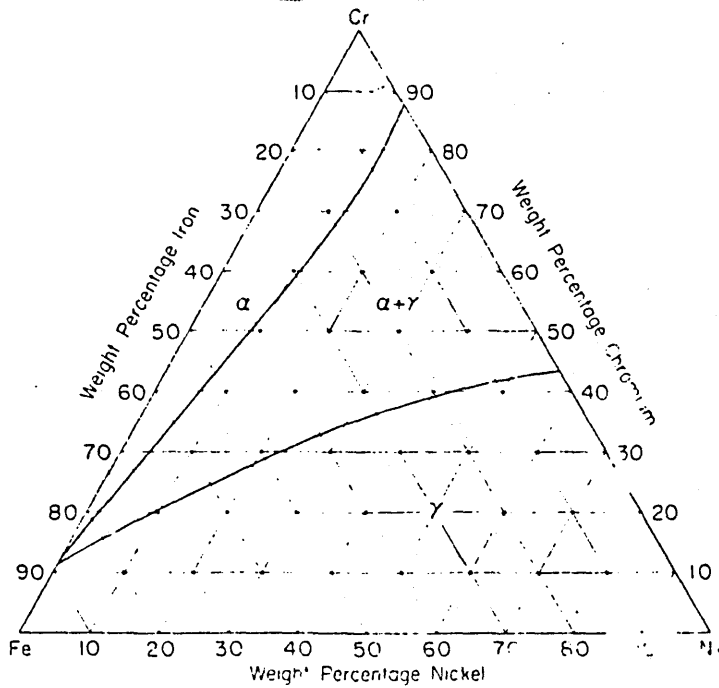


FIGURE 8: Cr-Fe-Ni ternary phase diagram. Isothermal section at 1100°C. (Am. Soc. Met.; Aborn & Bain, 1930; Schafmeister & Ergang, 1939).

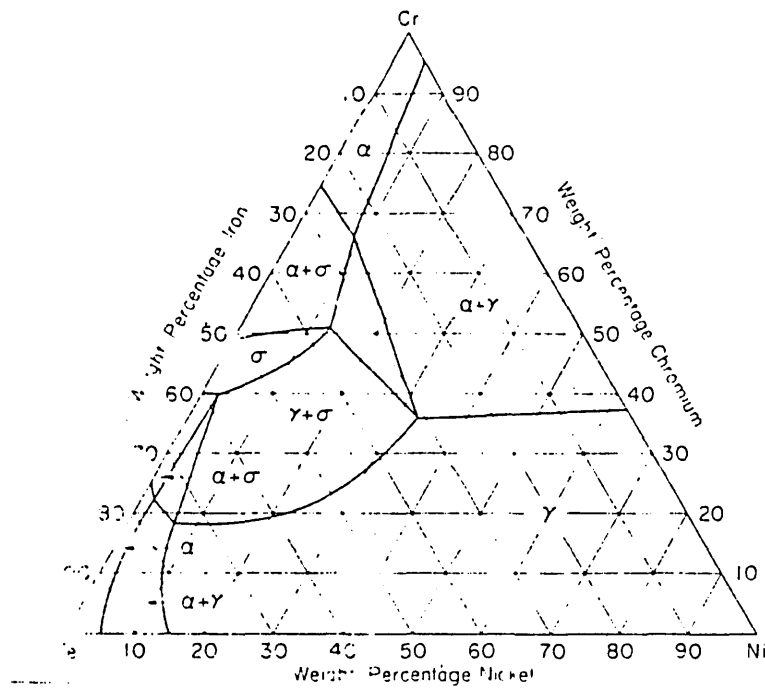


FIGURE 9: Cr-Fe-Ni ternary phase diagram. Isothermal section at 650°C. (Am. Soc. Met.; Aborn & Bain, 1930; Schaeffmeister & Ergang, 1939).

3. FRACTURE AND MICROSTRUCTURE

All mechanical properties are ultimately decided at the atomic level, for example the strength of a material is related to the energy necessary to separate the atoms in the structure. Hence the type of bonding influences the resulting mode of fracture, whether brittle or ductile.

The metallurgical factors which influence the toughness, or the resistance of a material to crack nucleation and propagation, are the strength level, the microstructure and the presence of inclusions or minor impurity elements which can give rise to embrittlement.

To measure a material's resistance to crack propagation, it is necessary to determine its fracture toughness. This can then be used to calculate the largest acceptable defect size at a particular operating stress, and the effect of the microstructure to resisting, or otherwise, the propagation of the crack through the material. To do this, it is necessary initially to explain the background theories used in determining these values, and then to correlate the values to the microstructure.

3.1 Theory of fracture toughness

All structures are bound to contain sharp, crack-like defects of some form or other, and it is necessary to know a numerical value for the applied stress which will cause a defect of known length to propagate in a catastrophic manner. The general method used to calculate such stresses was developed as a result of the work which A.A. Griffith carried out some fifty years ago to explain the anomalies between experimental values and theoretical predictions for the ideal fracture strengths of glasses.

The ideal fracture strength was first derived by Orowan by considering the stress necessary to cause a crystalline body to fracture across a particular cleavage plane. Figure 10 shows the bonding energy as a function of distance of separation of the atoms in a crystalline body. Assuming the atomic spacing within the lattice to be b_0 , and the lattice is subjected to a tensile stress σ , the stress required to cause fracture can be calculated as follows.

The bonding energy U , as a function of atomic separation, has a minimum at the equilibrium lattice spacing b_0 , and the total energy which must be supplied to separate the 2 atoms to infinity is given by U_0 (Fig.10). This work to cause a fracture in a

crystalline solid is often equated to twice the surface tension γ , because the work done has provided enough energy to create two new surfaces, each of energy γ . The force required to separate the atoms can be derived directly by differentiating the energy-distance curve with respect to distance (Figure 11), to give

$$F = \frac{dU}{db} \quad (1)$$

The force is at zero at equilibrium spacing $b = b_0$ and reaches a maximum at the point of inflection. The initial slope represents the stiffness of the atomic spring model, and is related directly to Young's modulus.

Thus this modulus depends on the form of the energy-distance curve and so general relationships between modulus and the type of atomic bonding can be deduced.

If $(b - b_0) = x$ then the strain can be written as x/b_0 . Since the stress $\sigma = F/b_0$, then the atomic stress-strain curve is as shown in Figure 12.

If this curve is assumed to be half that of a sine wave, then the relationship between σ and x is given by

$$\sigma = \sigma_{\max} \sin \left(\frac{2\pi x}{\lambda} \right) \quad (2)$$

where λ is the wavelength i.e. when

$$x = \lambda/4, \quad \sigma = \sigma_{\max}.$$

The total area under this curve represents the work supplied when the plane is fractured. So

$$\frac{\lambda \sigma_{\max}}{2\pi} \left(\cos \frac{2\pi x}{\lambda} \right) = U_0 = 2\gamma \quad (3)$$

$$\text{which gives } \frac{\lambda \sigma_{\max}}{\pi} = U_0 = 2\gamma \quad (4)$$

For small displacements the atomic stress can be written as

$$\sigma = \sigma_{\max} \frac{2\pi x}{\lambda} = \frac{E x}{b_0} \quad (5)$$

thus on rearranging

$$\lambda = \frac{\sigma_{\max} 2\pi b_0}{E}$$

and substituting for λ in equation 4 gives

$$\frac{2 \sigma_{\max}^2 b_0}{E} = 2\gamma \quad (6)$$

The expression for the ideal fracture strength can be rewritten as

$$\sigma_{\max} = \sqrt{\frac{E\gamma}{b_0}} \quad (7)$$

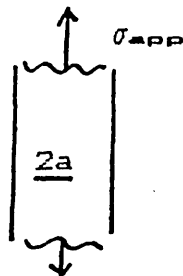
Thus high strength can be associated with a high surface energy and high stiffness and a small lattice spacing.

The theoretical fracture strength of a solid according to equation 7 is of the order of $E/10$. However, for most materials this value is unrealistic due to the presence of flaws, and Griffith extended his calculations of the energy required to form new fracture surfaces and the elastic strain energy release rate to take into account the fact that all materials have inherent crack-like defects. Thus defects of this nature produce a weakening effect because of the high local stresses concentrated at the crack tip.

The main achievement of Griffith in providing a basis for the fracture strengths of bodies containing cracks was his realisation that it was possible to derive a thermodynamic criterion for fracture by considering the total change in energy of a cracked body as the crack length was increased.

Briefly, if it is assumed that the crack length is $2a$,

in an infinite body of unit thickness, lying normal to a uniformly applied stress σ_{app} , and plane strain conditions are also assumed, for linear elastic behaviour, an energy balance exists



Elastic strain energy

$$W = \frac{-\sigma_{app} \pi a^2 (1-\nu^2)}{2E} \quad (8)$$

and

$$\text{Surface energy } S = 2\gamma a \quad (9)$$

where γ = surface energy/unit area

ν = Poisson's ratio

The total energy, which is the work done on the specimen

$$U = W + S \quad (10)$$

and the maximum occurs when (Figure 13)

$$\frac{dU}{da} = 0 = \frac{dW}{da} + \frac{dS}{da} \quad (11)$$

resulting in

$$\sigma_{app} = \left(\frac{2E\gamma}{\pi(1-\nu^2)a} \right)^{1/2} \quad (12)$$

So for a given stress, ^{and} a crack length greater than a

critical value the crack will propagate spontaneously to failure.

From Figure 14, where the lines intersect at the critical crack length a^*

surface energy / unit area = strain energy release rate

This occurs when the strain energy release rate $dW/da = G$ achieves a critical value $2\gamma = G_c$. Orowan and Irwin modified this equation for non brittle materials by $(2\gamma + \gamma_p)$ resulting in $\sigma = (E(2\gamma + \gamma_p)/\pi a)^{1/2}$ where $\gamma_p > 2\gamma$ for non brittle materials, and γ_p represents the energy expended in the plastic work necessary to produce unstable crack propagation.

To apply linear elastic fracture mechanics, it is assumed that the plastic zone ahead of the crack tip is small compared with the other dimensions of the specimen, and the fracture event can be characterised by a critical value of elastic strain energy release rate, G_{crit} which is a measure primarily of the amount of plastic work which must be done before the crack extends. This value is related to the stress intensity factor by

$$G = \frac{K^2 (1-\nu^2)}{E} \quad (13) \text{ in plane strain}$$

and $G = \frac{K^2}{E}$ (14) in plane stress

For plane strain situations, this term is called the plane strain fracture toughness K_{Ic} , where the suffix I refers to the mode of failure, in this case the tensile opening mode. The stress intensity factor can be related to the applied stress and the crack length by

$$K_I = \sigma_{app} (\pi a)^{1/2} \quad (15)$$

for a central crack of length $2a$.

Thus comparing equations for idealised fracture (i.e. no plastic deformation), K_{Ic} is equivalent to $(2E\gamma)^{1/2}$ and for fracture with plastic deformation $K_{Ic} = (E (2\gamma + \gamma_p))^{1/2}$ for plane stress.

So in a very brittle material less energy would be absorbed in fracture than in a ductile material, and the effective surface energy and the K_{Ic} value would be smaller. (Knott, 1973, 1977, 1978)

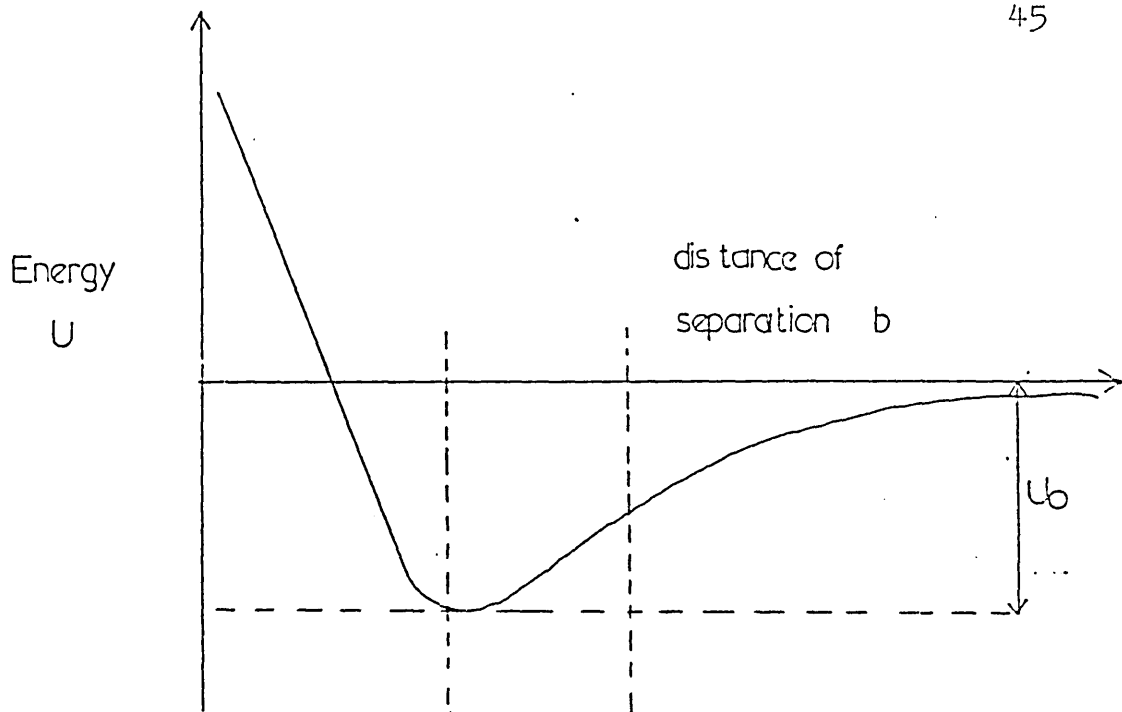


FIGURE 10: Bonding energy as a function of distance of separation (Lawn & Wilshaw, 1975; Knott, 1973).

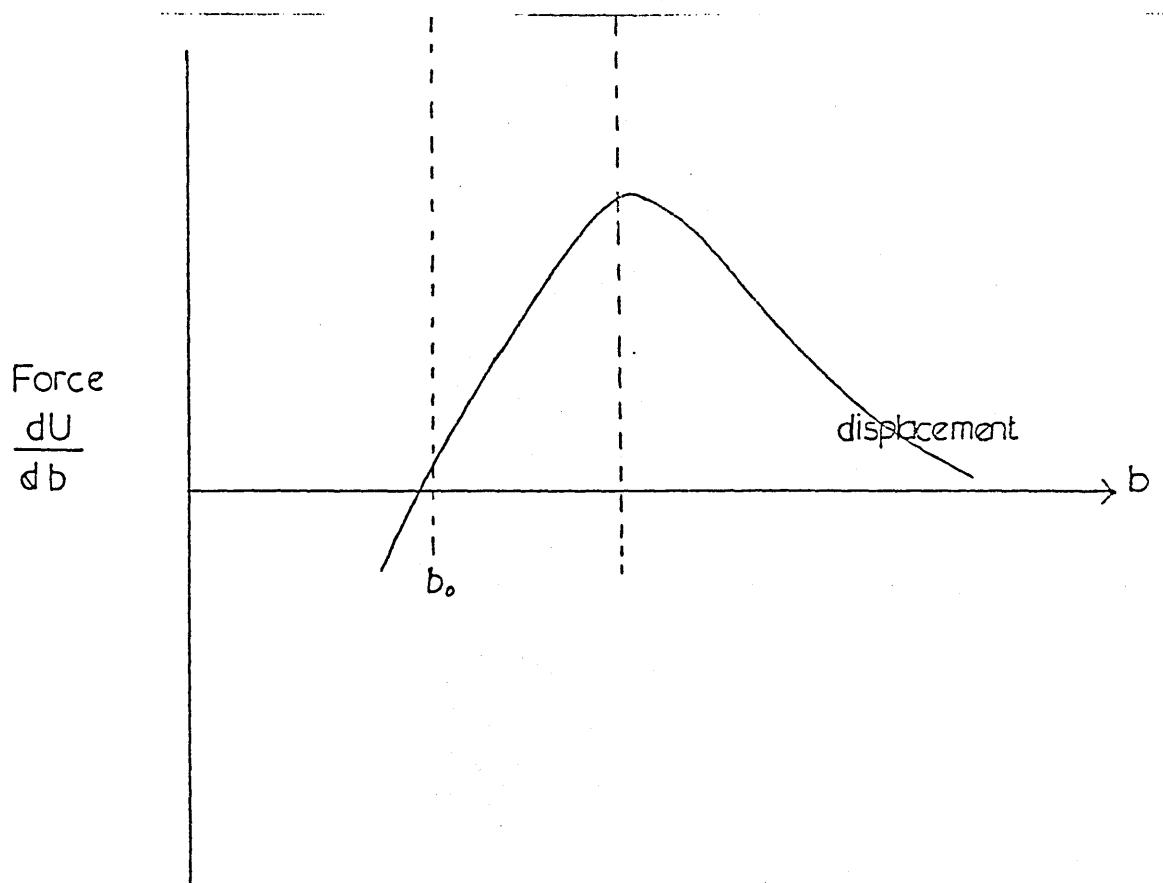


FIGURE 11: Force/Displacement curve (Lawn & Wilshaw, 1975; Knott, 1973).

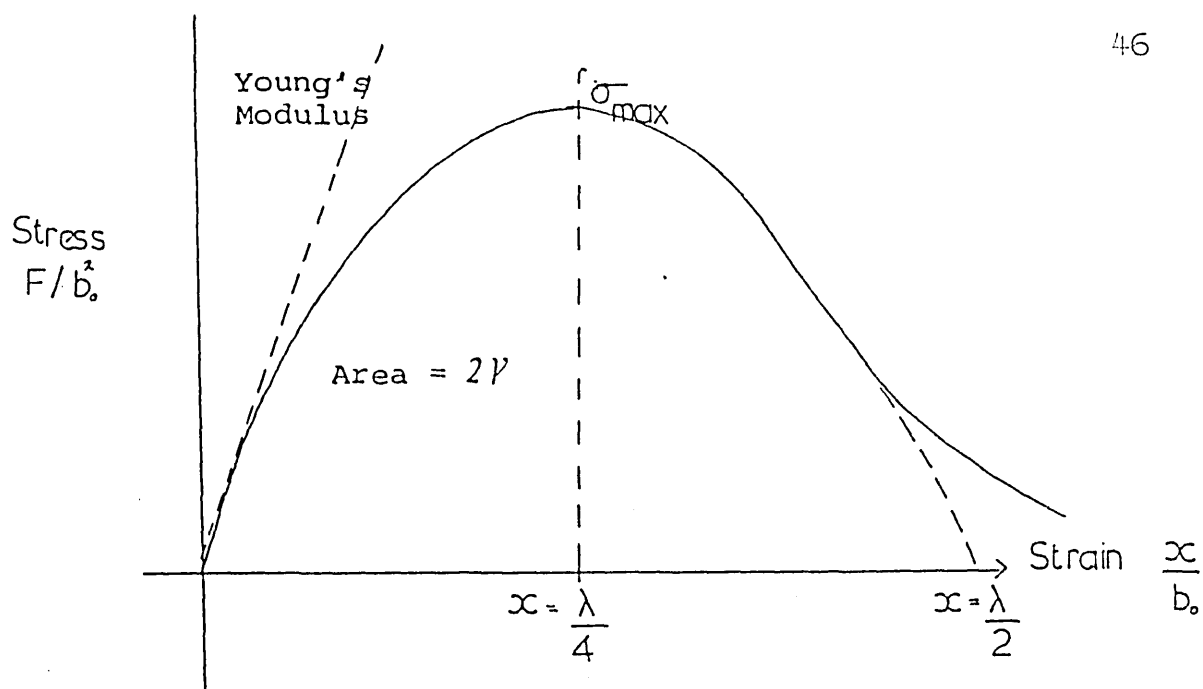


FIGURE 12: Atomic Stress-Strain Curve.

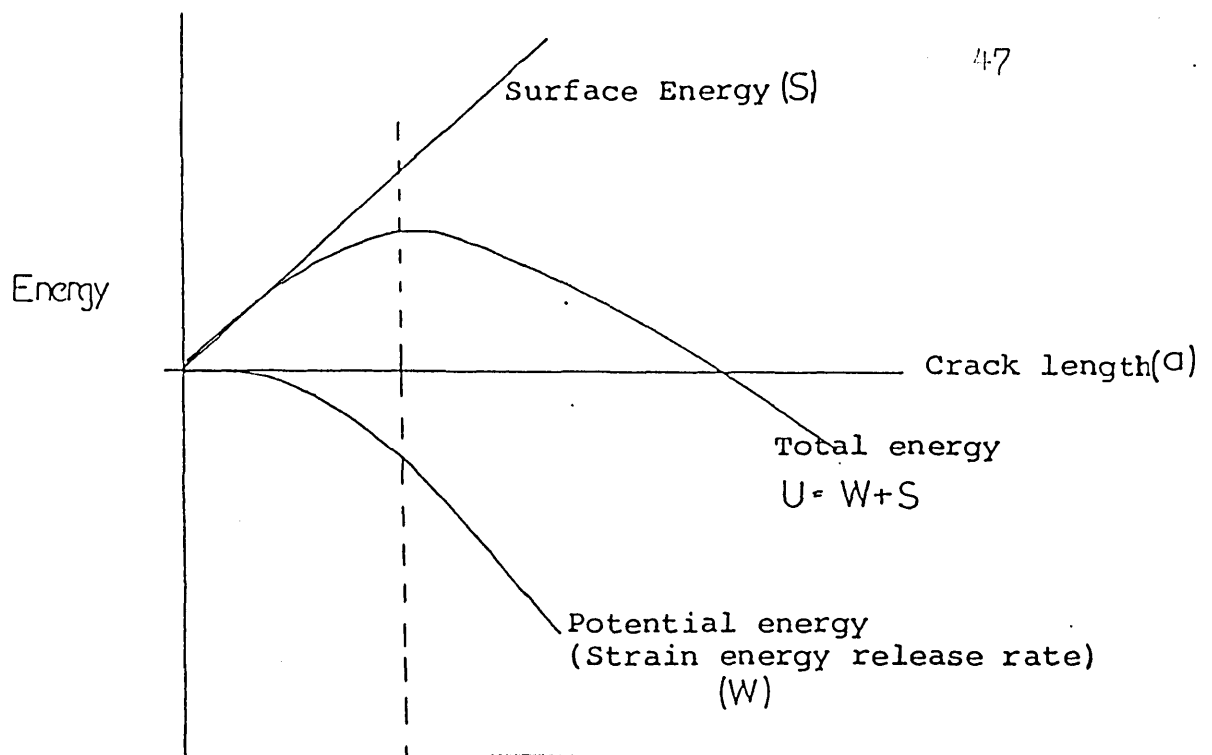


FIGURE 13: Variation of energy with crack length (Knott, 1973).

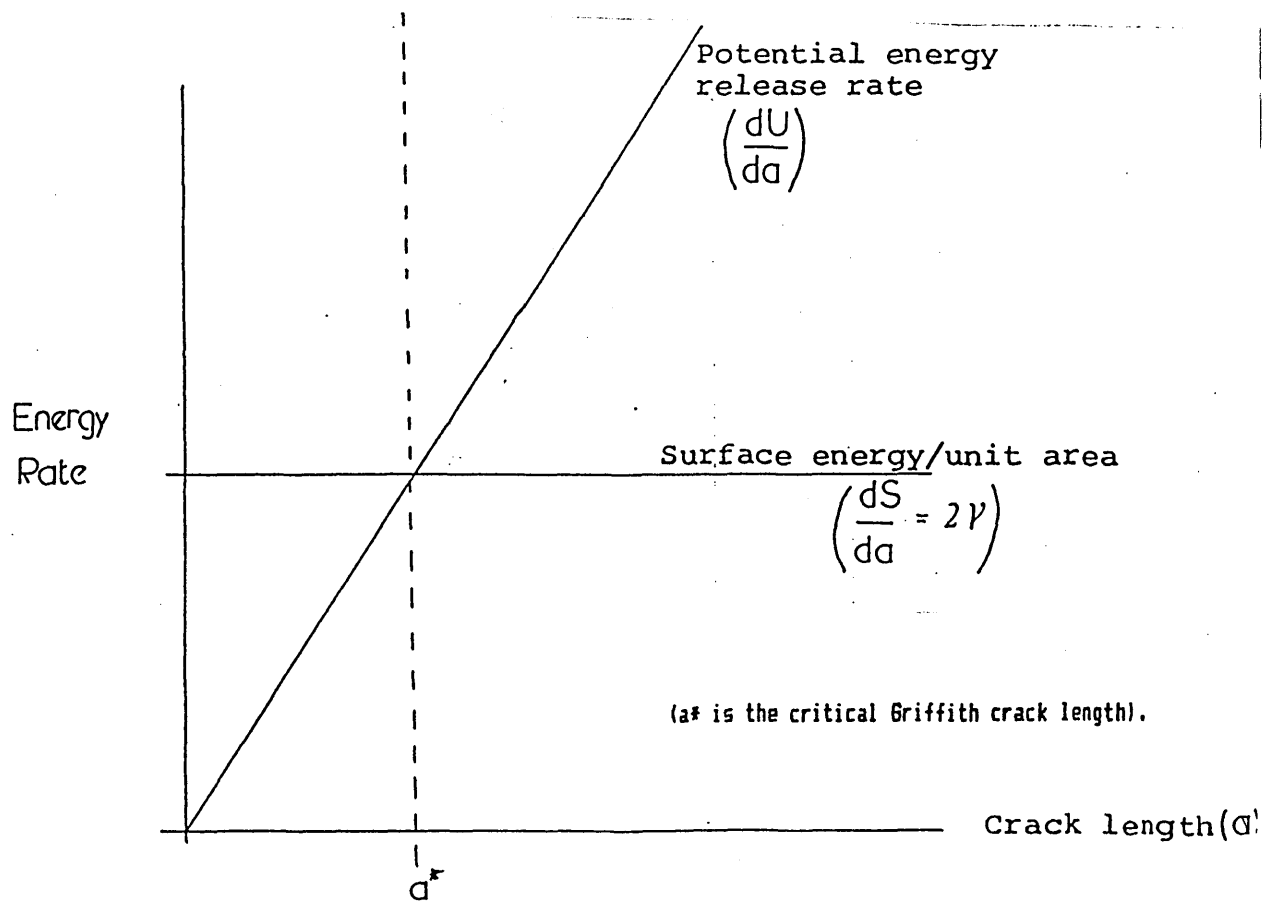


FIGURE 14: Variation of energy rates with crack length (Knott, 1973).

(a^* is the critical Griffith crack length)

3.2 Determination of K_{Ic} in real materials

To determine the plane strain fracture toughness of a material (K_{Ic}), it is necessary to have a cracked notched specimen of particular dimensions which is increasingly loaded (Knott, 1978; ASTM, 1983; British Standard, 1977). It is important to note from the equation $K \propto \sigma/\pi a$ ^{that} the stress intensity factor ($\sigma/\pi a$) is a mechanical parameter, its value determined by the geometry, stress level and crack length in the component, and is a measure of the cracking effort being applied to the component, whilst K_{Ic} is a material constant, a measure of the material's ability to resist rapid crack advance.

According to ASTM Method E 399-83, the following are the principal criteria for the validity of values of K_{Ic} , the plane-strain fracture toughness (ASTM 1983; British Standard, 1977).

1. Specimen thickness $B \geq 2.5(K_{Ic}/\sigma_{ys})^2$
2. Crack length $a \geq 2.5(K_{Ic}/\sigma_{ys})^2$.
3. Fatigue crack length $\geq 0.05a$ and ≥ 0.13 mm
4. Specimen proportions: normally $a = B = 0.5W$;
alternately for bend specimens $B = 0.25W$ to W .

5. K_{fmax} during fatigue cracking $\leq 0.00032mm^{1/2} \leq 60\%K_{Ic}$
6. Stress intensity range $\geq 0.9 K_{fmax}$
7. Crack front curvature, in middle third ≤ 0.05 average a ; also at edge > 0.9 average a
8. Crack plane parallel to $W-B$ plane within ± 10 deg.
9. Loading rate in the range 0.55 to 2.75 MPa $m^{1/2}/s$
10. $P_{max}/P_a < 1.10$

Of these requirements those of specimen size, fatigue stress intensity level, fatigue crack curvature, and P_{max} appear to be the most critical in the sense that they are the cause for most data invalidity (Kaufman, 1978).

A new wide range K_{Ic} stress intensity expression was proposed by Srawley (1976) which was valid for values of a/W in the range $0 < a/W < 1$ and is considered to be accurate within $\pm 0.5\%$ over this range for $L/W=4$, where L is the support span. (This L/W ratio is the minimum which avoids significant errors in the calculated K_{Ic} values arising from friction and indentation of the specimen at the supports).

The expression for the stress intensity is $K_{Ic} = Y \sigma \sqrt{a}$, where

$$Y^* = \frac{1.99 - (a/W)(1-a/W)(2.15 - 3.93a/W + 2.7a^2/W^2)}{2(1+2a/W)(1-a/W)^{3/2}(16)}$$

and since this new term for Y has a wider range, it has subsequently been adopted as the new ASTM Standard E-399.

3.2.1 Specimen Configuration

Formulae have been found from theoretical stress analysis for calculating K_{Ic} for various specimen geometries. Several test methods rely on an accurate assessment of the crack dimensions, since the stress intensity is inversely proportional to the square of the crack length.

An example of this method is the three point bend test. The advantage of this method is that the sample can be easily prepared and requires only a small amount of material. The notched beam is loaded until it fractures in three point bending apparatus as shown in Figure 15. The disadvantage of this method is that each specimen provides only one result.

3.2.2 Experimental requirements

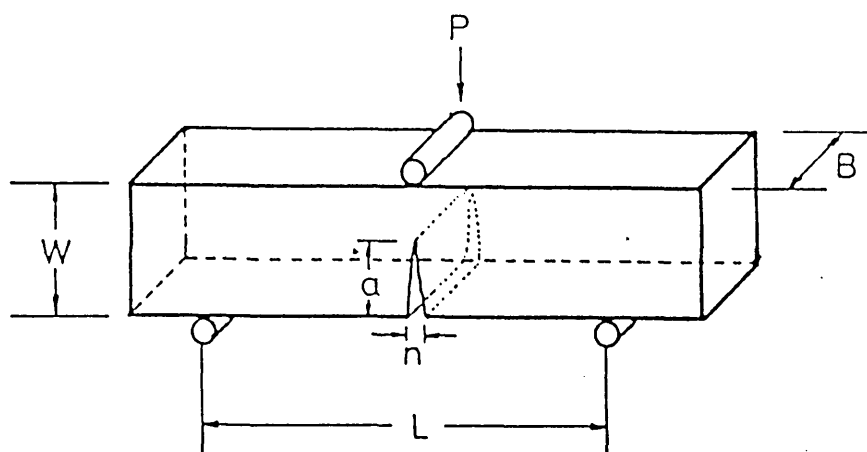
For linear elastic fracture mechanics (LEFM) to be applied to the cracked specimens, firstly the size of any plastic zone near the tip of the crack must be sufficiently small as to be negligible with respect to the specimen size (ASTM, 1983; Jones & Brown, 1970; Ritter, 1977), otherwise this would affect the

calculations involving the crack length measurements. Secondly, both the crack length a and thickness B must not be less than $2.5(K_{Ic}/\sigma_y)^2$ where σ_y is the 0.2% proof stress of the material under test conditions. A third requirement is that the specimen dimensions should be large compared with the microstructural features of the material, to ensure that the result reflects the properties of the bulk material and not individual grains: and fourthly it is necessary to establish a sharp-crack condition at the tip of the fatigue crack in order to measure the difficulty of propagating a crack as opposed to initiating one. However, the validity of the results depends on the third of the principal criteria mentioned in Section 3.2 concerning the fatigue crack.

Test pieces are usually precracked by fatiguing at low, and limited, alternating stress intensities (Knott, 1978). Although this is possible with normal ductile materials, precracking by fatigue in very brittle materials (e.g. ceramics and glass) is very difficult, and is also not easy in intermediate materials (e.g. brittle metals) since the stress intensity necessary to initiate a pre-crack at the root of a notch often approaches the critical fracture stress intensity value. Thus it may be necessary to employ other techniques to overcome the problem of precracking by fatigue. Various methods have been devised, including precracking by wedge

indentation (Almond & Roebuck, 1980; Almond & Roebuck, 1978). The most successful of these techniques is to insert a chevron notch into the specimen before three point bending (Munz, 1980), (Figure 16).

Specimens with a chevron starter notch have the unique advantage that a sharp natural crack is produced in the very early stage of test loading so that no precracking is required and then it is possible to apply LEFM. This method avoids curved crack fronts and ensures the initiation of a single crack front. Also, no post-test crack length measurement is required.



Recommended
dimensions SENB

Width = W (m)

Thickness = $B = \frac{1}{2} W$ (m)

Crack length = $a = (0.45 - 0.55) W$ (m)

Notch width = $n \leq \frac{1}{16} W$ (m)

Span = $L = 4W + 10\text{mm}$ (min)

Failure load = P (N)

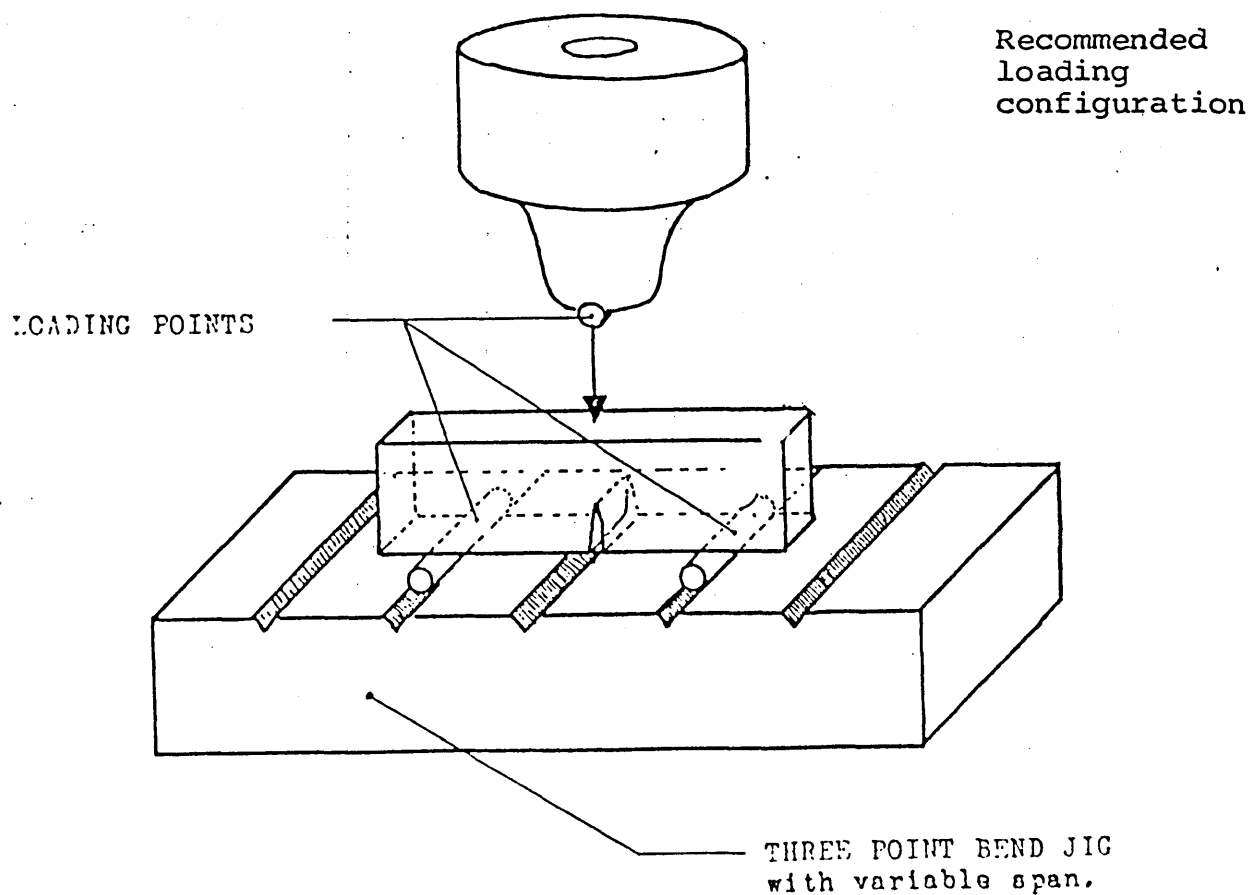
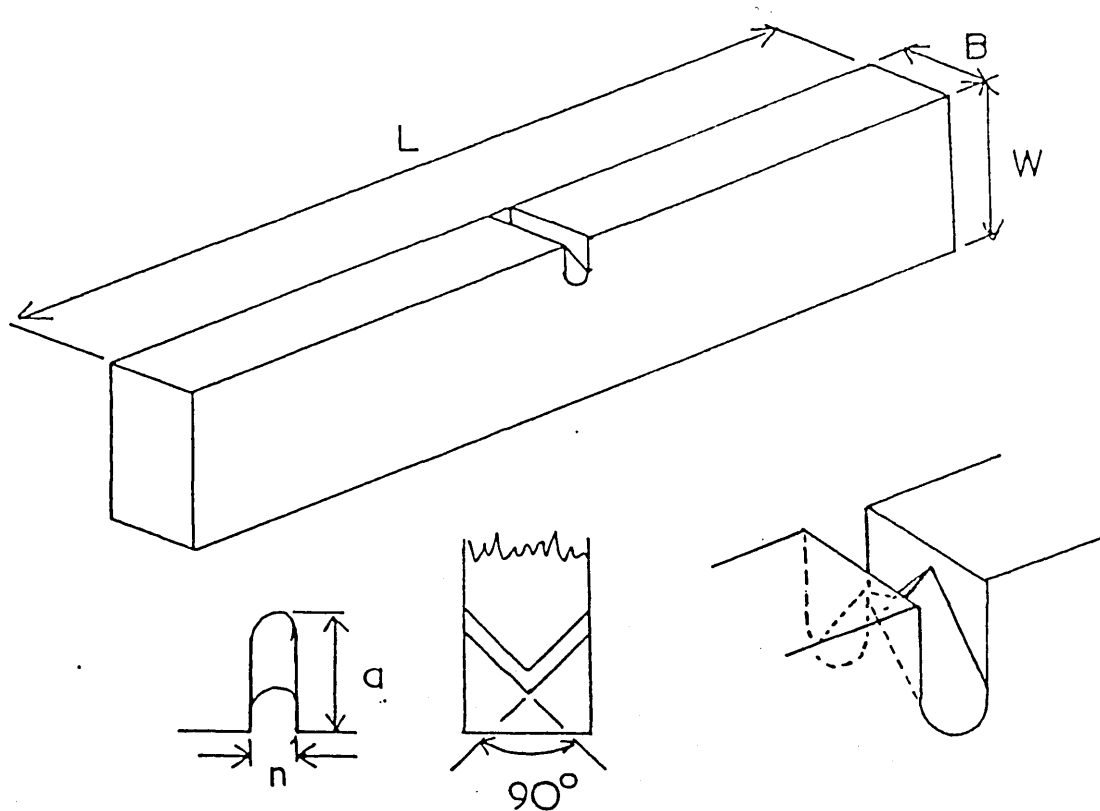


FIGURE 15: Three point bend fracture toughness testing.



Width = W

Thickness = T

Span = L

Notch Depth = a

Notch Width = n

FIGURE 16: Chevron notch for three-point bend specimens (Munz et al., 1980).

3.3 Microstructural and mechanical properties

3.3.1 Hardness and plastic deformation of Laves phases and Triballoys

A large fraction of all Triballoys consists of the intermetallic Laves phase $\text{Mo}(\text{Ni},\text{Si})_2$ which has an hexagonal structure. Work by Paufler and Schulze (Paufler, 1972; Paufler & Schulze, 1967) on the deformation of single crystals of MgZn_2 showed brittle behaviour and extensive $11\bar{2}1$ and $10\bar{1}1$ twinning. They found that MgZn_2 retains its strength up to about 723K (0.8 of its melting point), at which temperature plastic deformation occurred resulting predominantly from the onset of cross slip and the strength fell. However Bilski (1969), working on Fe_2Nb , another Laves phase with an hexagonal structure, found that softening occurred about 873K (0.45 of its melting point).

high temperature

The only work done so far on Triballoys has been that by Orrock (1981) on T-800. With initial compressive tests he found that softening occurred above 873K (approximately 0.5 of its melting point).

3.3.2 Microstructural aspects of fracture of Triballoys.

In the as-cast condition, Triballoy consists of large primary particles of the hard intermetallic phase (called a Laves phase) in a matrix of nickel solid solution. The mechanical properties would be expected to depend on the size,

morphology distribution, volume fraction and stability of the intermetallic phase and also on the stability of the nickel solid solution. Hence it is important to know something about the properties of Laves phases.

Halstead (1980), working on the cobalt-base Triballoys (T-400 and T-800), found that the initiation of cracks within both alloys was controlled by the amount of fcc cobalt solid solution present. It was suggested that its presence hindered the linking of microcracks through the matrix by accommodating the strain associated with the cleavage within the Laves phase. She found that where heat treatment resulted in a decrease in the volume fraction of Laves phase and a decrease in the amount of fcc cobalt solid solution, there was a compensating increase in the amount of eutectic (consisting of cobalt solid solution and Laves particles) which was coarser than the lamellar structure found in the as-cast alloys. As a result of the increase of this structure, cracks could be initiated more easily. So the heat treatment decreased its resistance to crack initiation.

However, she found that the propagation of cracks within both alloys was dominated by the cleavage strength and volume fraction of primary Laves phase which presented the weakest crack path regardless of whether the matrix of cobalt solid solution was the fcc or hcp form. However, on ageing heat treated specimens, precipitation in the form of

Widmanstatten type structure occurred, which presented an even weaker crack path.

3.3.3 Stress to propagate microstructural flaws

Cracks that start from a machined slit or notch extend the thickness of the specimen and the crack front is linear. In specimens that are fractured without being notched the flaws are not of this type but are usually associated with a particular microstructural feature such as a grain, and therefore tend to approximate more to semicircular or circular form.

The general fracture equation needs to be modified to allow for the flaw shape by introducing a constant σ_f , such that

$$\sigma_f = \frac{K_{Ic} z}{y a^{1/2}} \quad (17)$$

Sack (1946) showed that $z = \pi/2$ for an internal circular flaw, which is equivalent to a semi-circular surface flaw. A more detailed study was later carried out by Evans and Tapping (1972) and Bansal (1976) on semi-elliptical surface flaws with b/a varying (b is the semi-major axis and a is the semi-minor axis of the ellipse). Bansal (1976) demonstrated that for most elliptical flaws of practical significance $z^2 = 2.82b(A_f^{1/2})$ where A_f = area of the flaw. This leads to a modification of equation (17):-

$$\sigma_f = \frac{1.68 K_{Ic}}{Y A_0^{1/2}} \quad (18)$$

Y is a geometrical constant in the fracture toughness equation.

If the plane strain fracture toughness and the modulus of rupture are measured it is possible to estimate the critical defect size by use of equation (18). The flaw size can usually be linked to some microstructural flaws.

3.3.4. The stress to link flaws before failure.

In some instances flaws may link together at a stress lower than the stress needed to propagate a flaw. Paris and Sih (1965) investigating the linking of small flaws to form a large flaw, showed that, with an array of flaws, of length $2c$ and spacing $2s$ between centres, throughout the thickness of a specimen under tensile stress the factor Z in equation (17) is

$$z = \frac{2s}{\pi c} \tan \frac{\pi c}{2s} \quad (19)$$

z thus tends to 1 at large values of $2s$ and it only becomes significantly less than 1 when the flaws are close together. The validity of equations (18) and (19) was verified by Meredith and Pratt (1975) who identified the origins of fracture in a number of commercial aluminas. By applying the equations, they confirmed that the strength of individual specimens can be understood quantitatively provided that

sufficient detail is known about the distribution of flaws near the fracture origin.

3.4 Wear Resistance

3.4.1 Introduction to Wear

The Organizing Committee of the 1957 Conference on Lubrication and Wear of the Institution of Mechanical Engineers defines wear as "The progressive loss of substance from the surface of a body brought about by mechanical action (usually it reduces the serviceability of a body, but can be beneficial *in the* initial stages in running in)."

Consequently it is important to know the amount of wear over a given period of time and mechanical wear at a "steady rate" is the wear process of most economic interest to the engineering industry.

The course of wear can be influenced by

- a) general shapes of the contacting bodies *on* which the stresses depend
- b) applied load
- c) relative velocities between the surfaces
- d) surface roughness, particularly in the case of flat surfaces
- e) the bulk elastic and plastic properties of the contacting materials, and particularly those of surface layers

f) environment

and the different wear processes are as follows (the important related process is in brackets):

- a) adhesive, or galling. (Scuffing is gross damage characterised by the formation of local welds between surfaces and the breakdown of the surfaces subject to the sliding may be more or less continuous (Crook, 1980).
- b) abrasive and cutting. (Abrasion is the wear caused by fine solid particles).
- c) corrosion
- d) surface fatigue/fretting. (Pitting is where local wear is characterized by the removal of material to a depth comparable to surface damage).
- e) Minor types.

3.4.2 Mechanical Wear Tests

General laboratory wear tests are notoriously deficient in their ability to predict wear resistance in specific applications. However, the relative performance of a materials system in simplified tests is useful in providing guidelines for materials selection.

Figure 17 shows three examples of relatively simple adhesive

wear tests, which are as follows (Schmidt & Ferris, 1975; Ferris & Waldraedt, 1975).

- a) Oscillating slider test - a galling wear test which also gives information regarding friction.
- b) Drum and Rider test (also called alpha wear test), which can be performed in a corrosive environment.
- c) Rotary thrust test

3.4.3 Effect of microstructure on wear properties

Alloys designed to resist wear generally consists of a hard phase (carbide, boride etc.) dispersed throughout a softer metallic matrix. For such alloys, the abrasion process is complex, and depends not only upon the size, shape and hardness of the abrading species, but also on the volume fraction, morphology and nature of the alloy hard phase. Contrary to popular belief, the resistance to abrasion of these alloys is not necessarily related to bulk hardness. A large hard phase volume fraction and a coarse structure are generally of more benefit. (Crook & Richards, 1981; Silence, 1978).

According to the traditional theory for adhesive wear, strong interfacial bonds may occur at deformed surface asperities, mechanical degradation arising from subsequent shear failure in the weaker of the mating surfaces

(Rabinowicz, 1965). More recent approaches on metal-to-metal wear have concentrated on the subsurface crack nucleation and growth, following the shearing and flattening of surface asperities (Suh, 1973; Rignery & Glaeser, 1977).

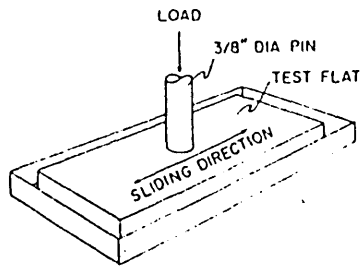
Engineering surfaces are generally covered by oxide films, and the growth of oxide upon freshly exposed metallic surfaces is rapid. Thus, in many wear systems, where conditions are such that the oxide film breakdown on both contact faces does not occur, true metal-to-metal contact is not established.

3.4.4 Wear of Triballoys

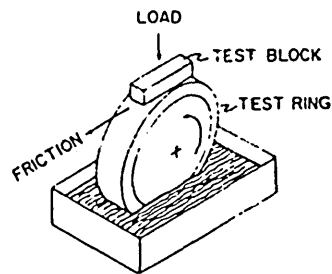
A number of papers have been published regarding the adhesive wear properties of the different Triballoys, and there is general agreement on their excellent wear properties.

Schmidt & Ferris (1974) found the cobalt-based Triballoys generally superior to the nickel-based Triballoy in corrosive environments in that there were no signs of corrosion on the test surfaces and weight loss was low or moderate. The nickel-based Triballoy showed some corrosion and moderate weight loss. Table 7 is an example of a comparative wear

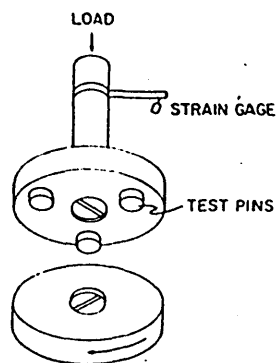
test undertaken for all three Tribaloy alloys.



a) Oscillating slider test



b) Drum & Rider test (also called Alpha wear test).



c) Rotary thrust tester

FIGURE 17: Examples of simple wear tests (Schmidt & Ferris, 1975; Ferris & Waldradt, 1975).

TABLE 7:

Corrosive wear test with drum and rider apparatus.
(1h in 5% HCl, speed 2 m/s under a load of 6.8 kg).

The results are for the weight loss of the rider.

Alloy	Weight Loss
T-400	G
T-700	F
T-800	G

where G describes a weight loss of less than 100mg,
with no visible score marks at 10X and no
surface damage or galling

F describes a weight loss of less than 100 mg,
with continuous grooving; pits or other
evidence of incipient corrosion; no galling.

(Schmidt & Ferris, 1975).

4 EXPERIMENTAL PROCEDURES

4.1 Materials

4.1.1 As received Tribaloy T-700

An ingot of T-700 was supplied by Deloro Stellite, Swindon, Wiltshire, and the typical alloy composition according to the manufacturer is given in Table 1.

4.1.2 Composition variations

Alloys based on T-700 were prepared by arc melting and were cast into small ingots (50g), approximately 60 mm in length.

Tests were carried out on the different alloys in an attempt to assess the effect of composition variations on the microstructure and mechanical properties. All the alloys produced were by alloying additions to T-700 e.g. 10% Fe added to 90% T-700 to give alloy of composition 10 wt% Fe.

4.1.2.1 Iron additions

Since iron may naturally cause dilution in Tribaloy when used as a hardfacing material, it was initially chosen as a prime candidate for alloying as explained earlier.

Ingots were cast in an argon arc furnace and contained 5, 10 and 15 by weight percent of iron added to T-700.

4.1.2.2 Silicon variation

As silicon appears to be important in the formation of the Laves phase, the next obvious candidate for alloy variation was that containing different amounts of silicon. Ingots were cast containing 0 and 6 by weight percent of silicon. These amounts of silicon were chosen as T-700 nominally contains 3 weight percent of silicon and thus falls into an intermediate position.

4.1.2.3 Iron/silicon variations

Based on the tentative results found for iron and silicon variations, it was decided that an interesting alloy would be one which could combine the preferred properties exhibited by the iron and silicon in T-700. Thus ingots of an alloy containing 0 by weight percent of silicon and 5 by weight percent of iron (denoted 0Si/5Fe) were cast. As a direct consequence of these results, an alloy containing 1 1/2 by weight percent of silicon and 5 by weight percent of iron was prepared (denoted 1 1/2Si/5Fe).

4.2 Heat Treatments

4.2.1 Temperature variation

Specimens of T-700 were heat treated for 4, 8, 12, 16, 20 and 24h at 400°C, 500°C, 700°C, 800°C and 900°C, followed by a rapid water quench, and the macrohardness values measured.

4.2.2 Variation in duration of heat treatment

As a result of the preliminary results found for the temperature variation, it was decided to confine the detailed study of the effect of time of heat treatments to 700°C. A number of the different composition alloys were heat treated at 700°C for 4h - 100h followed by a rapid water quench. (See 4.6 Summary of Experimental Procedures).

4.3 Microstructural Studies

4.3.1 Optical

Specimens (see 4.6 Summary) were prepared for optical examination by pregrinding on SiC papers, and polishing on diamond paste to 1 μ m. The most satisfactory etching procedure was found to be electrolytic etching in oxalic acid (5g/l) at a low voltage (3.2V) for between 1 - 2 mins at 0.054 Amps, (the shorter duration was for heat treated alloys).

4.3.2 Quantitative metallography

Two methods were used to determine the percentage of Laves phase present. The first method involved the use of a Bausch-Lomb microanalyser which entailed enlarging a micrograph of the specimen, and emphasizing the Laves phase by hand colouring as the equipment was unable to detect slight differences in shades. The area was then scanned and by applying a suitable computer program, information about

the Laves phase could be obtained.

A simpler, quicker and thus more satisfactory, method involved the use of a computer program from the Apple II Computer which involved tracing around the Laves phase over a chosen area from a micrograph, and similar information to that obtained from the image analysis described above was acquired, e.g. form factor, mean size. It was therefore decided to continue with this method.

The form factor of a particle gives a numerical value to a particle's shape (i.e. how round it is), and in this way any shape changes to particles can be followed numerically. The form factor is given by:

$$F = \frac{4\pi(\text{area})}{(\text{perimeter})^2}$$

So for a circle $F=1$.

For an ellipse of short dimension a and long dimension b this reduces to

$$F = \frac{2ab}{a^2 + b^2}$$

and for a rectangular shape it becomes

$$F = \frac{2\pi ab}{a + b}$$

So any particle can be given a form factor which will relate to shape. The form factor was considered as a possible way

of displaying any observed changes in the microstructural shapes.

The more elliptical a particle becomes, the lower the value of the form factor. So for an infinitely long and thin particle, it would have a value of F approaching zero. Unfortunately rectangular shapes have the same form factor as elliptical shapes. A square has a form factor of 0.785 and increasingly rectangular shapes have lower values. There is thus no real way of deciding whether the form factor given relates to an elliptical shape or to a rectangular one, unless the micrograph from which the form factor was taken is also consulted.

4.3.3 Microhardness

Microhardness results were obtained using a Vickers Microhardness Indenter, and an average of 6 indents were made per specimen. Where possible the microhardness of the major constituents for a number of the alloys was measured using a 100g load for the Laves phase and a 50g load for the other areas.

4.3.4 Scanning Electron Microscopy - using back scattered mode

Scanning electron microscopes (SEM) are normally used for examining rough surfaces such as fracture faces or heavily etched microstructures. Information can however be obtained

using a completely flat polished surface and back scattered high energy electrons. An image is then produced by atomic number contrast. An advantage of using this mode is that since the specimen surface is completely flat, there should be no anomalous effects due to differential polishing, and is thus suitable for chemical analysis. Subtle changes in the composition of a phase were seen which could not be picked up in the optical microscope or normal secondary mode of the SEM.

Various specimens (see 4.6 Summary) were polished to 1 μm finish for examination using two different SEMs, namely the JEOL T-200 and JEOL JSM-35.

Chemical analysis (EDX) of specimens was undertaken from images formed by back scattered atomic number contrast using the JEOL JSM-35.

4.3.5 Transmission Electron Microscopy (TEM)

Specimens were slit with a SiC wheel and then mechanically ground to (0.1mm). 3mm diameter discs were spark eroded from the slices followed by ion beam thinning (5kV and 0.5mA), then examined using a Philips 100kV transmission electron microscope.

4.3.6 X-ray diffraction

A Philips diffractometer, using $\text{CuK}\alpha$ radiation and scanning

at 1°/min, was used to obtain diffraction traces from specimens (see 4.6 Summary).

The diffraction traces yield plots of diffraction intensity against 2θ , where θ is the angle at which the incident X-rays impinge on the crystal plane. The spacing and positions of the peaks depend on the crystal planes satisfying the Bragg equation:

$$n \lambda = 2d \sin\theta$$

λ = wavelength of the X-rays = 15 4178 Å . CuK α
 d = distance between successive planes

The value of d is calculated for all the diffraction peaks.

Identification of the peaks was achieved by a comparison with published data. Results were obtained for pure nickel and solid solutions of Ni-Cr, Ni-Mo (International Centre for Diffraction Data, 1982). The Laves phases were compared using Gladyshevskii's work (Gladyshevskii and Kuzma, 1960).

The interplanar spacings (d parameter) of the nickel solid solution were calculated from the diffraction peaks associated with the structure. Cubic crystals give peaks whose $\sin^2\theta$ values satisfy:-

$$\frac{\sin^2 \theta}{h^2 + k^2 + l^2} = \frac{\lambda^2}{4a^2}$$

Knowing the wavelength, and the Miller indices of the planes giving rise to such diffraction peaks, enables a value of a to be calculated.

The hexagonal structure of the Laves phases are more complicated in that the relationship between the diffraction peak, the lattice parameter and the Miller indices is given by:-

$$\sin^2 \theta = \frac{\lambda^2}{3a^2} (h^2 + hk + k^2) + \frac{\lambda^2 l^2}{4c^2}$$

and substituting in ^{this} equation

$$A = \frac{\lambda^2}{3a^2} \quad \text{and} \quad C = \frac{\lambda^2}{4c^2}$$

it reduces to:-

$$\sin^2 \theta = A (h^2 + hk + k^2) + Cl^2 \quad (20)$$

As θ , λ and h , k , l , are known, a series of diffraction peaks can be seen to yield a set of simultaneous equations. Solution of which gives A and C and hence the lattice parameters. The equations were solved using a computer program enabling the parameters of the hexagonal system to be obtained.

4.4 Mechanical tests

4.4.1 Preparation of fracture toughness specimens

The single edge-notched beam specimen was chosen for the fracture toughness tests because of the ease of preparation and the economical amount of material needed. It has been

shown that this is a reliable test procedure for obtaining fracture toughness results (Bansal & Duckworth, 1979).

Figure 15 shows a sketch of a specimen with recommended dimensions and loading points (ASTM, 1983; British Standard, 1977). This type of specimen and testing mode minimises the effects of misalignment and gripping. The disadvantages are the need to precrack the specimen which as previously mentioned is one of the greatest problems in fracture toughness testing of brittle metallic materials.

4.4.2 Specimen dimensions

The three point bend specimens were approximately 40mm x 6mm x 3mm or 40mm x 5mm x 2.5mm and accurate dimensions were measured by a micrometer accurate to ± 0.005 mm.

4.4.3 Single edge-notched beam (SENB) testing

Some of the specimens were precracked by fatigue after a notch had been inserted to $1/3W$ with a thin slitting wheel (0.25mm). The rest were notched to $1/2W$. Specimens were placed exactly in the middle of the two supporting rods with the third directly above the notch. The tests were performed on an Instron at a cross-head speed of 0.5 cm/min.

The specimens were loaded until failure to obtain a value for the fracture load.

A chevron notch was inserted in some specimens since this

method should alleviate some of the problems encountered in precracking the material by fatigue (see 4.4.4).

The specimens were then broken in three-point bending (Figure 15) and a span of 30.4mm or 32.96mm (depending on W of the specimen).

4.4.4 Apparatus for inserting chevron notch

Figure 18 shows the apparatus used for the insertion of a chevron notch. The jig is held in a slitting machine with a beam specimen held in place by clamping plates and its position correctly ensured by an end stop. A first cut is made using a slitting wheel of thickness 0.5mm, and the specimen is then very carefully removed and reinserted on the second side of the jig and held such that the second cut is located alongside the first cut. (The end stop ensures the two sides of the notch are made in the same position of the beam specimen).

4.4.5 Compression test

A number of T-700 specimens were tested in compression at room temperature and at temperatures up to 900°C.

4.4.6 Modulus of Rupture (MOR)

The tensile strength of brittle materials is usually measured experimentally by a three-point bend test (Figure

15) without the inserted crack. The advantage of the test lies in its simplicity and the fact that no grips are needed. The disadvantage is that only a small area of the specimen surface is subjected to the maximum stress and stress gradients exist both along the bar and through the thickness. Un-notched specimens were tested in an identical way to that described previously (4.4.3).

4.4.7 SEM of fracture surfaces

Fracture surfaces of specimens tested for fracture toughness and modulus of rupture were examined using the T-200 SEM.

4.5 Wear

It was considered important to compare the wear properties of the new alloys with T-700, for which much information is already available in the literature (see section 3.4) and so a simple apparatus to test the wear properties of laboratory alloys and T-700 on a comparative basis was designed.

4.5.1 Apparatus designed for simple wear test

Figure 19 shows the apparatus designed to perform a simple wear test. It is based on the principle of adhesive wear, and, by using the chuck head in the lathe at a constant speed, the sliding distance can be simply calculated. Both the bearing and specimen were weighed before and after the duration of the test, and also any wear debris collected was

weighed.

The load applied was 80kg, and the duration of the test was confined to 1h and 80rpm. The diameter of the bearing was measured, and thus the sliding distance could be calculated.

This was found to be on average 7×10^2 m.

4.6 Summary of Experimental procedures

Specimen		Hv	μ Hv	XL	Experimental procedure						
					Comp Anly.	K _{1c}	MOR	SEM	TEM	X-ray	Wear
T-700	RT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	700°C	✓	✓	✓	✓	✓	✓	✓	-	-	✓
5%Fe	RT	✓	✓	✓	✓	✓	✓	✓	✓	✓	-
	700°C	✓	✓	✓	✓	✓	✓	✓	-	-	✓
10%Fe	RT	✓	✓	✓	✓	✓	✓	✓	-	✓	-
	700°C	✓	-	-	-	-	-	-	-	-	-
15%Fe	RT	✓	✓	✓	✓	✓	✓	✓	-	✓	-
	700°C	✓	-	-	-	-	-	-	-	-	-
0%Si	RT	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	700°C	✓	✓	✓	✓	✓	✓	✓	-	-	✓
6%Si	RT	✓	✓	✓	✓	✓	✓	✓	-	✓	-
	700°C	✓	✓	✓	-	-	-	✓	-	-	-
0Si/5Fe	RT	✓	✓	✓	✓	✓	✓	✓	-	✓	✓
	700°C	✓	-	-	-	✓	✓	-	-	-	-
1 1/2Si/5Fe	RT	✓	-	✓	✓	✓	✓	✓	-	✓	-
	700°C	-	-	-	-	-	-	-	-	-	-
Stellite 6	RT	✓	-	-	-	✓	✓	-	-	-	✓

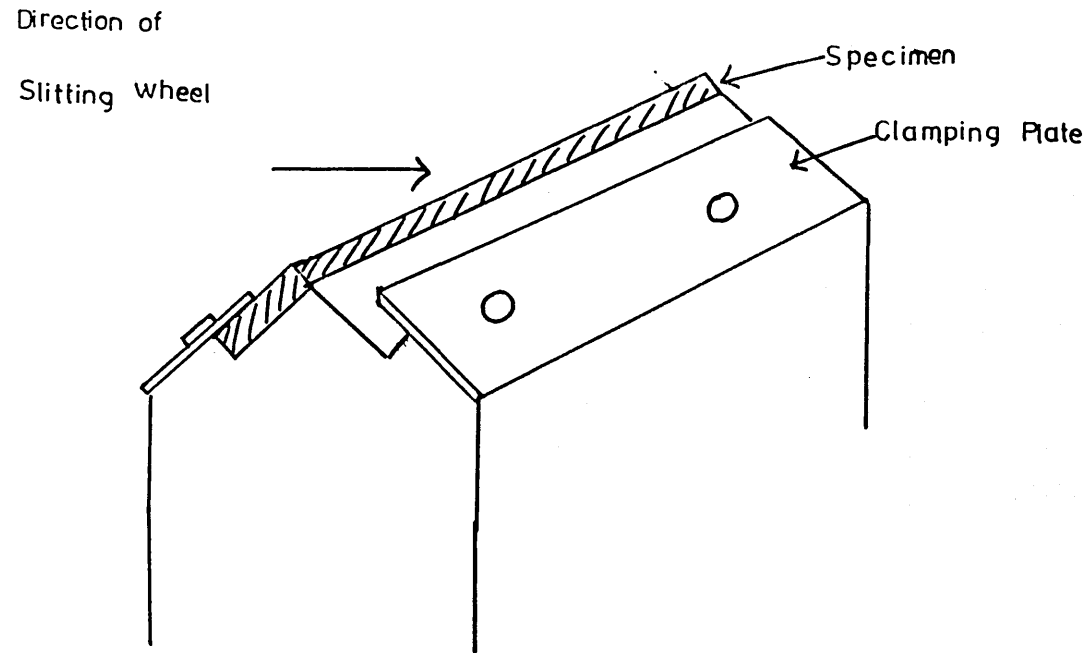


FIGURE 18: Apparatus for inserting chevron notch.

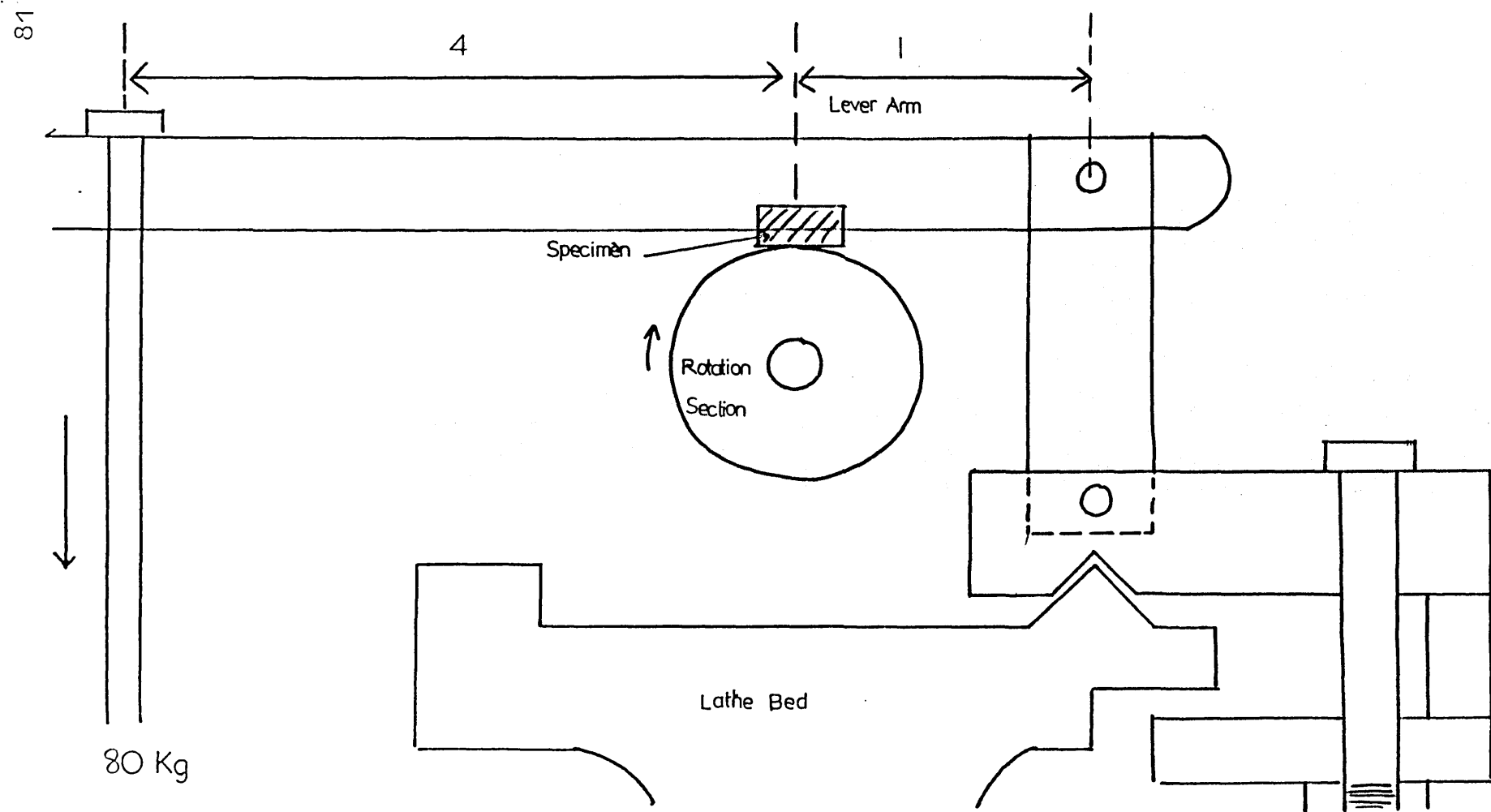


FIGURE 19a: Adhesive wear test.

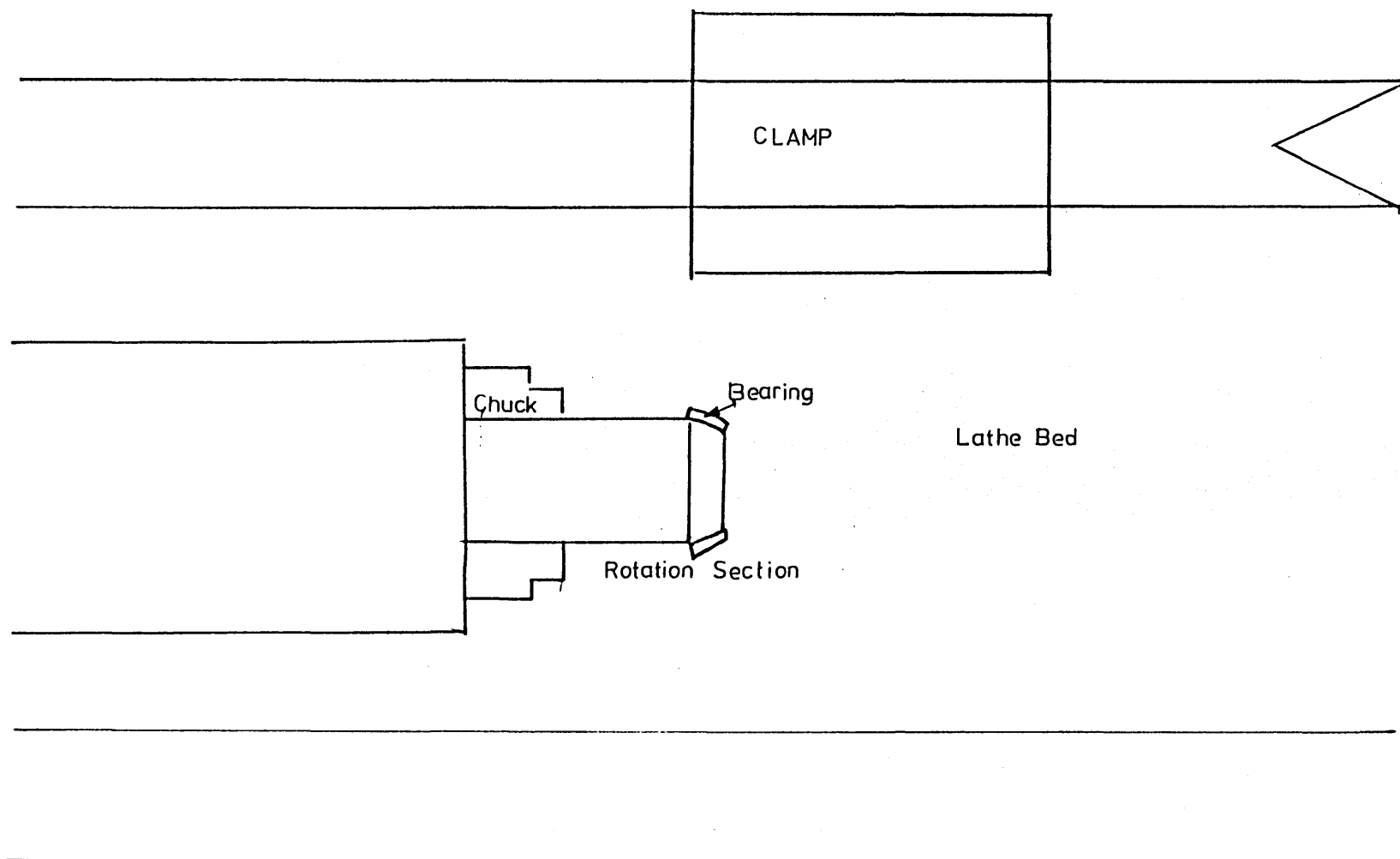


FIGURE 19b: Adhesive wear test (plan view).

5. RESULTS

The results are presented in terms of the material and alloy variations, except that for wear, which is summarised in Section 5.3.

5.1 Microstructure and mechanical properties of as-cast and heat treated T-700

5.1.1 Microstructural Studies

5.1.1.1 Metallography and Analysis

Figure 20 shows a typical micrograph of the as-cast T-700 which has been electrolytically etched. It is apparent that the eutectic of the T-700 alloy is not as well formed as that in the cobalt-base Triballoys, T-400 and T-800 (Halstead, 1980), and in the nickel-based Triballoy the microstructure consists of a primary Laves phase in a matrix of nickel solid solution. The volume fraction of the primary Laves phase is approximately 45%, (this value is similar to that given by the manufacturers), with an average size of $112\text{ }\mu\text{m}$. However, approximately 54% of the Laves particles were in fact less than $50\text{ }\mu\text{m}$ in *length*. The shape of the Laves particles was rectangular and the form factor was 0.56 ± 0.21 .

From examination using light microscopy it appeared that the Laves phase contained two regions, and this feature was observed more clearly using the back scattered atomic number contrast mode in the SEM (Figure 21). In this mode, the

region containing a higher average atomic number appears lighter, and it was found that the two regions within the Laves phase could thus be more clearly distinguished. Consequently it was decided that for further investigations of the microstructure the SEM should be used. Analysis (Table 8) using the JEOL JSM-35 Scanning Electron Microscope revealed that these two regions differed in their compositions: one region containing less nickel, but more molybdenum than the other region. However, the distribution of silicon between the two regions remained the same.

Even after heat treatments at temperatures between 600°C and 900°C, for 20h, 50h and 100h, there appeared to be no significant change in the microstructure (Figures 22, 23 and 24) and in the distribution of elements within the two regions of the Laves phase. Also no significant change was found for the percentage of primary Laves phase in the alloy (Student 't' test applied). No precipitation was found after heat treatment.

However, the shape of the Laves phase itself after 50h and 900°C became slightly less faceted, and more rounded in its appearance, although the form factor still remained the same (0.562).

5.1.1.2 X-ray diffraction

The lattice plane spacing, d , was calculated for the face centred cubic nickel solid solution of T-700, and in Table 9 it is compared with that from powder diffraction experiments (Powder Diffraction File, Card 31-404).

The metallographic evidence and chemical analysis which showed that the Laves consisted of two regions, was supported by the X-ray diffraction data which produced lattice spacings which could not be accounted for by only one hexagonal Laves phase structure type (Table 10).

X-ray diffraction data from the Laves phases of T-700, 0wt%Si and 6wt%Si were also analysed. Good agreement was found between the 0 wt% Si Laves phase diffraction peaks and those from the cubic Laves structure type, and between the 6 wt% Si Laves and those from the hexagonal Laves structure type. For T-700, some of the diffraction peaks coincided with those for an hexagonal Laves structure type, but some peaks remained which did not agree with either the cubic or hexagonal Laves structure types.

From these results (Table 10) it can be seen that the 0wt%Si alloy has a cubic type structure and the 6wt%Si alloy has an hexagonal type structure. The results also showed that since there was no correlation between the diffraction data

for the cubic Laves structure type and T-700, the cubic Laves phase is not present in T-700.

The lattice parameters calculated from the X-ray data are shown in Table 11 for the fcc nickel solid solution and for the hexagonal Laves phases. The results for the lattice parameters of the fcc nickel solid solution agree well with the published data. The calculated values for the lattice parameters in the a and c directions for the hexagonal Laves phase, shows more difference in the a direction, than in the c direction, confirming the Laves structures are different.

5.1.1.3 Transmission Electron Microscopy (TEM)

Due to the very brittle nature of the Laves phase present in the T-700, the initial preparation of specimens thin enough to be followed by ion beam thinning was difficult, since during the preliminary grinding, and indeed during ion beam thinning, the Laves phase usually fell out leaving only thick areas of the specimen. However, two specimens were eventually successfully thinned and Figures 25, 26 and 27 show the TEM micrographs of as-cast T-700. Within the primary Laves phase, ^{there are} regions composed entirely of stacking faults adjacent to regions which appear to be almost entirely devoid of stacking faults (Figure 26). There also appears to be an abrupt change between these two regions, with dislocations terminating at the boundary between the two regions. Figure 27 also shows an area containing

numerous twins.

Figures 28 and 29 show the diffraction patterns from both the matrix and Laves phase respectively. The structure of the nickel solid solution is identified as fcc from the diffraction pattern shown in Figure 28. The distance across the central reflection was measured from the pattern, and compared with the distance calculated from the lattice parameters and the camera constant. Table 12 shows a comparison of this data and the agreement is sufficiently good to identify the fcc structure.

A comparison of the diffraction spots produced by the Laves phase was made with transmission diffraction pattern data for hcp crystal structures, which are shown in Figures 29 and 30. They are sufficiently similar to identify the Laves phase as having an hcp structure. Comparison of the diffraction spots produced by the Laves phase was made with transmission diffraction pattern data for cph crystal structures, and Figure 30 shows the resulting indexed pattern.

TABLE 8: Distribution of Elements within the phases of T-700

Phase	Element	wt. % element
Laves (Dark region)	Ni	36.7 $\pm$ 0.1
	Cr	12.0 $\pm$ 1.0
	Mo	47.6 $\pm$ 0.5
	Si	3.6 $\pm$ 0.5
Laves (Light region)	Ni	35.5 $\pm$ 0.8
	Cr	11.0 $\pm$ 0.0
	Mo	51.6 $\pm$ 1.4
	Si	3.7 $\pm$ 0.2
Matrix	Ni	61.8 $\pm$ 0.3
	Cr	19.1 $\pm$ 1.2
	Mo	16.7 $\pm$ 0.1
	Si	2.1 $\pm$ 0.7

TABLE 9: Comparison of Theoretical and Experimental d spacing for nickel solid solution

Reflecting Planes (h,k,l)	Theoretical* d spacing nm	Experimental d spacing nm
111	.2034	.2036
200	.1762	.1807
220	.1246	.1232
222	.10172	.1025

*Comparison Made with Powder Diffraction File, JCPDS - International Centre for Diffraction Data, 1982. *for NiCrMo: 18Cr, 42Mo*

TABLE 10: Experimental 'd' spacing calculated from X-ray diffraction peak data from Laves phases of T-700, 0 wt% Si and 6 wt% Si.

T-700 nm	0wt%Si nm	6wt%Si nm	Ref. nm	Reflecting Planes (h,k,l)	Crystal
.2368		.2309	.2364	110	hexagonal
.2227					*
.2172		.2115	.2155	103	hexagonal
	.2127				cubic
.20804					*
.1994		.2025	.2009	112	hexagonal
.1963		.1963	.1978	201	hexagonal
	.1953				cubic
.19141					*
.1445					*
.1328		.1343	.1322	213	hexagonal
.1284		.1270	.1285	302	hexagonal
	.1227				cubic
.1225		.1212	.1220	205	hexagonal
	.1181				cubic
.1187		.1170	.1183	220	hexagonal
	.1093				cubic
.10855		.1074	.1085	215	hexagonal
.10498					*

Ref: Gladyshevskii & Kuzma (hexagonal)

* unaccounted for reflections (i.e. not cubic or hexagonal)

TABLE 11: Lattice parameters for the Laves phase and nickel solid solution for T-700

Nickel solid soln. nm	Nickel* solid soln. nm	Laves phase nm		
fcc a	fcc a	a	c	
.3526	.3523	.4738	.7709	hexagonal structure
		.4456	.7819	dihexagonal structure

*JCPDS- International Centre for Diffraction Data, 1982. *Si-404*
for Ni-Cr-Mo: 18 Cr 42 Mo

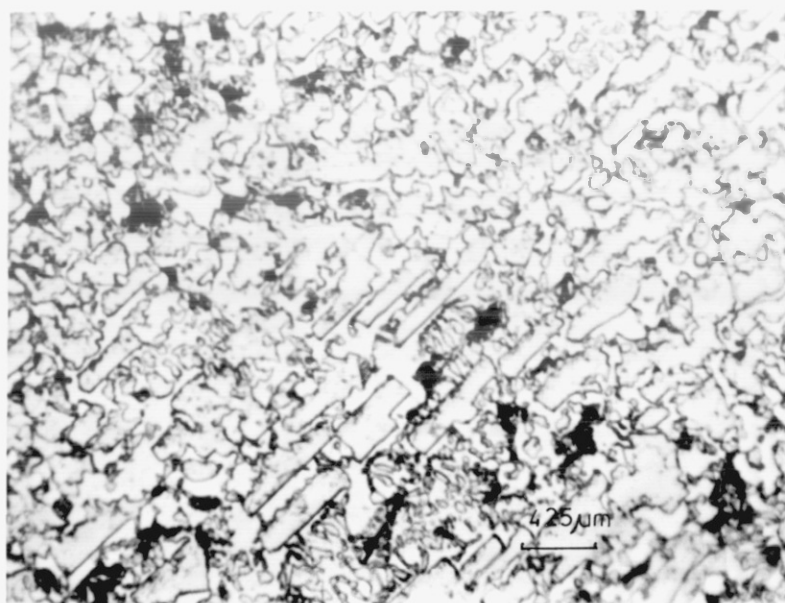


Fig. 20: As-Cast T-700 - Optical Micrograph (Electrolytic Etch)

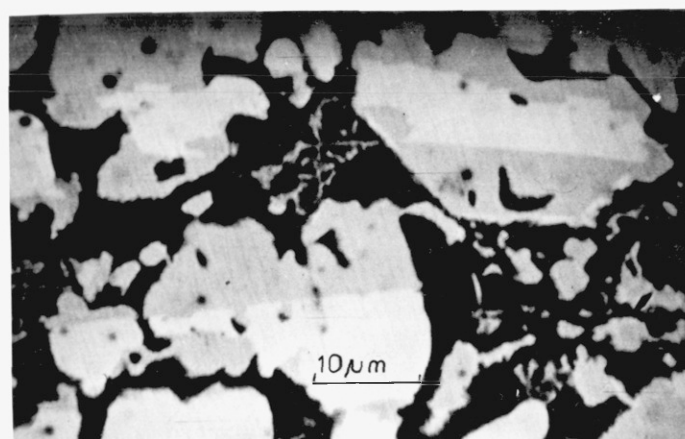


Fig. 21: As-Cast T-700 - SEM Atomic Number Contrast



Fig. 22: T-700 24h, 700°C (SEM)

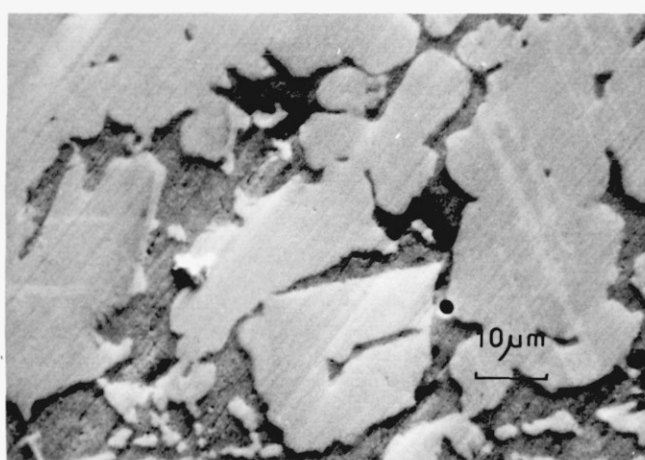


Fig. 23: T-700 50h, 700°C (SEM)

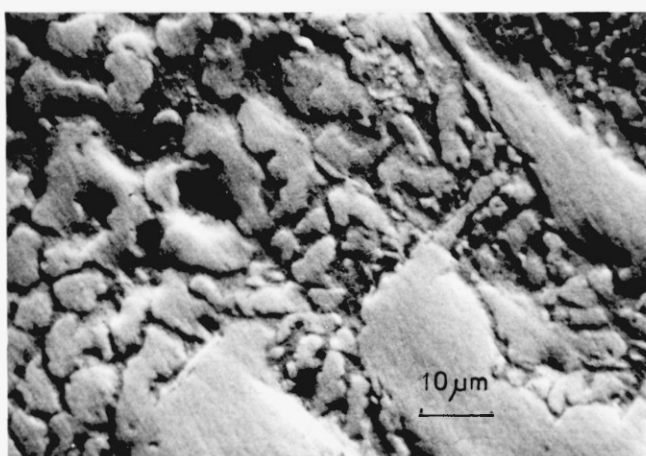


Fig. 24: T-700 50h, 900°C (SEM)

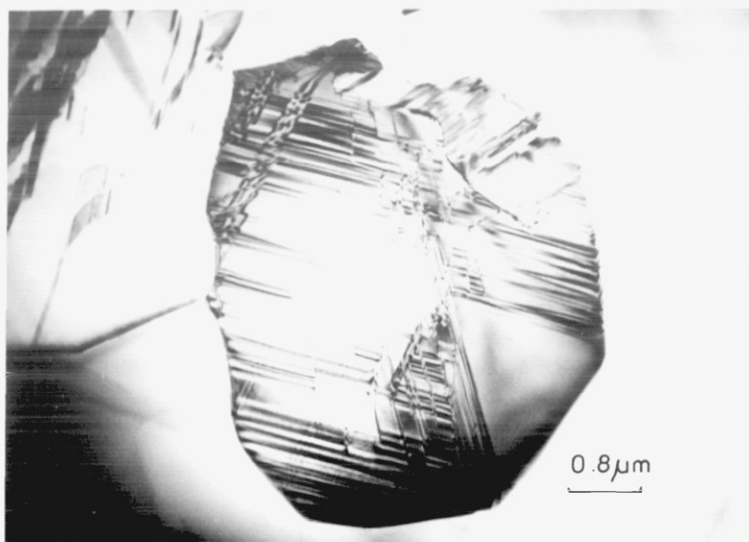


Fig. 25

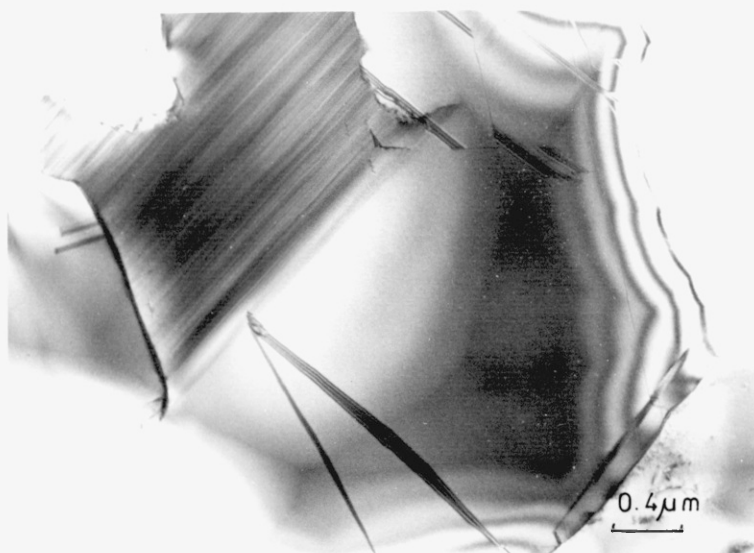


Fig. 26



Fig. 27

TEM Micrographs of as-cast T-700

TABLE 12: Comparison of SADP data identified as fcc nickel solid solution

Reflecting Planes	$d = \frac{a^*}{\sqrt{h^2 + k^2 + l^2}}$ nm	$D_{calc} = \frac{5.19}{d}$ nm	$D_{measured}$ from SADP nm
111	.2036	.255	.256
200	.1763	.294	.300
220	.1247	.416	.425
311	.1063	.488	.483
222	.1017	.510	.512

$a^* = 0.3523 \text{ nm}$ JCPDS International Centre for Diffraction Data 31-404.

5.1.2 Mechanical properties

5.1.2.1 Effect of heat treatment

The results of hardness values for specimens heat treated at 400°C, 700°C, 850°C and 900°C for up to 100h are shown in Figure 31. After applying suitable statistical analysis there was shown to be no significant difference between the results. For example comparing the hardness values of the as-cast specimens and specimens heat treated for 24h at 400°C, the difference between the mean values was only twice the standard error of the difference. Thus ^{there is} no evidence of any hardening occurring on heat treatment.

The microhardness of the primary Laves phase was found to be approximately 926 ± 35 kg/mm², and that of the nickel solid solution 322 ± 70 kg/mm². After heat treatment, there appeared to be very little change in the microhardness values, a result consistent with previously discussed macrohardness data.

Unfortunately, it was not possible to obtain microhardness values for the two regions within the Laves phase, because the Laves particles were relatively small and as mentioned earlier it was difficult to differentiate between the two regions using optical microscopy.

5.1.2.2 Compression testing

A number of specimens were compressed at room temperature and in the temperature range 700°C - 900°C, and the results are shown in Figure 32. From this curve it can be seen that at about 800°C, the ~~strength~~ value for T-700 is halved.

Figures 33 and 34 show examples of the typical shape of the stress/strain curves as a result of compression testing. (Figures 33 and 34 are at room temperature and 900°C respectively).

From the example at room temperature it can be seen that after the maximum stress is obtained, abrupt failure follows almost immediately, whereas for the specimen compressed at a higher temperature, some ductility is shown, and failure is no longer catastrophic.

The variation of 0.2% proof stress is shown in Figure 35, and a similar trend as previously show with the ~~compression~~ data was found.

The compression results have been compared to the Hot Hardness Curve (Cabot Corp., 1980) and from this comparison (Figure 36), it can be seen from the normalised curves that the two properties show very similar temperature dependences.

which 2 stress/strain strength or annealed yield.

5.1.2.3 Fracture behaviour

In Single Edge Notched Beam (SENB) three point bend test, the relationship between the crack length, specimen geometry and K_{Ic} is given by

$$K_{Ic} = \frac{3 PLYa^{1/2}}{2 BW^2} \quad (20)$$

where,

P = Failure load (N)

L = Span (m)

a = Crack length (m)

B = Width (m)

W = Depth (m)

Y is a geometrical factor which is a function of a/W . (Section 3.2, Equation 16). Equation 20 was used to calculate values for fracture toughness. Table 13 shows the average values of 0.2% yield stress, as determined in compression testing, and the maximum range of variation of K_{Ic} and the minimum thickness of the sample calculated according to ASTM standards. As the flow stress is high the plastic zone size ahead of the crack tip will only be small and hence it can be seen that plasticity does not impose a thickness constraint. The only thickness constraint that needs to be imposed, is that the section is large enough to be structurally representative of the material. Since the size of the primary Laves phase was found to be about 100 μm , it was decided that specimens 2.5mmx5mmx40mm or 3.0mmx6mmx45mm would satisfy the microstructural constraints, whilst being economic on material and large enough to handle.

All strain rates (down to 0.02cm/min), gave sharp cut off failure loads, with no deviation from linearity prior to crack propagation, and consistent K_{Ic} values were determined from the fracture loads. So, with this "ideal" behaviour there is no necessity to use clip gauge displacement measurements at the end of the crack, and it is quite adequate to use the crack propagation load to evaluate K_{Ic} .

A strain rate of 0.5 cm/min was chosen to carry out the fracture tests.

Since no significant change in the hardness of T-700 was found on ageing, it was decided to see whether more sensitive mechanical property tests also showed no change, 700°C for 24h and 50h was chosen arbitrarily as the times and temperature to which further heat treatment study would be confined.

Table 14 shows the results of the fracture toughness and modulus of rupture tests carried out on T-700 in both the as-cast and heat treated condition. The critical defect size in the as-cast condition has been calculated from equation (8) (0.51mm²), and has a similar value to the cobalt-based Tribaloy T-400, which has a result of 0.55mm².

Although the values for the fracture toughness and modulus of rupture for T-700 after heat treatment varied between 21.7 and 24.6 for the fracture toughness results, and 417

and 470 for the MOR results, the Student 't' test takes into account the number of specimens and results, and from this, it can be seen that there is little change between the fracture toughness and modulus of rupture values before and after heat treatment.

The brittle nature of T-700 can also be seen in the fracture surface of a specimen broken in 3 point bending (Figure 37).

Fracture occurred by transgranular cleavage with a faceted appearance to several regions. Region a shows a river like pattern formed on the cleaved surface, which is often seen in brittle materials.

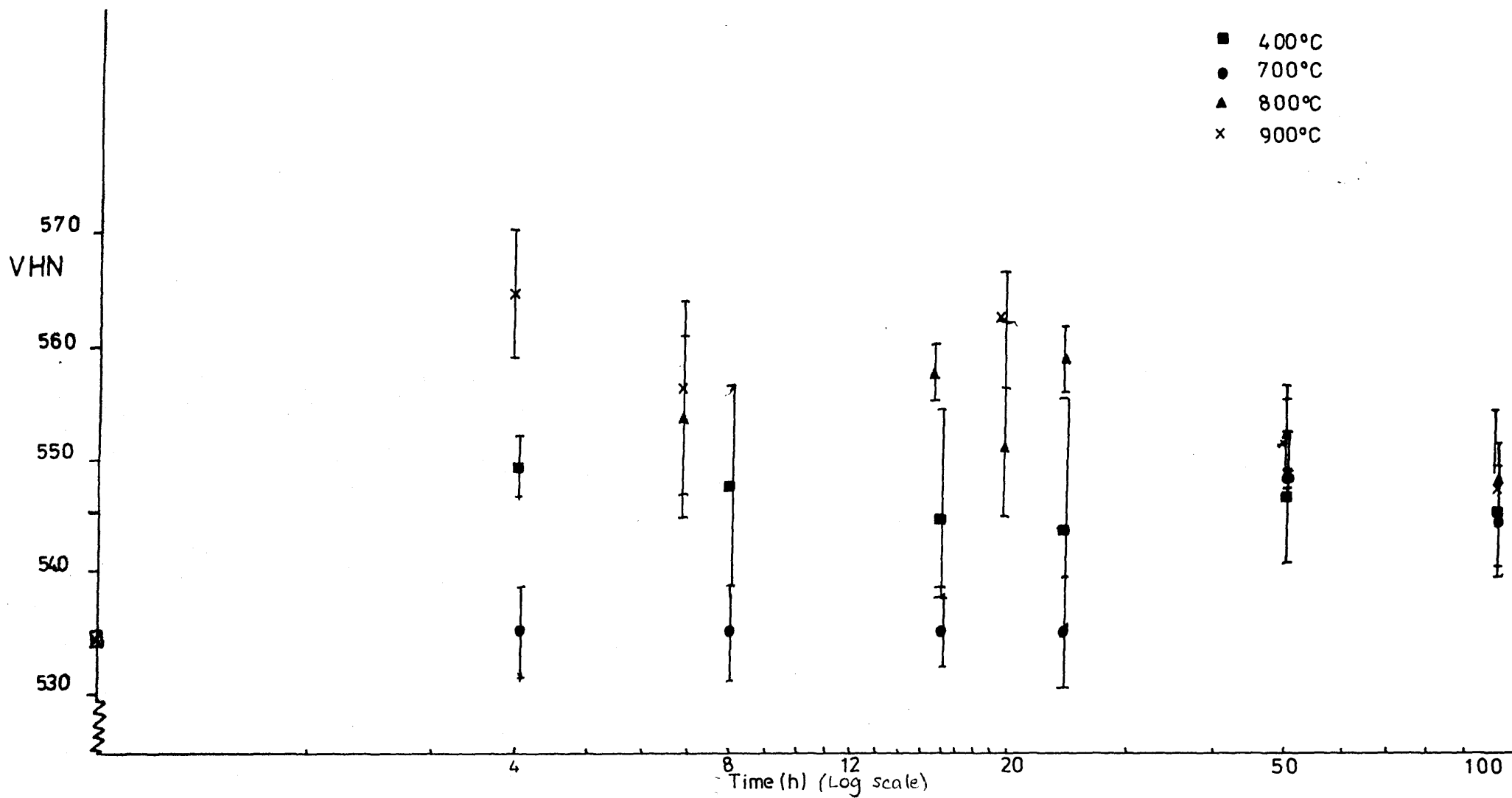


Fig. 31: Hardness variation of T-700 after heat treatment

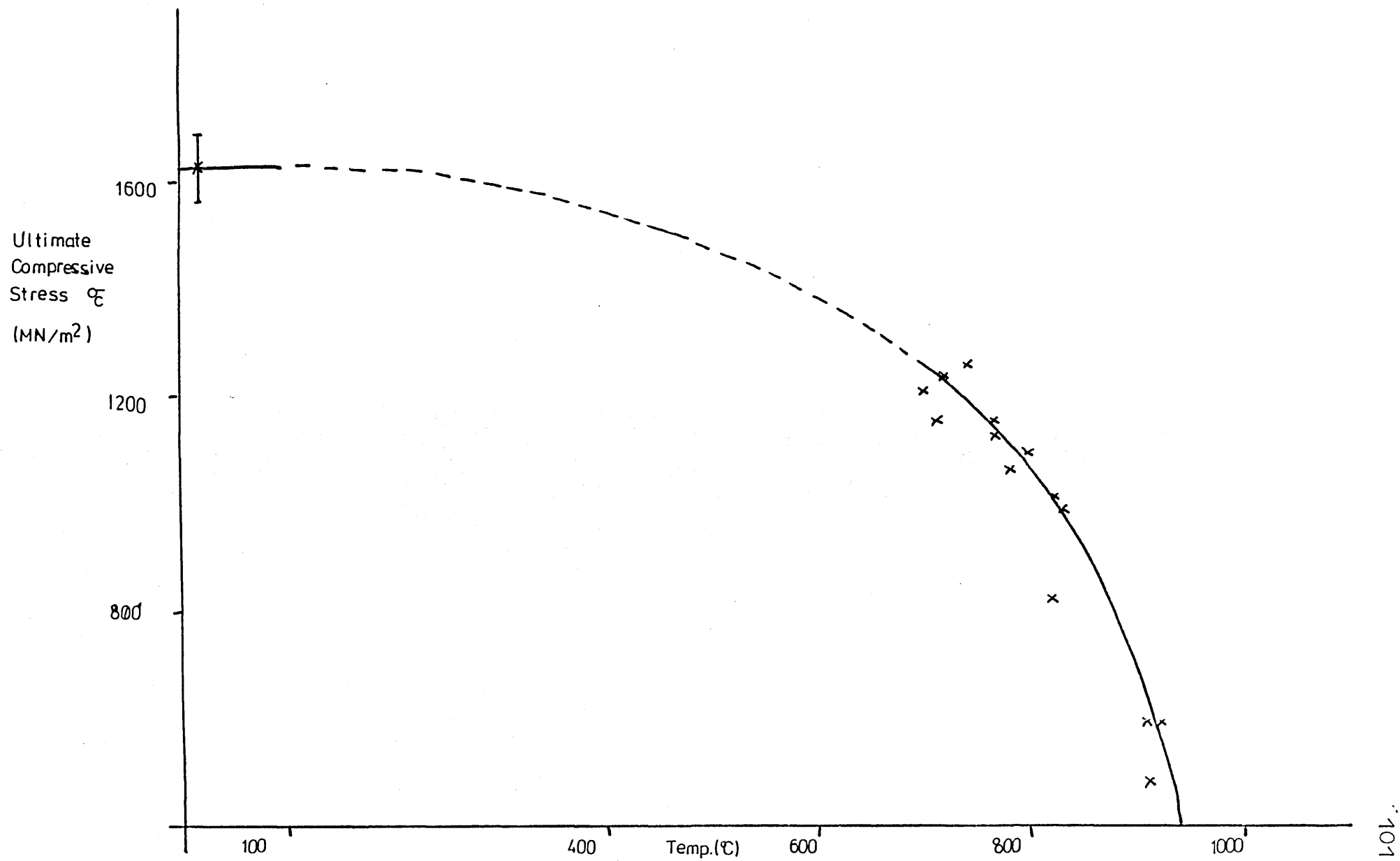
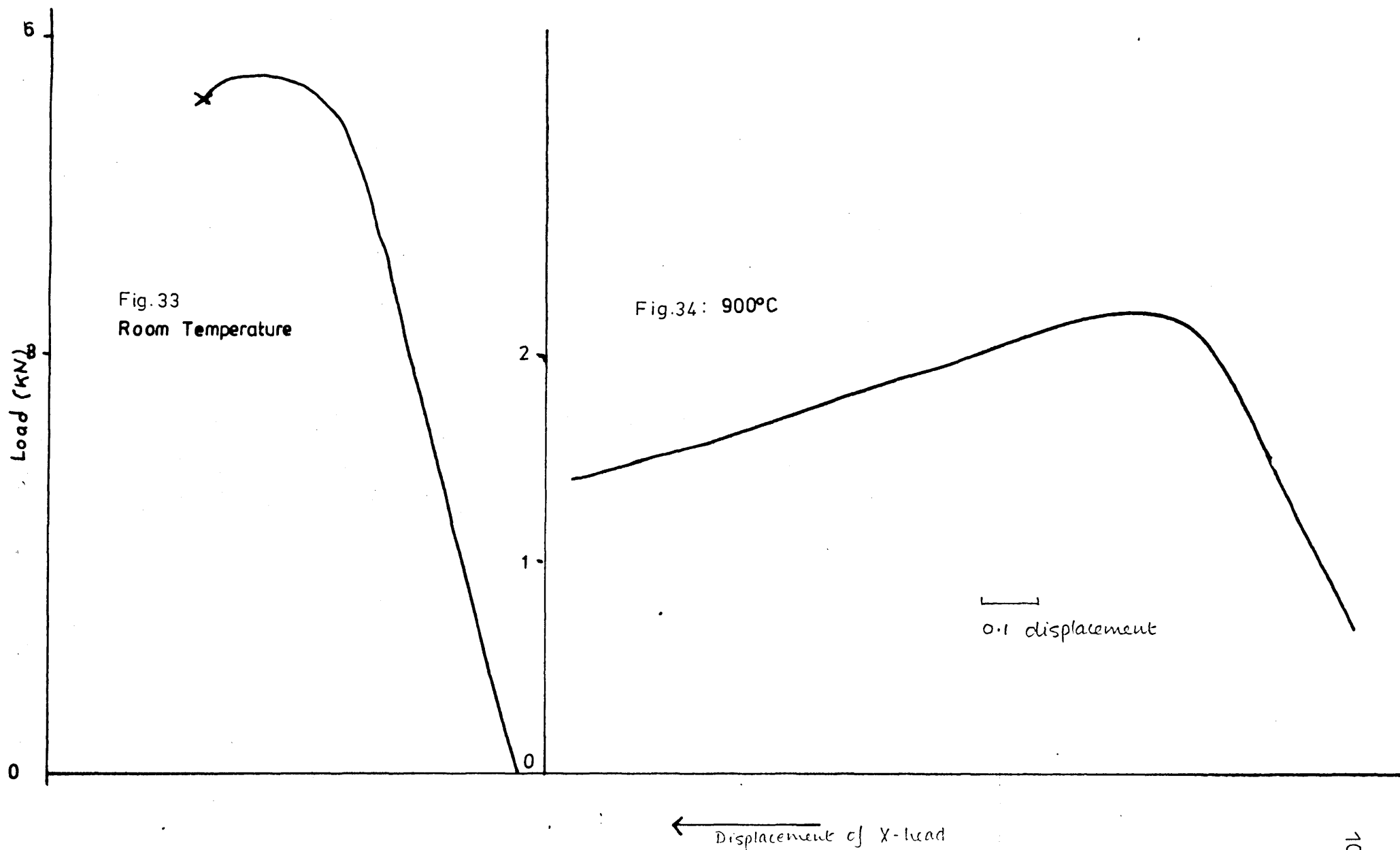


FIGURE 32: Compression variation of T-700 as a result of heat treataent.



Figs. 33 and 34 : Examples of the typical shapes of the compression testing curves.

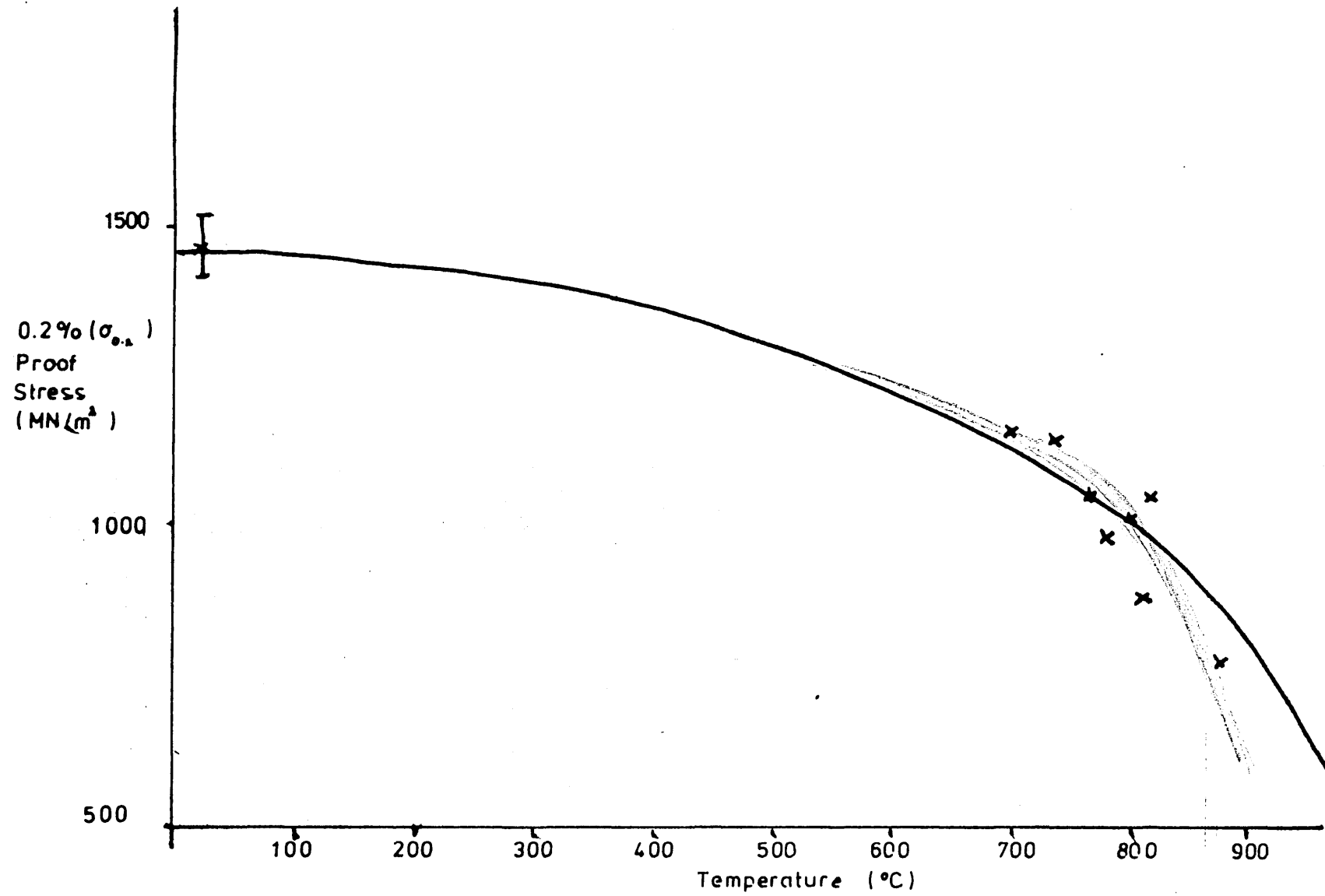


FIGURE 35: 0.2% Proof Stress of T-700

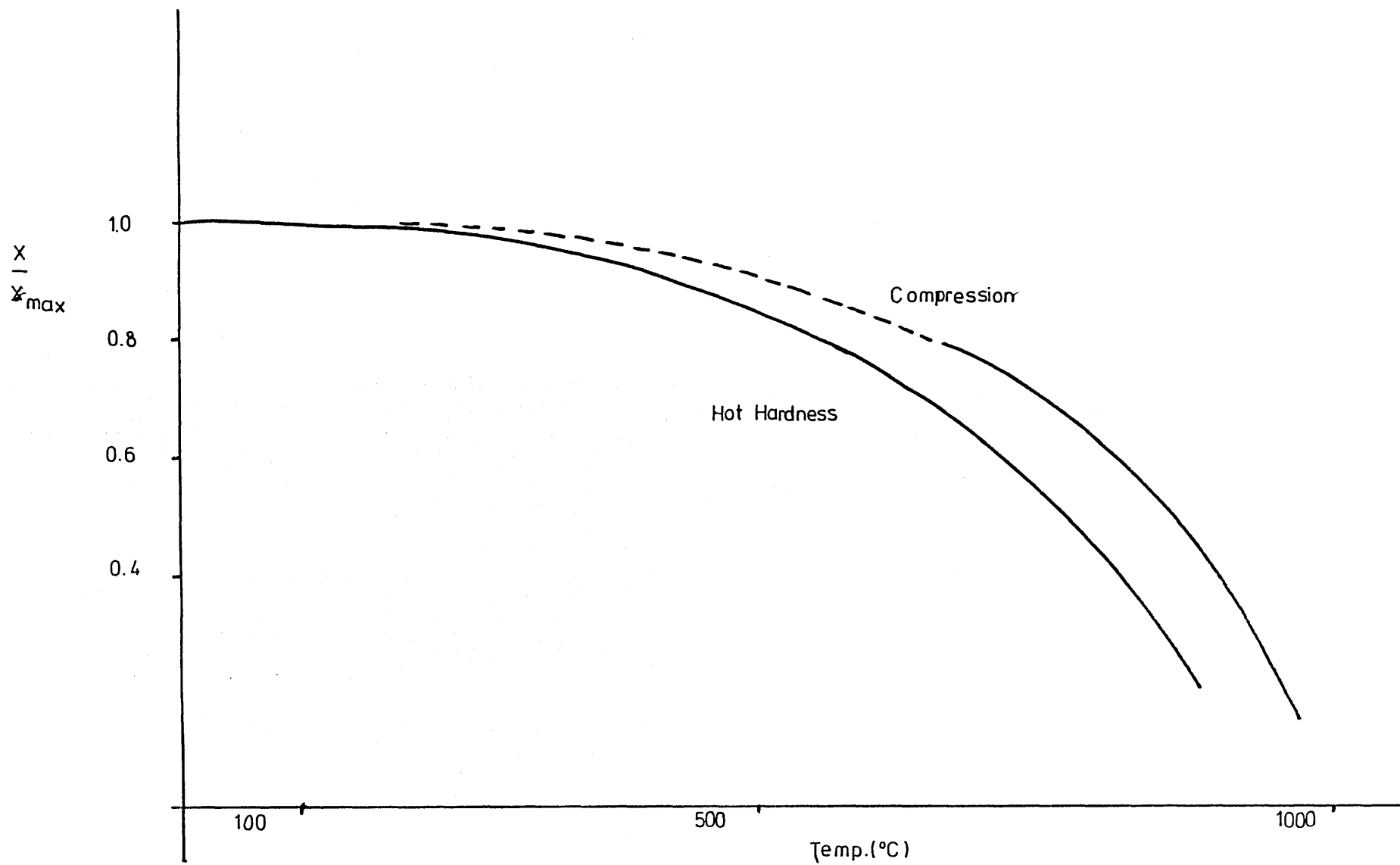


FIGURE 36: Hot hardness/Compression against Temperature where $\frac{X}{X_m}$ = normalised hot hardness or compression curve.



Fig. 37: As-cast T-700 Fracture Surface

TABLE 13: Estimation of specimen thickness		
Yield stress	K_{Ic} MN/m ^{3/2}	$B \geq 2.5 \left(\frac{K_{Ic}}{\sigma_y} \right)^2$ mm
1409	min 12.3	0.19
	max 22.3	0.63

TABLE 14: Mechanical properties of Tribaloy T-700 as-cast and heat treated					
Alloy Condition	Hardness Kg/mm ²	K_{Ic} MN/m ^{3/2}	MOR MN/m ²	% Laves	Flaw Size mm ²
As-cast	537 $\pm$ 17	20.1 $\pm$ 3	537 $\pm$ 49	46.6	0.52
24h 700°C	526 $\pm$ 18	24.6 $\pm$ 7	417 $\pm$ 36	41.4	(0.64)
50h 700°C	550 $\pm$ 6	21.7 $\pm$ 2	523 $\pm$ 176	42.0	0.79

5.2 Effect of Composition variation on the microstructure and mechanical properties of T-700

5.2.1 Iron additions

Alloys containing additions of 5, 10 and 15 wt% Fe were made to T-700. As a result of initial microstructural and mechanical property tests, it was decided to continue most of the investigations only with the alloy containing 5 wt% Fe. The results of all the mechanical property tests concerned with alloy variations are summarised in Table 15.

5.2.1.1 Microstructure

For the alloy containing iron additions, the two regions of the Laves phase could not be distinguished, however compositional analysis and X-ray diffraction results show that the two regions were present.

Compositional analysis was undertaken for all three alloys (Table 16) in an attempt to assess the distribution of the elements within the phases of these new alloys, and also to see if any further information could be gained concerning the dual nature of the Laves. As with T-700 in the 5 and 10 wt% Fe alloys, the greater percentage of molybdenum appeared in the Laves, although the difference in distribution of molybdenum between the two Laves is relatively small. The iron appeared to partition itself more in the matrix than the Laves, however its presence affected the distribution of

the chromium, which was now more evenly distributed between the phases. From these analyses no information could be gained regarding the two regions of the Laves in the 15 wt% Fe alloy.

An initial reduction in the percentage of primary Laves phase present to about 34% for the addition of 5 wt% Fe was found; this amount remained constant for up to 15 wt% Fe. This behaviour was in contrast with that of the cobalt-base Triballoys, where the volume fraction of Laves phase continued to fall with increasing iron content (Table 17).

However, after heat treatment of the alloy containing 5 wt% Fe, there was an increase in the percentage of Laves phase, and after 50h at 700°C, this amount was similar to that for T-700 (i.e. 46%) the similarity being confirmed by suitable statistical analysis.

Correlation was found between the X-ray diffraction data peaks for the iron bearing alloys and those for the hexagonal Laves but peaks were also present which could not be accounted for by the hexagonal Laves structure type (Table 18); these extra peaks correlated with peaks found in T-700 which suggests that the same Laves type structure which was found in T-700 is also present in these alloys. The lattice parameters of the matrix for these alloys calculated from this data are shown in Table 19, from which

it can be seen that a reduction in the lattice parameter results on adding iron.

Figures 38, 39, 40, 41 show the microstructure of the alloys containing 5, 10 and 15 wt% Fe before and after heat treatment. As mentioned above, the two regions of the Laves phase could not be distinguished for the alloys containing iron additions.

In addition to a reduction in the volume fraction of Laves phase for all the alloys, it was also noted that there had been an alteration in the general shape of the Laves phase, which now appeared more "rounded" in its appearance. A comparison of the form factors for the different alloys is shown in Table 20. There did, however, appear to be very little difference between the microstructures of the new alloys, even after heat treatment. Also, similar to T-700 no precipitation after heat treatment was observed.

As mentioned previously, most of the investigations into the addition of iron to T-700, were restricted to 5 wt% Fe, and Figures 42, 43, and 44 show typical transmission electron micrographs of the alloy containing 5 wt% Fe. From these it can be seen that the Laves phase is still composed of large areas of stacking faults, but there is a reduction in the amount of fault free regions of the Laves. However, in

contrast to the change in the appearance of the Laves phase with the addition of iron there appeared to be no visible difference between the matrix of the iron bearing alloys and that of T-700.

TABLE 15: Summary of Mechanical Properties for Alloy Variations

Alloy	K_{IC} MN/m ^{3/2}	MOR MN/m ²	% Laves	VHN	Flaw size mm ²
T-700 a.c. 24h 700°C 50h 700°C	20.1±3.0 24.6±6.6 21.7±1.5	537±49 470±126 417±36	46.6±7 41.4±5 42.0±9	537±17 526±12 549±13	0.51
Fe additions:					
5 wt% Fe a.c. 24h 700°C 50h 700°C	23.3±0.8 21.1±3.3 21.3±4.9	764±150 527±114 576±148	33.0±4 38.0±9 46.2±11	488±6 524±9 581±12	0.29
10wt% Fe a.c.	24.7±5.0	800±195	36.8±6	479±6	
15wt% Fe a.c.	23.6±0.7	822±29	31.5±6	455±17	0.54
Si variations					
0 wt% Si a.c. 24h 700°C 50h 700°C	20.6±5.4 15.2±2.1 14.3±4.1	899±74 1605±354 1602±555	24.6±11 34.9±4 -	536±20 606±9 608±9	0.04
6 wt% Si a.c.	19.2±4.6	285±11	62.8±2	565±21	4.29
T-400 a.c.	22.3±2.0	917±54	42.0±8	658±25	0.55
T-800 a.c.	19.2±1.8	752±35	70±12	728±15	0.27
Stellite 6	64.5±4.8	1452±86		406±9	
0Si/5Fe a.c. 24h 700°C 50h 700°C	52.8±18 54.7±4.1 51.1	1387±538 1789±576 1727±416	30±5	475±45 493±100 488±8	
1 1/2Si/5Fe ac	45.1±17.8	920±10	30	526±20	

TABLE 16: Distribution of elements and average atomic weights within the phases of T-700 with iron additions.

Alloy	Ni	Cr	Mo	Si	Fe	
5% Fe						
Matrix	66.17±1.4	11.00±0.9	10.29±2.1	1.36±0.4	11.17±0.4	
Laves(L)	49.49±4.4	8.72±0.5	29.52±6.4	2.65±0.4	9.62±2.0	
Laves(D)	39.34±1.1	7.41±0.2	33.01±1.2	2.40±0.2	17.87±2.7	
Av.At.Wt.						Total
Matrix	3885	572	987	38	624	
Laves L	2906	434	2832	74	537	6783
Laves M	2310	385	3167	67	998	6927
10% Fe						
Matrix	65.69±1.0	11.67±1.0	9.36±3.6	1.21±0.2	12.61±4.5	
Laves(L)	40.05±1.8	9.62±1.1	40.31±1.6	3.2±0.6	6.92±1.9	
Laves(D)	47.40±0.5	8.61±0.3	35.69±0.7	2.53±0.2	5.78±0.3	
Av.At.Wt.						Total
Matrix	3857	607	898	34	704	
Laves L	2351	500	3867	90	387	7195
Laves D	2783	448	3424	71	323	7049
15% Fe						
Matrix	63.63±0.4	9.92±0.4	9.13±0.9	1.14±0.2	16.19±0.9	
Laves	41.84±0.1	7.95±0.1	35.76±0.1	2.60±0.1	11.88±0.1	
Av.At.Wt.						
Matrix	3736	516	876	32	904	
Laves	2456	413	3431	73	663	

TABLE 17: Volume fraction of Laves phase as a result of iron additions

Alloy	As-cast	5 wt% Fe	10 wt% Fe	15 wt% Fe
T-700	47 $\pm$ 7	33 $\pm$ 4	37 $\pm$ 6	32 $\pm$ 6
T-400	42 $\pm$ 8	35 $\pm$ 7	25 $\pm$ 3	17 $\pm$ 7
T-800	70 $\pm$ 12	57 $\pm$ 7	43 $\pm$ 8	26 $\pm$ 6

TABLE 18: Experimental 'd' spacing calculated from X-ray diffraction peak data for the iron bearing alloys.

5 wt% Fe /nm	10 wt% Fe /nm	15 wt% Fe /nm	T-700/nm (Ref: Table 1)
.4058	.4058	.4058	
.2014 (47%)	.2008 (41%)	.2013 (36%)	
.1973 (24%)	.1972 (50%)	.1982 (24%)	
.1941 (18%)	.1972 (43%)	-	
.1903 (11%)	.1899 (7%)	.1908 (6%)	.1914*
.1435 (3%)	.1446 (4%)	.1438 (4%)	.1446*
.1300 (29%)	.1300 (14%)	.1304 (9%)	

Figures in brackets refer to the percentage of the main peak intensity, which was a matrix peak.

* - refer to diffracted lines from T-700.

TABLE 19: Lattice parameters for the nickel solid solution of the iron bearing alloys calculated from X-ray data.

T-700/nm	5 wt% Fe/nm	10 wt% Fe/nm	15 wt% Fe/nm
a = .3588	a = .3596	a = .3556	a = .3551

TABLE 20: Form factors for the Laves phase particles of the as-cast iron bearing alloys

T-700	5 wt% Fe	10 wt% Fe	15 wt% Fe
0.562 $\pm$ 0.21	0.582 $\pm$ 0.03	0.615 $\pm$ 0.05	0.627 $\pm$ 0.02

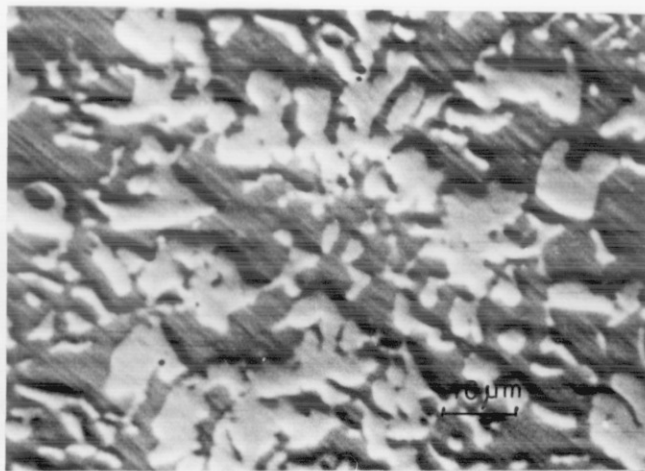


Fig. 38 : As Cast T-700 + 5 wt % Fe (SEM)

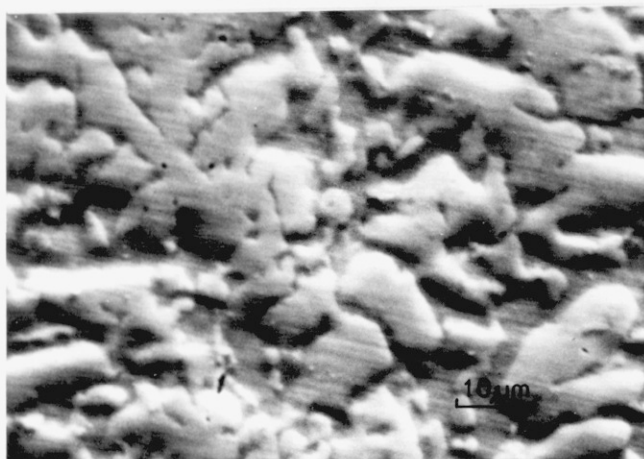


Fig. 39 : T-700 + 5wt % Fe, 24h 700° C (SEM)

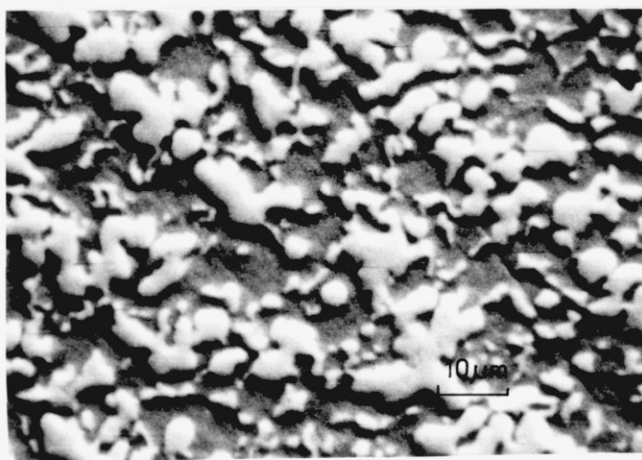


Fig. 40 : As Cast T-700 + 10 wt % Fe (SEM)

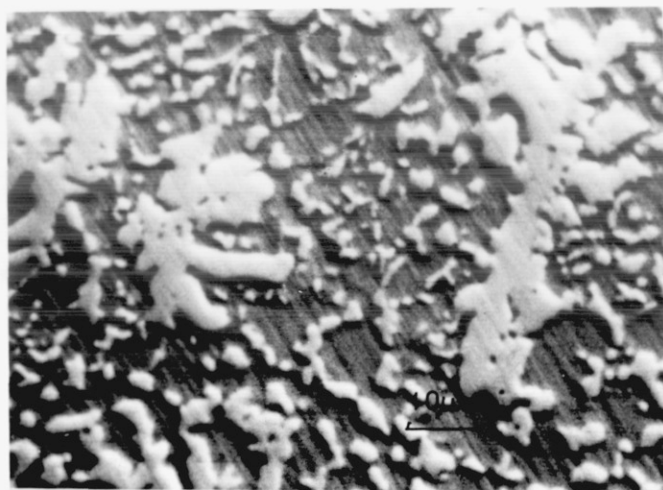


Fig. 41 As Cast T- 700+15wt % Fe (SEM)

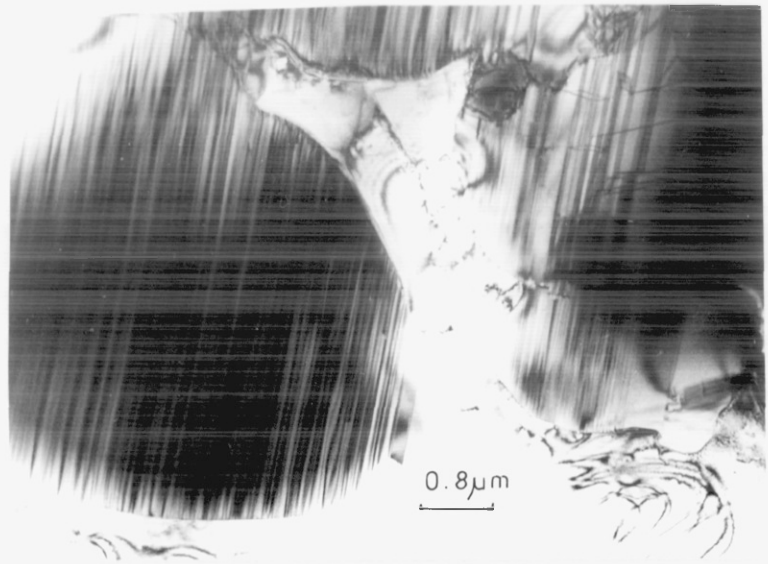


Fig. 42



Fig. 43

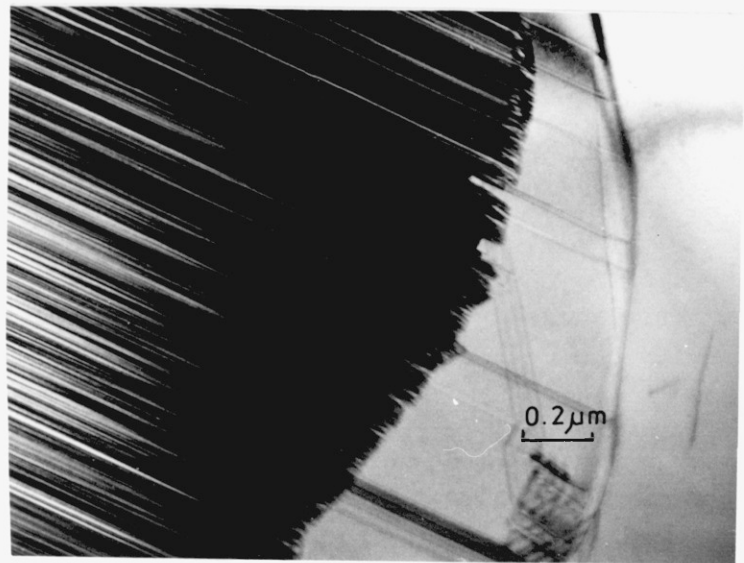


Fig. 44

TEM Micrographs of As Cast T-700 + 5wt%Fe

5.2.1.2 Mechanical properties of as-cast and heat treated iron bearing alloys

5.2.1.2.1 Hardness variation with addition of iron, as-cast and heat treated

The effect of heat treatment on the hardness of the different iron additions is presented graphically in Figure 45. Reference is also made to Table 15 for the tabulated results.

From this it is interesting to note that although initially the hardness was considerably less in the iron bearing alloys than in T-700, after heat treatment at 700°C an improvement in the hardness was evident for both the 5 and 10 wt% Fe alloys. Although the hardness of the 5wt% Fe stopped increasing during further heat treatment, the hardness of the 10wt% and 15wt% alloys continued to increase.

The microhardness results for these alloys are shown in Table 21 and are compared to those for the cobalt-base Triballoys. These show similar results in that for the Laves, after an initial reduction in hardness for the 5 wt% Fe addition, there is no further reduction in hardness for further iron additions. The reduction is however more marked than for the cobalt base Triballoys. The matrix shows no significant change.

5.2.1.2.2 Fracture behaviour

The results of these tests are summarised in Table 15. The trend is similar to that shown by the cobalt-based Triballoys (Table 6) i.e. the fracture toughness remained constant, and the modulus of rupture increased for increased iron additions.

For the 5 wt% Fe alloy no change was found in the fracture toughness, after heat treatment, although there was a reduction in the modulus of rupture.

Figures 46, 47 and 48 are typical micrographs showing the fracture surfaces of the as-cast condition of the three iron bearing alloys. The brittle nature of the alloys is again evident from the very faceted fracture surface, which is similar to T-700; fracture has occurred by transgranular cleavage.

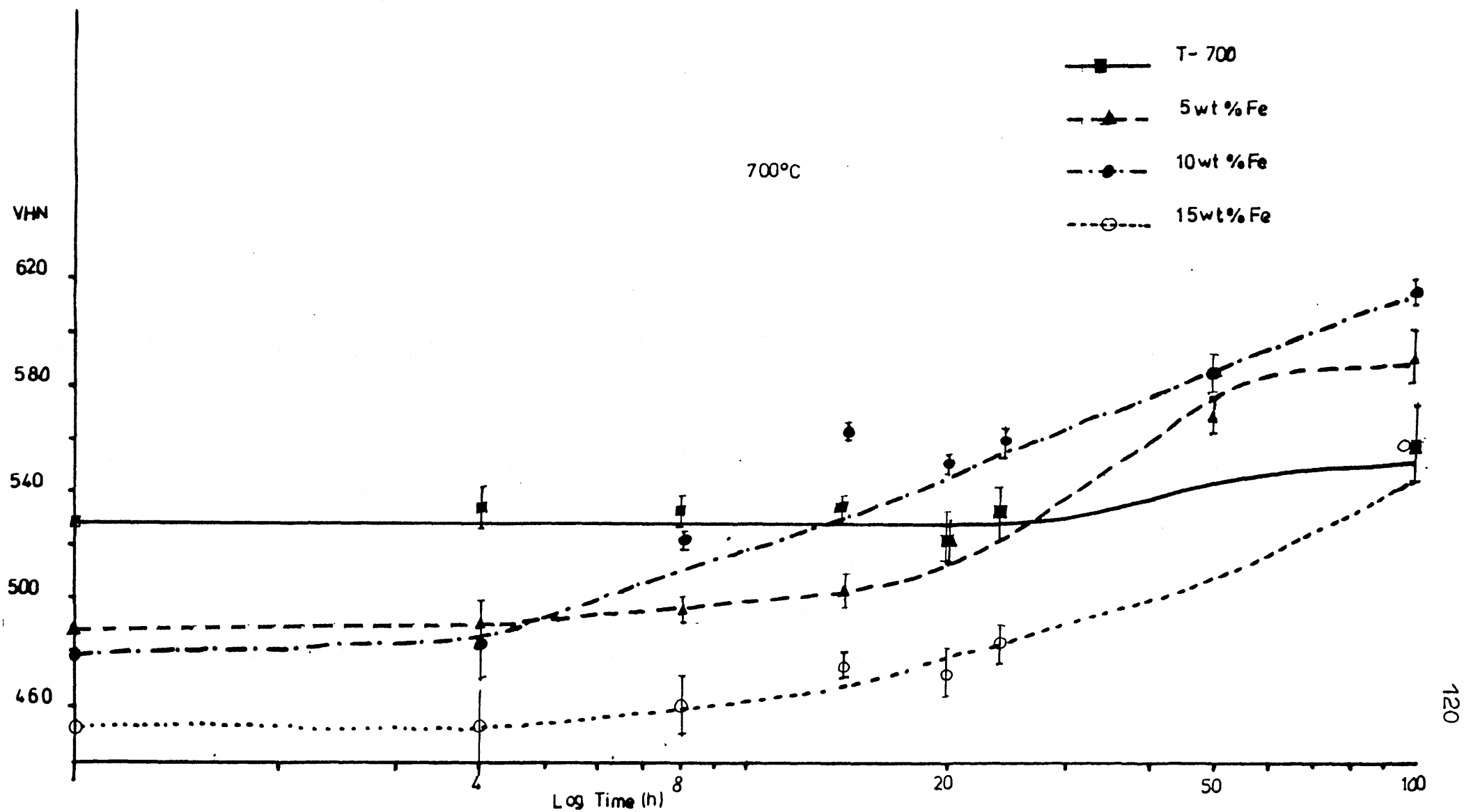


FIGURE 45: Hardness variation of iron bearing alloys of T-700 as a result of heat treatment.

TABLE 21: Variation of Microhardness of Triballoys as a result of iron additions

Alloy	As-cast	5 wt% Fe	10 wt% Fe	15 wt% Fe
T-700				
Laves	926	443 $\pm$ 92	429 $\pm$ 38	476 $\pm$ 76
Matrix	322	210 $\pm$ 80	208 $\pm$ 46	188 $\pm$ 20
T-400				
Laves	1068 $\pm$ 90	1018 $\pm$ 100	1013 $\pm$ 90	1018 $\pm$ 70
Matrix	598 $\pm$ 41	588 $\pm$ 70	590 $\pm$ 90	575 $\pm$ 50
T-800				
Laves	1081 $\pm$ 70	1017 $\pm$ 50	1027 $\pm$ 70	1020 $\pm$ 90
Matrix	-	610 $\pm$ 60	589 $\pm$ 50	590 $\pm$ 40
Laves 100g load Matrix 50g load				

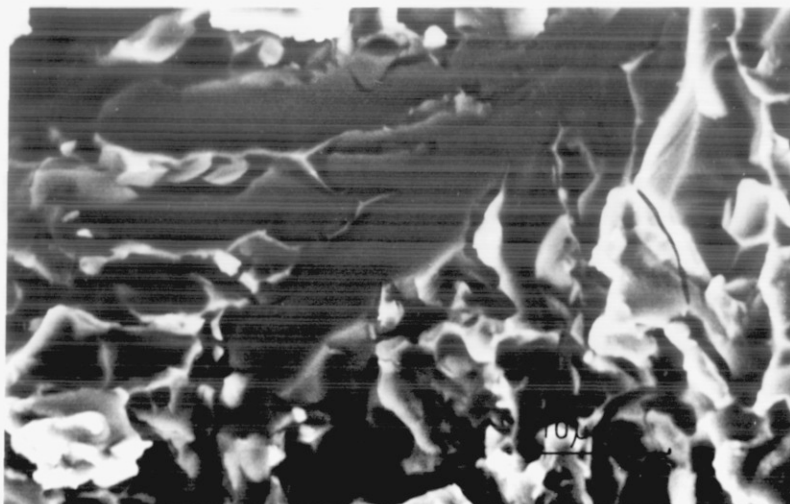


Fig. 46: Fracture Surface a.c. T-700 + 5wt% Fe

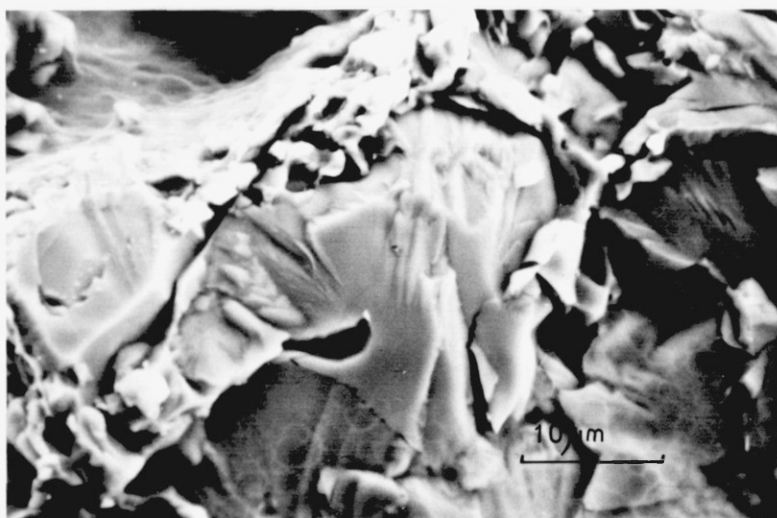


Fig. 47: Fracture Surface a.c. T-700 + 10wt% Fe

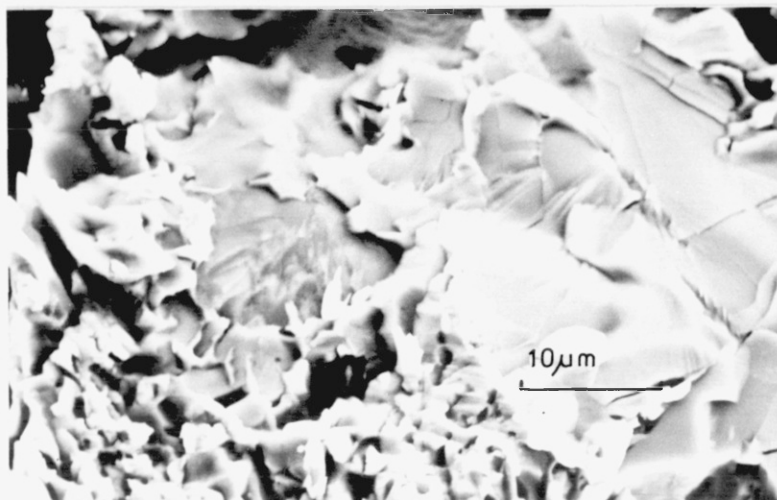


Fig. 48: Fracture Surface a.c. T-700 + 15wt% Fe

5.2.2 Silicon variations

Alloys containing 0 wt% and 6 wt% Silicon were arc-cast and subsequent heat treatments were carried out at 700°C and 850°C up to 100h.

5.2.2.1 Microstructure

Table 22 shows the percentage of Laves phase in the alloys of differing silicon content. The percentage of Laves phase present increases almost linearly with increased silicon content, but heat treatment of the 3 wt% Si alloy (T-700), caused no significant increase in the volume fraction of Laves phase.

A marked variation between the microstructures was also observed. The 0 wt% Si alloy (Figure 49) contained primary Laves phase particles of various shapes and sizes, but the most notable feature was the matrix, which was now lamellar in appearance. For the 3 wt% Si (T-700) (Figure 21) and 6 wt% Si (Figure 50) the matrix consisted of nickel solid solution, the eutectic no longer being present. However, in the 6 wt% Si, the primary Laves phase particles were "rounded", and were of two sizes: large particles which were 20-50 μm in diameter, and small particles of the order of 2-3 μm diameter which appeared to be evenly distributed. The form factors and sizes of the particles in the alloys with different silicon content are included in Table 22. The two

regions previously seen in the Laves phase for T-700 (3wt%Si) were however not observed in 0 wt% Si or 6 wt% Si.

After heat treatment there was a change in the morphology of the alloys. Figure 51 shows the 0 wt% Si alloy after 4h at 850°C, and there is still evidence of the dendritic nature of the Laves phase. Although the particles appeared to be grouped in colonies there was no change in size. After further heat treatment (up to 50h), the size appeared more uniform, and the eutectic had started to lose its lamellar structure. The lamellar structure of the eutectic had completely disappeared after 100h, and the Laves particles were of a larger uniform size than previously.

In the 6 wt% Si alloy, there was not such a marked change in the microstructure during heat treatment. Initially the Laves particles became more uniform in shape and increased slightly in size and then there was no further appreciable change in the microstructure.

The compositional analysis of the alloys revealed some marked trends with increasing silicon content, the results of which are shown in Table 23. Although the percentage of nickel varies from system to system, the proportions by which it partitioned itself between the phases always remained constant i.e. approximately 40:60. The proportions by which the silicon partitions itself between the Laves and

the matrix also appears approximately constant for 3 and 6 wt% Si (i.e. about 65:25 respectively), the silicon going preferentially into the Laves phase.

More importantly was the effect of chromium, which imparts corrosion resistance, which was equally partitioned between the Laves phase and the matrix for 0 wt% Si. As the silicon content increased, the chromium partitioned itself more in the matrix than the Laves, and the reverse was true of the molybdenum which came out of the matrix and was transferred to the Laves phase.

Figure 52 shows a typical TEM micrograph for the as-cast 0 wt% Si alloy. The shape of the eutectic as lamellar particles is clear and the Laves phase contained considerably less stacking faults than that of the 3 wt% Si (T-700).

TABLE 22:

Variation in percentage Laves phase as a result of silicon variation to T-700

Specimen Condition	% Laves	Max. Diam. (μm)	Length (μm)	Form Factor
0 wt% Si As-cast	24.6 $\pm$ 11	11.3 $\pm$ 8	32.3 $\pm$ 33	0.71 $\pm$ 0.2
4h 850°C	24.4 $\pm$ 4	12.6 $\pm$ 7	35.6 $\pm$ 27	0.63 $\pm$ 0.2
24h 850°C	17.9 $\pm$ 6	13.7 $\pm$ 8	38.5 $\pm$ 24	0.70 $\pm$ 0.2
50h 850°C	22.7 $\pm$ 3	11.5 $\pm$ 6	28.9 $\pm$ 19	0.70 $\pm$ 0.2
3 wt% Si As-cast (T-700)	46.6 $\pm$ 7	22.5 $\pm$ 13	72.3 $\pm$ 41	0.56 $\pm$ 0.2
4h 850°C	45.7 $\pm$ 5	24.7 $\pm$ 7	71.4 $\pm$ 23	0.54 $\pm$ 0.2
24h 850HSoC	45.1 $\pm$ 6	20.5 $\pm$ 8	67.3 $\pm$ 26	0.51 $\pm$ 0.3
50h 850°C	43.9 $\pm$ 6	26.3 $\pm$ 12	98.6 $\pm$ 53	0.50 $\pm$ 0.4
6 wt% Si As-cast	62.8 $\pm$ 2	11.6 $\pm$ 11	30.4 $\pm$ 37	0.68 $\pm$ 2.0
4h 850°C	64.7 $\pm$ 5	21.6 $\pm$ 12	58.8 $\pm$ 43	0.62 $\pm$ 0.03
50h 850°C	71.1 $\pm$ 4	49.6 $\pm$ 27	130.9 $\pm$ 75	0.64 $\pm$ 0.2

TABLE 23: Distribution of elements in the Laves and matrix as a result of silicon variation.

		Laves		Matrix	Ratio of Laves:Matrix
0 wt% Si	Ni	30		47	39:61
	Cr	18		19	49:51
	Mo	52		34	61:39
	Si	0		0	
3 wt% Si (T-700)	Ni	37	35	62	37:63
	Cr	12	11	19	38:62
	Mo	48	51	17	48:52
	Si	3	3	2	60:40
6 wt% Si	Ni	37		62	37:63
	Cr	9		24	27:73
	Mo	47		11	81:19
	Si	7		3	70:30

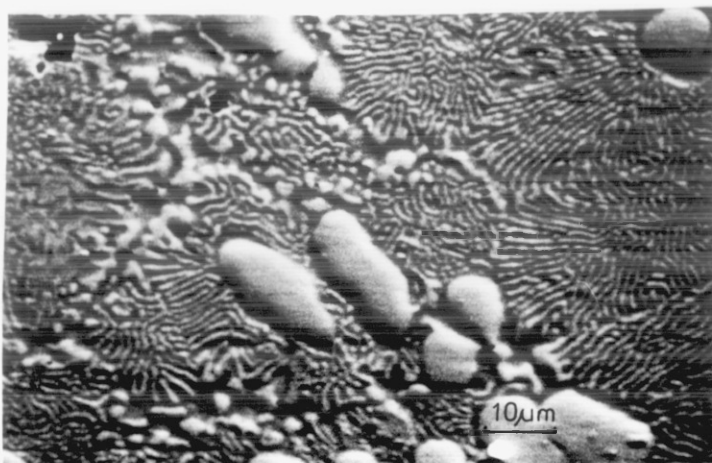


Fig. 49: A.C. 0 wt % Si

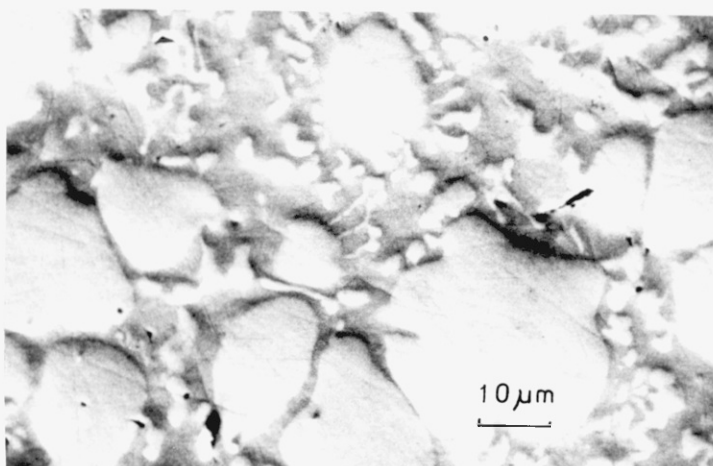


Fig. 50: A.C. 6 wt % Si

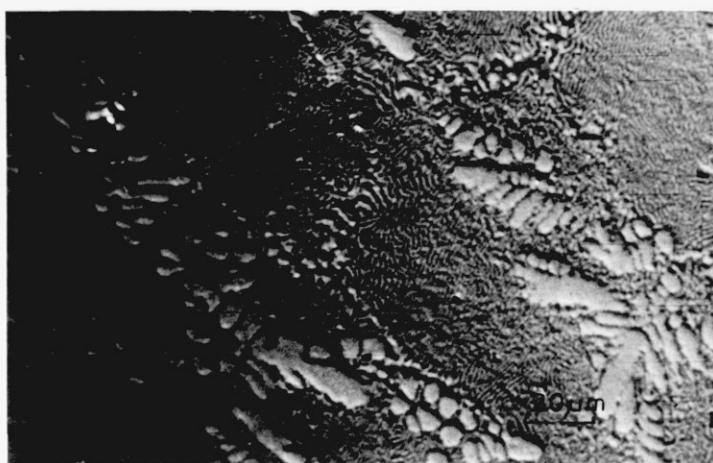


Fig. 51: 0 wt % Si 4 h at 850°C

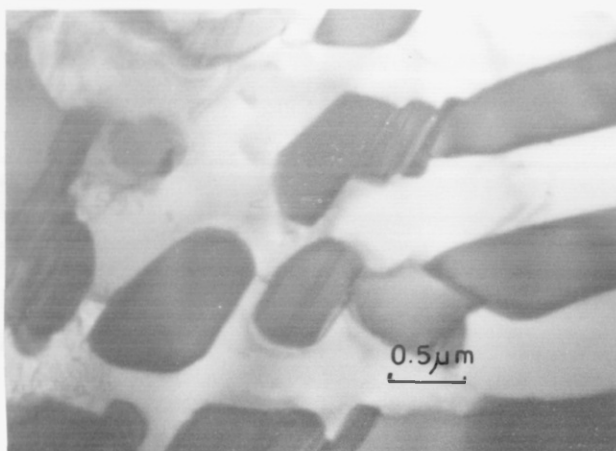


Fig. 52 : TEM Micrograph a.c. 0 wt % Si

5.2.2.2 Mechanical properties of as-cast and heat treated alloy

The summary of mechanical property tests described below is shown in Table 15.

5.2.2.2.1 Hardness variation of as-cast and heat-treated alloy.

Both alloys were heated at 700°C and 850°C up to 100h and the results compared to those for 3 wt% Si (T-700). The results are shown graphically in Figures 53 and 54. All three alloys showed similar hardness values in their as-cast conditions, but the hardness of both the 0 wt% Si and 6 wt% Si changed as a consequence of the above heat treatment conditions. It is possible that the difference in the crystal structure of the Laves phase caused by the different silicon contents may have an effect on the hardness, reaching a maximum at 3 wt% Si. Both alloys also showed hardness peaks during the heat treatment at 700°C showing they are less stable than T-700 at this temperature. However this peak was only repeated for the alloy containing 0 wt% Si for the heat treatment at 850°C. Even though the hardness of the 6 wt% Si alloy was measured after 2h at 850°C, a peak hardness was not obtained, but this may not necessarily indicate stability of the alloy, but may be due to the

very rapid kinetics involved in the reaction producing a hardness peak in less than 2h, which was consequently missed in this heat treatment study.

The variation in the microhardness of the Laves phase and matrix at 850°C are given in Table 24. The Laves phase in the alloys containing silicon had higher hardness values than that in the 0 wt% Si alloy. After heat treatment, both 0 wt% Si and 6 wt% Si showed an increase in the hardness of the Laves phase, with that of the 6 wt% Si being considerably greater.

The matrix however showed different trends as might be expected from the different microstructures. The eutectic of the 0 wt% Si alloy exhibited the highest hardness value, but the 6 wt% Si showed a higher matrix hardness than the 3 wt% Si alloy, which is probably due to the presence of increased solute. After heat treatment, the 0 wt% Si alloy showed an initial increase in hardness followed by a decrease. However, no significant change was found in the hardness of the matrix after heat treatment of both the 3 wt% Si and 6 wt% Si alloys (student 't' test).

5.2.2.2.2 Fracture behaviour

The results are summarised in Table 15. There was no

significant difference in the fracture toughness of the as-cast alloys (3wt%Si (T-700), 0 wt% Si and 6wt% Si); this was also the effect shown for the hardness values of all three as-cast alloys. However, there was a very large change in the modulus of rupture values with a very low value of 285 MN/m² being obtained for the as-cast 6 wt% Si alloy.

After heat treatment of the 0 wt% Si alloy, the modulus of rupture increased substantially, and this was accompanied by an improvement in the hardness and a reduction in the fracture toughness value for the alloy.

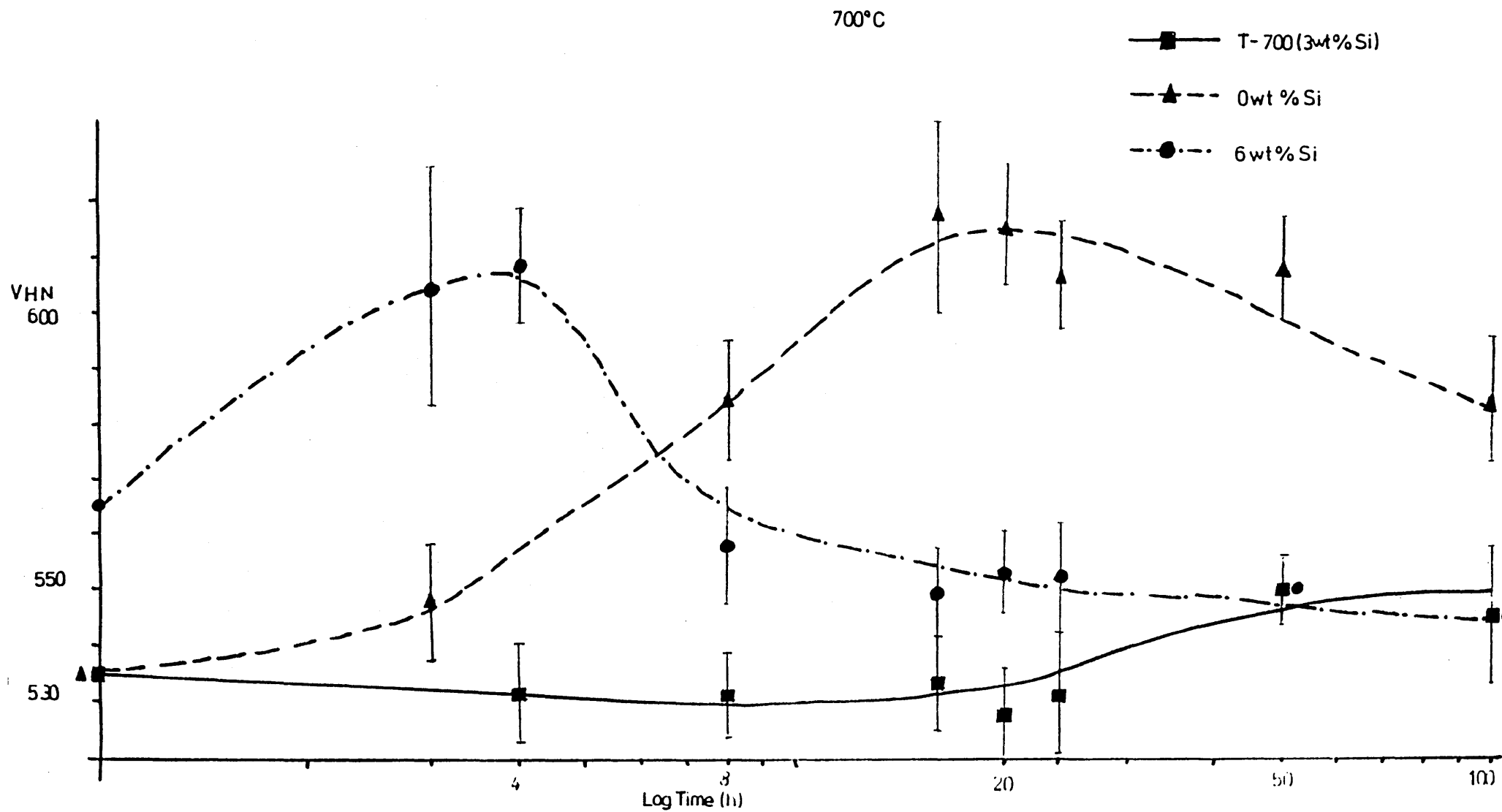


FIGURE 53: Hardness variation of alloys of different silicon content as a result of heat treatment at 700°C.

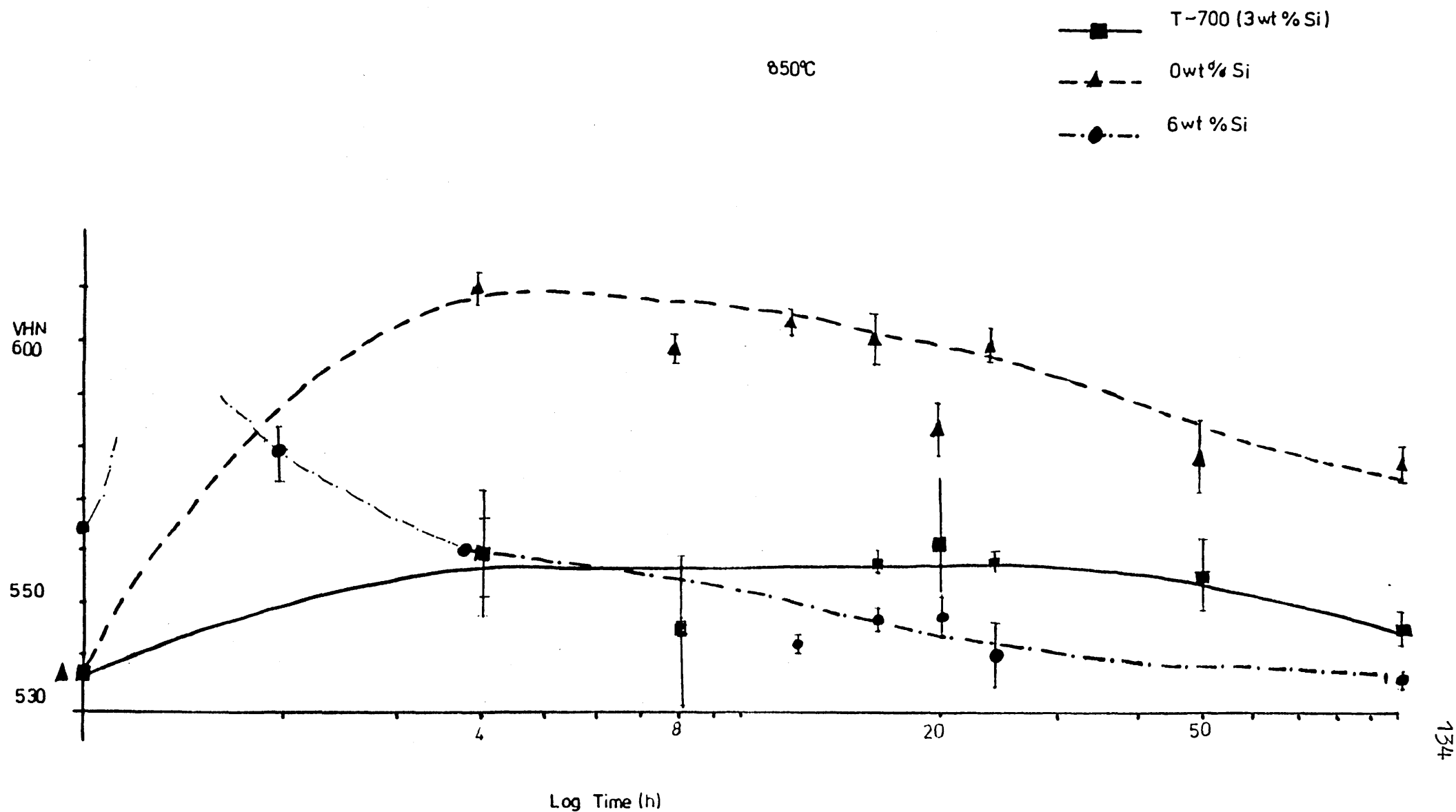


FIGURE 54: Hardness variation of alloys of different silicon content as a result of heat treatment at 850°C.

TABLE 24: Microhardness results for silicon variation alloys

Alloy	Laves (100g)	Matrix (50g)
0 wt% Si a.c.	650 $\pm$ 110	501 $\pm$ 23
4h 850°C	891 $\pm$ 28	590 $\pm$ 15
50h 850°C	751 $\pm$ 62	458 $\pm$ 14
3 wt% Si a.c. (T-700)	926 $\pm$ 58	322 $\pm$ 39
50h 850°C	948 $\pm$ 36	344 $\pm$ 49
6 wt% Si a.c.	782 $\pm$ 66	472 $\pm$ 17
4h 850°C	927 $\pm$ 69	448 $\pm$ 51
50h 850°C	905 $\pm$ 71	456 $\pm$ 13

5.2.3 Iron/Silicon variations

From seeing the effect of adding various quantities of iron and silicon, it was decided to investigate the properties of an alloy containing 5 wt% Fe and 0 wt% Si (0Si/5Fe), and as a result of tests undertaken on this new alloy, another alloy containing 5 wt% Fe and 1 1/2wt% Si (1 1/2Si/5Fe) was made.

5.2.3.1 Microstructure

Figure 55 shows the typical microstructure of an as-cast specimen which contains 0 wt% Si and 5 wt% Fe (0Si/5Fe). There is a distinct similarity in the lamellar appearance of the matrix of this alloy and the alloy containing no iron (0 wt% Si) (Figure 49). On addition of 1 1/2 wt% Si, some regions of the matrix were still lamellar in appearance (Figure 56), with a large reduction in the percentage of primary Laves phase compared with the 0/5 but in other regions there was an even distribution of smaller primary Laves phase particles with an ill-defined eutectic matrix (Figure 57). At first this was thought to be due to poor mixing of the specimen when originally cast, but on remelting and very thorough mixing the same microstructure was still present.

The two regions within the Laves phases were not visible

in either alloy, as was similarly the case with 0 wt% Si.

The volume fraction of the primary Laves phase for the 0Si/5Fe alloy was found to be approximately 36%, and this did not alter after heat treatment. In the 1 1/2Si/5Fe alloy the volume fraction of Laves phase particles was determined by point counting to be approximately 30%.

Compositional analysis in the SEM was undertaken for both the alloys and the results are shown in Table 25. This method is unfortunately only satisfactory where the primary Laves particles to be analysed are greater than 5 μm in diameter. In the case of 1 1/2Si/5Fe, the particles were too small to be analysed individually and so the results for 1 1/2Si/5Fe are for the whole alloy. The amount of iron present is greater than 5wt% because when making up this alloy from the "raw ingredients", an additional amount of iron was added comparable to that in the original T-700 alloy, as detailed by the Cabot Corporation (1979).

X-ray analysis was undertaken for both alloys, and the lattice plane spacings were compared to the cubic, hexagonal and the possible dihexagonal form (found in T-700) of the Laves phase structure types (Table 26). The results showed both the cubic and hexagonal Laves

structure types were present in the 0Si/5Fe alloy, and one d spacing was found which coincided with that found in the dihexagonal Laves structure type. However, although both the cubic and hexagonal structures were also found in the Laves phase of the 11/2Si/5Fe, more diffraction peaks were found which coincided with the possible dihexagonal form previously found in T-700.

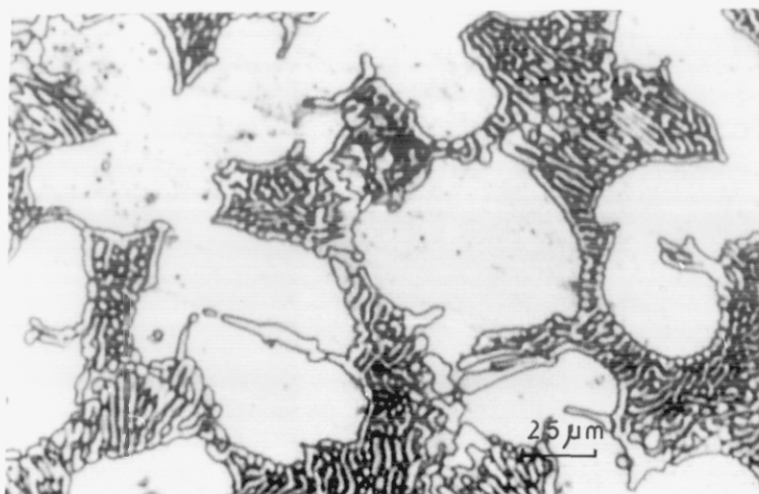


Fig. 55: As-Cast 0wt%Si/5wt%Fe (Optical)

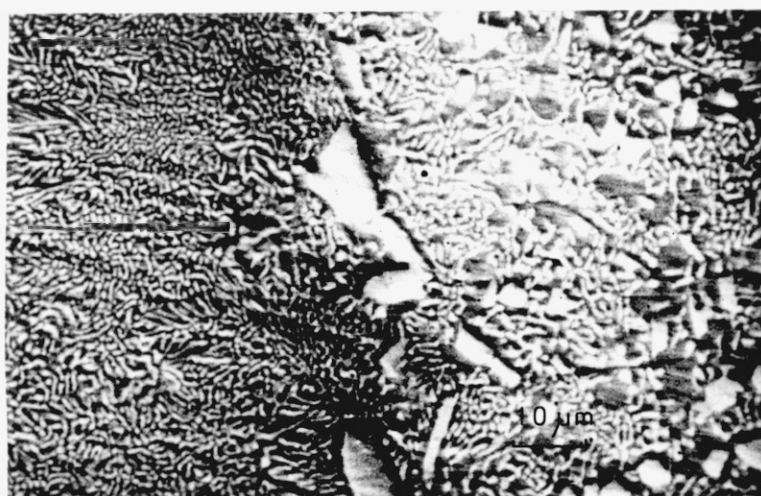


Fig. 56: As-Cast 1 1/2 wt % Si / 5wt % Fe (SEM)



Fig. 57: As-Cast 1 1/2 wt % Si / 5wt % Fe (SEM)

5.2.2.2 Mechanical properties of as-cast and heat treated alloy

The summary of mechanical property tests described below is shown in Table 15.

5.2.2.2.1 Hardness variation of as-cast and heat-treated alloy.

Both alloys were heated at 700°C and 850°C up to 100h and the results compared to those for 3 wt% Si (T-700). The results are shown graphically in Figures 53 and 54. All three alloys showed similar hardness values in their as-cast conditions, but the hardness of both the 0 wt% Si and 6 wt% Si changed as a consequence of the above heat treatment conditions. It is possible that the difference in the crystal structure of the Laves phase caused by the different silicon contents may have an effect on the hardness, reaching a maximum at 3 wt% Si. Both alloys also showed hardness peaks during the heat treatment at 700°C showing they are less stable than T-700 at this temperature. However this peak was only repeated for the alloy containing 0 wt% Si for the heat treatment at 850°C. Even though the hardness of the 6 wt% Si alloy was measured after 2h at 850°C, a peak hardness was not obtained, but this may not necessarily indicate stability of the alloy, but may be due to the

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The matrix however showed different trends as might be expected from the different microstructures. The eutectic of the 0 wt% Si alloy exhibited the highest hardness value, but the 6 wt% Si showed a higher matrix hardness than the 3 wt% Si alloy, which is probably due to the presence of increased solute. After heat treatment, the 0 wt% Si alloy showed an initial increase in hardness followed by a decrease. However, no significant change was found in the hardness of the matrix after heat treatment of both the 3 wt% Si and 6 wt% Si alloys (student 't' test).

5.2.2.2.2 Fracture behaviour

The results are summarised in Table 15. There was no

significant difference in the fracture toughness of the as-cast alloys (3wt%Si (T-700), 0 wt% Si and 6wt% Si); this was also the effect shown for the hardness values of all three as-cast alloys. However, there was a very large change in the modulus of rupture values with a very low value of 285 MN/m² being obtained for the as-cast 6 wt% Si alloy.

After heat treatment of the 0 wt% Si alloy, the modulus of rupture increased substantially, and this was accompanied by an improvement in the hardness and a reduction in the fracture toughness value for the alloy.

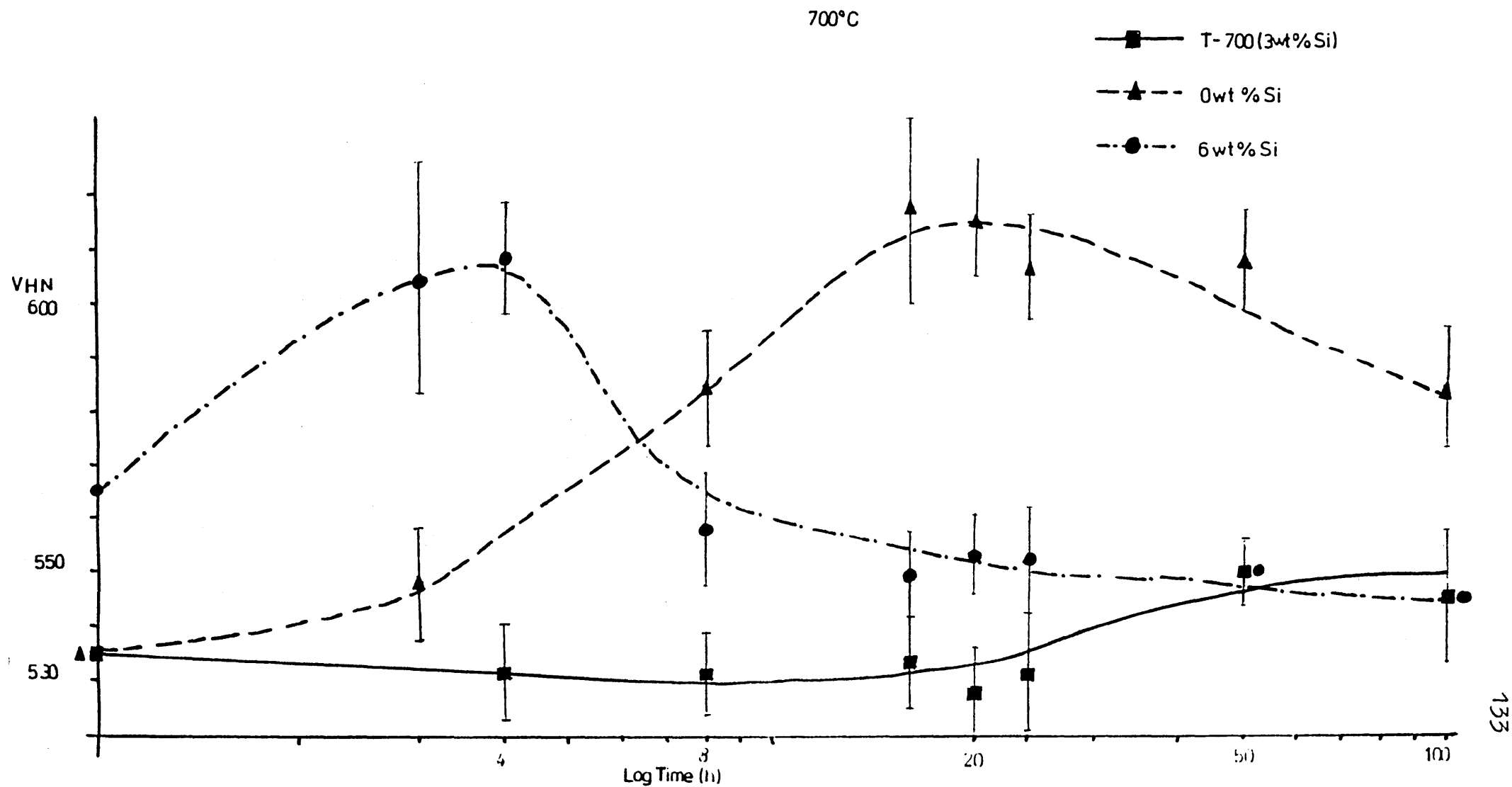


FIGURE 53: Hardness variation of alloys of different silicon content as a result of heat treatment at 700°C.

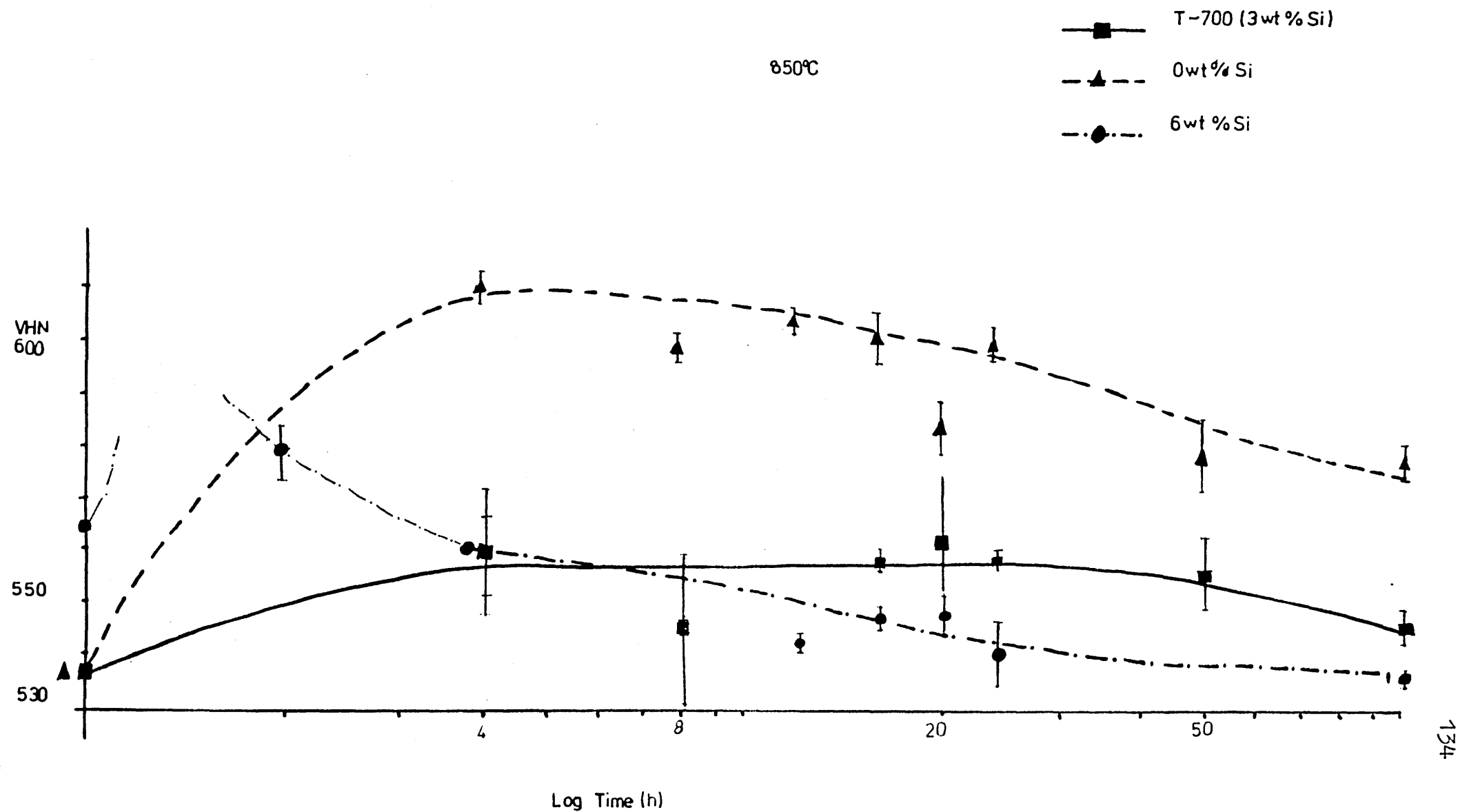


FIGURE 54: Hardness variation of alloys of different silicon content as a result of heat treatment at 850°C.

TABLE 24: Microhardness results for silicon variation alloys

Alloy	Laves (100g)	Matrix (50g)
0 wt% Si a.c.	650 $\pm$ 110	501 $\pm$ 23
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50h 850°C	751 $\pm$ 62	458 $\pm$ 14
3 wt% Si a.c.	926 $\pm$ 58	322 $\pm$ 39
(T-700)		
50h 850°C	948 $\pm$ 36	344 $\pm$ 49
6 wt% Si a.c.	782 $\pm$ 66	472 $\pm$ 17
4h 850°C	927 $\pm$ 69	448 $\pm$ 51
50h 850°C	905 $\pm$ 71	456 $\pm$ 13

5.2.3 Iron/Silicon variations

From seeing the effect of adding various quantities of iron and silicon, it was decided to investigate the properties of an alloy containing 5 wt% Fe and 0 wt% Si (0Si/5Fe), and as a result of tests undertaken on this new alloy, another alloy containing 5 wt% Fe and 1 1/2wt% Si (1 1/2Si/5Fe) was made.

5.2.3.1 Microstructure

Figure 55 shows the typical microstructure of an as-cast specimen which contains 0 wt% Si and 5 wt% Fe (0Si/5Fe). There is a distinct similarity in the lamellar appearance of the matrix of this alloy and the alloy containing no iron (0 wt% Si) (Figure 49). On addition of 1 1/2 wt% Si, some regions of the matrix were still lamellar in appearance (Figure 56), with a large reduction in the percentage of primary Laves phase compared with the 0/5 but in other regions there was an even distribution of smaller primary Laves phase particles with an ill-defined eutectic matrix (Figure 57). At first this was thought to be due to poor mixing of the specimen when originally cast, but on remelting and very thorough mixing the same microstructure was still present.

The two regions within the Laves phases were not visible

in either alloy, as was similarly the case with 0 wt% Si.

The volume fraction of the primary Laves phase for the 0Si/5Fe alloy was found to be approximately 36%, and this did not alter after heat treatment. In the 1 1/2Si/5Fe alloy the volume fraction of Laves phase particles was determined by point counting to be approximately 30%.

Compositional analysis in the SEM was undertaken for both the alloys and the results are shown in Table 25. This method is unfortunately only satisfactory where the primary Laves particles to be analysed are greater than 5 μm in diameter. In the case of 1 1/2Si/5Fe, the particles were too small to be analysed individually and so the results for 1 1/2Si/5Fe are for the whole alloy. The amount of iron present is greater than 5wt% because when making up this alloy from the "raw ingredients", an additional amount of iron was added comparable to that in the original T-700 alloy, as detailed by the Cabot Corporation (1979).

X-ray analysis was undertaken for both alloys, and the lattice plane spacings were compared to the cubic, hexagonal and the possible dihexagonal form (found in T-700) of the Laves phase structure types (Table 26). The results showed both the cubic and hexagonal Laves

structure types were present in the $0\text{Si}/5\text{Fe}$ alloy, and one d spacing was found which coincided with that found in the dihexagonal Laves structure type. However, although both the cubic and hexagonal structures were also found in the Laves phase of the $11/2\text{Si}/5\text{Fe}$, more diffraction peaks were found which coincided with the possible dihexagonal form previously found in T-700.

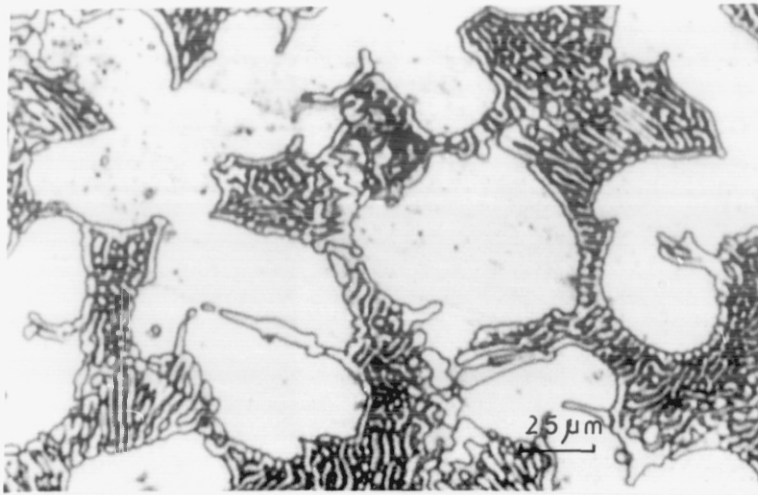


Fig. 55: As-Cast 0wt%Si/5wt%Fe (Optical)

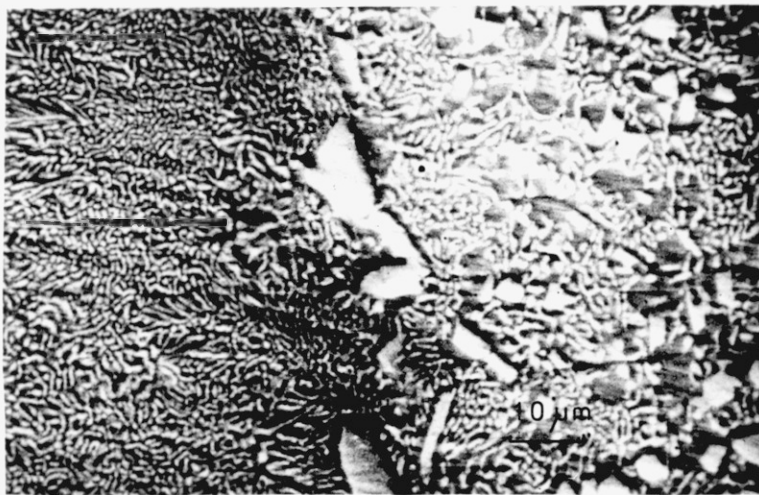


Fig. 56: As-Cast 1 1/2 wt % Si / 5wt % Fe (SEM)



Fig. 57: As-Cast 1 1/2 wt%Si / 5wt % Fe (SEM)

TABLE 25: Distribution of elements for the alloys containing varying amounts of silicon and iron.

Alloy	Element	Laves (%)		Matrix (%)
0wt%Si/5wt%Fe	Ni	43		51±0.7
	Cr	16		17±0.0
	Mo	34		24±0.5
	Si	0.0		0.1±0.1
	Fe	7		9±0.0
1 1/2Si/5Fe	Ni		44.5±2	
	Cr		15.2±0.5	
	Mo		31.4±2	
	Si		1.1±0.0	
	Fe		8.2±0.1	
T-700 (3wt%Si) (Ref: Table 8)	Ni	36.7	35.8	61.8
	Cr	12.0	11.0	19.1
	Mo	47.6	51.6	16.7
	Si	3.6	3.7	2.1

TABLE 26: Experimental 'd' spacings calculated from X-ray diffraction peak data from the Laves phases.

0wt%Si/5wt%Fe		1 1/2wt%Si/5wt%Fe	
d _{exp} /nm	crystal	d _{exp} /nm	crystal
0.2368	hexagonal	0.2368	hexagonal
0.2222	dihexagonal	0.2237	dihexagonal
		0.2176	hexagonal
		0.2137	cubic
0.2089	dihexagonal	0.2076	dihexagonal
0.2039	cubic	0.2050	cubic
		0.1957	hexagonal
		0.1910	dihexagonal
0.1890	cubic		
0.1814	cubic	0.1810	cubic
		0.1390	dihexagonal
		0.1390	hexagonal
0.1281	hexagonal	0.1278	hexagonal
0.1184	hexagonal	0.1185	hexagonal
0.1090	cubic	0.1090	cubic
0.1046	dihexagonal	0.1048	dihexagonal

5.2.3.2 Mechanical properties of as-cast and heat treated alloy.

The hardness of the alloy 0Si/5Fe was less than that of T-700, but similar to that of T-700 + 5 wt% Fe. After heating at 700°C for up to 50h there was no variation in the hardness. This is a similar result to that for T-700, but dissimilar to the alloy T-700 + 5 wt% Fe, and also to that containing no silicon and no iron.

On the addition of a small amount of silicon (1 1/2Si/5Fe) to the alloy, it was found that the hardness was nearer to that of the original T-700 alloy.

As can be seen from Table 15, the fracture toughness values of both alloys were considerably greater than that of T-700. As with T-700, after heat treatment there was no change in the fracture toughness for the alloy 0Si/5Fe.

It is considered that there is also no change in the modulus of rupture, bearing in mind the size of the standard deviations. The tests were repeated a number of times in an attempt to substantially reduce this spread of results, but it was not possible. (Student 't' test confirmed no significant difference between the results).

With the small addition of silicon the fracture toughness value and modulus of rupture were reduced, but both values were still somewhat greater than T-700.

5.2.4 Summary of wear test

Table 27 shows the results of the simple wear test for a number of different specimens.

The equation used to calculate the wear coefficient for this test is

$$V = \frac{k PL}{3H_v} \quad (21)$$

(Archard, 1953; Bhansali, 1980).

where V = volume loss

k = wear coefficient

P = load

L = sliding distance

H_v = hardness

Where possible the results were compared with previous work for a similar type of adhesive wear test (Bhansali, 1980). Since there is generally such a variation in the performance of wear tests and in the interpretation of results gained, wear coefficients tend to be quite variable. However, very good agreement was found between wear coefficients from this present work and those reported by Bhansali.

For good wear resistance the wear coefficient should be as small as possible, and from the list of alloys on Table 27 it can be seen that T-400 has the lowest value, but the wear coefficient for T-700, even after heat treatment remained fairly constant and low. This is again in agreement to the stability shown after heat treatment.

With the addition of iron heated at 700°C for 24h, a similar low value for the *weight loss* was produced. However, for the alloy containing no silicon there is a greater fractional weight loss and after heat treatment this increased quite considerably, together with the wear coefficient, showing that the wear resistance of the material without silicon had decreased.

The alloy 0Si/5Fe showed an even greater fractional weight loss and a considerably larger wear coefficient resulted.

Stellite-6 is also included in Table 27 on a comparative basis, since it is a well documented material. It is interesting to note its wear resistance is not as great as that of T-700, and it also showed considerable percentage weight loss in comparison with most of the other alloys for this wear test.

TABLE 27: Results of simple wear test

Alloy	% wt loss	Wear Coeff (k) ($\times 10^{-6}$)	VHN	C (k/3VHN) ($\times 10^{-9}$)
T-700	0.18	8.55	536	5.32
24h 700°C	0.09	7.8 (1)	526	2.76
50h 700°C	0.10	4.36	550	3.36
0wt% Si a.c.	0.22	5.54	536	7.08
24h 700°C	0.61	11.38	600	16.4
T700+5wt%Fe				
24h 700°C	0.091	4.15	524	2.64
0Si/5Fe a.c	7.61	329.1	475	230.6
Stellite 6	2.28	86.4	406	70.95
		88.9 (1)		
T-400 a.c.		0.77 (1)	690 (2)	0.37

(1) Bhansali (1980)

(2) Halstead (1980)

6. DISCUSSION

6.1 Microstructure of as-cast and heat treated T-700

Until now the only information available about the microstructure of T-700 has been in the form of optical micrographs produced by the manufacturer (Deloro Stellite) together with confirmation of the presence of the Laves phase (Cameron & Ferris, 1973; Cabot Corpn., 1979). Using the scanning electron microscope in the back scattered electron emissive mode the present work revealed the unexpected presence of two regions within the Laves phase, which were initially designated as "light" and "dark" to distinguish them. X-ray diffraction data, transmission electron micrographs and compositional analysis show that these two regions were both Laves phases with differing structures (hexagonal and dihexagonal) which can co-exist at the particular alloy composition of T-700.

Hume-Rothery et al. (1969) describe the coexistence of different types of Laves phases in terms of the electron concentration (the average number of valence electrons per atom), " e/a ". As this increases one or more of the Laves phase types are formed in the order of increasing e/a , that is cubic ($MgCu_2$), dihexagonal ($MgNi_2$), and hexagonal ($MgZn_2$). In the Mg-Cu-Zn ternary system, they found that the dihexagonal structure was formed which they considered as being intermediate, in terms of its structural relationship and electron concentration, to the other two types. It was

also found that in this ternary system the Laves cubic structure was stable over a range 1.33 to approximately 1.80 electrons per atom and the hexagonal structure was stable from about 1.90 electrons per atom. Thus the electron concentration of the dihexagonal structure type is likely to exist between the electron concentrations of the other two types.

The e/a ratios of the two parts of the Laves phase in T-700 were calculated using the data from the analysis of the phase composition of the alloy. For the light Laves phase this was found to be in the range 1.31 to greater than 2.60, and for the dark Laves phase the e/a range was 1.33 to greater than 2.56. The range of e/a for the various valencies of chromium and molybdenum are shown in Table 28. However, the difference between the e/a values for "light" and "dark" Laves is smaller than the experimental errors. According to the data produced by Hume Rothery et al. (1969), these values in fact overlap throughout the cubic - dihexagonal - hexagonal structure types. However, no evidence was found to support the existence of the cubic structure type in T-700, and so if the suggestion of Hume-Rothery et al. (1969) that the dihexagonal structure type forms at e/a ratios greater than about 1.70 is correct, then it would appear that the univalent molybdenum is absent, leaving the di- and tri-valent forms.

Mittal et al. (1978) found that on adding silicon to binary

TABLE 28: Electron concentration (e/a) of T-700				
Light Laves				
Mo Cr		1	Valency 2	3
V a l e n c y	1	1.312	1.954	2.596
	2	1.386	2.028	
	3	1.46	2.102	
Dark Laves				
Mo Cr		1	Valency 2	3
V a l e n c y	1	1.33	1.944	2.557
	2	1.415	2.028	
	3	1.499	2.112	

and ternary systems which contained the cubic Laves structure, the hexagonal type was invariably formed. They found the hexagonal Laves type was formed on the addition of silicon, even if previously no Laves phase had been present in the alloy. This was seen in the case of the Mn-Ni-Si system, for which no Laves phase exists in the binary system (Mn-Ni), but the cubic type Laves phase is stable in the ternary system with low silicon content and the hexagonal type Laves phase is stable at higher silicon content.

On the basis of this it was decided to try to establish which Laves phase types were present in T-700, which has 3 wt% Si, by analysing the X-ray diffraction data produced by T-700 and comparing this to the X-ray diffraction data produced by the alloys containing 0 wt% Si and 6 wt% Si, where the low silicon content alloy was likely to have the cubic type Laves, and the higher silicon content alloy was likely to contain the hexagonal type. Since the original T-700 Triballoy alloy contained 3 wt% Si, and thus occupied an intermediate position, it was expected that the diffraction data produced from its two Laves phases would be of the cubic and hexagonal types.

There was good agreement between data for the cubic Laves phase structure (Wood & Compton, 1958; Compton & Matthias, 1959) and the X-ray diffraction data of the 0 wt% Si alloy. This confirms that the 0 wt% Si alloy contains the cubic form of the Laves phase, but no correlation was found

between the cubic type Laves phase and the X-ray diffraction data produced by the 3 wt% Si alloy (T-700), which indicates that the cubic structure type does not exist in T-700. A number of the X-ray diffraction peaks for T-700 (3 wt% Si) were similar to those obtained from the alloy containing 6 wt% Si, and those from the hexagonal Laves type in the Mg-Ni-Si system produced by Gladyshevskii and Kuzma (1960).

Some X-ray diffraction peaks produced by the T-700 alloy could not be accounted for in this way, so these may be produced by the dihexagonal structure, but no X-ray diffraction data of the dihexagonal Laves structure could be found in the literature for comparison.

The lattice plane spacing values of the hexagonal and dihexagonal Laves structures were calculated from the X-ray diffraction data and compared to the Hull-Davey (or Bunn) chart (1956) for hexagonal crystals. The c/a ratios were found to be 1.614 for the hexagonal and 1.898 for the dihexagonal. These results compare well with the calculated values for a and c (Table 11), which result in c/a ratios of 1.627 and 1.755 for the hexagonal and dihexagonal forms. It is therefore unlikely that these phases have any other morphology.

Further confirmation of the coexistence of the two types of Laves phase is shown in the transmission electron micrographs. Allen et al. (1972) suggested that Laves

structures differ only in the stacking of similarly built layers and which may depend on the exact composition, and that the dihexagonal structure is only a distorted version of the hexagonal type. They also suggested that transformation between the different structure types can occur as a result of temperature variation and that the stacking fault energy should be small for alloys undergoing transformation between structure types. In their experimental studies they found that a TiCo_2 alloy was able to adopt two different structure types at room temperature depending on its composition. An excess of cobalt caused the structure to be dihexagonal; whereas the stoichiometric alloy TiCo_2 had been shown to be cubic. They found after undertaking extinction experiments that the stacking faults were extrinsic as a result of a double glide process. As in T-700, they found numerous stacking faults, but they also observed superstructures which suggested low stacking fault energy.

However, for T-700 (which contained 3 wt% Si), two Laves structure types were identified, the hexagonal and dihexagonal forms, and at the temperatures of heat treatment and the particular duration of the test the complete transformation to only one Laves type did not take place, as might have been expected, showing that under these conditions the alloy was particularly stable.

This is in contrast to the situation encountered by Allen et

al. (1972), where a transition between structure types of $TiCr_2$ was found to occur after heat treatment. However it is quite possible that if the heat treatment for T-700 had been extended for some considerable time beyond 100h then a transformation would take place. It is interesting to note that after the heat treatments undertaken for T-700 no precipitation particles were observed in the matrix, unlike the situation for the cobalt-base Triballoys which did show precipitation in the matrix, showing that T-700 is more stable than the cobalt base Triballoys.

It is also worthy of note that, in the cobalt-base Triballoy T-800, primary particles containing two Laves phases can be observed after 2h at 1250°C followed by 13 days at 800°C (Halstead, 1980). This effect was not however seen after similar treatments to T-400, the cobalt-base Triballoy which contains more cobalt than T-800, or where T-800 was only heat treated for 13 days at 800°C.

In T-700 the diffraction patterns produced from the basal planes of both hexagonal and dihexagonal Laves types were identical to each other and show the structure to be hexagonal (Figures 29 and 30) since the cubic form would produce a completely different diffraction pattern. It is also suggested that within the T-700 alloy, the region containing the greater density of stacking faults is the hexagonal type structure (see section Results 5.1.1.3) since, according to Hume-Rothery (1969), this type is more

sup
154

stable than the dihexagonal structure, and could possibly have a lower stacking fault energy. However no published information could be found which relates directly to the Laves phase structure types and stacking fault energies.

Working with copper, Salonen et al. (1969) found a variation in the stacking fault energy as a direct result of alloying additions. They found that increasing the aluminium content reduced the stacking fault energy, but increasing the manganese content not only increased the stacking fault energy but also reduced the electron concentration (e/a). Although their primary work concerned the binary alloys, they found this relationship applied equally well to the ternary.

Carter and ~~Holmes~~ (1977), also found the same relationship between e/a and stacking fault energies in copper alloys by using a slightly different approach.

Both investigations showed the same for all the alloying additions considered, that is the e/a increased exponentially as the stacking fault energy decreased.

Smallman and Green (1964), working on the relationship between the rolling texture and stacking fault energy of brasses, also observed the exponential relationship between stacking fault energy and e/a , but they also found that the variation of the stacking fault energy in various alloy

systems could be affected if there is an appreciable atomic misfit or a difference in valency between solute and solvent. Unfortunately, they did not investigate this relationship in any more detail since their work primarily concerned rolling texture, and they concentrated on eliminating both atomic misfit and valency difference in an attempt to explain that the stacking fault energy was the fundamental factor controlling texture transition. In T-700, the "light" Laves phase contains a greater weight percentage of molybdenum than the "dark" phase (from the compositional analysis results) and from atomic size considerations alone this is likely to cause more misfit in the structure. Also there is a valency difference between both nickel and chromium and nickel and molybdenum.

In summary, the sequence of argument is as follows:

- a) the "light" Laves phase appears lighter in the SEM because the greater molybdenum content produces greater atomic number contrast
- b) the higher molybdenum content increases lattice parameter misfit
- c) the increased misfit leads to a greater density of stacking faults
- d) a greater number of stacking faults implies a lower stacking fault energy, and hence less stability, which is associated with the dihexagonal structure.

This suggests that the "lighter" Laves is the dihexagonal

structure.

6.2 Microstructural changes as a result of alloy variation

Having already discussed the structure of the two Laves phases in T-700, which contains 3 wt% Si, the effect of varying the quantity of iron and silicon on the microstructure will now be considered.

In all the alloys containing iron, although two Laves phases could be identified by X-ray and composition analysis, they could not be distinguished using the SEM. A possible explanation for this could be due to an increasing similarity in the percentage of molybdenum content of the two Laves phases as the amount of iron increased. This caused a reduction in the average atomic number difference and thus could no longer be detected using the SEM, which depends on average atomic number difference to produce a contrast.

X-ray diffraction data produced for all three iron bearing alloys (5, 10 & 15 wt% Fe) shows that both types of Laves are present, but more diffraction peaks were compatible with the hexagonal type than the dihexagonal type for all the iron additions. With increasing iron the intensity and number of the peaks compatible with the possible hexagonal Laves structure type increased and the number and intensity of peaks compatible with the dihexagonal structure type decreased (Table 4). It is therefore suggested that the

addition of iron to T-700 causes a transition to occur between Laves structure types, resulting in domination by the more stable hexagonal Laves structure type.

Another change observed was that the volume fraction of the Laves phase was less in the iron bearing alloys than in T-700. This effect was also seen for the addition of iron to the cobalt-base Triballoys (Halstead, 1980). However, the decrease was more noticeable for the cobalt alloys in that the volume fraction of Laves phase continued to decrease monotonically for increasing iron content, whereas for T-700 after an initial reduction in the volume fraction of about 30%, there was no further change for iron additions (up to 15 wt% Fe). The change in volume fraction as a function of iron content is important because it is later related to changes in the mechanical properties.

There was also a change in the general shape of the Laves phase particles in the iron bearing alloys, and attention is drawn to Table 20 for a comparison of form factors. From this it can be seen that with increasing iron content, there is an increase in the form factor which suggests that the shape of the particles is becoming more rounded. Although no alteration in the morphology of the matrix was observed for these alloys, it is quite possible that this subtle change in shape of the Laves phase particles may be due to the transition between hexagonal and dihexagonal Laves phase structure types discussed earlier.

This change in shape was also noted for the alloys containing varying amounts of silicon. Here too, the Laves phase particles became less faceted and more rounded in appearance than in T-700, but for both increasing and decreasing silicon content. Again there was an associated increase in the form factor corresponding with the increase and decrease in silicon content. It is also interesting to note at this point that as mentioned previously during this experimental work only one Laves phase structure type was observed in the 0 wt% Si alloy where the cubic form was identified, and in the 6 wt% Si alloy, where the hexagonal structure type was identified. It is thus quite possible that, where mixed Laves structure types are found to co-exist, the shape of the Laves phase particles is affected. Unfortunately, the workers who observed the co-existence of different Laves structure types (Allen et al., 1973) did not describe an overall shape of the Laves phase particles.

Although the phase diagrams are described in the Introduction they show only the ternary systems for Ni-Cr-Mo, Cr-Mo-Si and Ni-Si-Cr it may be possible to identify the phase of the quaternary Ni-Cr-Mo-Si alloy with a phase on the ternary diagram.

According to the phase diagram of the Ni-Cr-Mo system produced by Bloom & Grant (1951) (Figure 4), if T-700

contained no silicon the position the alloy would occupy would be in the $P + (Ni)$ region. From the investigations undertaken for the 0 wt% Si alloy, the presence of a cubic Laves phase structure has been confirmed, and as a result it is suggested that the P phase which they called an intermetallic compound of unknown structure is in fact the cubic Laves phase.

From the ternary diagram for Fe-Mo-Ni (Figure 6) it can be seen that without silicon or chromium a solid solution composed of Fe+Ni is formed together with the P phase. It is suggested that if the silicon or chromium does not change the phase type, then the P phase in this ternary is a Laves phase of either dihexagonal or hexagonal structure.

Why?

The results of compositional analysis reveals that a greater percentage of the iron added was present in the matrix than in the Laves phase. If the iron goes preferentially into the Laves phase by replacing nickel, the depletion of nickel from the Laves phase allows more nickel to be available for nickel solid solution. Since the solid solution now also contains iron, the overall result is a reduction in the percentage of the Laves phase present.

Since the effect of silicon in stabilising a particular form of Laves phase has already been discussed, the microstructural changes as a result of the different silicon content are now considered.

The most dramatic differences in these alloys was in the appearance of the matrices, and the very large difference between the amounts of Laves present in the alloys. The 0 wt% Si alloy contained a small amount of primary Laves phase and a fine lamellar eutectic of Laves and nickel solid solution. The alloy containing 6 wt% Si however contained very large amounts of primary Laves in a matrix of nickel solid solution. (Indeed as noted in the results in section 5.2.2.1 there is an almost linear relationship between the increasing percentage of Laves phase and increasing silicon content shown in Table 22).

In the Ni-Cr-Mo phase diagram (Figure 4), the alloy containing approximately 52%Ni, 32.5%Mo 15.5%Cr and 0%Si is within the region containing the cubic Laves structure (previously termed the P phase) and (Ni). However, it is important to note that this phase diagram is only the isothermal section at 1250°C.

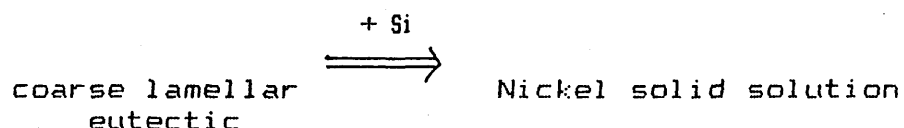
A comparison between this phase diagram and the isothermal section at 1200°C produced by Rideout et al. (1951) shows a slight difference in that the composition of the alloy has moved further away from the region containing cubic + σ + (Ni) to a position well within the cubic + (Ni), nearer to (Ni). Although there is only a slight difference between the temperatures of the two phase diagrams, it is suggested that, during the solidification process of this alloy and

after the formation of the primary cubic Laves phase, the alloy composition moves into the region containing (Ni), and that the lamellar eutectic is secondary Laves within the nickel solid solution.

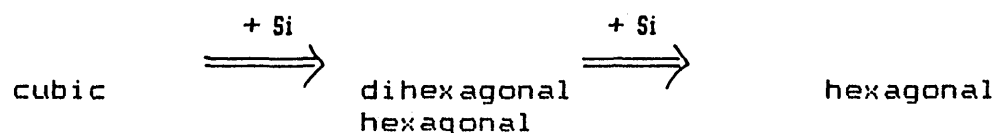
It thus appears that as silicon is added to the alloy, although it increases the amount of Laves phase formed, it inhibits the formation of the lamellar eutectic, producing a matrix of nickel solid solution. Compositional analysis revealed that the presence of the silicon directly affected the proportions in which chromium and molybdenum were distributed in the matrix and the Laves phase (Table 23). With increasing silicon content there was more chromium in the matrix than the Laves and the reverse was true for molybdenum.

The effect of silicon variation can briefly be summarised as follows:

In the matrix



in the Laves structure:



In the alloys where both the iron and silicon contents were varied, additional microstructural changes were observed.

The alloy containing 0 wt% Si/5 wt% Fe (0Si/5Fe) showed a remarkable similarity to the alloy with 0 wt% Si, but was quite different to the alloy with 3 wt% Si (T-700)/5 wt% Fe.

The similarity to the 0 wt% Si alloy was primarily in the appearance of the matrix, which again contained what appeared to be a lamellar eutectic composed of secondary Laves and nickel solid solution, and the overall appearance of the Laves phase was also similar. However, the volume fraction occupied by the primary Laves phase particles (30%) was greater than that of the 0 wt% Si (25%).

As reported in the results for the alloy containing 11/2Si/5Fe, regions containing a fine lamellar eutectic were observed (Figure 56) as well as regions containing small primary particles within a matrix of nickel solid solution (Figure 57).

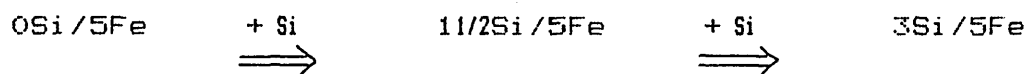
As discussed when comparing 0 wt% Si and 3 wt% Si (T-700), the presence of silicon again tends to inhibit the formation of a lamellar eutectic, although in the case of the 11/2Si/5Fe alloy, it is appears that this process is incomplete.

The X-ray diffraction data produced for both the 0Si/5Fe and 11/2Si/5Fe alloys showed diffraction peaks from the hexagonal form, which was expected because of the presence

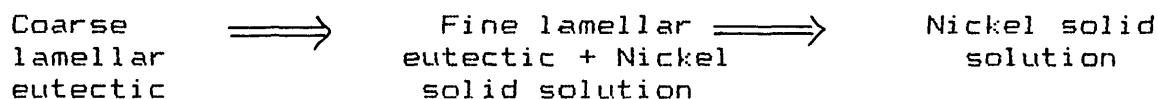
of iron, but also showed peaks produced by the cubic structure. For the alloy containing 0Si/5Fe the cubic form dominated, and for the alloy containing 11/2Si/5Fe the hexagonal form dominated.

Also diffraction peaks, which were compatible with the presence of the di-hexagonal form in T-700, were observed from both these alloys, but more peaks compatible with this structure type were found in the 11/2Si/5Fe alloy than the 0Si/5Fe alloy.

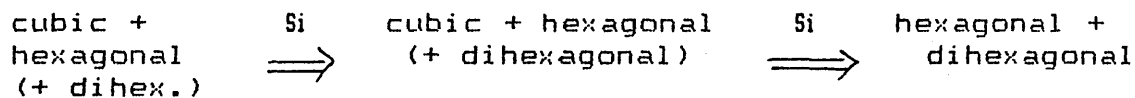
From both the microstructural observations and the X-ray diffraction data produced, it is suggested that a transition is occurring in both the matrix and the Laves phase, which is shown below:



in the matrix -



in the Laves -



In the case of a transition between the dihexagonal and hexagonal structure types, it is likely that since only a

change between stacking sequences is involved, this could occur by a shear mechanism. However, there is a greater structural difference between the cubic and both the hexagonal Laves structures than between the two hexagonal structures themselves (Hume Rothery et al., 1969; Allen et al., 1972). Thus a transition between the cubic and hexagonal structure types could involve a more dramatic change in the size, shape and distribution of the Laves phase particles than that between the two hexagonal structure types, and this could be why small particles were observed in $11/2\text{Si}/5\text{Fe}$.

Obviously to verify these suggestions, considerable further investigation of the microstructure is necessary.

6.3 Mechanical properties of T-700

As mentioned in the Results section the microstructure of T-700 after heat treatment appeared to be virtually unchanged and the structural stability was also evident in the hardness, fracture toughness and modulus of rupture results which showed no significant change after heat treatment (student 't' tests applied), (Table 15), therefore the following discussion applies to both the as-cast and heat treated condition.

The brittle nature of T-700 is evident from the appearance of the fracture surface and the low fracture toughness values obtained. It was observed that crack propagation in T-700 occurred predominantly by cleavage of the Laves phase (Figure 37), which presented the weakest crack path, (although there appeared to be no preference for the type of Laves through which the crack propagated) and this agrees with the low fracture toughness results showing ease of crack propagation.

The fracture toughness results for T-700 were found to be similar to that for the as-cast cobalt-based Triballoys, and the fracture toughness values for all three Triballoys are comparable to the WC-Co hardmetals (Table 5).

Fracture toughness values can also be used to calculate the minimum acceptable defect size which is the lowest value that can be tolerated under a given design stress, and is proportional to the square of the stress intensity factor (K_{Ic}). It should be pointed out that the simple fracture mechanics approach to determine flaw size can only be applied to single phase homogeneous materials, but since correctly determining the flaw size involves the use of finite element analysis, which is beyond the scope of this work, the simplistic approach has been used. For T-700, the minimum acceptable defect size was found to be very similar to T-400, (Table 15: T-700=0.51mm², T-400=0.55mm², T-800=0.27mm²), which is not surprising since similar fracture toughness results were found. It should also be noted that T-700 contained a similar Laves volume fraction to the T-400 alloy.

Thus the similarities between T-700 and the cobalt-base Tribaloy T-400 are:

- a) fracture toughness and flaw size
- b) volume fraction of Laves phase

In contrast to the fracture toughness data, the modulus of rupture results for T-700 were found to be quite different to the cobalt-base Triballoys.

The modulus of rupture of a material can be considered as a measure of the failure strength of a material under a tensile

stress and as such in brittle materials can give an insight into the initiation of cracks and their propagation. Halstead (1980), working on the cobalt-base Triballoys, monitored crack initiation by acoustic emission and found the Laves cleaved at a stress well below that necessary to produce catastrophic failure. As a result of investigation of the as-cast and heat treated alloys, she postulated that with a high volume fraction of brittle primary phase, cleavage within the Laves phase took place easily. In addition, she found that improved tensile strength could be obtained by increasing the amount of fcc cobalt solid solution present, because the fcc cobalt solid solution is able to accommodate the strain produced on cleavage of the primary Laves and hinders the linking of microcracks through the matrix to reach the critical flaw size necessary for catastrophic failure. The fcc cobalt solid solution was able to accommodate more easily the stresses produced at a crack tip than hcp since the number of independent slip systems available for dislocation motion is 5, whereas for hcp slip is confined to the basal plane. An exception to this was found where precipitation occurred in the matrix as a result of ageing. This resulted in hindering the dislocation motion which increased the brittleness of the matrix and thus the microcracks were able to link together. This effect was more noticeable where Widmanstätten precipitation resulted.

Since in T-700 the nickel solid solution matrix is similarly fcc and the percentage of Laves is similar to T-400, it would

be expected that a reasonably high modulus of rupture should result. However, this was not the case, and it was at first considered that the most important difference was in the matrices of the two alloys. As already mentioned the microstructure for T-700 showed the matrix was composed of nickel solid solution, but in T-400 the matrix was composed of a layer of cobalt solid solution surrounding the primary Laves and a lamellar eutectic. The presence of this solid solution layer hinders the linking of microcracks by effectively blunting the cleavage cracks in the Laves phase, and therefore stopping the propagation of cracks through the eutectic matrix. Hence the higher modulus of rupture values obtained for the cobalt-based Triballoys are probably due to this solid solution layer and also to the very nature of the lamellar eutectic which may offer more resistance to dislocation motion, than the nickel solid solution. Thus of these two Triballoys, T-700 can be considered as having the weaker matrix.

It was also noted that the size of the primary Laves phase particles for T-400 are smaller than those of T-700. Although the value quoted by Halstead (1980) for the mean size of the Laves phase particles for T-400 was $6\text{ }\mu\text{m}$, a re-examination of the micrographs suggest a mean size of about $20\text{ }\mu\text{m}$. This value is however still smaller than that found for the Laves phase particles of T-700 (mean length $70\text{ }\mu\text{m}$, mean diameter $20\text{ }\mu\text{m}$), thus for the same flaw size there is more linking together of microcracks than in T-700, which is a more

difficult process, and thus propagation of cracks is more difficult.

Another difference is in the actual appearance of the Laves phase particles; the Laves phase in the cobalt-base Triballoys appearing "rounded" whereas in T-700 they appeared "faceted". A number of papers have been published concerning the size, shape and distribution of second phase particles and non-metallic inclusions present in steels and cast iron and their effect on mechanical properties (Luyckz et al., 1970; Brooksbank & Andrews, 1972; Baker & Charles, 1972; Petrichenko et al., 1974; Bernard et al., 1975; Eriksson, 1975).

Petrichenko et al. (1974) investigated the effect of the shape and size of graphite particles on the strength, ductility and toughness of nodular cast iron, and concluded that particles of poor shape (that is, departing seriously from the spheroidal form) impaired the mechanical properties of some cast irons. But Gensamer (1946), examining the distribution of iron carbide in steels and its effect on their mechanical properties, found the strength of this material depended on the mean spacing between the particles in such aggregate structures, and not at all on the shape of the particles except as this affected the mean spacing.

The effect of brittle second phase particles such as Laves phases can in some way be considered as similar to inclusions in terms of strength and fracture toughness.

However investigations on the effect of inclusions have generally been undertaken on steels, which on failure show fibrous fracture. Also, the sizes (5-10 μm) and volume fractions (0.5%) of inclusions are very much smaller than those of Laves phase particles. Bernard et al., (1975) working on the effect on non-metallic inclusions on the mechanical properties of steels, emphasised that the sensitivity of the material to fracture initiation is partly a fundamental property of the matrix; they also showed that the effect of inclusions on the fracture initiation at the root of a notch depended upon complex mechanistic interactions, and thus both the inclusion geometry and matrix properties were important with respect to the fracture mechanism.

They also emphasised the importance of taking into account an inclusion shape factor when discussing the control of the different parameters. The work covered only elongated and spherical inclusions, rather than the complex and unusual shapes such as the faceted Laves particles which occur in T-700, but the elongated forms showed the worst results. Certainly in T-700 their shape is more elongated than spherical.

Brooksbank & Andrews (1972) however were able to show that where particles are close together there is an overlap of stress fields which causes the matrix to yield eventually.

Supporting this, Eriksson (1975) showed that the fracture toughness of a material is preserved if the most frequent inclusion distance is always kept larger than the extent of the intensely strained region of the material. Brooksbank and Andrews also concluded that sharp corners raise the stress potential and can be considered as having a greater potential to form voids than smooth or "rounded" corners. It is again emphasised that their results applied to a fibrous failure mode.

Evans, ^{Ref} however, working on the structural and microstructural properties of brittle materials showed that the type of failure of a material depended on the elastic modulus and fracture toughness of the inclusion, compared to the matrix. When the inclusion has a larger fracture toughness than the matrix, fracture initiates with the matrix, usually from microflaws located within (or adjacent to) the interface between the matrix and inclusion, and this process resembles what happens during the void fracture described above. This then supports the suggestion of sharp corners raising the stress potential again contradicting the work by Gonsamer.

On the basis of this, it is suggested that the shape of the Laves phase particles in T-700 are more favourable to crack nucleation than the "rounded" shape Laves particles present in T-400.

But Laves will
have a lower
fracture toughness

It is suggested that the higher modulus of rupture of T-400 is due to the combination of the solid solution around the Laves phase which hinders crack propagation, and the higher strength of the lamellar eutectic. The smaller primary Laves phase particles found in T-400 and the more "rounded" shape may also contribute to the higher modulus of rupture of T-400.

Thus in summary the important factors affecting the modulus of rupture appear to be

- a) the structure of the matrix
- b) the size and volume fraction of the Laves phase particles
- c) the shape of the Laves phase particles.

6.4 Mechanical properties as a result of alloy variation

6.4.1 As-cast condition

Although no changes in the matrix were detected on the addition of iron to T-700, the Laves particles became more rounded in appearance, indicated by the change in the form factor with a value tending more to 1 as iron was added (Table 20). As shown by Bernard et al. (1975) this is a better shape for improved mechanical properties than that seen in T-700. The addition of iron was also accompanied by a reduction in the volume fraction of Laves phase. In terms of overall performance, an improvement in the modulus of

rupture and fracture toughness, but reduced the macrohardness.

At this point it is interesting to consider the effect of changes in the matrix and in the volume fraction of the Laves on the mechanical properties. Figures 58, 59, 60, 61 and 62 show the modulus of rupture, fracture toughness and macrohardness respectively as a function of the volume fraction of primary Laves phase. These also include the effect of the silicon additions, which will subsequently be discussed.

From these graphs, it can be seen that the modulus of rupture is more sensitive to changes in the volume fraction of primary Laves phase than the other two properties. As already discussed, the important factors affecting the modulus of rupture appear to be the morphology of the matrix, the size of the primary Laves and its volume fraction. Note that after an initial reduction in the volume fraction of Laves phase on adding iron the microstructure, and consequently the modulus of rupture, remain constant.

For the alloys containing additions of iron to T-700, a comparison can be made with the as-cast condition of the cobalt-base Triballoys containing iron additions (Table 6). For these alloys, a reduction in the volume fraction of the Laves phase as a result of iron addition also gave an

increase in the MOR result, however for the cobalt based Tribaloys on adding more iron, there was a further increased in the modulus of rupture.

Of the alloys containing silicon variations, that containing 0wt%Si had a lamellar eutectic matrix similar to that seen in the cobalt base alloys, but had more rounded Laves particles with a reduced volume fraction than the nickel based T-700; all factors which are favourable to producing the higher modulus of rupture which was in fact found. With increased silicon (6 wt% Si), however, there was a very large increase in the volume fraction of the primary Laves phase, which resulted in a considerably reduced modulus of rupture.

So it can be seen from these results that the shape, size, and volume fraction of the Laves phase are important in determining the modulus of rupture and the most dominant is the volume fraction, as has already been concluded from the literature.

If one now considers the fracture toughness aspect of iron additions, the effect is dissimilar to modulus of rupture in that a reduction in the percentage of Laves for iron additions to T-700 only gave a relatively small increase in the K_{Ic} value (Fig. 59). This may in part have been due to a change in the morphology of the Laves phase particles as

well as the decrease in volume fraction after adding iron in comparison to T-700; and there was little difference in the morphology of the Laves phase particles of the iron addition alloys themselves. Overall the reduction in the percentage of Laves phase had the effect of increasing the fracture toughness by a small amount.

For the cobalt-base Triballoys, since the matrix is a brittle lamellar eutectic, the addition of iron hindered the formation of the solid solution layer around the Laves phase and so the propagation of cracks is easy. Thus the decrease in the volume fraction of Laves as a result of iron addition is insignificant since the eutectic and Laves phase were now as brittle as each other. Although for the cobalt-based Triballoys the modulus of rupture continued to increase for increased iron due to a decrease in the percentage of Laves phase, in contrast the K_{Ic} values remained constant (Table 6). The constancy of K_{Ic} in this case could be attributed to the fact that the eutectic matrix does not hinder crack propagation in a manner similar to the iron free cobalt based Triballoy.

In the as-cast condition, the macrohardness of all three Triballoys, decreased with increasing additions of iron. However, as can be seen from Table 21, the presence of the iron in T-700 considerably reduced the hardness values of both the Laves and matrix, which in itself is detrimental.

This decrease in macrohardness must however be weighed against the favourable increase in MOR results.

In the 0 wt% Si alloy the eutectic matrix counteracted the effect of the reduced volume fraction of Laves phase as in the cobalt based Triballoys, as producing a K_{IC} value similar to that in T-700. However, for increased silicon content (6 wt% Si) which produced a large Laves volume fraction (63%), there was very little reduction in the fracture toughness results, which indicates that once about 40% volume fraction of Laves has been achieved, there appears to be no further change in K_{IC} (Fig. 60).

It can be seen that the morphology of the matrix must be considered as a significant factor as well as the volume fraction. So a reduction in the volume fraction of Laves phase is favourable for a higher K_{IC} , but a lamellar eutectic should be avoided.

The considerable increase in ductility of the alloy containing 0 wt%Si/5wt% Fe (0Si/5Fe) was apparent from the high modulus of rupture and fracture toughness results, similar to Stellite-6 which has a nominal composition by weight percentage of 66.5 Co, 29.0 Cr, 4.5 W and 1.0 C. Again a low volume fraction of Laves phase particles (30%) was found which were rather rounded in appearance and the macrohardness was found to be lower than that of the

original T-700 alloy, having a value similar to that found for the alloys containing iron additions to T-700. This was surprising since an increase was expected because the matrix was now a lamellar eutectic. Also surprising was the very high K_{Ic} , even though the volume fraction of the Laves phase was not much greater than that of the 0 wt% Si alloy.

As can be seen in Table 15, with a small addition of silicon (1 1/2 wt% Si / 5 wt% Fe) to the 0 Si / 5 Fe alloy although there was a reduction in the fracture toughness and modulus of rupture values, the results still showed a vast improvement in comparison to T-700. There was also an increase in the hardness to a value more in line with that expected for a lamellar eutectic. These changes must be related to the microstructure of 1 1/2 Si / 5 Fe both in terms of the matrix, which was now intermediate between a Nickel solid solution and a lamellar eutectic, and the Laves phase particles, which were now no longer large faceted Laves phase particles as seen in T-700. As discussed previously, it is possible that the transition to a different type of structure and the dispersion of Laves particles much smaller than those previously seen, leads to an increase in modulus of rupture because the smaller particles offer greater resistance to the nucleation and propagation of cracks.

The possibility of this transition is suggested on the basis of the decrease in the fracture toughness and modulus of

rupture of the alloy in comparison to that of the 0Si/5Fe alloy, and the previously discussed X-ray results. The macrohardness value approaches that of the T-700 alloy, even though the primary Laves is considerably less, and this reduction in volume fraction may be due to the even distribution of the small Laves particles in the intermediate type matrix. Since the mechanical properties look interesting, it would be particularly useful to see which effect was produced as a result of heat treatment, and whether or not this alloy remained stable.

Referring again to Figure 58 in which the effect of the volume fraction of the Laves phase and change in the matrix morphology on the modulus of rupture is shown, it appears that a similar relationship occurs in the 0Si/5Fe and 11/2Si/5Fe alloys where there is a change from a lamellar eutectic to a nickel solid solution, as well as the postulated change between types of Laves structure. However no comment can be made about the effect of the lamellar eutectic at these compositions to the fracture toughness results.

The importance of the presence of silicon cannot be overlooked, and attention is drawn to Figures 61 and 62 which show the effect of the presence of silicon and silicon plus iron on the mechanical properties. As previously discussed, although the presence of silicon tends to inhibit

the formation of a lamellar eutectic which is favourable for and increase in the modulus of rupture, it is equally important in controlling the formation of a particular type of Laves phase structure. However, as can be seen from Figures 61 and 62 for the iron bearing alloys, the addition of too much silicon quickly affects the mechanical properties, and so a large improvement is seen on the addition of iron.

6.4.2. Effect of heat treatment to the alloy variation

Where heat treatments were undertaken the temperature was comparable with those reached during machine operation and thus it is important that reasonable stability of the material is maintained. One of the problems encountered so far was that concerning the addition of iron, which reduced the stability of the alloy, particularly when silicon was not present.

Although only one time and temperature test was undertaken for the cobalt alloys with iron additions (Table 6) an increase in the hardness was found with each of the alloys after heat treatment, although with T-400 this was much less marked than with T-800. Generally the hardness of the cobalt-based alloys decreased with increasing iron content after the heat treatment. This effect of an increase in the macrohardness after heat treatment, was also shown for the nickel-base Tribaloy (T-700) containing 5 wt% Fe. However,

only the as-cast iron alloys for the cobalt-based alloys was investigated, and this was not done in detail, since the work concentrated on compositional variation rather than heat treatment, thus the data on the cobalt alloys is limited.

It is interesting that the matrix of the 0 wt% Si alloy becomes less lamellar after heat treatment, which resulted in the K_{Ic} value decreasing with a complementary increase in the hardness and modulus of rupture. The increase in the modulus of rupture was far more dramatic than might have been expected since there was no change in form factor but the Laves volume fraction increased. This again shows the sensitivity of modulus of rupture to changes in the volume fraction of Laves phase.

Although the 0Si/5Fe alloy appeared to show an improvement in the modulus of rupture after heat treatment, no conclusions could be drawn from the fracture toughness and hardness values, except that the standard deviations of all the measurements suggest instability of the alloy.

6.5 Wear

To produce a good wear performance, the key properties of the hardfacing material are generally considered to be its resistance to deformation, as measured by hardness and its

resistance to microfracture, as measured by K_{IC} and modulus of rupture. Ideally, therefore, the alloy with the highest fracture toughness result and hardness should yield the best wear results.

Attention is again drawn to Table 27, and the effects of the alloying addition on the wear properties. Unfortunately, wear tests are renowned for their poor reproducibility, and it is here emphasised that the results are for one test run only. Nevertheless excellent agreement was found with the present results for T-700, T-400 and Stellite-6 and with those reported by Bhansali (1979).

From the wear test results, the alloys with smaller wear coefficient together with low percentage weight loss, indicate better wear properties. From Figure 27, it can be seen that T-700 together with T-700 + 5wt%Fe produced the best wear resistance results.

It is thus apparent that silicon is a necessary addition for better wear resistance as can be seen from the alloys 0wt%Si (both as-cast and after heat treatment) and 0Si/5Fe. The latter alloy had very poor wear resistance results, which could be due to the reduction in macrohardness as a result of the iron addition as well as the lack of silicon.

From these tests on the various alloys of T-700, it appears

that silicon probably plays an important role in increasing the wear resistance of the alloy, by aiding the formation of Laves phases.

In summary, from these tentative results, it appears important that a certain amount of silicon must be retained in the alloy, the suggested amount being that coincident with the actual formation of the larger Laves phase particles, i.e. 1 1/2 wt% Si or slightly greater.

It appears from these results that the alloys which contain a Laves phase with an hexagonal structure (i.e. T-700 and T-700 + 5 wt% Fe) show superior results to those where the Laves phase structure type is the cubic form. As has been discussed previously the presence of silicon is necessary for the formation of the hexagonal forms of the Laves phase.

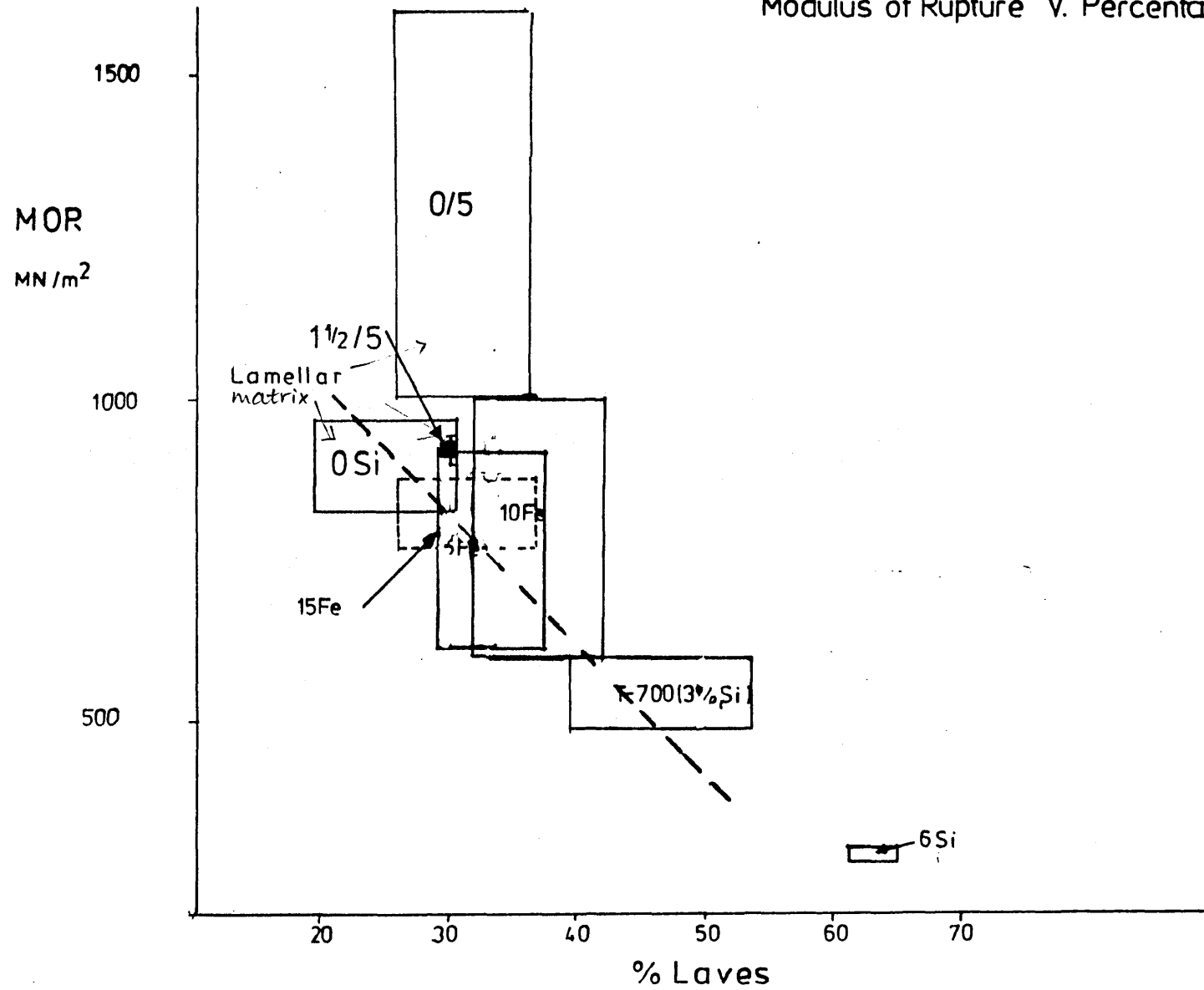
It has been shown that, even if the iron content remains constant, the variation in silicon has an effect on the modulus of rupture. However, as can be seen with the 6 wt% Si, too much Laves phase can be formed by the increased silicon content, which in this particular case resulted in a low modulus of rupture value. Also with the increased silicon there is a reduction in the fracture toughness of the alloy, which also shows a transition from a ductile to a more brittle alloy.

However, the importance of silicon in retaining good wear resistance in the alloy is clear.

It may be possible to find a compromise situation by retaining a small amount of silicon which, together with some iron addition, gives vastly improved mechanical properties compared with the original T-700 alloy. However, it is also important that this compromise alloy should be stable.

Fig 58

Modulus of Rupture V. Percentage Laves Phase



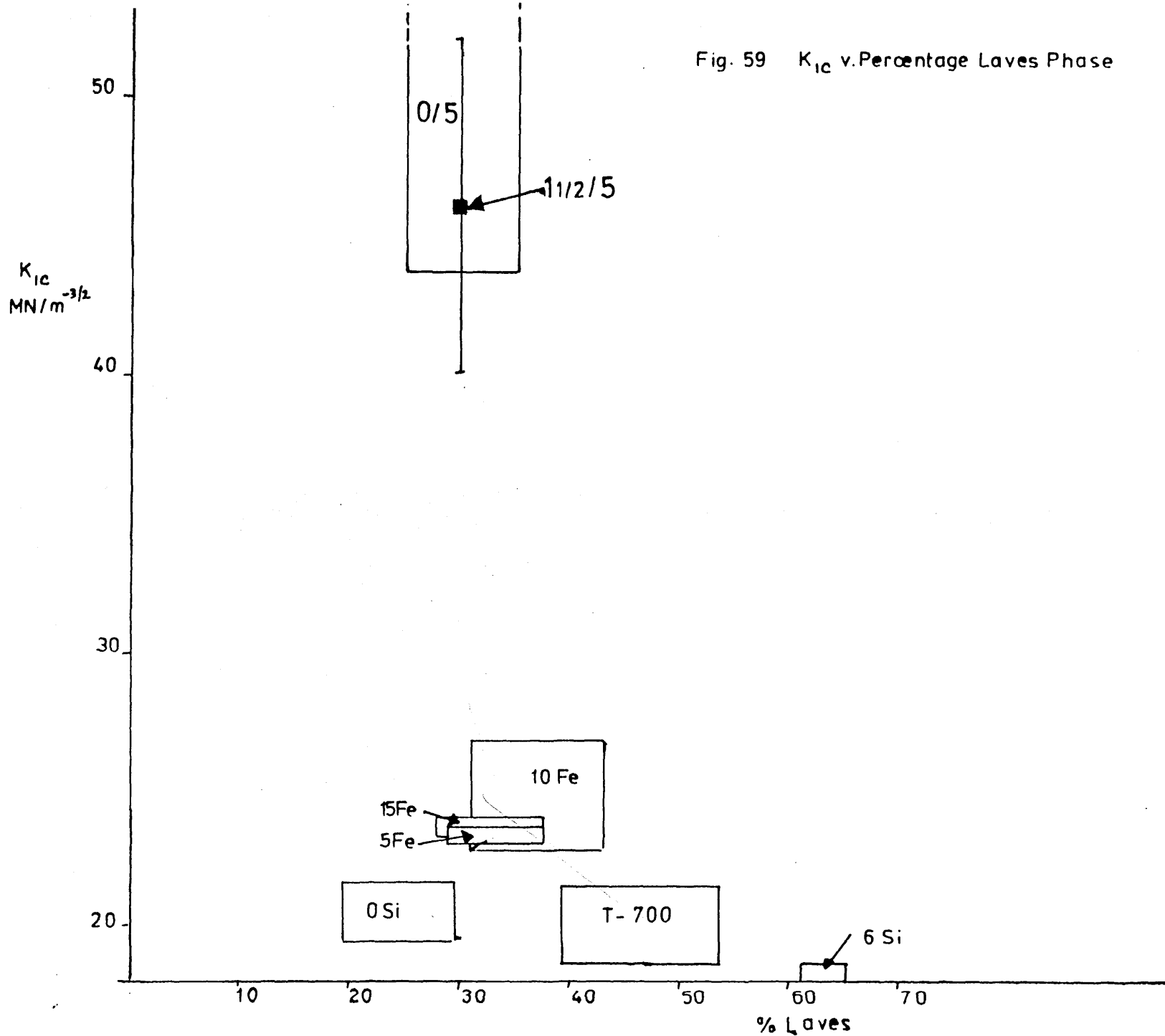


Fig 60

Hardness V. Percentage Laves Phase

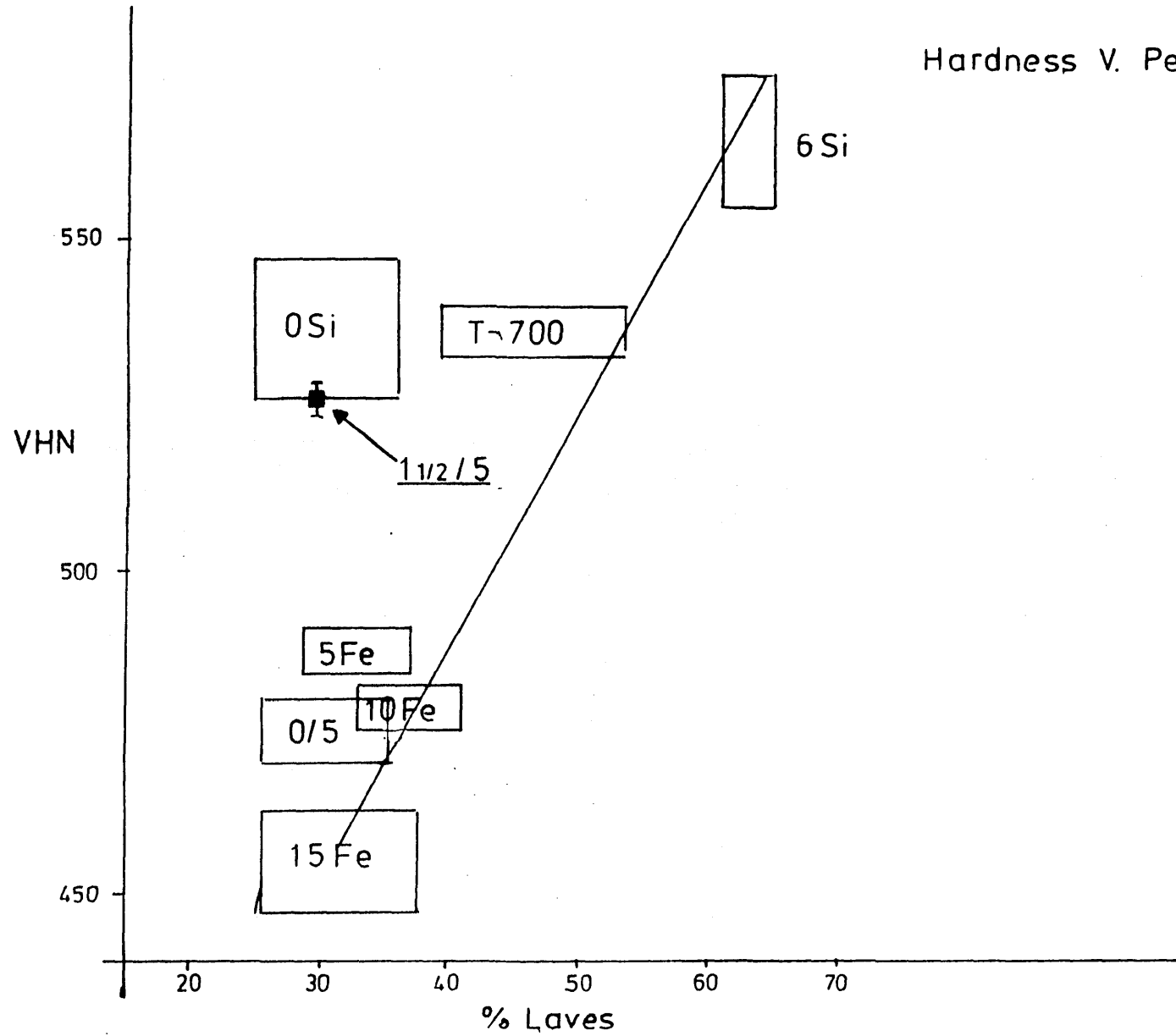


Fig. 61

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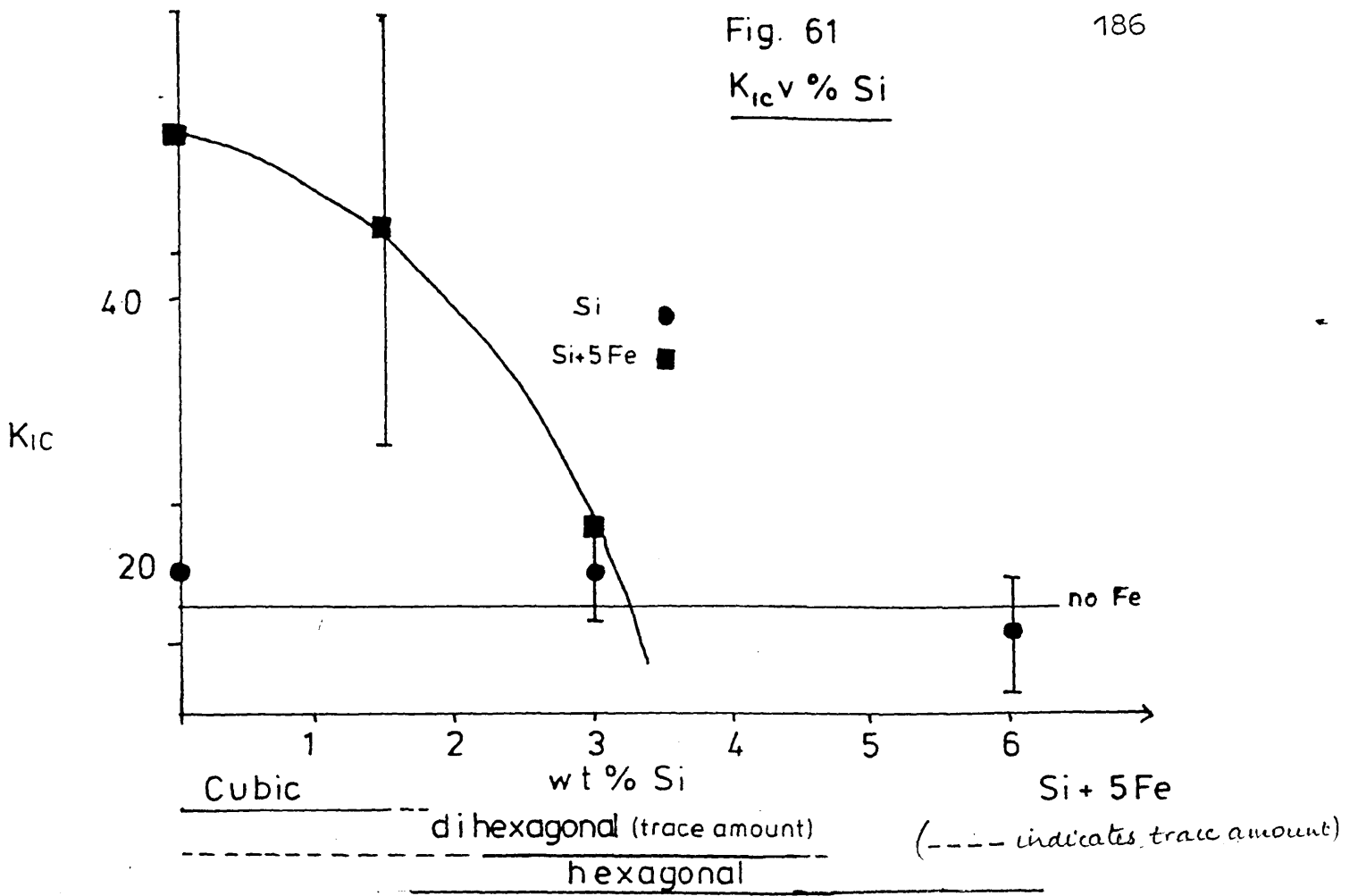
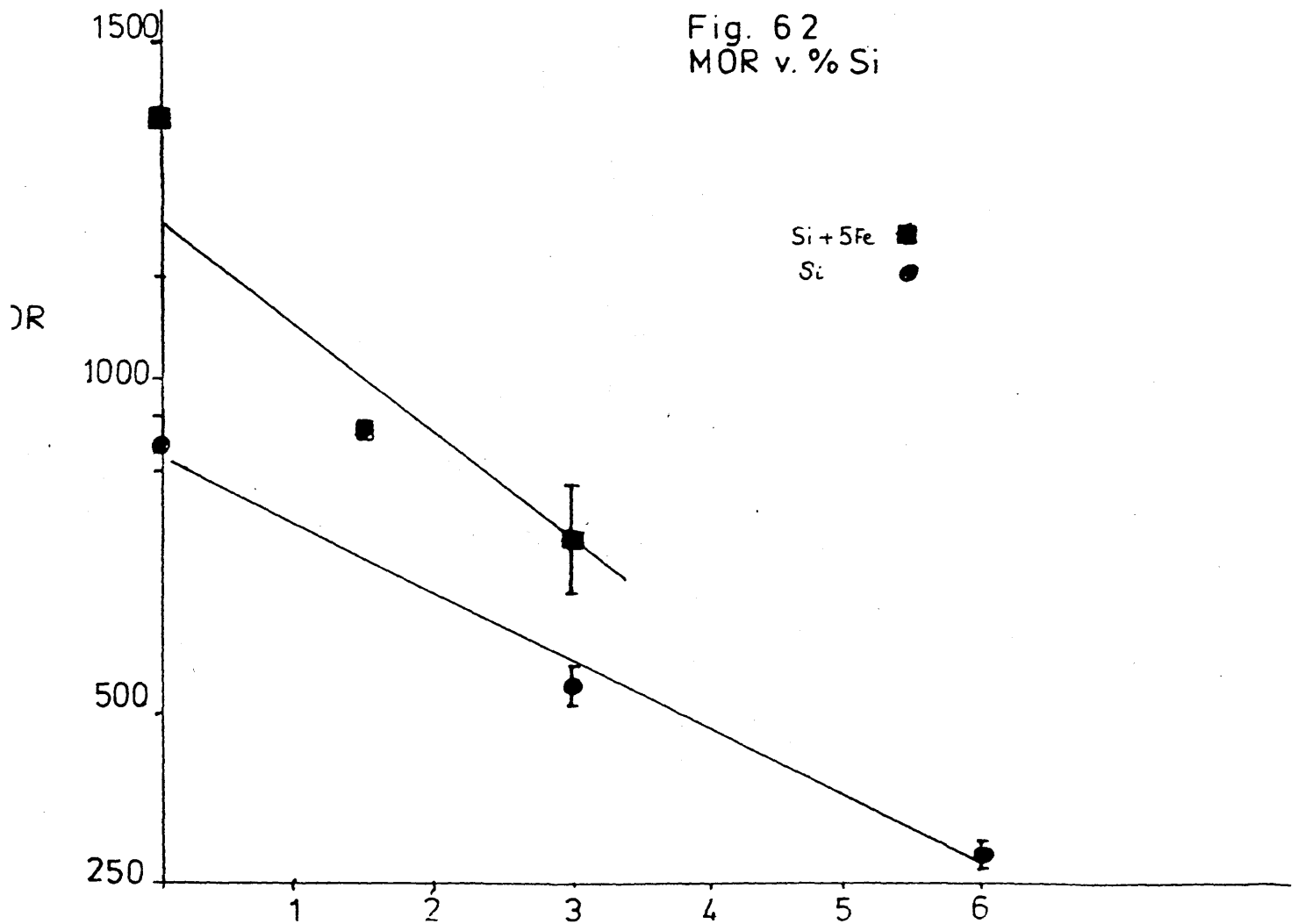
 K_{Ic} v % Si

Fig. 62

MOR v. % Si



7. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

7.1 Conclusions

1. Two Laves phases are formed in T-700, having the hexagonal and dihexagonal structure types (MgZn_2 and MgNi_2 respectively), these two forms differing primarily in their stacking sequence.
2. The phase previously termed P in the Ni-Cr-Mo phase diagram is the cubic Laves structure type (MgCu_2).
3. Stability of T-700 up to 950°C is confirmed.
4. The fracture toughness and Modulus of Rupture values for T-700 are $20.1 \text{ MN/m}^{3/2}$ and 537 mn/m^2 respectively.
5. The addition of iron to the alloy is not detrimental to the original alloy; in the as-cast condition there is only a slight decrease in the macrohardness, but an increase in the fracture toughness.
6. However after heat treatment at 700°C for 24h, the alloy containing 5 wt % iron shows no change in the above noted mechanical properties
7. No detrimental behaviour to the wear resistance of the

alloy on the addition of 5 wt % iron is shown even after a heat treatment of 24h at 700°C.

8. Silicon is a very necessary addition to the alloy, primarily in the formation of the hexagonal type Laves phase since this Laves phase structure type shows increased wear resistance properties to that without silicon (which results in the formation of the cubic structure type).

9. The presence of silicon inhibits the formation of a lamellar eutectic, which from the results of this work and that of Halstead (1980) are necessary for improved MOR and fracture toughness results.

7.2 Suggestions for further work

1. The work undertaken at present only provides a very limited amount of linking between the microstructure and mechanical properties of the alloys. Further information can be obtained by investigating the deformed material

a) to determine the presence of slip steps (optical microscopy)

b) to determine the dislocation density, since this gives information about the ease or difficulty of dislocation motion and slip (TEM)

c) to determine whether any changes in the crystal structure were present after deformation (TEM, X-ray).

2. Since identification of the diffraction pattern of the Laves phase was only a small part of this present research, it was determined by comparing published data on indexed diffraction patterns. Although beyond the scope of this present work, the possible orientation dependence of the crystal structure should be investigated (TEM).

3. The initial results for the alloy containing 1 1/2wt% Si/5 wt% Fe showed some interesting variations and improvements, and heat treatments similar to that already undertaken should be done to confirm or otherwise the variations in mechanical properties.

4. From the results it appears that 1 1/2wt% Si is probably the minimum weight percent of silicon for the transition between Laves phase structure types and it would be interesting to compare the results for an alloy with a silicon content of say between 2 and 2 1/2 weight percent.

5. Extended heat treatment for T-700 to perhaps 15 days, to see whether there is a transition in the Laves phases to the hexagonal form only.

6. Wear tests should be undertaken on all the different alloys made before and after heat treatment to obtain a more complete picture.

7. Further TEM study should be made to investigate further the Laves structure types particularly for the alloy containing 1 1/2wt%Si/5wt%Fe which from the results contained herein indicates a transition between the three Laves phase structure types.

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