

PHASE EQUILIBRIA
IN
RECYCLED NICKEL-BASED SUPERALLOYS.

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I dedicate this work to my parents.

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ABSTRACT

Nickel-base superalloys are used for their outstanding resistance to deformation and oxidation in the combustion sections of aircraft and land-based gas turbine engines. Typically, the combustion chamber, nozzle guide vanes and turbine blades. These blades are situated immediately after the combustion chamber and 'see' the hottest temperatures in the engine.

However, during manufacture, up to 60% of the initial material ends up as scrap. This consists of the runners, risers and headers. The cost of these materials is such that it would be advantageous to re-use this 'revert' material, either directly or as a certain percentage of material of which the rest would be 'virgin'. It has been observed, however, that the performance of blades containing 'revert' material is poorer and this has been linked with the observation of 'new' phases in the microstructure.

In particular, a Ni-Hf and Ni-Zr rich phase was identified in Hf and Zr containing superalloys, such as MarM002 and MarM246. Silicon was associated with the phases and it was found that by doping 'heats' of MarM002 with small amounts of silicon the volume fraction of the Ni-Hf phase was found to increase.

Therefore, the identity of these phases was required, to ascertain whether they were the cause of the poorer mechanical properties. Also, an understanding of the exact association of silicon with these phases was desirable.

Studies of the nickel-rich regions of the Ni-Hf-Si and Ni-Zr-Si alloy systems showed that silicon was in solid solution in Ni_5Hf and Ni_5Zr up to at least 10 at. % at 1125°C. The $\gamma/\text{Ni}_5\text{Hf}$ and $\gamma/\text{Ni}_5\text{Zr}$ phase fields were found to be quite extensive. A ternary eutectic was tentatively observed in both systems at Ni-6.0 Hf-16 Si and Ni-6 Zr-16 Si. Phases found to be rich in nickel and hafnium and nickel and zirconium were observed in MarM002+Si, IN939+Si and MarM246. Higher silicon contents were measured in these phases than in the surrounding phases.

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Table 1 Compositions of a variety of nickel base superalloys

ALLOY	COMPOSITION (wt %)									
	Ni	Cr	Co	Ti	Al	Mo	C	Zr	B	Others
<i>Turbine disc</i>										
Waspaloy	Balance	19.5	13.5	3.0	1.3	-	0.08	0.06	0.006	
Astroloy	Balance	15.0	17.0	3.5	4.0	5.25	0.06	-	0.030	
API (Powder Astroloy)	Balance	15.0	17.0	3.5	4.0	5.0	0.025	0.04	0.025	
<i>Wrought turbine blades</i>										
Nimonic 80A	Balance	19.5	-	2.4	1.4	-	0.07	0.07	0.003	
Nimonic 90	Balance	19.5	16.5	2.4	1.4	-	0.08	0.07	0.003	
Nimonic 105	Balance	15.0	20.0	4.7	1.3	5.0	0.13	0.10	0.006	
Nimonic 115	Balance	14.5	13.3	3.8	5.0	3.3	0.15	0.045	0.016	
<i>Cast turbine blades</i>										
IN713LC	Balance	12.0	-	0.6	5.9	4.5	0.05	0.10	0.010	2.0Nb
IN100 (Nimocast PK24)	Balance	10.0	15.0	4.7	5.5	3.0	0.18	0.06	0.014	1.0V
B1900	Balance	8.0	10.0	1.0	6.0	6.0	0.10	0.10	0.015	4.0Ta
MarM200	Balance	9.0	10.0	2.0	5.0	-	0.15	0.05	0.015	12.0W; 1.0Nb
MarM002	Balance	9.0	10.0	1.5	5.5	-	0.15	0.05	0.015	10.0W; 2.5Ta; 1.5Hf
MarM247	Balance	8.3	10.0	1.0	5.5	0.7	0.15	0.05	0.015	10.0W; 3.0Ta; 1.5Hf
René 77	Balance	14.5	15.0	3.3	4.3	4.2	0.07	0.04	0.016	
René 80	Balance	14.0	9.5	5.0	3.0	4.0	0.17	0.03	0.015	4.0W

Purpose	Cr	Al	Co	Mo	W	Ti	Ta	Nb	Hf	C	B	Zr
Matrix Strengthenener	+		-	-	-							
Gamma Prime Former		-				-	-	-				
Carbide Former	-			-	-	-	-	-	-			
Oxide Scale Former	-	-										
Grain Boundary Strengthenener									-	-	-	-

Table 2. The effect of elements on the microstructure of cast nickel-base alloys.

1. LITERATURE SURVEY

1.1 Nickel-base superalloys

1.1.1 What is a nickel-base superalloy?

The following definition is given in "The Superalloys", by Sims and Hagel (1):

'A superalloy is an alloy developed for elevated temperature service, usually based on group VIII A elements, where relatively severe mechanical stressing is encountered and where high surface stability is frequently required'.

1.1.2 Basic Structure and Composition of Some Commercial Nickel-Base Superalloys

Nickel-base alloys are used for their outstanding strength and oxidation resistance over a wide range of temperatures. They have a fully austenitic, face-centred cubic structure which maintains good tensile, rupture, and creep properties up to temperatures much greater than those to which body centred cubic materials can exhibit similar characteristics, and these alloys are used to within 80% of their solidus temperature (°C) , for times up to 100,000 hours at lower temperatures.

In practice commercial alloys can contain ten to twelve elements. The compositions of some typical nickel-base superalloys are shown in table 1. The effect that each element has on the microstructure is shown in table 2.

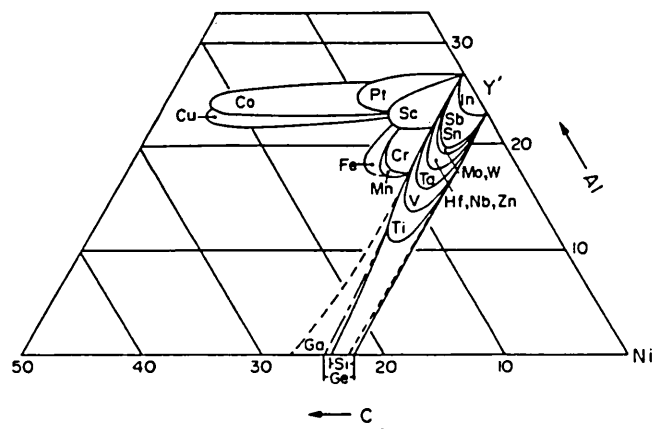


Fig. 1. Semischematic depiction of the solubility lobes of ternary Ni_3Al phase at 1273 K for various elements. .

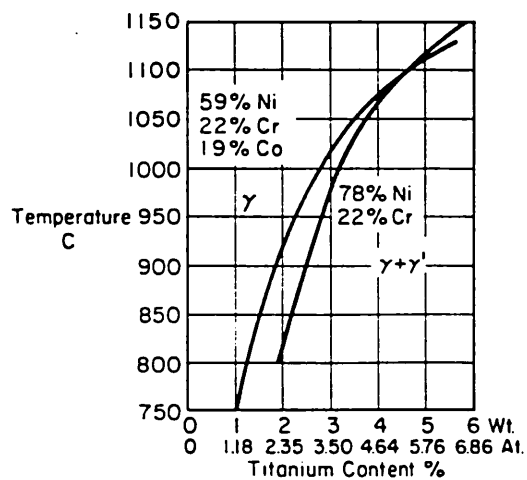


Fig. 2 Effect of substituting cobalt in a nickel-base system on the γ' solvus. Ti - Al ratio = 1 : 1 Heslop [].

1.1.3 Nickel-Base Alloys: The Constituent Elements and their Function

Oxidation Resistance: Chromium additions of 15-30 at.% are made for optimum resistance to oxidation. Nickel alloys provide protection to oxidation by the formation of a chromia, Cr_2O_3 , layer. If the chromium content is lowered, microstructural stability is maintained, but more γ' forming elements can be added. The accompanying loss in oxidation resistance is compensated for by increasing the aluminium content. Aluminium provides resistance to oxidation by the formation of aluminium oxide, Al_2O_3 . This stable oxide forms in the oxide scale at high temperatures.

Strengthening elements and carbide formers: Chromium also forms carbides which are important for strengthening mechanisms, but the most important strengthening phase in nickel-base alloys is γ' , $\text{Ni}_3(\text{Al},\text{Ti})$, which forms on addition of aluminium and titanium to nickel. Niobium, and a number of other elements can, however, substitute for aluminium and titanium in γ' . The ternary phase diagram of Ni-Al-X, where X is the third element, shows how this is possible (fig.1)- if the substituted niobium content is greater than 4%, a separate hardening phase is formed. Titanium and niobium also form carbides.

Cobalt is a solid solution strengthener and can be used in place of nickel. It reduces the solubility of aluminium and titanium in the nickel-chromium matrix and as a result increases the γ' solvus temperature to maintain strength at elevated temperatures (fig.2). Cobalt has a greater

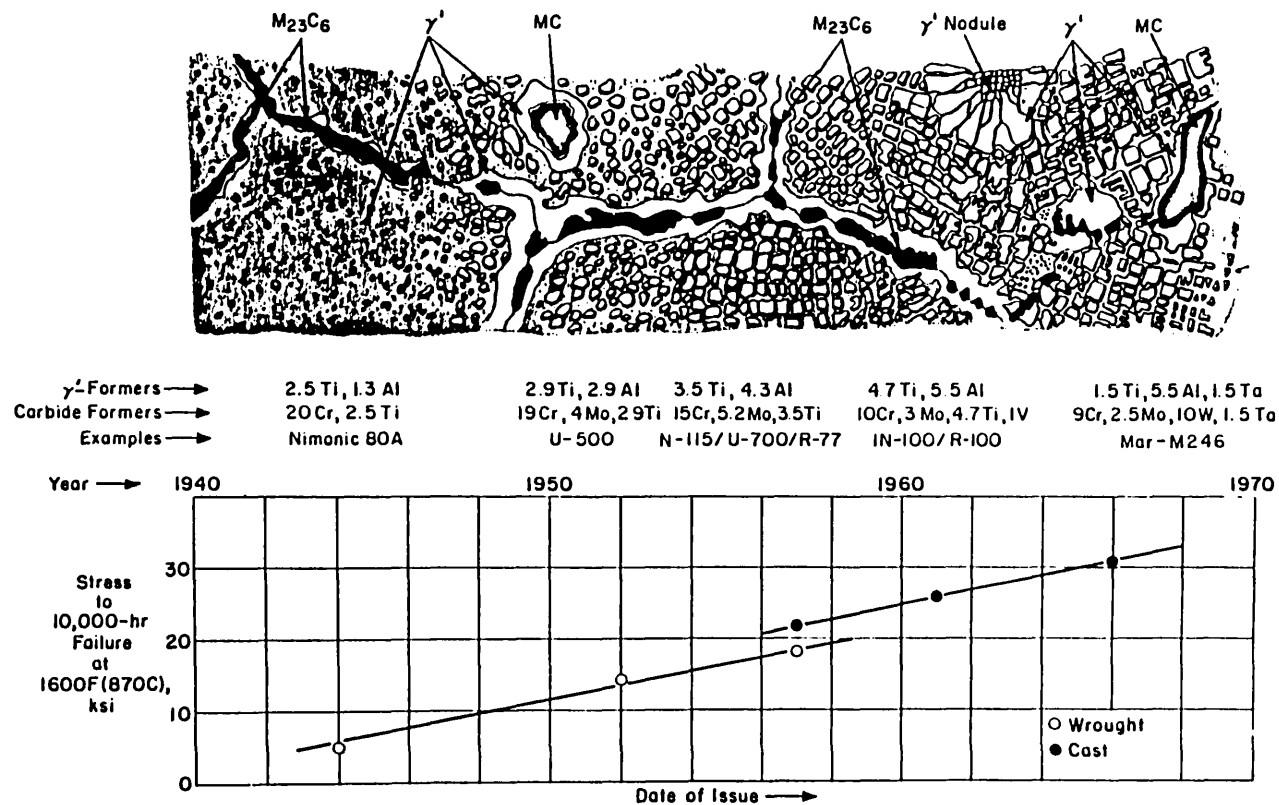


Fig. 3 Genesis of nickel alloy microstructure, 1940 - 1970, 5000X. Plot shows stress capability of the alloys as a function of approximate date of issue. Structure shown is heat treated for best rupture properties, major features only. Compositions are generalized and typical.

solubility for carbon than nickel, which leads to a reduction in the volume fraction of carbides present in the structure. Molybdenum, tungsten and tantalum are solid solution strengtheners at high temperatures and they form complex carbides in the structure - tantalum is soluble in γ' . (In the Soviet Union molybdenum has been replaced by tungsten when possible, and the use of cobalt has been restricted because it is in short supply. Aluminium and titanium additions have been reduced and vanadium added).

Hafnium, used especially in cast alloys, improves ductility, increases strength at low and intermediate temperatures, and raises the hot tear resistance in directionally solidified alloys (The effects of hafnium will be dealt with more fully in section 1.1.5).

Boron and zirconium improve the creep strength and ductility of the matrix. These elements segregate to grain boundaries where they modify the formation of grain boundary carbides.

Carbon is also used to improve creep strength, which it does by the formation of carbides.

Trace elements: Calcium, magnesium and yttrium are three trace elements introduced to improve workability.

1.1.4 Phases in Nickel-Base Superalloys

The wide range of alloying additions made to nickel-base superalloys gives rise to a variety of phases, produced by the reactions that occur between the elements in the matrix. Each phase contributes in some way towards the properties of

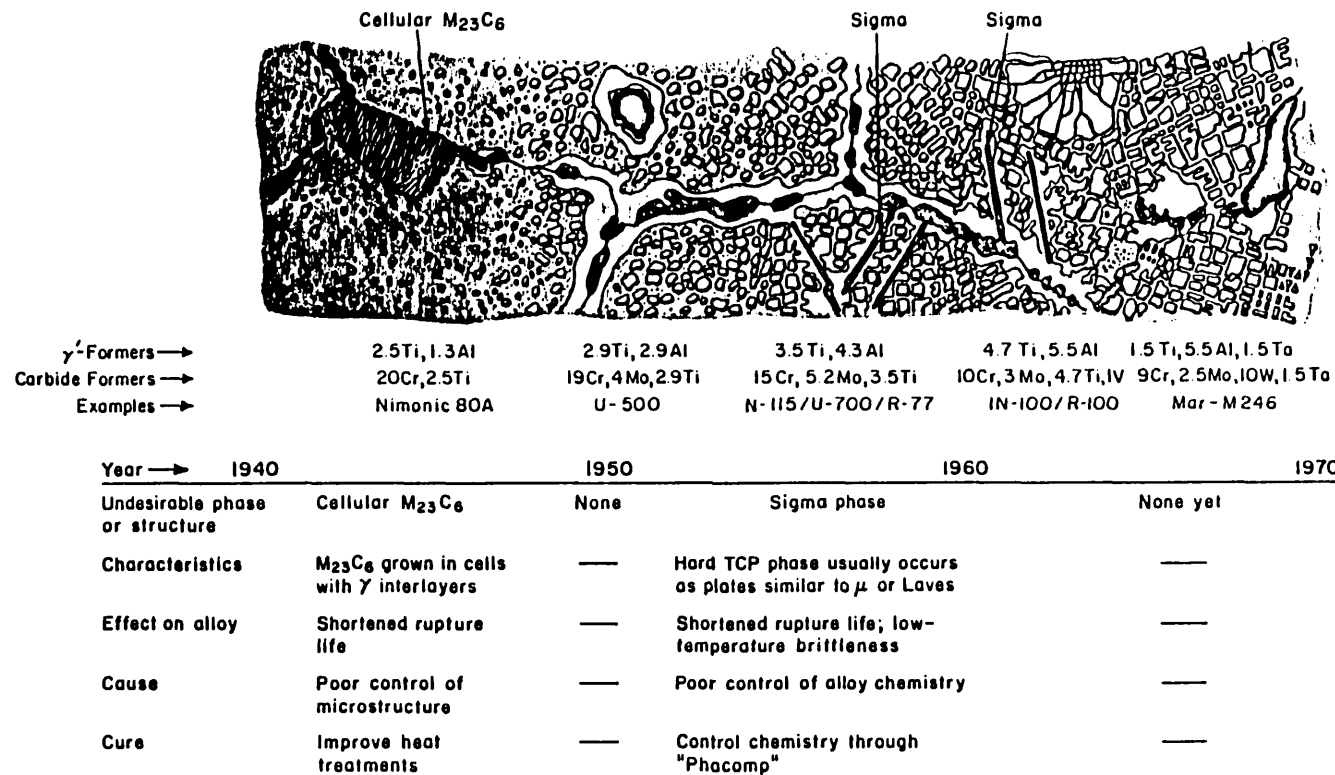


Fig. 4 Common unwanted phases or structures in nickel alloys, 1940 – 1970, 5000X [3].

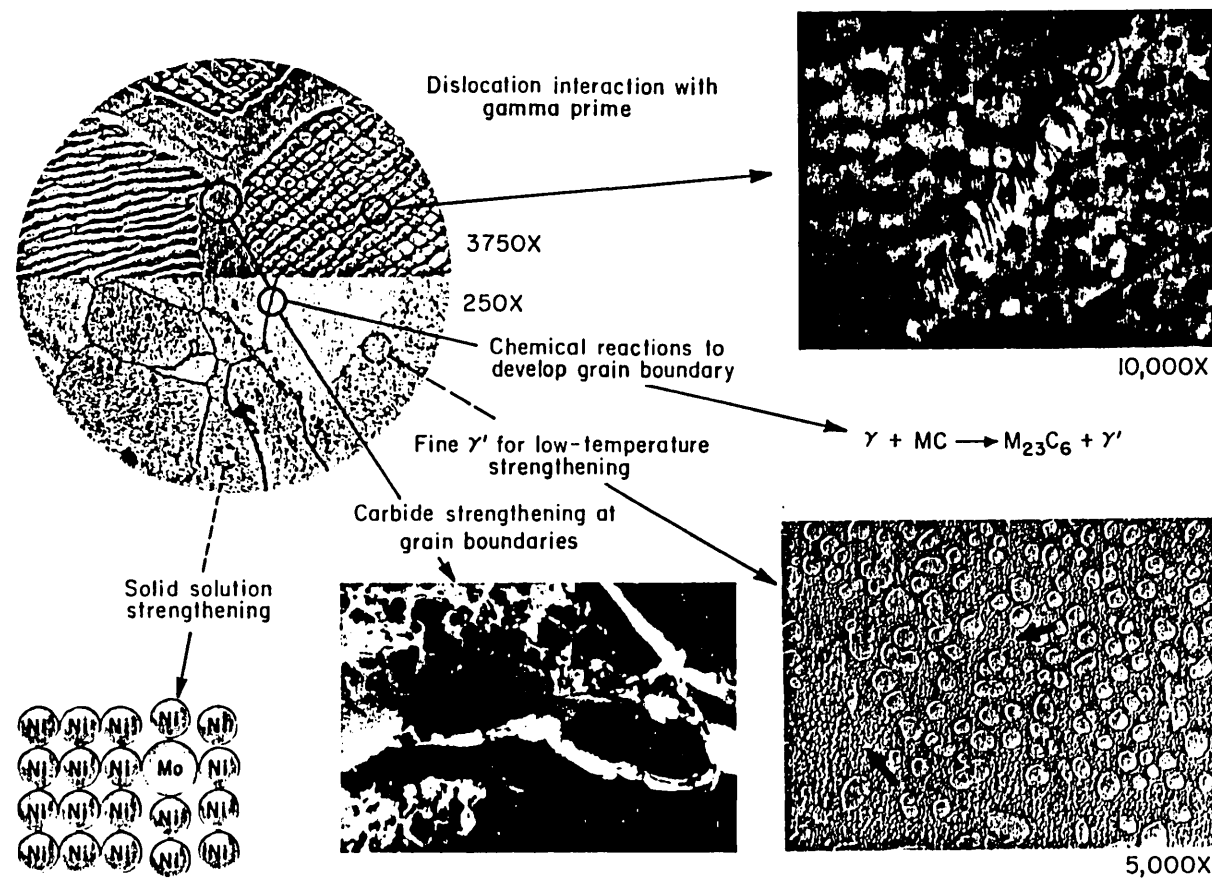


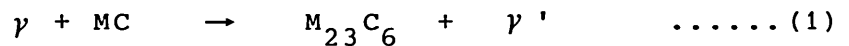
Fig. 5 Major features for achieving useful strength in nickel-base alloys.

the metal. Some are favourable and their formation is encouraged (fig.3). Other phases can be deleterious and their formation is suppressed as much as possible (fig.4).

Carbides: Carbides are a good example of beneficial phases - those which, in the right form, help to improve the desired properties of the alloys (figs.3&5). Carbides exist as MC, $M_{23}C_6$, M_6C , and M_7C_3 , although M_7C_3 formation is rare.

MC carbides have a face-centred cubic structure and are stable compounds. They form in the liquid or at high temperatures after solidification has taken place. They exist, with blocky, script morphologies, in grains and at grain boundaries. The main MC forming elements are titanium, tantalum, niobium and hafnium, although molybdenum and tungsten are also involved.

$M_{23}C_6$ carbides form in alloys with high chromium contents. Indeed, in these alloys this type of carbide predominates. They form during normal heat treatments, and as a result of MC breakdown.

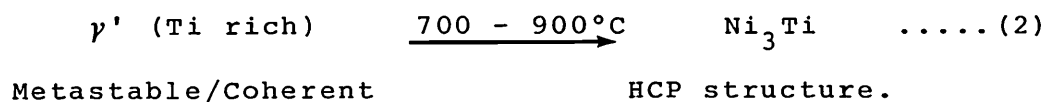


They tend to inhibit grain boundary sliding when found as discrete particles on grain boundaries. However, $M_{23}C_6$ can form with a cellular structure and this has adverse affects on the properties of the alloys (fig.4).

M_6C forms during heat treatments and also in materials having high molybdenum contents. It, also, can form as a result of MC breakdown. Chromium, nickel, or cobalt may replace the major alloying elements, molybdenum and tungsten, in this carbide.

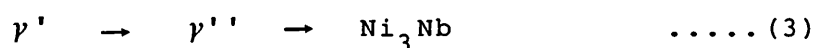
γ' : One of the most important phases in nickel-base alloys is based on the ordered face-centred cubic structure, and is known as γ' . It is a precipitate hardening constituent which is normally found as $\text{Ni}_3(\text{Al},\text{Ti})$, although it has a nominal composition of Ni_3Al in which 65% of the aluminium content can be replaced by titanium and other elements (fig.1) Nickel can be replaced by chromium, cobalt, iron or molybdenum. Ageing after a solution treatment causes precipitation of γ' , which is coherent with the matrix. It exists as fine homogeneous particles which have a spherical morphology, although as they grow and coherency is lost, they become cuboidal. This phase forms at grain boundaries, and at second phase particle interfaces during relatively high temperature ageing treatments or during partial solution treatments (figs.3-5).

There also exists a metastable form of γ' . This phase is titanium rich and the structure is coherent with the matrix. It exists in equilibrium with Ni_3Ti , which is hexagonal close-packed and which is non-coherent with the matrix.



This reaction is accelerated by stressing. Ni_3Ti forms as duplex cells with the γ matrix and at grain boundaries at temperatures less than 750°C or intergranularly as Widmanstätten precipitates if the transformation occurs at a temperature greater than 750°C . If the titanium/aluminium ratio is increased there is an increase in the particle/matrix misfit parameter which decreases the overall

stability of the alloy. A decrease in alloy strength is produced when metastable γ' changes to Ni_3Ti . This is highly undesirable. If, on the other hand, the alloy contains greater than 4% niobium, as in Inconel 718, then γ' decomposes as follows:



γ'' has a body centred tetragonal structure and precipitates as platelets. The platelets are coherent with the matrix and can co-exist with γ' . However, Ni_3Nb has an orthorhombic structure and forms as large platelets which are undesirable. To maintain creep properties, grain boundary particles are essential, and so the formation of platelets is avoided as far as possible.

Borides: Borides are yet another series of compounds formed in these alloys. They are associated with M_{23}C_6 particles. If the alloy contains greater than 0.01% boron, M_3B_2 compounds will form. These are usually molybdenum rich, although titanium, nickel, or chromium may also be present. M_3B_2 has a tetragonal unit cell and precipitates at grain boundaries.

TCP phases: Other phases which have a detrimental effect on the properties of nickel-base alloys are topologically close packed phases, TCP phases. There are a number of different types that are known to exist, e.g. Sigma and Laves phases (fig.4).

Sigma phase is a precipitate found in nickel-chromium rich alloys between the temperatures of 650°C and 925°C, especially when the alloy is subject to stress. It is an

intermetallic compound and has a tetragonal structure. It is formed by a nucleation and growth process which takes place at grain boundaries, on twin boundaries, and at the interface of carbides and borides.

Topologically close packed phases are detrimental to the mechanical properties of the alloys because they themselves are brittle, hard, and liable to cause fracture. They have a plate-like morphology and can act as a source of crack initiation and propagation which reduces the impact strength of the alloy.

A phase computation technique, called PHACOMP, was successfully developed and applied to nickel-base alloys to predict and control the tendency for austenitic alloys to precipitate TCP compounds.

1.1.5 Effects of Hafnium Additions to Nickel-base Superalloys

Microstructure & Mechanical Properties: Before the development of hafnium-containing alloys, commercial material such as MarM200 was found to suffer from inconsistent creep life and limited ductility at 1033K and 689 MPa (3). Improvements in both properties were found after 2 wt.% Hf had been added to the alloy. In amounts much greater than this MarM200+Hf began to suffer from embrittlement due to the formation of intermetallic compounds (4).

Hf additions have also been found to improve intermediate temperature creep properties and there is a reduced tendency to grain boundary tearing in directionally solidified superalloys compared with alloys not containing Hf. The effect of grain boundary embrittlement has also been minimised and is due to the high affinity of hafnium for sulphur (4-7).

It was also found that in MarM200 an addition of 2 wt.% Hf decreased the volume fraction of microporosity (3).

The solubility of Hf in the γ matrix is < 1 at.% and in γ' it is < 7 at.% (8,9). During solidification, therefore, Hf will tend to partition to γ' , and this has several effects. Firstly, it strengthens the γ' phase and improves the ductility of the alloy. By partitioning to the γ' phase no extraneous phases are formed (8). This increase in strength means that the γ' that forms along the grain boundary provides increased resistance to grain boundary sliding. The γ' which forms at the grain boundary has been found to transform from a planar configuration to a convoluted configuration which is a consequence of the 'dendritic' morphology of the γ' . It has been suggested that this also helps to improve ductility and leads to high creep resistance (9). In higher Hf-containing superalloys blocky grain boundary γ' forms (8). Again, an improvement in the creep properties was found and is said to be due to the fact that γ' can accommodate slip better than other phases at the grain boundary due to the slip deformation

mechanism that operates in this phase.

Carbide morphology & composition changes: In revert MarM002 the majority of carbides were Ti/Ta rich (See section 1.1.9 for definitions of virgin & revert material). A minority of carbides were Hf rich and these were found at the edges of Ti/Ta carbides (10).

Hf rich carbides have been found by many workers in Hf modified alloys. In one case the primary carbide had been Zr and Ti rich before the addition had been made (8).

In MarM002, heated at 1323K the original Ti/Ta/Hf 'script' carbide was replaced by a precipitate of M_6C and a Hf rich MC phase. The volume fraction of this phase was found to increase with time (11).

Changes in the morphology of carbides in Hf-modified alloys have also been noted. In one case the 'Chinese script' morphology disappeared and a carbide with a discrete particulate morphology replaced it. Improved ductility in this alloy was explained in terms of a reduction in the available paths for brittle fracture (9).

A summary of the effect of Hf additions on carbides has been given (12). Hf has a high affinity for C. This is associated with the change in primary MC carbide from a 'script' to a blocky discrete morphology which is more resistant to crack propagation. Hf causes additional primary carbide precipitation at low carbon activities when precipitation would otherwise tend to cease. Hence, since there are primary carbides with Hf rich surface zones and there is less carbon in solution at grain boundaries

secondary carbide precipitation tends to occur in a more controlled manner. No continuous carbide networks form at the grain boundaries and precipitation occurs with the formation of small discrete particles.

1.1.6 Effects of silicon additions to nickel-base superalloys

When a cast superalloy, MarM002, was deliberately doped with 0.16 wt.% Si several effects were noted (13). The carbide particles were more acicular; microporosity was less extensive; and there was a fourfold increase in the volume fraction of a nickel-hafnium phase within the γ/γ' eutectic regions. Deliberate additions of silicon have been made to superalloys to try to improve the properties of the alloys. High concentrations of silicon in Unitemp 718 (14) and B-1900 (15) have been found to be deleterious to mechanical properties through the stabilisation of Laves phases (12). It was found that 0.1-0.9 wt.% Si in a wrought alloy, Ni-15Cr-6W-3Mo-2Al-2Ti, brought about a reduction in tensile strength and ductility (16). This was attributed to changes in the amounts, types and morphologies of carbides. A minimum in the tensile properties occurred between 0.4-0.6 wt.% Si. Silicon was found by EPMA to be uniformly distributed in intragranular carbides and in grain boundary carbides, in alloys with less than 0.4 wt.% Si, and the dominant carbide was $M_{23}C_6$. Between 0.4-0.6 wt.% Si considerable segregation of silicon to grain boundary carbides occurred and the silicon content in grain

boundary carbides was three to four times greater than in intragranular carbides. Precipitation of M_6C carbide was enhanced. In specimens containing greater than 0.6 wt.% Si the relative amount of M_6C with respect to $M_{23}C_6$ was found to be greater than 90%. A minimum in tensile strength, ductility and impact toughness occurred between 0.4 & 0.6 wt.% Si; this was thought to be due chiefly to the morphology and distribution of M_6C carbide which as a continuous film at the grain boundaries, weakens it and consequently lowers the strength and ductility of the alloy.

A 1 wt.% Si addition to alloy B1900 improved thermal fatigue and sulphidation resistance (15). However, silicon was detrimental to stress rupture properties at 1273K when the alloy was given a standard heat treatment for 4 hours at 1353K followed by 10 hours at 1173K. At these high solution treatment temperatures and with an addition of 0.6 wt.% Si an increase in the rupture life of the alloy was obtained. A refinement of the γ' distribution also occurred. Silicon was the cause of precipitation of γ' as massive nodules during solidification rather than by precipitation from the matrix on subsequent cooling. Silicon additions also promoted the formation of $Mo(Ni, Si)_2$, Laves phase. Finally, the oxidation resistance of γ' was greatly improved by replacing 1-3 at.% Al with silicon.

Holt (12) summarised work that had been done on the effects of Si in nickel-base superalloys. When 1 wt.% Si

was added to Inconel 718 it caused the alloy to fragment during hot forging (17). By increasing the silicon content from 0.2 to 0.8 wt.% a reduction in the 922K/690Mpa rupture life of heat treated samples, from 95 to 32 hours, was observed (17). In Unitemp 718, silicon contents greater than or equal to 1 wt.% were the cause of M_6C formation and a decrease in room temperature ductility occurred (14). The hot workability of Hastalloy X and Inconel 600 decreased as the silicon content increased. This was related to the inclusion count which increased with silicon content (18). In Hastalloy X (19,20) and Inconel 718 (21) weldability was improved by the addition of silicon. Silicon segregated to the fusion zone in welds of Hastalloy X and reduced the tendency to hot cracking when present up to 0.46 wt.% (19). It was also mentioned that in Unitemp 718 as well as in B1900 silicon stabilised the Laves phases which under certain circumstances were thought to be detrimental (14,15).

1.1.7 Processing of Superalloys.

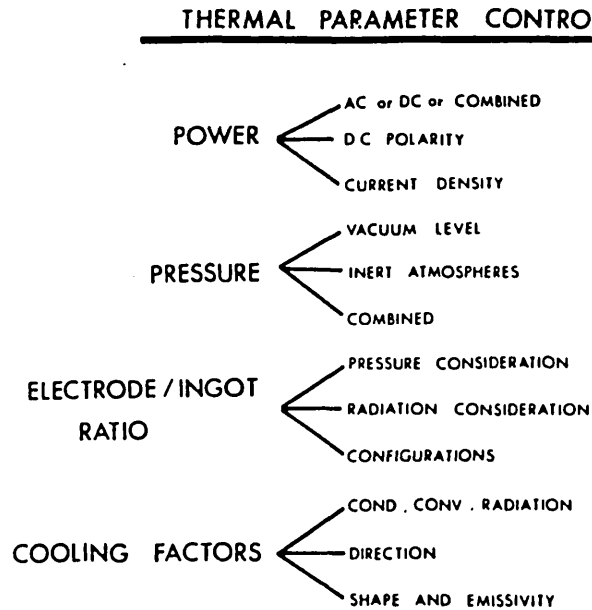
Advent of Vacuum Processing and Materials Production

Early advances in superalloy technology came with the addition of significant amounts of Al and Ti to oxidation resistant nickel-base alloys. Thus, the volume fraction of γ' in the structure was increased which led to higher operating temperature capabilities in aircraft engines. However, these increased additions could only be made under

AAM = air-arc melted (electric furnace)
AIM = air-induction melted
~~VIM = vacuum-induction melted~~
VAR = vacuum-arc remelted from air-melted electrodes
VIR = vacuum-arc remelted from vacuum-induction-melted electrodes
ESR = electroslog-remelted from air-melted electrode
EVR = electroslog-remelted from vacuum-induction-melted electrodes
PMR = plasma melted into refractory crucible
PMS = plasma melted into a skull-lined crucible (water-cooled copper or graphite mold)
PMV = plasma-melted electrode plus vacuum-arc remelting
NAR = non consumable arc-melted into a refractory mold
NAS = non consumable arc-melted into skull-lined crucible (water-cooled copper or graphite)
NAV = Nonconsumable arc-melted electrodes plus vacuum-arc remelting
NER = Nonconsumable arc-melted electrodes plus electroslog remelting
EBM = electron-beam melting (drip or direct)
VEB = vacuum-induction melting plus electron-beam (EB) cascading hearth
NEB = non consumable plus EB refining
NEV = NEB plus vacuum-arc remelt

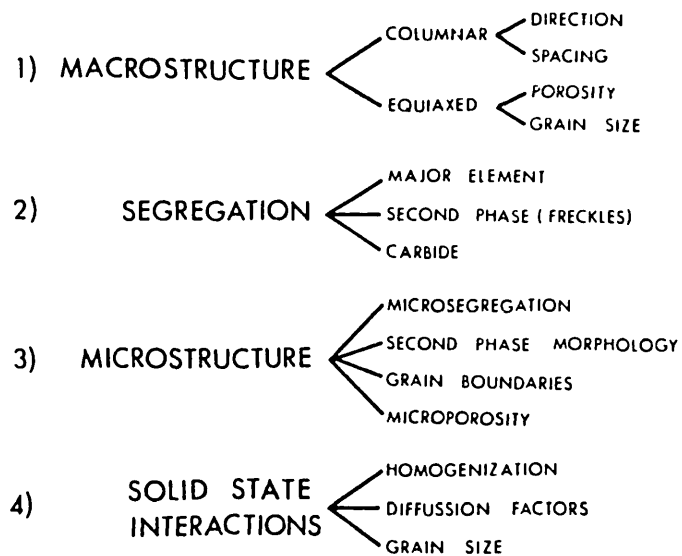
Table 3. Processing practices and shorthand notation used to designate current and future superalloy melting methods and combinations.

Table 4 Specific-VAR-Process-Control Parameters and Related Factors



VACUUM-ARC REMELTING

Table 5 Superalloy-Structural Factors Related to Vacuum-Arc-Control Characteristics and Procedure



vacuum because of the ease with which these elements were oxidised in air. The two most commonly used vacuum melting techniques are Vacuum Induction Melting (VIM) and Vacuum Arc Remelting (VAR) although table 3 shows a list of current and future superalloy melting methods and combinations (21):

The advantages of VIM are (22):

1. Allows independent control of temperature and pressure during melting.
2. Elimination of contaminating reactions with atmospheric gases.
3. Purification of melts by vaporization of unwanted gases and volatile trace elements.
4. Exceptional and reproducible control over alloy composition.
5. The chemically reactive elements could be used effectively as alloying additions.

The disadvantages of VIM are:

1. Material/crucible reactions can re-introduce oxygen and other elements into the melt (much lower levels than in air).
2. Large statically charged ingots tend to have very coarse grains, significant shrinkage porosity, and segregation of solute elements.

Tables 4 & 5 show some of the specific VAR Process Control Parameters and Superalloy Structural Factors related to vacuum-arc control characteristics and procedure. *No further comment;*

1.1.8 Turbine Blade Production

Nickel-base alloys are currently used in the manufacture of turbine blade components for aircraft engines, particularly in those parts which are subject to the highest temperatures and stresses, and where the materials have to withstand severe chemical attack from the combustion and exhaust gases. These components are precision parts which must retain their original shapes throughout in-service life.

These components are thus very expensive to manufacture and there are difficulties associated with manufacturing routes involving mechanical working, because turbine airfoils are designed to resist the very hot deformation needed to shape them.

Some typical manufacturing routes by which turbine blades are manufactured are:

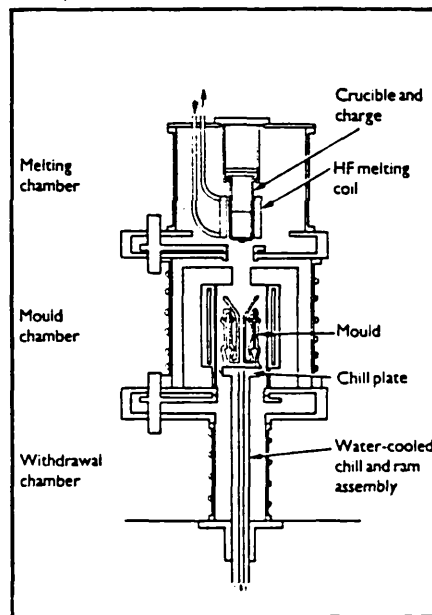
1. Investment casting
2. Directional Solidification
3. Single Crystal Technology

a. Investment Casting

Precision casting, by the lost wax process, for example, became the only practical manufacturing method to achieve the desired shapes for the stronger alloys. Some advantages of precision casting are:

1. Relatively precise dimensional tolerances
2. Excellent surface finish

Fig 6 Schematic of Rolls-Royce directional solidification plant



3. Great flexibility in intricate design including
blind holes and passages

4. Relatively low cost

In order to design suitable materials the metallurgist
had to control many process variables such as:

1. Control of Residual elements

2. Porosity

3. Grain size and grain orientation.

4. Type of mould

5. Degree of superheat

6. Mould temperature

7. Degree of inoculation

8. Cooling rates

9. Soundness of casting

All of these effects will vary to some extent
depending on the composition of the superalloy.

b. Directional Solidification and Single Crystal Technology.

Directionally solidified blades were developed in
order to eliminate one source of weakness in cast blades,
namely, transverse grain boundaries which were the source
of creep failure in these materials. By enclosing a mould
of molten metal within a hot zone from which the majority
of heat is removed through a chill plate, nucleation can be
restricted to the chill region (fig.6). Columnar grains
then develop along the blade, as the mould is withdrawn

Table 6 Single crystal alloy compositions

ALLOY	COMPOSITION (wt %)								
	Ni	Cr	Co	Ti	Al	Mo	W	Ta	Others
Alloy 444	Balance	8.6	—	1.98	5.1	—	11.1	—	
Alloy 454	Balance	10.0	5.0	1.5	5.0	—	4.0	12.0	
(P & W 1480)									
Nasair 100	Balance	9.0	—	1.2	5.75	1.5	10.5	3.3	<0.01C
SRR 99	Balance	8.5	5.0	2.2	5.5	—	9.5	2.8	0.02C
RR 2000	Balance	10.0	15.0	4.0	5.5	3.0	—	—	1.0V 0.02C
RR 2060	Balance	15.0	5.0	2.0	5.0	2.0	2.0	5.0	0.02C

from the hot zone. By incorporating a geometric constriction in the mould , or by the use of a seed crystal, grain boundaries can be eliminated entirely, resulting in single crystal blades. Although grain boundary elimination was the original motivation for directional solidification , it was the favoured [100] growth direction and the improved heat treatment characteristics from which most benefit could be accrued. The advantage of [100] alignment along the blade axis is its intrinsic high creep resistance, together with a low Young's modulus which enables thermal stresses, caused by temperature gradients across the blade, to be kept to a minimum. The lack of grain boundaries in single crystals allows removal of those elements introduced primarily for grain boundary strengthening, ie carbon, boron, zirconium and hafnium. Since these elements tend to lower the incipient melting point, their loss allows higher solution heat treatment temperatures to be safely employed , with resultant improvement in chemical homogeneity and a more uniform distribution of γ' precipitation. The compositions of some single crystal materials are given in table 6.

One problem associated with directional solidification and single crystal technology is the long contact time between the ceramic mould wall and the material which is usually about one hour for nickel-base superalloys. Good melt/mould compatibility is required otherwise composition changes can occur.

1.1.9 Use of Virgin and Recycled material

Material is known as 'virgin' when it is produced directly from its constituent elements without the addition of any scrap material. Material is known as 'revert' when high quality scrap material, produced by individual foundries and recycled, is remelted to produce new material for turbine blade manufacture. Additions are made to the melt in order to achieve the desired alloy composition. The sources of scrap material are the risers, runners and headers of the castings.

The percentage of scrap generated by any one foundry may be of the order of 60% of the initial material, and at a cost of about £10/kg, considerable savings can be made if the scrap is recycled and used in the production of more components. Other good reasons for the use of scrap material are that some elements, ie Hf and Ta, are scarce, and others are strategically vulnerable ie. Cr and Co. Even though the major element concentration of recycled material is adjusted during reverting to meet the original specification it is generally believed that the foundry performance of 'revert' alloy is inferior to that of 'virgin' (23). This inferiority, which can result in increased microporosity or in hot-tearing, may be due to small changes in the content of minor elements such as zirconium, silicon, nitrogen and oxygen as a result of contamination from the mould, cores and furnace environment.

Table 7 Electron Probe Microanalysis data of Ni-Hf and Ni-Zr phases in various superalloys from this work and from references 24, 25 and 74.

Element	Ni	Cr	Co	Mo	W	Ti	Ta	Fe	Al	Nb	Zr	Hf	Si
Alloy													
MarM002	66.9	1.9	7.8	0.1	-	0.8	0.0	0.02	0.0	-	3.9	15.9	2.7
MarM246	64.1	4.9	7.9	0.1	0.3	1.2	1.5	-	1.3	-	14.1	0.6	4.1
IN939+Si	52	14	14	0.0	0.2	3.5	0.6	-	2.5	3.9	8	-	1.0
IN939+Zr	59	6	13	0.0	0.04	2.9	0.7	-	1.2	1	14	-	1.2
MarM200+Hf (74)	58	3	10	-	-	1	-	-	-	4	12	10	2
Alloy B (24)	66.7	4.8	16.7	-	1.0	0.8	-	-	-	-	-	10.0	-
MarM200+Hf (25)	70.4	3.8	0.8	-	0.3	4.5	-	-	4.7	1.9	-	13.7	-

1.1.10 Observation of Ni-Hf and Ni-Zr phases in Nickel-base Superalloys.

A problem associated with hafnium containing nickel-base superalloys which are processed by directional solidification was first reported by Burke (24). Castings made from recycled MarM200+Hf showed a tendency to crack along grain boundaries (hot tearing) and an increase in the volume fraction of a phase within the γ/γ' eutectic regions was noted. Wavelength dispersive x-ray analysis investigations showed that the phase was Ni-Hf rich and contained small amounts of hafnium and silicon. The analysed levels of silicon were determined to be about 1 wt.%. The 'revert' heats which contained this phase had higher overall concentrations of zirconium and silicon and had lower solidus temperatures than 'virgin' heats (1200°C compared with 1240°C). It was suggested that this phase might be associated with the hot tearing observed in 'revert' heats.

Yunrong and Yulin (25) studied the formation of a Ni-Hf rich phase, in several alloys containing hafnium, and concluded, from x-ray diffraction, EPMA (Table 7), and electron diffraction methods, that the phase was Ni_5Hf . It was suggested that cobalt substituted for nickel and chromium, and that tungsten and titanium substituted for hafnium, although the reasons why this should be so were not given. The phase was unstable at about 1100°C,

decomposing into secondary HfC and γ . Although different amounts of Ni_5Hf were found in different alloy systems with the same hafnium contents, no figures for the silicon or zirconium contents were reported.

More recently, plane front solidification experiments have been carried out by Sellamuthu and Giamei (26). MarM200+Hf alloy was directionally solidified as bar under very slow growth conditions and a steep temperature gradient so that throughout solidification there would be no mixing in the solid and complete mixing in the liquid. Under these conditions the solidification sequence of the alloy could be followed. The last liquid to solidify was a ternary eutectic containing the γ phase, a carbide and Ni_5Hf : no silicon or zirconium analysis was performed.

1.1.11 Doping Experiments on Nickel-base Superalloys.

The effects mentioned in the last section have been modelled to some extent by making additions of silicon to nickel-base superalloys. Durber et al. (13) added 0.1 wt.% Si to a heat of MarM002 and observed a four-fold increase in a phase associated with the γ/γ' eutectic. This was reported as being predominantly Ni-Hf with small amounts of Si and Zr but it was not possible to identify the phase. It dissolved at about 1100°C with the formation of HfC. From differential thermal analysis studies a small peak was located which was correlated with the formation of the phase at 1105°C.

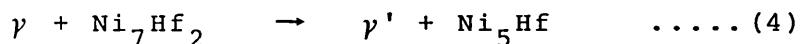
1.2 Model alloy systems for use in studying Ni-Hf and Ni-Zr intermetallic compound formation in nickel-base superalloys.

Basis of alloy selection for^{the} present investigation

The model alloy systems that were studied in order to understand Ni-Hf and Ni-Zr intermetallic compound formation in nickel-base superalloys and the association of these phases with silicon were:

1. Ni-Al-Hf
2. Ni-Hf-Si
3. Ni-Zr-Si
4. Ni-Al-Si
5. Ni-Al-Hf-Si

The Ni-Al-Hf system was chosen because work on two isothermal sections at 1000°C and at 1200C had already been carried out (27). Thus new data would serve to check certain parts of the existing information; the x-ray reflections observed for Ni₅Hf could be determined experimentally and the following reaction postulated by Nash and West (27) could be checked:



The Ni-Hf-Si and Ni-Zr-Si ternary systems were studied in order to determine the extent of solid solution of silicon in Ni₅Hf and Ni₅Zr. Also, very limited information was available on these systems and data was needed to construct the quaternary Ni-Al-Hf-Si system.

The Ni-Al-Hf-Si system was studied in order to obtain a better understanding of the phase regions in a superalloy type structure ie. γ/γ' , when hafnium and silicon are also

present.

Data was available in the literature of isothermal sections in the nickel-rich corners of the Ni-Al-Hf (27), Ni-Zr-Si (28,29), and Ni-Al-Si (30) systems and binary alloy phase diagrams were available for the following:

1. Ni-Hf (31)
2. Ni-Zr (32)
3. Ni-Si (33)
4. Ni-Al (34)

1.2.1 Isothermal Sections and Alloys to be Studied in the Ni-Hf-Si, Ni-Zr-Si and Ni-Al-Hf-Si systems.

The isothermal sections in the nickel-rich corner of the Ni-Hf-Si system, and the other alloys and heat treatment temperatures, are listed below in table8:

System	Temperature °C	No. of alloys
1. Ni-Al-Hf	1000 1200	1
2. Ni-Hf-Si	1125 1070 926	4 1 3
3. Ni-Zr-Si	1070	1
4. Ni-Al-Hf-Si	1000	1

Table8 Model alloy systems, heat treatment temperatures and number of different compositions.

The temperatures for heat treatment of the specimens in the Ni-Al-Hf system were chosen to coincide with the isothermal sections studied by Nash and West (27).

In the Ni-Hf-Si system specimens were initially heat treated at 1125°C and the temperature was chosen on the basis of the temperature of the binary γ / Ni₅Hf eutectic

reaction, aiming to avoid incipient melting but to obtain the maximum possible diffusion during heat treatment. The other temperatures were selected on the basis of DTA experiments carried out on specimens of the different alloys.

In the Ni-Zr-Si system the temperature was chosen on the basis of experience with the Ni-Hf-Si alloys at 1125°C, some of which had undergone incipient melting.

1.2.2 Nominal Compositions of Alloys to be Studied and their respective heat treatment temperatures.

The nominal compositions of the alloys studied in the different systems and their respective heat treatment temperatures are listed below in table9:

Alloy System	No.	Composition (at.%)			Heat Treatment Temperatures (°C)		
		Ni	Hf	Si			
Ni-Hf-Si	1	83.0	2.0	15.0	926		1125
	2	75.0	10.0	13.0	926		1125
	3	75.0	2.0	23.0	926	1070	1125
	4	93.0	2.0	5.0			1125
	5	81.0	16.0	3.0		1050	
		Ni	Zr	Si			
Ni-Zr-Si	1	90.0	5.0	5.0		1070	
	2	80.0	5.0	15.0			
	3	75.0	5.0	20.0			
	4	75.0	12.0	13.0		1070	
	5	81.0	16.0	3.0		1050	
		Ni	Al	Hf			
Ni-Al-Hf	1	83.0	12.0	5.0	1000		1200
		Ni	Al	Hf	Si		
Ni-Al-Hf-Si	1	83.0	7.0	5.0	5.0	1000	

Table 9: The Nominal Compositions of the specimens and the temperatures at which they were heat treated.

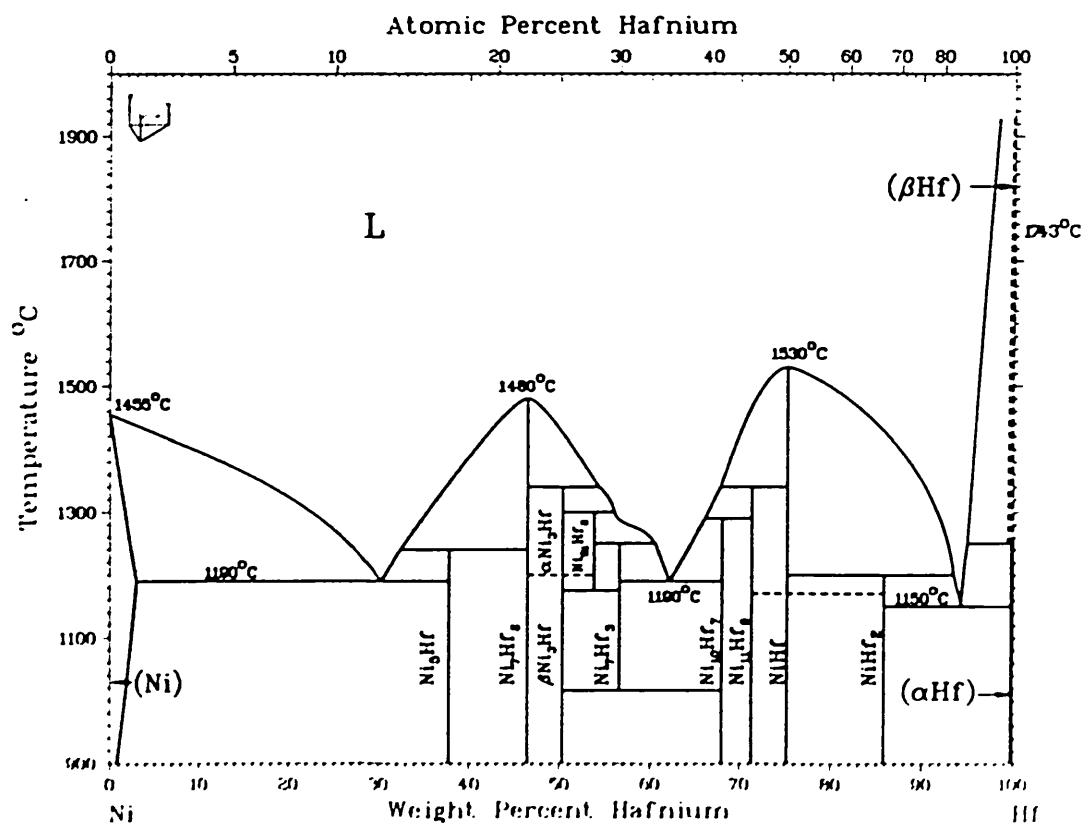
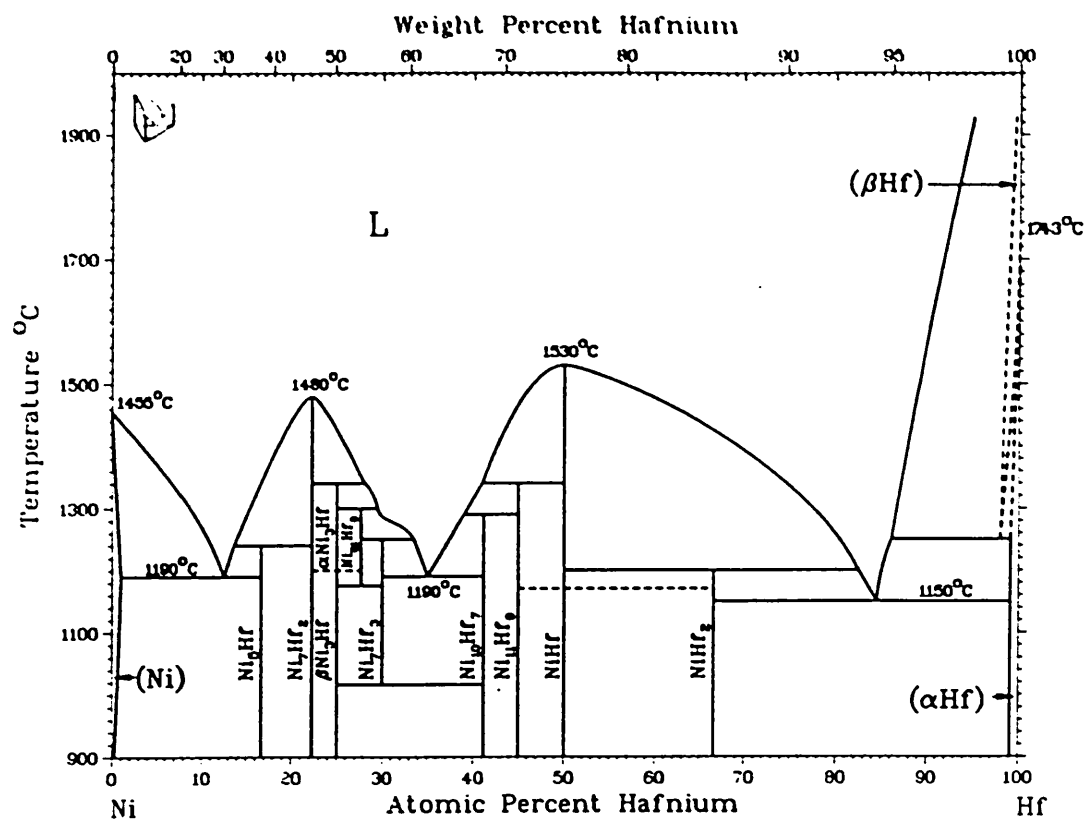


Fig.7 Assessed Ni-Hf binary phase diagram.

Hf-Ni (Hafnium-Nickel)

178.49

58.69

P. Nash and A. Nash; *Bull. Alloy Phase Diagrams*, 4(3), Nov 1983

Ni-Hf Crystal Structure Data

Phase	Composition, at.% Hf	Pearson symbol	Space group	Struktur- bericht designation	Prototype
(Ni)	0 to 1	cF4	Fm3m	A1	Cu
Ni ₃ Hf	16.7	cF24	...	...	AuBe ₃
Ni ₇ Hf ₂	22.2	(a)	...	...	Ni ₇ Zr ₂
αNi ₃ Hf(b)	25.0	...	R3m	...	BaPb ₃
βNi ₃ Hf(c)	25.0	...	P6 ₃ /mmc	...	γTa(Pd,Rh) ₃
Ni ₂₁ Hf ₆	27.6	...	P1	...	...
Ni ₇ Hf ₃	30.0	(d)	P1	...	...
Ni ₁₀ Hf ₇	41.2	(e)	C2ca	...	Ni ₁₀ Zr ₇
Ni ₁₁ Hf ₆	45.0	(f)	I4/m	...	...
NiHf	50.0	oC8	Cmcm	B ₇	CrB
NiHf ₂	66.7	tI12	I4/mcm	c16	Al ₂ Cu
(βHf)	98 to 100	cI2	Im3m	A2	W
(αHf)	99 to 100	hP2	P6 ₃ /mmc	A3	Mg

Metastable phases

NiHf ₃	80	oC16	Cmcm	E1 ₂	BRe ₃
Amorphous NiHf	11 to 80	...	...	...	...

(a) Monoclinic. (b) Stable above 1200 °C. (c) Stable below 1200 °C. (d) Triclinic. (e) Base-centered orthorhombic. (f) Body-centered tetragonal.

Table 10

Ni-Hf Invariant Reactions

Reaction	Composition, at.% Hf			Temper- ature, °C	Reaction type
L = (Ni) + Ni ₃ Hf	12.5	1.0	16.7	1190	Eutectic
L + Ni ₇ Hf ₂ = Ni ₃ Hf	13.6	22.2	16.7	1240	Peritectic
L = Ni ₇ Hf ₂	...	22.2	...	1480	Congruent
L + Ni ₇ Hf ₂ = Ni ₃ Hf	28.6	22.2	25	1340	Peritectic
βNi ₃ Hf = αNi ₃ Hf	...	25	...	1200	Polymorphic
L + αNi ₃ Hf = Ni ₂₁ Hf ₆	29.5	25	27.6	1300	Peritectic
L + Ni ₂₁ Hf ₆ = Ni ₇ Hf ₃	33.5	27.6	30	1250	Peritectic
L = Ni ₇ Hf ₃ + Ni ₁₀ Hf ₇	35	30	41.2	1190	Eutectic
L + Ni ₁₁ Hf ₆ = Ni ₁₀ Hf ₇	39	45	41.2	1290	Peritectic
L + NiHf = Ni ₁₁ Hf ₆	41	50	45	1340	Peritectic
L = NiHf	...	50	...	1530	Congruent
NiHf (HT) = NiHf (LT)	...	50	...	1170	Polymorphic
L + NiHf = NiHf ₂	82.5	50	66.7	1200	Peritectic
L = NiHf ₂ + (αHf)	84.5	66.7	99.1	1150	Eutectic
(βHf) = L + (αHf)	98	85.6	99.1	1250	Metatectic

Table 11

PHASE	STRUCTURE TYPE	PEARSON SYMBOL SPACE GROUP	a	ALPHA	ATOMS	POINT SET	x	y	z	OCC.	SPACE LATTICE	REMARKS	NAME CODEN	
			b [nm]	BETA [D]			• 1000 or 10000	100	(c)	(T)	(p)		YEAR VOL	PAGE
			c	GAMMA									[NO]	
HfNi ₃	Pd ₃ Ta	hP40 P6 ₃ /mmc	0.52822		Hf ₁	2b	0000	0000	2500	100		SD, R=0.098; LT	BSENK ASBSUK	
					Hf ₂	4f	3333	6667	3488	100	phase [-1473K]; prep arc; ann	78 34	P3201	
			2.13916		Hf ₃	4f	3333	6667	5458	100	1273K/120h			
					Ni ₁	6h	5117	2330	2500	100				
					Ni ₂	12k	1560	3119	5140	100				
					Ni ₃	12k	8316	6633	1495	100				
HfNi ₃	BaPb ₃	hR12 R3m	0.52787		Hf ₁	3a	0000	0000	0000	100		SD, R=0.095; HT	BSENK ASBSUK	
					Hf ₂	6c	0000	0000	2185	100	phase [1473K-]; prep arc; ann	78 34	P3201	
			1.92324		Ni ₁	9e	5000	0000	0000	100	1573K/24h			
					Ni ₂	18h	1780	3560	1099	100				
HfNi ₅	AuBe ₅	cF24 F43m	0.6683		Hf	4a	000	000	000	100		PP (ref1)	DWIGH TASEA7	
					Ni ₁	4c	250	250	250	100			61 53	P479
					Ni ₂	16e	625	625	625	100			SVECH RMLYAQ	
													67 No6	P95

Table 12 Relative positions of the atoms in the unit cell in Ni₅Hf.

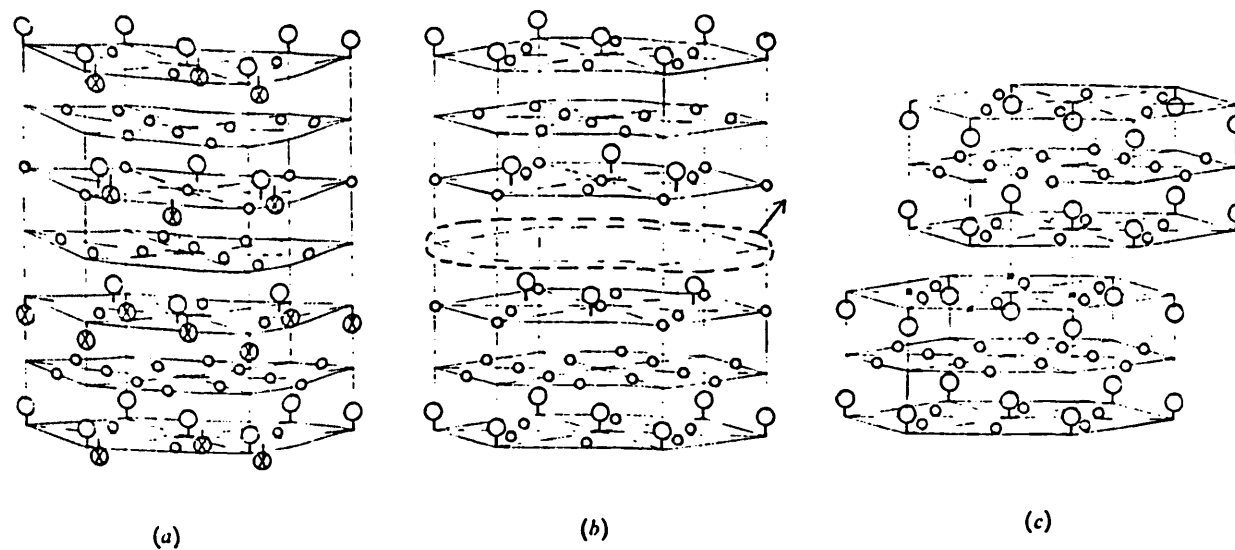


Fig. 8 Relationship of the Zr_2Ni_7 structure to the ZrNi_5 structure. (a) ZrNi_5 structure with the [111] direction normal to the layers. The large open circles, O, represent Zr atoms and the small open circles, o, and the large crossed circles, $\odot$, represent Ni atoms. (Note: if the $\odot$ positions are occupied by the larger, rather than the smaller, species, this is the MgCu_2 structure.) (b) Alternate Ni layers have been removed and the Ni atoms at the $\odot$ positions have had their vertical displacement eliminated. (c) The alternate Zr layers have been inverted and realigned, and the upper structural motif has been displaced laterally and downward to produce the stacking arrangement of Zr_2Ni_7 .

The compositions above were selected on the basis of information available in the literature which is reviewed in the next section.

1.2.3 Relevant information from the binary phase diagrams.

Ni-Hf(31): The binary Ni-Hf system (fig.7) has a large number of intermetallic compounds (table 10) which are associated with a large number of reactions (table 11). Those of interest in this study, namely Ni_5Hf and Ni_7Hf_2 , occurred in the nickel-rich end of the system. The structure of Ni_5Hf is FCC but it has a large and complex unit cell (table 12). The structure is thought to be similar to that of Ni_5Zr which is shown in fig.8. The positions of the atoms in the cell are given in table 12. Ni_7Hf_2 has a monoclinic structure. The positions of the atoms on the lattice are thought to be similar to those in Ni_7Zr_2 . These can be seen in fig.8 and the values are given in table 12.

The solubility of hafnium in γ is low and has been given as 0.7 at.% at 1200°C (35) and 1 at.% at 1050°C (36). The solubility of aluminium in Ni_5Hf and Ni_7Hf_2 has been determined at 1000°C and at 1200°C (27). The solid solubility of aluminium in Ni_5Hf was found to be very limited at both temperatures. However, the solid solution of aluminium in Ni_7Hf_2 at 1000°C extended up to 11 at.% Al and at 1200°C it extended up to 13 at.% Al.

Ni_5Hf forms by a peritectic reaction at 1240°C:

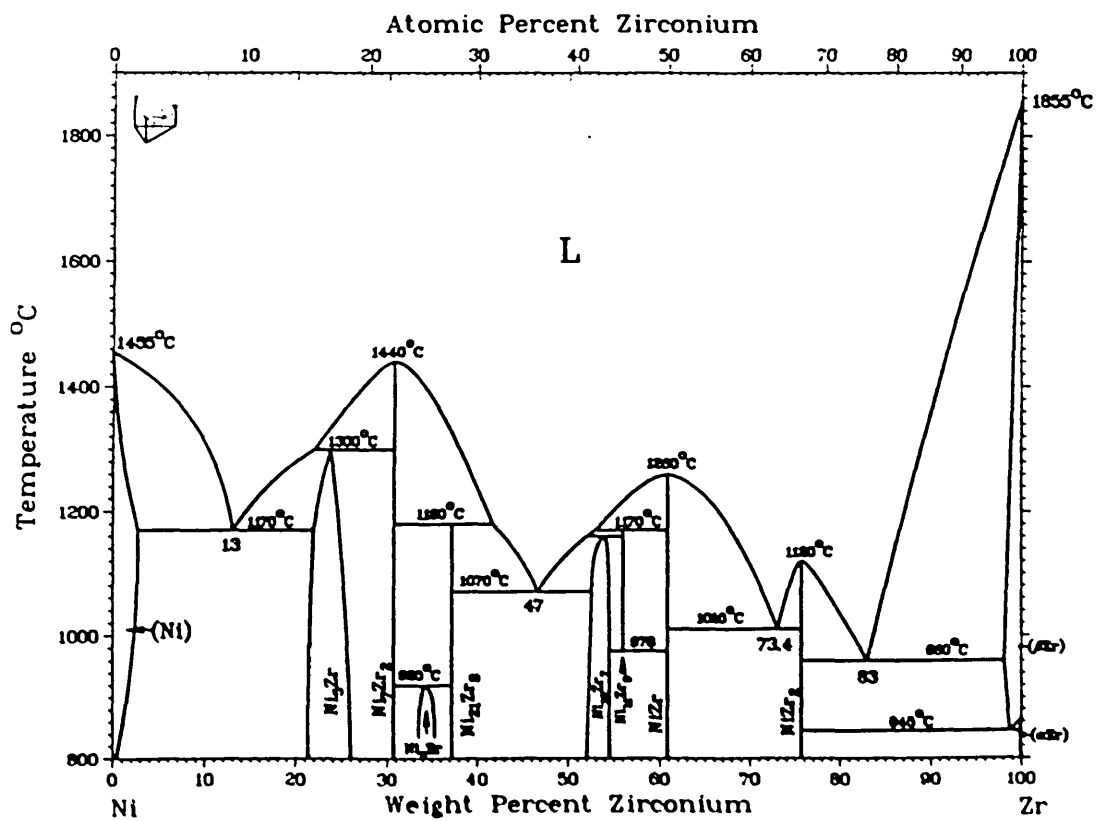
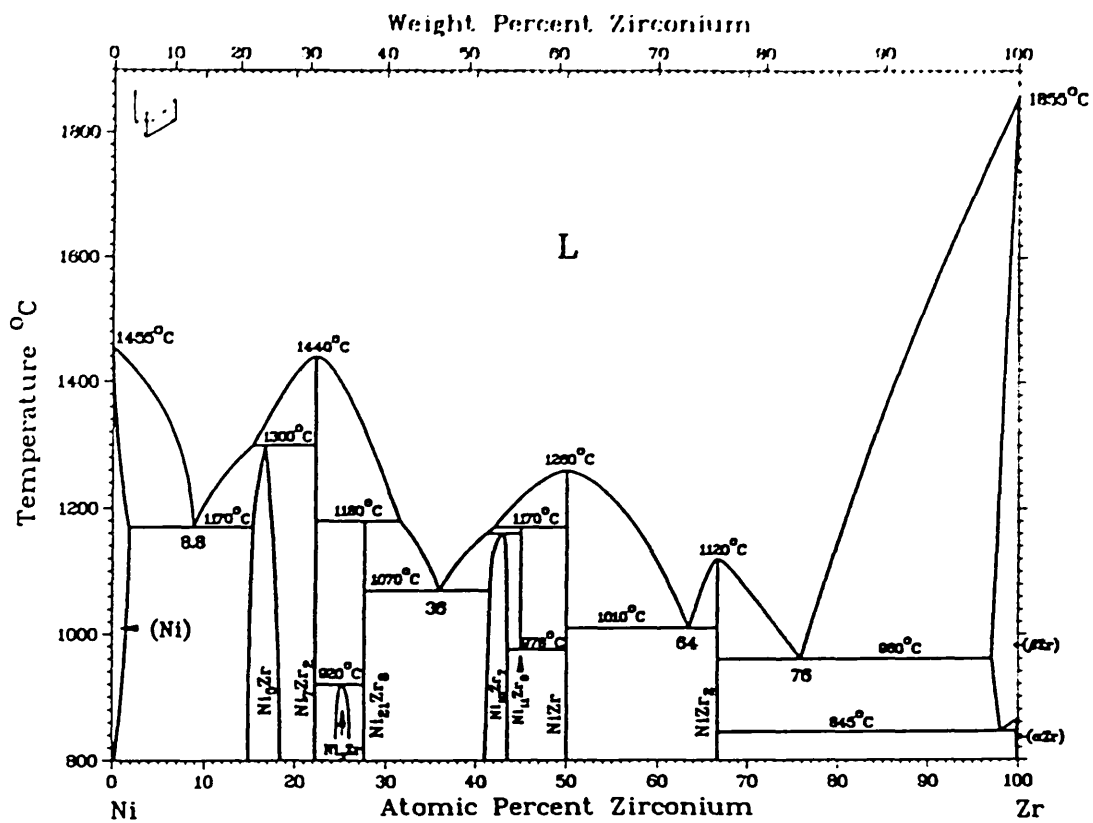


Fig.9 The assessed Ni-Zr binary alloy phase diagram.

Ni-Zr (Nickel-Zirconium)

58.69

91.22

 P. Nash and C.S. Jayanthi; *Bull. Alloy Phase Diagrams*, 5(2), Apr 1984

Ni-Zr Crystal Structure Data

Phase	Composition, at.% Zr	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Ni) or γ	0 to 1.78	cF4	Fm3m	A1	Cu
Ni ₅ Zr	14.85 to 18.40	cF24	F43m	C15 ₂	AuBe ₅
Ni ₇ Zr ₂	22.22	mC36	C2/m	...	...
Ni ₉ Zr	24.50 to 26.00	hP8	P6 ₃ /mmc	D0 ₁₉	Ni ₃ Sn
Ni ₂₁ Zr ₈	27.60	(a)	...	...	Hf ₆ Ni ₂₁
Ni ₁₀ Zr ₇	41.07 to 43.54	oC68	C2ca(b) Pbca(c)	...	...
Ni ₁₁ Zr ₉	45.00	tI40	I4/m	...	...
NiZr	50.00	oC8	Cmcm	B ₇	CrB
NiZr ₂	66.7	tI12	I4/mcm	C ₁₆	Al ₃ Cu
(β Zr)	97.08 to 100	cI2	Im3m	A2	W
(α Zr)	99.80 to 100	hP2	P6 ₃ /mmc	A3	Ng

(a) Triclinic. (b) Stoichiometric. (c) Zr-rich.

Table 13

PHASE	STRUCTURE TYPE	PEARSON SYMBOL SPACE GROUP	a b [nm] c	ALPHA BETA [D] GAMMA	ATOMS	POINT SET	x • 1000 or 10 000	y	z	OCC. •	SPACE LATTICE (c) (T) (p)	REMARKS	NAME CODEN YEAR VOL PAGE [NO]
Ni ₂ Zr	Cu ₂ Mg	cF24 Fd $\bar{3}$ m	0.6925		Ni Zr	16d 8a	625 000	625 000	625 000	100 100		PP; T _m =1463K, icm; prep argon arc; ann 1173K/8d	PETKO RMLYAQ 72 No2 P137
Ni ₂₁ Zr ₈	Hf ₈ Ni ₂₁	aP29 P $\bar{1}$	0.64721 0.80645 0.85878	75.19 68.04 75.26								PP (ref1)	BSENK JOOMAH 79 63 P171 GACHO JOOMAH 83 92 P307
												REMARKS: Incompl c-T diagram [64-80a%Ni] (ref1); compl c-T diagram (ref2)	
Ni ₃ Zr	Ni ₃ Sn	hP8 P6 ₃ /mmc	0.5309 0.43034		Ni Zr	6h 2c	829 333	658 667	250 250	100 100		PD, Q=0.06; T _m = 1213K, icm; chem an 67.6w%Ni, 33.5%Zr (ref1); (ref2) gives a=0.53125, c=0.43029	BECLE JOOMAH 79 66 P59 BSENK JOOMAH 79 63 P171
Ni ₅ Zr	AuBe ₅	cF24 F $\bar{4}$ 3m	0.6702		Ni ₁ Ni ₂ Zr	4c 16e 4a	250 625 000	250 625 000	250 625 000	100 100 100		PP; prep argon arc; ann 1273K/6h	KRAME TMSAAB 59 215 P256
Ni ₇ Zr ₂	Ni ₇ Zr ₂	mC36 C2/m	0.4698 0.8235 1.2193	95.83								SD, R=0.091; AP see STT	ESHEL ASBSDK 72 28 P1594

- 56 -

Table 14 Relative positions of the atoms in the unit cell in Ni₅Zr and Ni₇Zr₂.

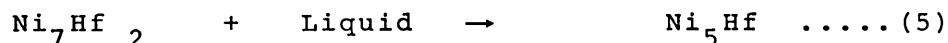
Table 15 Structural parameters for Zr_2Ni_7 in space group $C2/m$

(a) Positional parameters

Set		x	y	z
4(<i>i</i>)	Zr(1)	0.2115 ± 0.0007	0	0.6133 ± 0.0003
4(<i>i</i>)	Zr(2)	0.2695 ± 0.0007	0	0.8840 ± 0.0003
4(<i>i</i>)	Ni(1)	0.2561 ± 0.0011	0	0.2460 ± 0.0004
8(<i>j</i>)	Ni(2)	0.2075 ± 0.0007	0.1625 ± 0.0005	0.0762 ± 0.0003
8(<i>j</i>)	Ni(3)	0.2974 ± 0.0006	0.1679 ± 0.0004	0.4208 ± 0.0002
8(<i>j</i>)	Ni(4)	0.5033 ± 0.0007	0.2464 ± 0.0007	0.2507 ± 0.0003

(b) Temperature factors (β 's $\times 10^4$)Anisotropic temperature factors of the form $T = \exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{13}hl + 2\beta_{23}kl + 2\beta_{12}hk)$.

Set		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
4(<i>i</i>)	Zr(1)	4 ± 8	8 ± 3	2 ± 1	0	-3 ± 2	0
4(<i>i</i>)	Zr(2)	9 ± 9	15 ± 4	12 ± 2	0	6 ± 3	0
4(<i>i</i>)	Ni(1)	34 ± 7	15 ± 2	8 ± 1	0	9 ± 2	0
8(<i>j</i>)	Ni(2)	53 ± 8	34 ± 4	12 ± 1	6 ± 5	5 ± 3	1 ± 2
8(<i>j</i>)	Ni(3)	65 ± 8	15 ± 3	7 ± 1	10 ± 4	4 ± 3	2 ± 1
8(<i>j</i>)	Ni(4)	33 ± 4	16 ± 2	12 ± 1	-3 ± 2	4 ± 1	0 ± 1



Ni_7Hf_2 forms congruently from the melt at 1480°C.

Ni-Zr(32): The Ni-Zr system is very similar to the Ni-Hf system (fig.9). The intermetallic compounds Ni_5Zr and Ni_7Zr_2 both have the same crystal structure and very similar lattice parameters to the corresponding Ni-Hf compounds (table 13). The structure of the crystal and the positions of the atoms in the unit cells are shown in fig.8 and tables 14 & 15. However, whereas Ni_5Hf has a very limited homogeneity range, Ni_5Zr has been shown to maintain its homogeneity between 15-18 at.% Zr at 1000°C (37). The composition range over which Ni_7Hf_2 exists has not been established.

The extent to which aluminium is found in solid solution in Ni_5Zr and Ni_7Zr_2 has been determined at two temperatures in a similar way to the Ni-Hf compounds (38). There was found to very limited solubility of aluminium in Ni_5Zr , but extensive solubility of aluminium in Ni_7Zr_2 at 1000°C and at 1200°C.

Ni_7Zr_2 forms congruently from the liquid. The temperature at which the reaction occurs varies according to author (table 16).

Phase	Temperature °C			
	(40)	(41)	(41)	(42)
Ni_7Zr_2	1440	1420	1450	1575±25

Table 16 Temperatures at which Ni_7Hf_2 has been reported to form congruently from the melt.

The favoured reaction temperature was 1440°C (32).

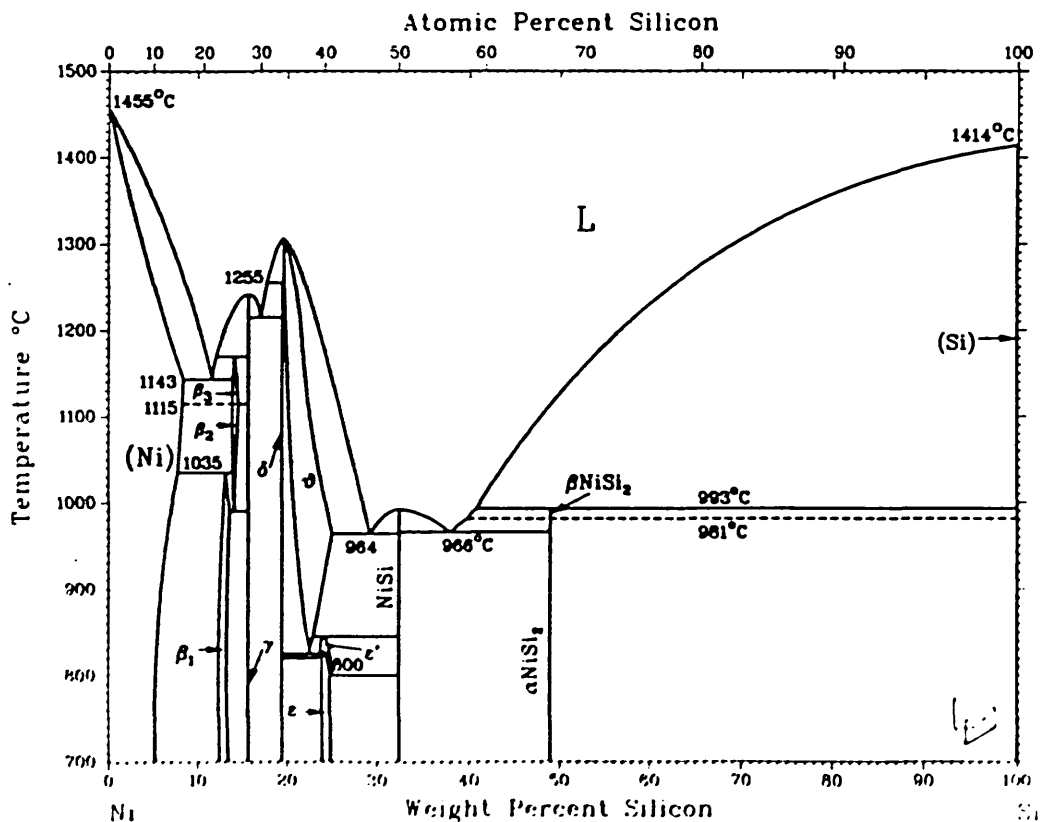
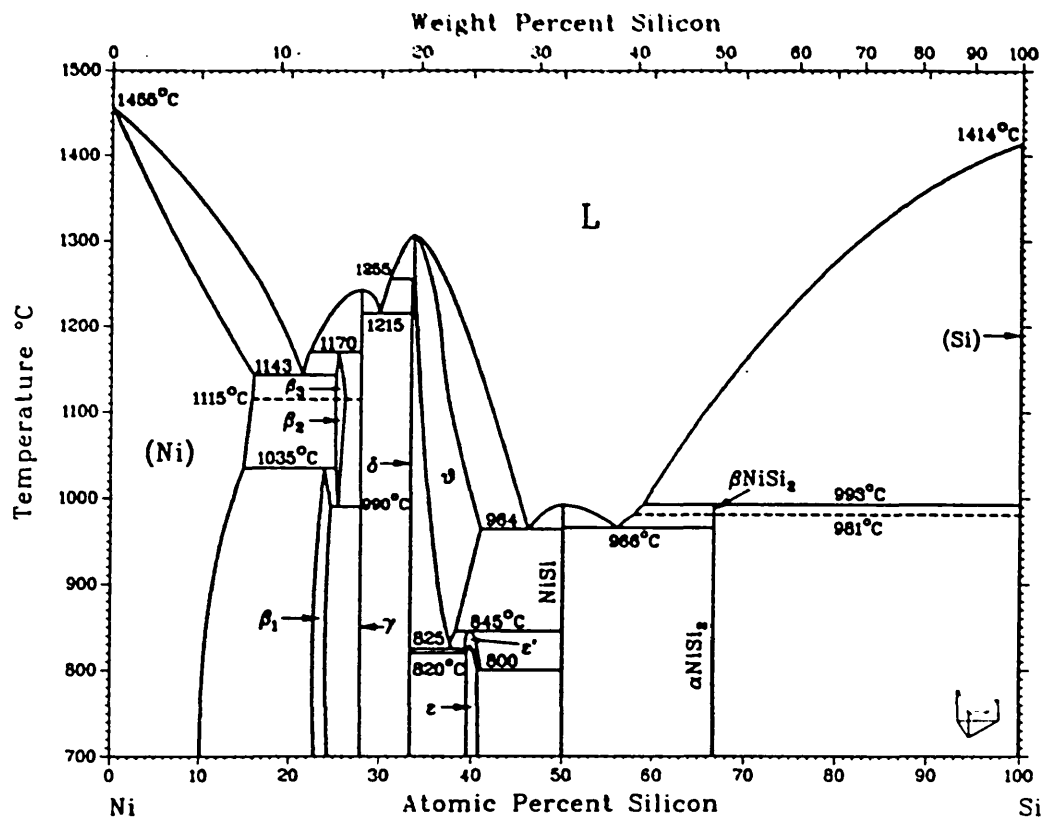


Fig.10 The assessed Ni-Si binary phase diagram.

Ni-Si (Nickel-Silicon)

58.69

28.0855

P. Nash and A. Nash; submitted to the APD Program

Ni-Si Crystal Structure Data

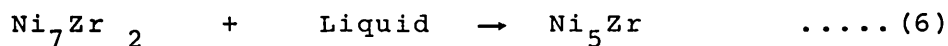
Phase	Composition, at.% Si	Pearson symbol	Space group	Struktur- bericht designation	Prototype
(Ni)	0 to 15.8	<i>cF4</i>	<i>Fm3m</i>	A 1	Cu
β_1 (Ni ₃ Si)	22.8 to 24.5	<i>cP4</i>	<i>Pm3m</i>	<i>L1₂</i>	AuCu ₃
β_2 (Ni ₃ Si)	24.5 to 25.5	<i>mC16</i>	...	...	GePt ₂
β_3 (Ni ₃ Si)	24.5 to 25.5	<i>mC16</i>	...	...	GePt ₂
γ (Ni ₁₁ Si ₁₂)	~26.5 to 29.5	<i>hP14</i>	...	...	...
δ (Ni ₂ Si)	...	<i>hP6</i>	...	...	...
δ (Ni ₂ Si)	32.5 to 34.5	<i>oP12</i>	...	...	...
Ni ₃ Si ₂ (ϵ)	39 to 42	<i>oP80</i>	...	...	...
NiSi	49.5 to 51	<i>oP8</i>	<i>Pnma</i>	B 31	MnP
β NiSi ₂	66.6	?	...	...	?
α NiSi ₂	66.6	<i>cF12</i>	<i>Fm3m</i>	C 1	CaF ₂
(Si)	~100	<i>cF8</i>	...	...	...

Ni-Si Invariant Reactions

Reaction	Composition, at.% Si		Temperature, °C	Reaction type	
$L \rightarrow (Ni) + \beta_3$	21.4	15.8	25	Eutectic	
$\beta_2 = \beta_3$	...	...	~1115	Polymorphic	
$(Ni) + \beta_2 = \beta_1$	14.7	25.1	23.7	1035	Peritectoid
$\beta_2 = \beta_1 + \gamma$	25.2	24.5	27.9	990	Eutectoid
$L - \gamma = \beta_3$	22	27.9	25.2	1170	Peritectic
$L = \gamma$	...	27.9	...	1242	Congruent
$L = \gamma - \delta$	29.8	27.9	33.3	1215	Eutectic
$L - \delta = \delta$	30.8	33.4	33.3	1255	Peritectic
$L = \delta$	...	~33.5	...	1306	Congruent
$\delta = \delta + \epsilon'$	37.8	33.3	39.2	825	Eutectoid
$\epsilon' = \delta - \epsilon$	39.2	33.3	39.5	820	Eutectoid
$\epsilon' = \epsilon - NiSi$	41	40.7	50	800	Eutectoid
$\delta + NiSi = \epsilon'$	38.5	50	40	845	Peritectoid
$\epsilon = \epsilon'$	...	40	...	~830	Polymorphic
$L = \delta - NiSi$	46	41	50	964	Eutectic
$L = NiSi$	...	50	...	992	Congruent
$L = NiSi + \alpha NiSi_2$	56.2	50	66.7	966	Eutectic
$L + (Si) = \beta NiSi_2$	59	~100	66.7	993	Peritectic
$\beta NiSi_2 = \alpha NiSi_2$	...	66.7	...	981	Polymorphic

Table 17

Ni_5Zr forms at 1300°C as a result of the reaction between Ni_7Zr_2 and Liquid:



The solubility of Zr in Ni was found to be about 0.6 at.% Zr (40), in agreement with other results (41,43) found in the literature, which indicated a Zr solubility less than 1 at.%. The maximum solubility of Zr in Ni has been given as 1.8 at.% Zr (39). There is no confirming experimental evidence for this particular value, other than inferring that it is small, but greater than the 0.6 at.% found at a lower temperature.

Ni-Si(33) (fig.10): There are two intermetallic compounds in the Ni-Si system which were of interest in this study, namely Ni_3Si and $\text{Ni}_{31}\text{Si}_{12}$ (table 17).

Ni_3Si has been reported to change its crystal structure twice on heating. Between 1040°C and 1125°C the β_2 form has been reported to be stable (44,45). A more recent assessment of the Ni-Si system was in fairly good agreement with these temperatures (33). Ni_3Si β_1 was shown to be stable up to 1035°C , Ni_3Si β_2 was stable between 990°C and 1115°C and Ni_3Si β_3 was stable from 1115°C to 1170°C . However, an alternative interpretation was suggested in which Ni_3Si β_2 was reported to exist between 970°C and 1225°C . The phase was given a different stoichiometry, $\text{Ni}_{25}\text{Si}_9$, but was essentially considered to

be the same phase (46,33) (fig.11). The structure of $\text{Ni}_{25}\text{Si}_9$ was reported to be hexagonal. Ni_3Si β_2 and Ni_3Si

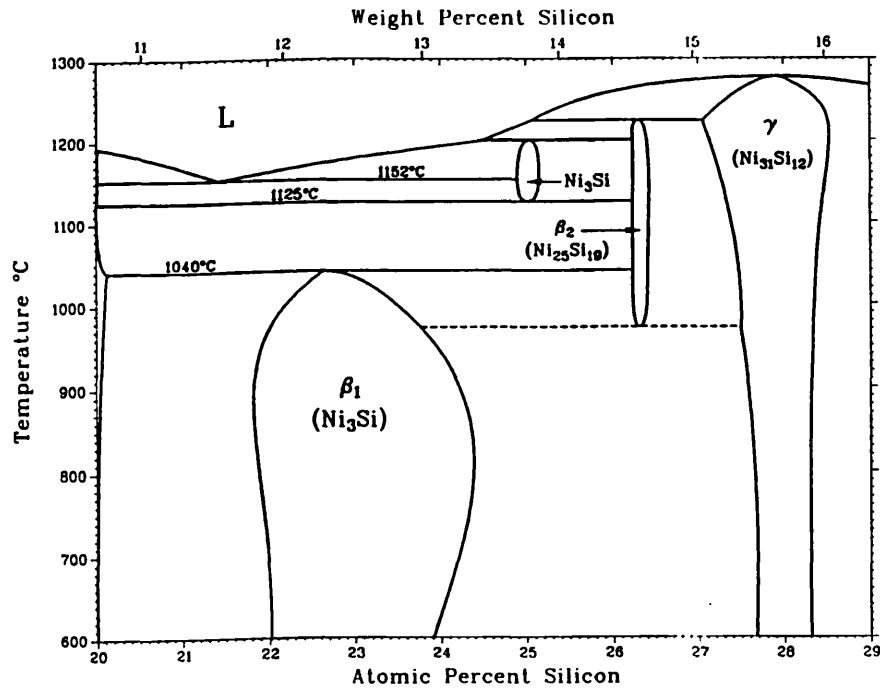
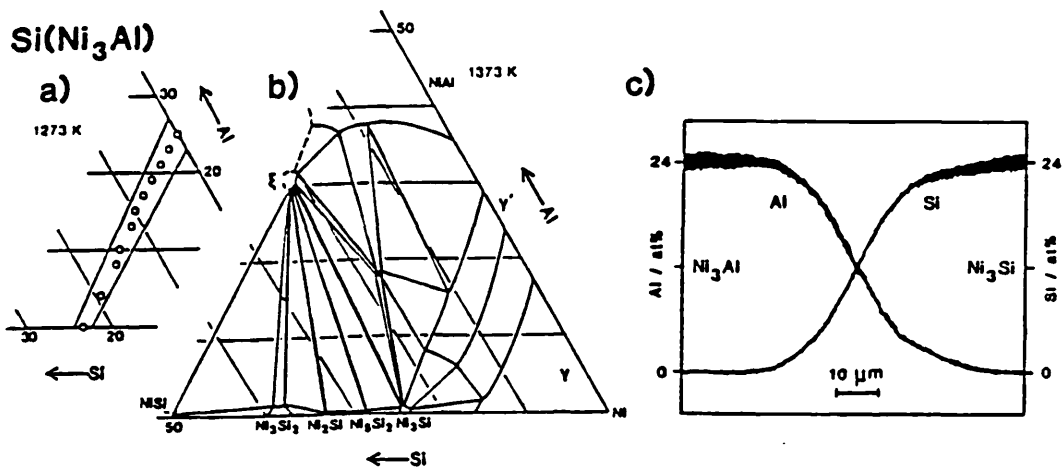


Fig.11 The composition range and phase relationships between $\text{Ni}_{25}\text{Si}_9$ (Ni_3Si β_2) and other phases and compounds.



Ni_3Al and Ni_3Si forms a continuous solid solution below 1273 K(a), which is further confirmed with the diffusion experiment by Oya et.al. The micro-analysis profile of the diffusion couple treated at 1173K for 2 Ms is shown(c). At 1373 K in the isothermal section of Ni-Al-Si ternary phase diagram proposed by Guard and Smith(b), Ni_3Si has been transformed to a distorted L_{12} type crystal structure, which could not accommodate ternary additions in solution.

- (1) R.W.Guard and E.A.Smith, J.Inst.Metals 88(1959-60) 369.
- (2) Y.Oya,S.Ochiai and T.Suzuki,unpublished work,Tokyo Inst.Tech.,1983.

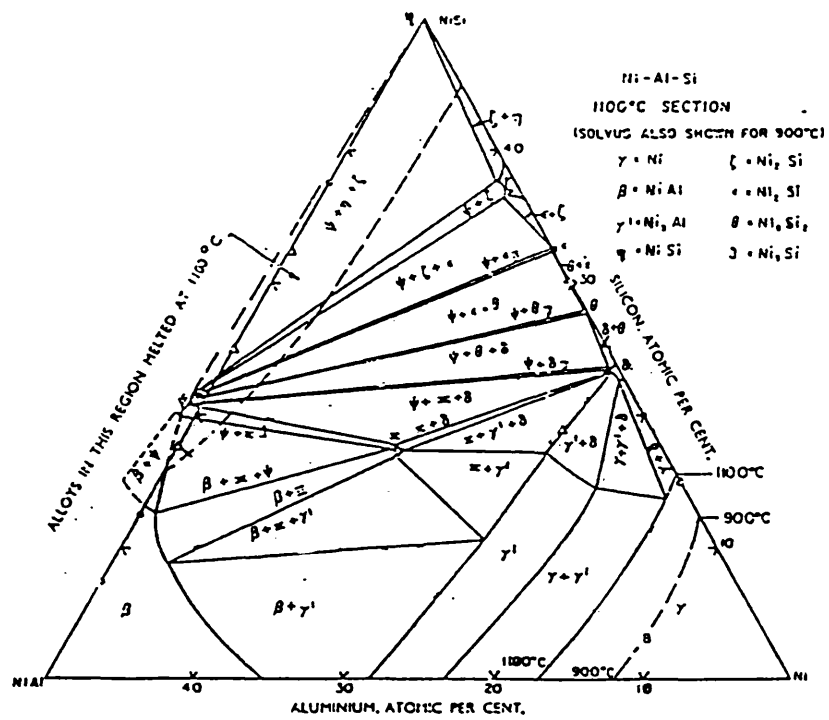


Fig 13 Isothermal section of the nickel-aluminium-silicon system at 1100° C, showing also the γ solvus for 900° C.

Table 18 Substitution behavior of ternary additions in Ni_3Si . Symbols with circle substitute for Si-site, with square for Ni-site and with triangle for both sites. Those unmarked exhibit very limited solubility. Asterisks are the components of the base compound.

[illegible]

$\beta 3$ are reported to have distorted $L1_2$ type structures, pseudocubic unit cells, or they could be considered as monoclinic structures (table 17). Ni_3Si $\beta 1$ is reported to have the $L1_2$ type structure (33). Certain elements have been found to form a solid solution with Ni_3Si $\beta 1$ (47). Aluminium substituted for silicon sites below $1000^\circ C$ and Ni_3Al and Ni_3Si form a continuous solid solution (47) (fig.12). At $1100^\circ C$ in the isothermal section of the Ni-Al-Si ternary phase diagram proposed by Guard and Smith (30) (fig.13), Ni_3Si has probably been transformed to a distorted $L1_2$ type structure which will only exhibit limited solid solubility. Zirconium was reported to exhibit limited solubility at $1000^\circ C$ (table 18). In general the solid solubility of ternary additions in Ni_3Si was reported to be more limited than in Ni_3Al (47) (fig.14).

$Ni_{31}Si_{12}$ is often referred to in the literature by the symbol γ . However, in this work γ refers to the nickel solid solution, therefore, the intermetallic compound will be referred to by its stoichiometric composition. The structure of $Ni_{31}Si_{12}$ was first reported to be trigonal (48,49). The phase was designated Ni_5Si_2 (48) and $Ni_{31}Si_{12}$ (49). The lattice parameters reported by both authors were in good agreement. More recently the stoichiometric composition of the phase was given as 27.9 at.% Si (50,51) which is slightly more nickel-rich than the compositions given elsewhere (44,52,53). Thus the change in designation from Ni_5Si_2 to $Ni_{31}Si_{12}$ was made. The composition range of $Ni_{31}Si_{12}$ was reported by Badiev et

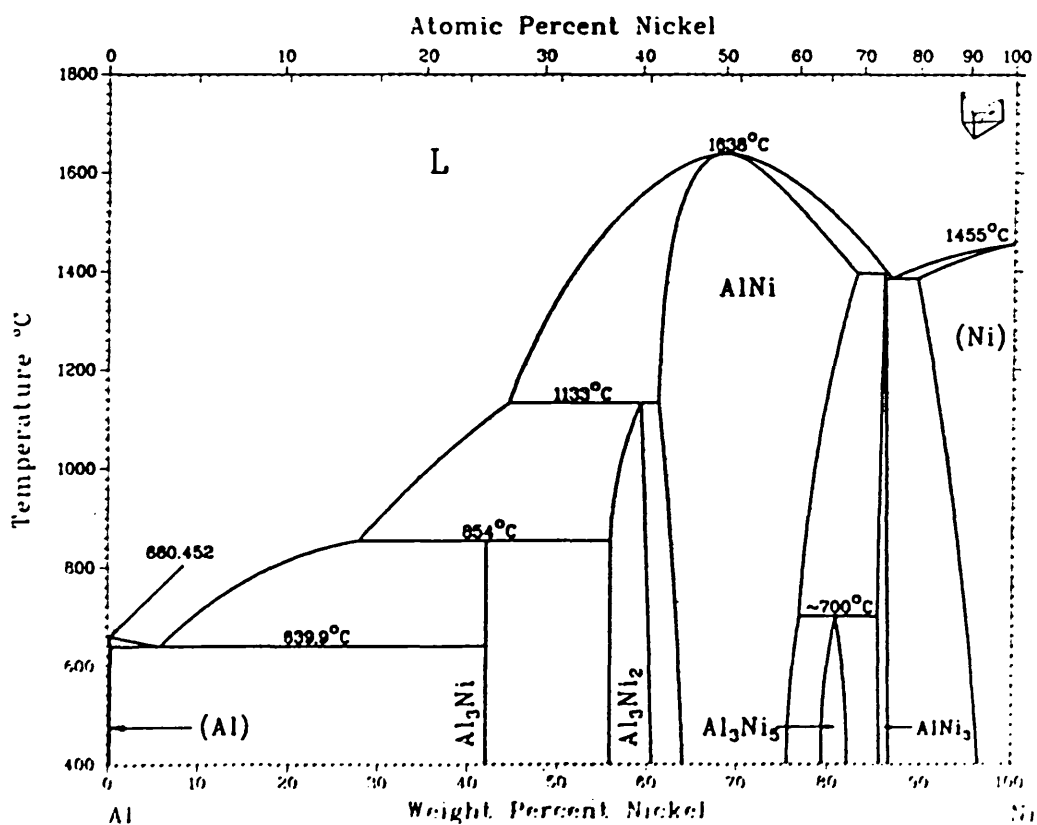
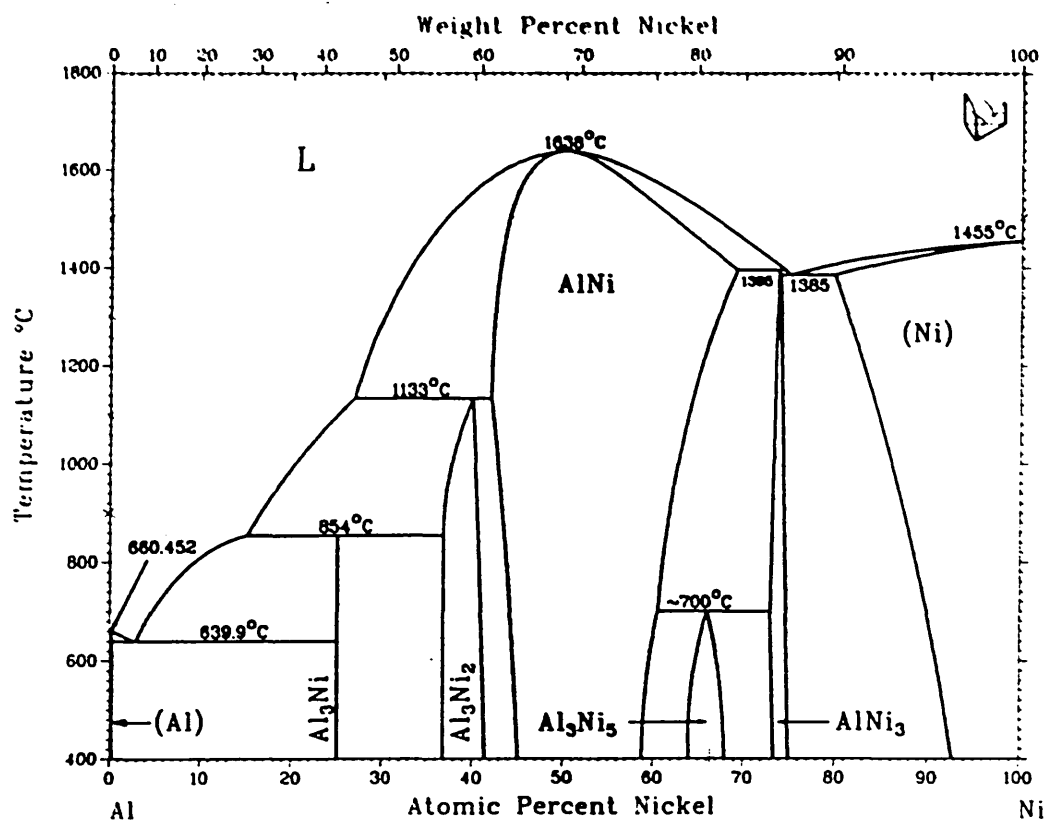


Fig.15 The assessed Ni-Al binary phase diagram.

Al-Ni Invariant Reactions

Reaction	Composition, at.% Al			Temperature, °C	Reaction type
$L \rightleftharpoons (Ni) + AlNi_3$	25	20.2	26	1385	Eutectic
$L + AlNi \rightleftharpoons AlNi_3$	25.5	30.8	26.25	1395	Peritectic
$AlNi + AlNi_3 \rightleftharpoons Al_3Ni_2$	39.5	27	34	700	Peritectoid
$L + AlNi \rightleftharpoons Al_3Ni_2$	73.1	58	60	1133	Peritectic
$L + Al_3Ni_2 \rightleftharpoons Al_2Ni$	85	63.2	75	854	Peritectic
$L \rightleftharpoons Al_3Ni + (Al)$	97.3	75	99.89	639.9	Eutectic

Al-Ni Crystal Structure Data

Phase	Composition, at.% Al	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Ni)	0 to 21.2	<i>cF4</i>	<i>Fm3m</i>	A1	Cu
$AlNi_3$	24 to 27	<i>cP4</i>	<i>Pm3m</i>	<i>L1_2</i>	AuCu ₃
Al_3Ni_4	~32 to 36	...	<i>Cmmm</i>	...	Ga ₃ Pt ₄
$AlNi$	30.8 to 58	<i>cP2</i>	<i>Pm3m</i>	B2	CsCl
Al_3Ni_2	59.5 to 63.2	<i>hP5</i>	<i>P3m1</i>	<i>D5_1</i>	Al_3Ni_2
Al_2Ni	75	<i>oP16</i>	<i>Pnma</i>	<i>D0_11</i>	CFe ₃
(Al)	99.89 to 100	<i>cF4</i>	<i>Fm3m</i>	A1	Cu

Table 19

Table 20 Substitution behavior of ternary additions in Ni_3Al . Symbols with circle substitute for Al-site, with square for Ni-site and with triangle for both sites. Those unmarked exhibit very limited solubility. Asterisks are the components of the base compound.

Sc	Ti	V	Cr	Mn	Fe	Co	*	Cu	Zn	Ga	Ge	—
Y	Zr	Nb	Mo	—	—	—	Pd	—	—	In	Sn	Sb
—	Hf	Ta	W	—	—	—	Pt	—	—	—	—	—

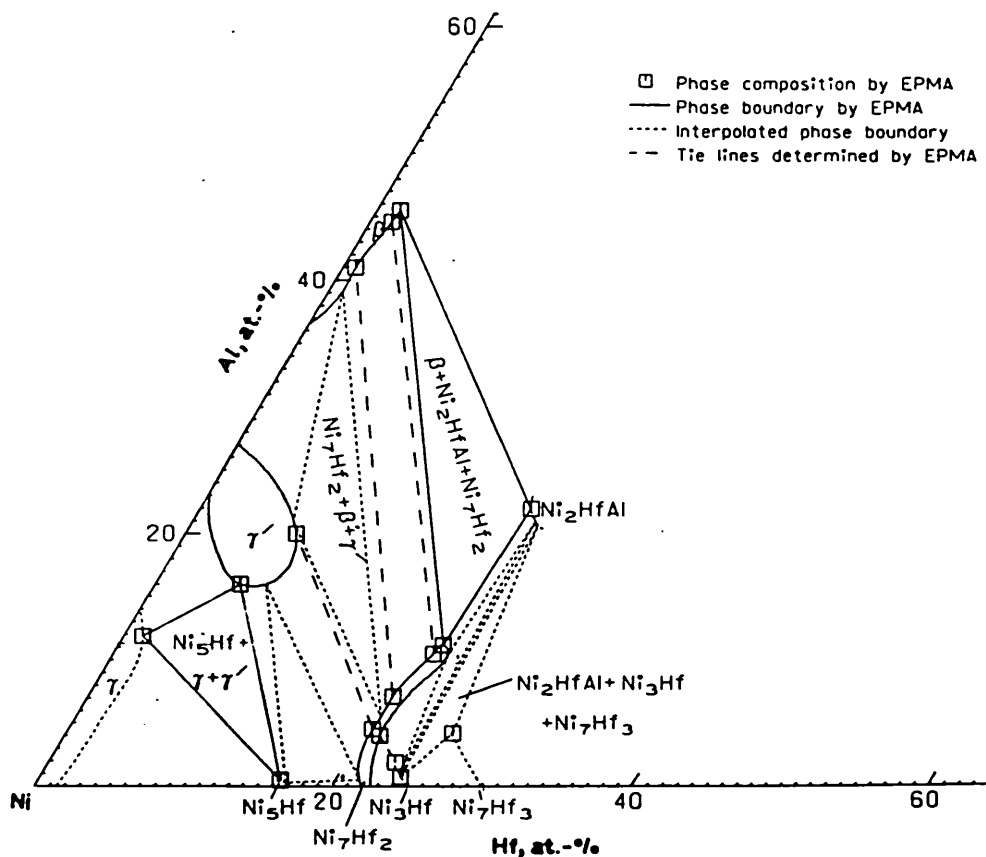


Fig 16 Partial isothermal section of Ni-Al-Hf system at 1273 K

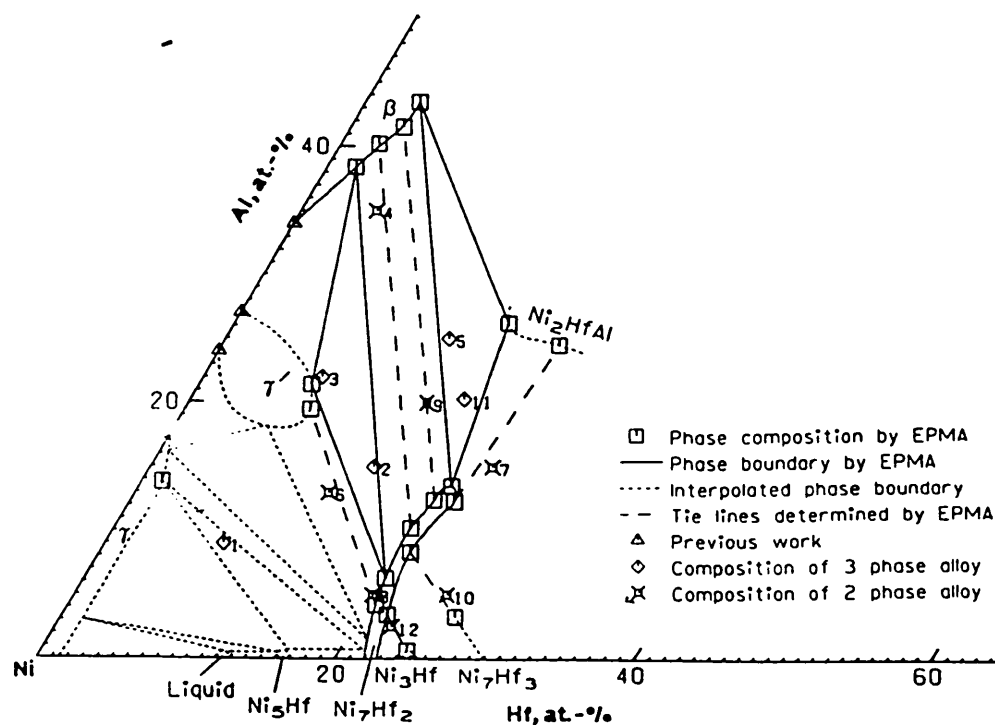


Fig 17 Partial isothermal section of Ni-Al-Hf system at 1473 K

al.(52), but other workers reported a narrow composition range covering the stoichiometric composition (46,51).

The various liquid and solid state reactions associated with these phases are given in table 17.

The nickel solid solution has been reported to extend to 15.8 at.% Si at 1143°C. Rapid solidification of Ni-rich alloys has been reported to increase the solid solubility of silicon in nickel to about 18 at.% (54).

Ni-Al(34) (fig.15): Besides the γ solid solution the only phase of interest from this system was Ni_3Al (table 19). Ni_3Al has the L1_2 type structure. The phase is stable up to 1395°C and forms as a result of a peritectic reaction (34) (table 19). The form of the phase diagram has been well established in the nickel-rich end of the diagram. Extensive work has been carried out to establish in greater detail the substitution behaviour of different elements in Ni_3Al (55) (table 20). Zr has been found to be soluble in Ni_3Al up to 4 at.% in the temperature range 1000-1100°C (38). Ochaia et al.(55) reported very limited solubility of Zr in Ni_3Al . Hafnium on the other hand has been found to be soluble in Ni_3Al up to 7 at.% (27). The direction of the lobe suggested that hafnium substitutes for aluminium (fig.1). This was confirmed by Ochaia et al.(55).

1.2.4 Relevant information from the Ternary Diagrams.

Ni-Al-Hf (27,55): Isothermal sections of the nickel-rich corner of the Ni-Al-Hf system at 1000°C and 1200°C were established by Nash and West (27) (figs.16&17).

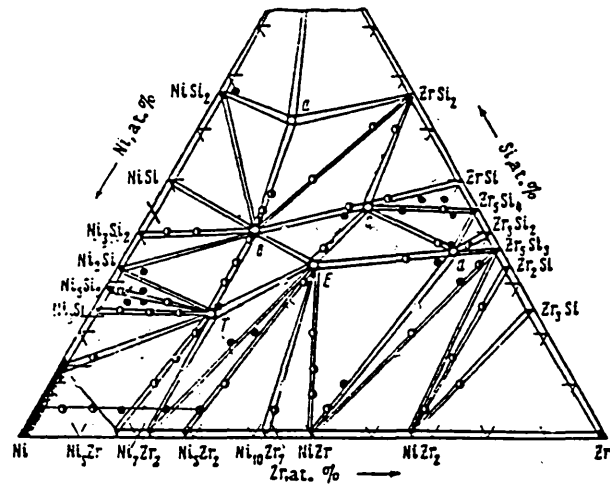


Fig. 18 Isothermal section of the Zr-Ni-Si system at 800°C.

TABLE 21: Ternary Intermetallic Compounds of the Ni-Al-Hf,
Ni-Al-Si, Ni-Hf-Si and Ni-Zr-Si Systems

TERNARY INTERMETALLIC	AT % 2ND ELEMENT	SPACE GROUP	PROTOTYPE	a (nm)	b (nm)	c (nm)	REFS	
HfNiSi	33.3 Hf-33.3 Ni-33.3 Si			0.639	0.72	0.389	(65)	
HfNi _{1.8} Si _{3.2}	16.7 Hf-30.0 Ni-53.3 Si			0.378		2.428	(66)	
HfNiSi ₂	25.0 Hf-25.0 Ni-50.0 Si		TiNiSi ₂	1.287		0.509	(67)	
Hf ₃ Ni ₂ Si ₃	37.5 Hf-25.0 Ni-37.5 Si	Cmcm (63)	MgAl ₂ Cu	0.383	0.986	1.300	(64)	
Hf ₆ Ni ₁₆ Si ₇	20.7 Hf-55.2 Ni-24.1 Si		Mg ₆ Cu ₁₆ Si ₇	1.139			(68)	
Ni ₂ HfAl	50.0 Ni-25.0 Hf-25.0 Al	Fm3m (255)	MnCu ₂ Al	0.608			(62)	
Ni ₁₆ Hf ₄ Al ₅	64.0 Ni-16.0 Hf-20.0 Al		Cu ₂ Mg	0.691			(57)	
Ni _{1.9} HfAl _{0.1}	63.0 Ni-33.0 Hf- 3.0 Al		MgCo ₂	0.691			(57)	
HfNi _{0.6} Al _{1.4}	20.0 Ni-33.0 Hf-47.0 Al		MnZn ₂	0.518		0.841	(57)	
Hf ₆ Ni ₈ Al ₁₅	28.0 Ni-21.0 Hf-52.0 Al		Mg ₆ Cu ₁₆ Si ₇	1.200			(58)	
Hf ₆ Ni ₇ Al ₁₆	24.0 Ni-21.0 Hf-55.0 Al	Fm3m (255)		1.201			(59)	
Hf ₆ NiAl ₂	11.0 Ni-67.0 Hf-22.0 Al		Zr ₆ FeAl ₂	0.783	0.329		(60)	
Hf ₃ Ni ₆ Al ₁₆	24.0 Ni-12.0 Hf-64.0 Al		Zr ₃ Ni ₆ Al ₁₆	0.401	1.412		(60)	
Hf ₅ Ni ₄ Al	40.0 Ni-50.0 Hf-10.0 Al						(60)	
HfNiAl	33.3 Ni-33.3 Hf-33.3 Al	P62m (189)	Ni ₂ In/Fe ₂ P	0.689 0.709		0.684 0.711	(61)	
HfNi _{0.35} Al _{1.65}	12.0 Ni-33.0 Hf-55.0 Al	Fd3m (227)	MgCu ₂	0.735			(62)	
Ni ₂ AlSi	50.0 Ni-25.0 -25.0 Si	P213(198)	FeSi	0.454			(62)	
Ni ₃ (AlSi) ₇	30.0 Ni-35.0 Al-35.0 Si		Ru ₃ Sn ₇	0.829			(63)	
Zr ₆ Ni ₁₆ Si ₇	20.7 Zr-55.2 Ni-24.1 Si		Mg ₆ Cu ₁₆ Si ₇	1.147			(69)	
ZrNiSi	33.3 Zr-33.3 Ni-33.3 Si		TiNiSi	0.735 0.615	0.544 0.702	1.147 0.367	(70)	
Zr ₂ Ni ₃ Si ₈	15.4 Zr-23.1 Ni-61.5 Si		Only interplanar spacings available					(28)
ZrNi ₂ Si ₂	20.0 Zr-40.0 Ni-40.0 Si		CeGa ₂ Al ₂	0.375	0.968		(28)	
Zr ₄ Ni ₂ Si ₅	36.2 Zr-18.2 Ni-45.5 Si		Only interplanar spacings available					(28)
Zr ₁₄ Ni ₂ Si ₉	56.0 Zr- 8.0 Ni-36.0 Si		Only interplanar spacings available					(28)

Data on the extent of solubility of various elements in solid solutions and binary intermetallic compounds has been given in the section above.

Eleven ternary intermetallic compounds have been found in this system, none of which lie in the region of interest. These compounds are presented in table 21 (56-62).

Ni-Al-Si (30,47): An isothermal section of the nickel-rich corner of the Ni-Al-Si system was determined at 1100°C (30) (fig.13). The γ phase field extends right across the diagram. No continuous solid solution was observed between Ni_3Si and Ni_3Al , although as was mentioned in the section above, at 1100°C the structure of Ni_3Si would have changed to a distorted L1_2 type structure which would be unable to accommodate ternary additions.

Two ternary intermetallic compounds have been found in this system (62,63) (table 21). Neither are in the region of interest.

Ni-Hf-Si : No isothermal sections of the Ni-Hf-Si system have been published.

Five ternary intermetallic compounds have been found (64-68) (table 21). None of these phases are in the region of interest.

Ni-Zr-Si (28,29): An isothermal section of the Ni-Zr-Si system was constructed at 800°C by x-ray analysis (28,29) (fig.18). Very limited solubilities of Si in Ni_5Zr and of Zr in Ni_3Si were found. The following phase regions in the nickel-rich corner of the section were established:

1. γ
2. $\gamma + \text{Ni}_5\text{Zr}$.
3. $\gamma + \text{Ni}_3\text{Si}$.
4. $\gamma + \text{Zr}_{16}\text{Ni}_7\text{Si}_6$.
5. $\gamma + \text{Ni}_5\text{Zr} + \text{Zr}_{16}\text{Ni}_7\text{Si}_6$.
6. $\gamma + \text{Ni}_3\text{Si} + \text{Zr}_{16}\text{Ni}_7\text{Si}_6$.

Six ternary intermetallic compounds have been reported in the Ni-Zr-Si system (28,69,70) (table 21).

2. EXPERIMENTAL

2.1 Casting of alloys

2.1.1 Specimen preparation

All model alloys were cast using the vacuum-arc melting technique. The constituent elements were washed in ethanol to degrease them and were weighed to an accuracy of three decimal places. Aluminium was deoxidised in a sodium hydroxide solution, then degreased in ethanol. The nickel, aluminium and silicon used were approximately 99.99% pure. Hafnium contained approximately 3 at.% zirconium, the maximum level of other impurities was 0.38 mass percent. The silicon used in the Ni-Hf-Si alloys was in powdered form, "Special product 80/00", normally used for flame spraying. Semiconductor grade silicon was used in the Ni-Zr-Si alloys and in the Ni_5Hf and Ni_5Zr alloys. The total weight of elements for one ingot was 30g.

2.1.2 Vacuum-arc melting of alloys.

All alloys were cast in a vacuum-arc furnace. The chamber was flushed three times with argon prior to melting. The copper hearth had been cleaned with an abrasive paper (grade 600, silicon carbide paper) and washed with tissues and ethanol. The elements were melted in the chamber using a tungsten arc operating at approximately 3000°C. To ensure homogeneity the ingot was

Before Casting (at.%)	After Casting (at.%)
Ni - 12.0% Al-5.0% Hf	
Ni-2.0% Hf-16.0% Si	Ni-2.0% Hf 14.1% Si
Ni-10.0% Hf-12.0% Si	Ni-10.0% Hf 7.8% Si
Ni-2.0% Hf-24.0% Si	Ni-2.0% Hf-22.0% Si
Ni-2.0% Hf-5.0% Si	
Ni-7.0% Al 5.0% Hf-5.0%Si	

Table 22 Compositions of Ni-Al-Hf, Ni-Hf-Si and Ni-Al-Hf-Si alloys. Compositions given for 'after-casting' were calculated on the assumption that all weight loss was due to silicon being 'blown away'.

remelted several times before casting. At the end of the casting stage the electrode was run slowly along the length of the ingot to move most of the impurities to one end of the bar. This end was sliced off and was not used for analysis. All cast ingots were cut into two pieces. One was kept to examine the as-solidified structure. The other was heat treated at the required temperature.

Problems were encountered using silicon powder as one of the elements for casting. Evacuating the furnace caused the powdered silicon in the hearth to rise and form a cloud within the chamber. This produced a change in the intended composition of the cast product.

By weighing the elements before casting and the bar after casting the weight loss was obtained. By attributing all weight loss to the loss of silicon powder from the hearth the composition of the cast bar was predicted (table 22). A more accurate value for the composition of the bar was sought by means of EPMA. No such loss of silicon was found by using semiconductor grade material.

2.2 Heat treatment

That part of the ingot to be heat treated was sealed in a silica tube under a partial pressure of argon. This was hung from a piece of nichrome wire and suspended in the hot zone of an upright furnace. The temperature of the furnace had previously been checked with a Pt-Pt. 13% Rh thermocouple and was accurate to within $\pm 2^{\circ}\text{C}$. Following heat treatment at given temperatures and for specified

times (table 9), ingots were quenched in ice-water to retain the high temperature structure. When quenched, however, the silica tubes did not usually break on hitting the water, and they had to be broken by hand as soon as possible after entering the water.

A significant amount of oxide formed during the solidification of hafnium containing ingots. Before heat treatment as much as possible of this oxide scale was removed on a grinding wheel.

An as-solidified and heat-treated cross section of each alloy was then cut from the ingot halves on a carborundum slitting wheel. Specimens were mounted in bakelite and polished using diamond sprays. Polishing times were cut down to approximately 5 minutes by using an automatic polishing machine. As-solidified and heat treated specimens were prepared in this way for x-ray diffraction, EPMA and interference film microscopy.

2.3 Alloys

2.3.1 Ni-Al-Hf, Ni-Hf-Si, Ni-Zr-Si, Ni-Al-Hf-Si

Alloys of most interest from the constitutional point of view were those of the Ni-Hf-Si, Ni-Zr-Si and Ni-Al-Hf-Si systems.

Weight losses after solidification were of the order of 0.35g (equivalent to 1.3 at.%) for the Ni-Hf-Si alloys, but weight losses were less than 1 at.% for the Ni-Zr-Si alloys in which semiconductor grade silicon had been used.

Alloys containing high percentages of hafnium were

avoided because it has been reported (27) that a reaction to a depth of 1mm could occur during heat treatment between the hafnium in the alloy and silicon from the tube. At a heat treatment temperature of 1125°C there would be a partial pressure of silicon within the tube. The argon present should slow down any reaction between the two but heat treatment times were in the order of 168 hours and some reaction could occur in this time.

Even with these low hafnium containing alloys there was evidence that at the heat treatment temperature of 1125°C some reaction had occurred. On quenching, that area of the silica tube containing the ingot was coated with a very thin metallic layer - a vapour deposition process seemed to have taken place. In alloys containing no hafnium no metallic layer was discovered on the inside of any of the silica tubes.

To cast the Ni-7%Al-5%Hf-5%Si (atomic percentages) alloy a Ni-Si master alloy was produced to which the relevant weight percentages of aluminium and hafnium were added.

2.3.2 Ni₅Hf and Ni₅Zr alloys.

Two alloys of similar composition were cast. One contained hafnium and the other zirconium. The aim was to obtain two single phase alloys, one of Ni₅Hf and the other of Ni₅Zr, both containing about 3 at% silicon. At 1000°C Ni₅Zr has a homogeneity range of ≈ 3 at.% , 14.85-18.4 at.%. It was assumed that silicon would substitute for

nickel in Ni_5Zr . If 3 at.% silicon was added then the composition of the alloy was $\text{Ni-16.6\%Zr-3.0\%Si}$. The composition of the hafnium containing alloy was chosen to be $\text{Ni-16.0\%Hf-3.0\%Si}$. A piece of each alloy was heat treated at 1050°C for 13 days in a silica tube under a partial pressure of argon. These specimens were then quenched in ice water in the same way as the other specimens had been.

2.4 Experimental techniques for phase analysis

Analysis of the phases in these alloys was carried out using the following techniques :

1. X-ray diffraction: diffractometer.
2. Electron back-scattering patterns.
3. Quantitative x-ray microanalysis and digimapping.
4. Interference film microscopy.
5. Differential thermal analysis.

Having 'calibrated' these techniques to identify the different phases in the model alloy systems, they were used to try to identify the Ni-Hf and Ni-Zr phases found in some nickel-base superalloys.

2.4.1 X-Ray Diffraction.

A Phillips 1710 diffractometer system was used to establish the phases and intermetallic compounds present, the interplanar spacings and thus, the lattice parameters of their unit cells.

Specimens were prepared by cutting a cross-section of

the ingot, grinding on silicon carbide paper to 600 grade, and finally polishing with a 30 μ m diamond spray.

The specimens were then mounted in the x-ray diffractometer and the following parameters set for the scan. The instrument was microprocessor controlled.

RON	- Recorder on
PON	- Printer on
WAV 1.54178	- wavelength (λ).
RFS 1E3	- full scale deflection
RTC 2	- recording time constant (seconds).
RSP 10	- recorder speed paper (mm/ $^{\circ}$ 2θ).
SPE 0.016	- scan speed ($^{\circ}$ 2θ /second).
INT 3.10	- Sampling interval time (seconds).
SAN 10	- Send to angle 10 ($^{\circ}$).
CSP 60	- Continuous scan with peak labelling over 60 $^{\circ}$.
WAV 1.54051	- Wavelength (λ).
CSP 60	- Continuous scan with peak labelling over 60 $^{\circ}$.

The diffractometer scanned from 10 $^{\circ}$ 2θ to 130 $^{\circ}$ 2θ .

The diffractometer moved at a rate determined by SPE, which in this case was at 0.016 $^{\circ}$ 2θ /sec, 0.96 $^{\circ}$ 2θ /min. The whole scan took approximately 2 hours.

The diffractometer sampled in steps which were governed by the product of SPE and INT. In this case the sampling step was 0.0496 $^{\circ}$, since the interval over which counts were measured was 3.10 seconds. The values of SPE and INT are very important and a balance had to be achieved between the processor labelling broad peaks or very narrow peaks only. In these experiments it was important to select a slow scan speed so as to obtain as many peaks as possible. The interval chosen was found to label the majority of peaks.

A computer program was written to compare the values

obtained from the experiments above with values from the powder diffraction file. The axes could be scaled to any values and the lattice parameters of cubic reflections calculated (Appendix 1).

2.4.2 Electron Back-Scattering Patterns.

Electron back-scattering patterns were obtained from two scanning electron microscopes (71,72). The first, a Nanometrics Field Emission microscope, in which the patterns were viewed directly on a phosphor screen. The second was a Cambridge S4 microscope in which the patterns could be recorded on photographic film placed directly in the chamber. For lattice parameter measurements the second instrument was found to be the best in that sharp patterns containing a large amount of information could be obtained.

Specimens were sliced from a bar or ingot and ground on silicon carbide paper to 600 grade. They were then polished to $\frac{1}{4}$ μm diamond spray, and finally polished with a Struers O.S. suspension for anything between 45 minutes and 3 hours. This produced substantial relief on the specimen surface although this seemed to be of little consequence in obtaining good patterns from the majority of phases in the alloys prepared. Unfortunately, pattern quality of the Ni_5Hf phase was drastically impaired by polishing in this way. A freshly fractured surface was found to give the best results. The polishing treatment in fact helped to relieve the majority of phases of strain so that patterns could be obtained. The specimens were then degreased in arklone and

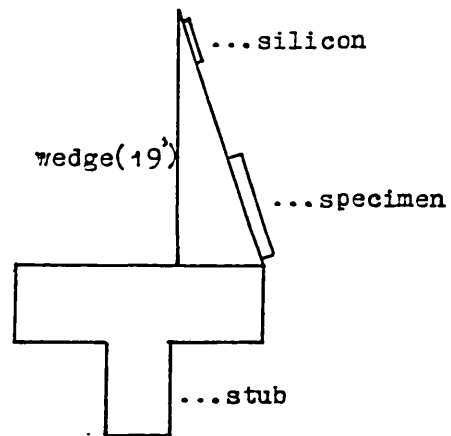


Fig. 19 Arrangement for mounting specimen and
silicon in the SEM to obtain Electron Back-
Scattering Patterns.

mounted on a stub inclined at 19° to the vertical (fig.19). The stub had also been degreased beforehand. Colloidal graphite was used to mount the specimen. In order to obtain the pattern centre and hence calculate the specimen to screen distance which was necessary to calculate lattice parameters a piece of single-crystal silicon was mounted above the specimen. The silicon had been cut along its cleavage plane, and chemically polished in a solution of 1 part hydrofluoric acid to 10 parts nitric acid for 10 minutes. It was later realised that this was not necessary because the pattern centre could be obtained by consideration of the symmetry of the acquired pattern. The specimen was then mounted in the SEM chamber so that the specimen surface was parallel to the phosphor or photographic film.

With the microscope operating at most voltages above 5kV, with a high probe current, patterns were obtained.

Patterns were obtained from the Ni_5Hf alloy, which after heat treatment was substantially single phase. The only pattern that could be obtained was from a fractured surface. Patterns were also obtained from two nickel-base superalloys prepared in the same way. Excellent patterns could be obtained from the majority of phases but it was not possible to acquire one from the Ni-Hf phase. The pattern acquired from the single phase alloy proved to be useful in identifying which phases were not Ni_5Hf .

Pattern analysis was carried out with the aid of a BBC microcomputer. Once the pattern centre had been located the

specimen to film distance was calculated. Patterns were then generated on the BBC microcomputer and the actual pattern was reproduced by the computer pattern. Once the poles had been identified and the widths of lines checked the lattice parameters of all the reflections were calculated.

2.4.3 Quantitative x-ray microanalysis and digimapping.

Specimens were prepared by slicing sections from a rod or ingot, mounting them in bakelite, grinding with silicon carbide paper down to 600 grit, and polishing with diamond paste to $\frac{1}{4}$ μm . It was important to prepare the specimens carefully to ensure that the upper surface was flat. This is required to minimise errors in quantitative analysis. Specimens were finally coated with a carbon layer using an Edwards sputtering unit. They were then mounted in a brass block in which four standards had been mounted also. These were samples of nickel, aluminium, hafnium and silicon. Each standard was coated with approximately 200 Angstroms of carbon. These standards were used for quantitative WDS analysis (table 23). It was found necessary to use this technique due to the resolving power of the EDS technique which could not adequately resolve the hafnium $M\beta$ and $SiK\alpha$ peaks.

Impurity list for standards.

nickel	22 ppm
aluminium	99.999%
hafnium	Ag<1,Ca<1,Cu<1,Fe<30,Si<3,Zr<10 All in ppm.
silicon	Single crystal.

Table 23. Impurity lists for standards for quantitative WDS

analysis.

Analysis was carried out using a Camscan-series 2, Cambridge Scientific instrument. The quantities of nickel, aluminium, hafnium and silicon in the different phases were measured. Quantitative analysis was achieved by focussing the electron beam onto the area or spot of interest. Not all of the phases and intermetallic compounds in the alloys could be analysed in this way because they were less than 3 μm in size. The overall composition of the alloys were obtained by performing a series of area analyses. The ZAF4/FLS Link program was used to perform EDS analysis. Link's SPECTA software was used to control the Cambridge Instruments Microspec System - a wavelength dispersive spectrometer - which is itself microprocessor controlled. This package was set up according to appendix 2.

2.4.4 Interference film microscopy.

Interference film microscopy (73) was used to study the microstructure of the various alloys optically since this technique gave excellent phase contrast. The number of phases or compounds in a given alloy was easy to determine by colour recognition and it enabled image analysis to be performed in order to establish volume fractions.

An Edwards S150 Sputter coater, modified to allow the sputtering of an iron oxide film onto the sample was used. The iron oxide film thus produced was approximately 40 nm thick. On looking through the optical microscope at the

specimen the different phases could be clearly seen. This method was particularly useful for identifying the Ni-Hf phase in some nickel-base superalloys and for distinguishing between this phase and the carbide phases.

Specimens were prepared for this technique by grinding on silicon carbide paper to 600 grade, followed by polishing with diamond paste to $\frac{1}{4}$ μm . Finally the specimen was polished with a Struers O.S. suspension to ensure that the surface was scratch free. This technique was particularly susceptible to scratches but the overall polishing time could be kept to about 10 minutes by using an automatic polishing machine. The sputtering process took about 1 hour depending on the colour of the sputtered layer. A golden colour was found to give best contrast in the nickel-base superalloys and a magenta colour gave best results with the model Ni-Hf-Si and Ni-Al-Hf-Si alloys. A pressure of oxygen of approximately 0.0345 N/mm² was leaked in to the sputtering chamber to enable a discharge to be established. The system was run at a voltage of 5 on the scale and with an operating current of between 10-15 mA.

Slides and photographs of the microstructures were taken using a UNIVAR optical microscope with Kodak 25 ASA slide film and Polaroid Land film.

2.4.5 Differential Thermal Analysis.

Samples were cut from the following alloys. These samples were approximately 2mm x 2mm.

1. Ni-12.0% Al - 5.0% Hf

- 2. Ni- 2.0% Hf - 16.0% Si
- 3. Ni-10.0% Hf - 12.0% Si
- 4. Ni- 2.0% Hf - 24.0% Si
- 5. Ni- 2.0% Hf - 5.0% Si

Alloy 1 had been heat treated at 1000°C for 6 days before the experiment. Between 1000°C and 1200°C a reaction was postulated by Nash and West (27). It was hoped to identify that reaction and its temperature. The conditions under which the experiment was performed are given in appendix 3.

Alloys 2-5 were all heat treated at 1125°C in silica tubes, under partial pressures of argon prior to differential thermal analysis.

The experiments were carried out according to appendix 3.

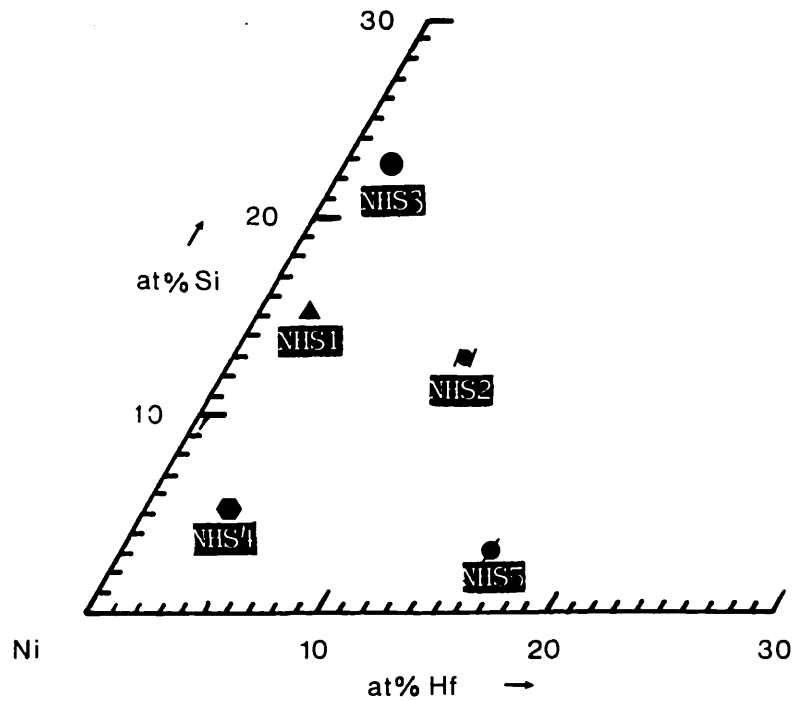


Fig.20 Schematic representation of the compositions of the model Ni-Hf-Si alloys.

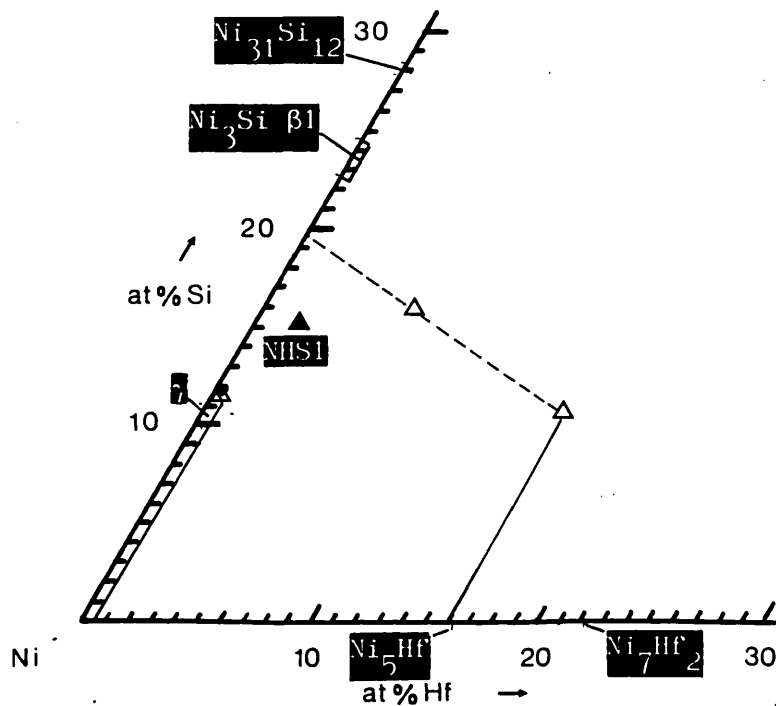
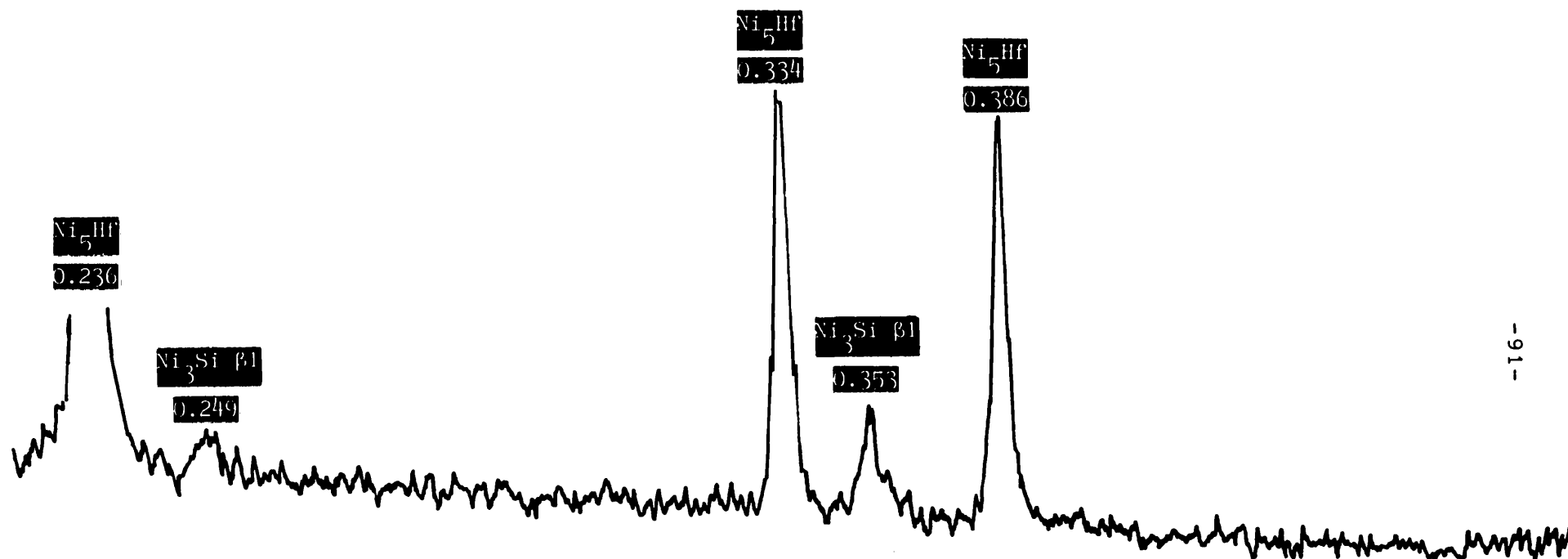


Fig.22. Ni-Hf-Si: A tie line, joining the compositions of Ni_5Hf and the ternary eutectic in NHS1 -as solidified, lies between γ and $\text{Ni}_3\text{Si } \beta 1$.



-91-

Fig.23. N5S1-as solidified: γ and Ni_5Hf positively identified. Reflections at 0.35304 nm and 0.24946 nm were tentatively ascribed to $\text{Ni}_3\text{Si } \beta 1$.

As-solidified	NHS1			NHS2			NHS3			NHS4			NHS5		
	Ni	Hf	Si	Ni	Hf	Si	Ni	Hf	Si	Ni	Hf	Si	Ni	Hf	Si
Composition	83.0	1.8	15.2	77.0	9.9	13.0	75.1	1.9	22.8	91.6	3.3	5.2	81.0	16.0	3.0
γ solid soln.	88.3	0.2	11.6	84.2	0.5	15.3	82.2	0.9	17.0	96.0	0.5	3.4	@		
Ni ₅ Hf	73.3	15.8	10.9	74.2	15.7	10.1	74.0	17.1	10.5				83.0	16.1	0.9
Ni ₇ Hf ₂													77.7	21.5	0.8
Ni ₃ Si β 1				79.1	0.5	20.3	79.3	0.8	21.2						
Ni ₃ Si β 2 or β 3							73.3	0.3	26.4						
Ni ₃₁ Si ₁₂							72.3	0.04	27.7						
Eutectic	77.6	6.4	16.0	80.4	6.2	13.4	76.4	7.4	16.2	86.2	9.4	4.4	87.3	8.0	4.6

Table 24a: EPMA results showing the compositions of the Ni-Hf-Si alloys in the as-solidified state, and of the phases and eutectics observed in them.

1125°C	NHS1			NHS2			NHS3			NHS4		
	Ni	Hf	Si	Ni	Hf	Si	Ni	Hf	Si	Ni	Hf	Si
Composition	82.7	1.8	15.5	76.5	11.2	12.3	75.3	2.1	22.5	91.6	3.3	5.2
γ solid soln.	85.7	0.0	14.3				82.0	0.2	17.7	94.4	0.8	4.8
Ni ₅ Hf	72.5	16.9	10.6	74.3	15.4	10.3	72.5	15.2	12.3	80.5	15.2	4.3
Ni ₇ Hf ₂				64.0	21.4	14.6						
Ni ₃ Si β 1	79.0	0.6	20.4				79.0	0.6	20.4			
Ni ₃ Si β 2 or β 3							73.3	0.3	26.4			
Ni ₃₁ Si ₁₂												
Eutectic (1)	76.5	6.3	17.2	77.3	6.4	16.3						
Eutectic (2)	76.2	6.9	16.9	80.8	6.6	12.6						
Particle	15.7	83.4	0.8									

Table 24b: EPMA results showing the compositions of the Ni-Hf-Si alloys heat-treated at 1125°C, and of the phases and eutectics observed in them.

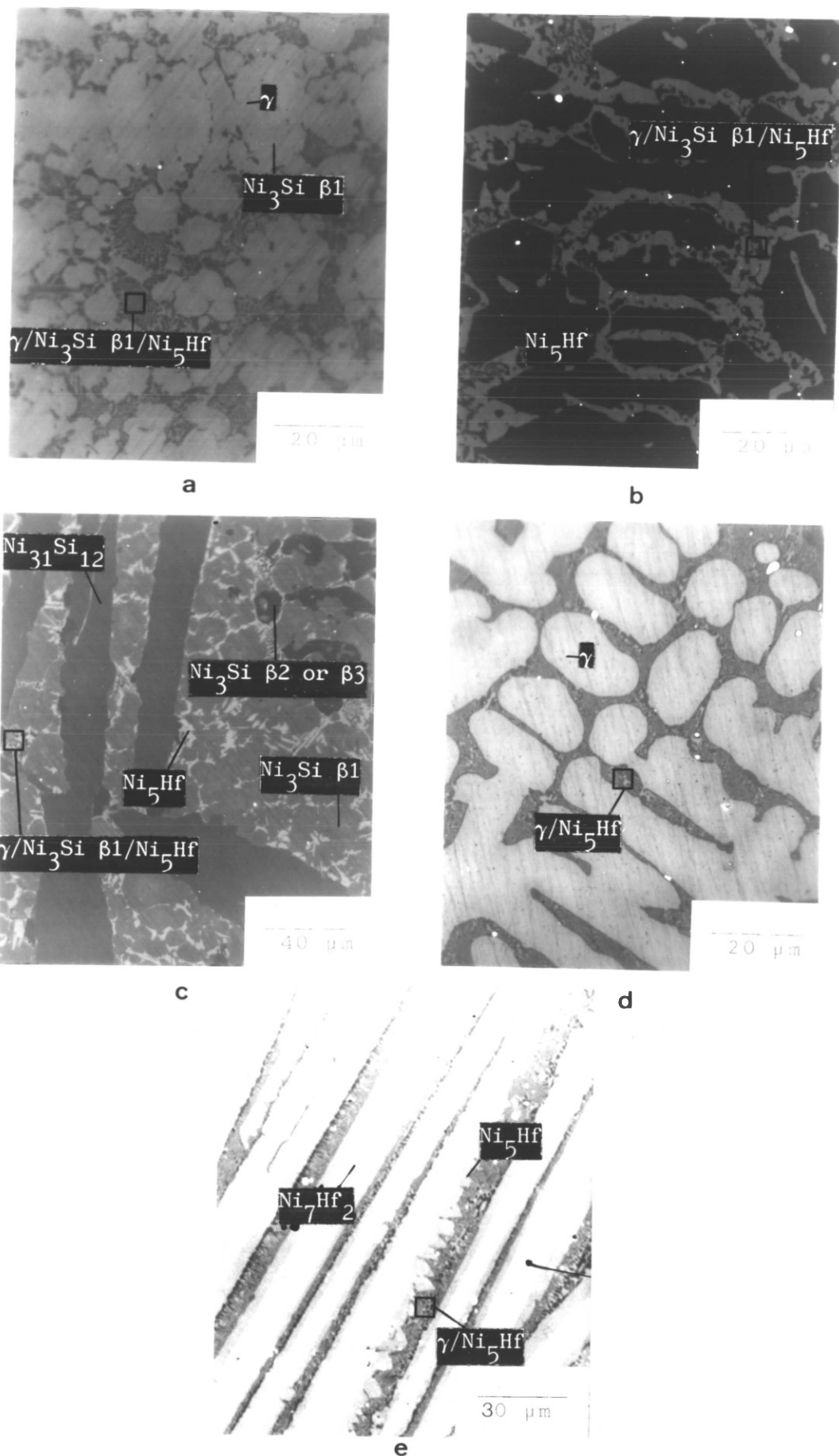


Fig 21

3. RESULTS

3.1 Ni-Hf-Si Alloys.

The compositions of the alloys are shown schematically in fig.20.

3.1.1 As-solidified Alloys.

a. Ni-1.8 at.% Hf-15.2 at.% Si (NHS1 As-solidified)

The structure, as viewed by light microscopy and SEM, consisted of primary dendrites of Ni (γ), a second phase outlining the γ phase, a coarse eutectic and a very fine-structured eutectic (fig.21a).

The compositions of the phases, as determined by EPMA, are shown in table 24. The composition of the γ phase is in good agreement with the literature at temperatures less than 920°C. The interference film micrograph showed that Ni_5Hf was present in the eutectics (fig.21a). The phase outlining the primary γ dendrites was interpreted to be Ni_3Si $\beta 1$ because the Si content, as determined by EPMA, was 20.4 at.% (see section 4.1.2.c). A tie line drawn through the eutectic composition, from Ni_5Hf , meets up with the Ni-Si binary alloy line between γ and Ni_3Si $\beta 1$ (fig.22). Thus, the finely-dispersed-eutectic was interpreted to consist of Ni(γ), Ni_5Hf and Ni_3Si $\beta 1$.

By x-ray diffraction γ and Ni_5Hf were positively identified, however, Ni_3Si $\beta 1$ was only tentatively identified. Weak reflections were observed at 0.353 nm and at 0.249 nm (fig.23).

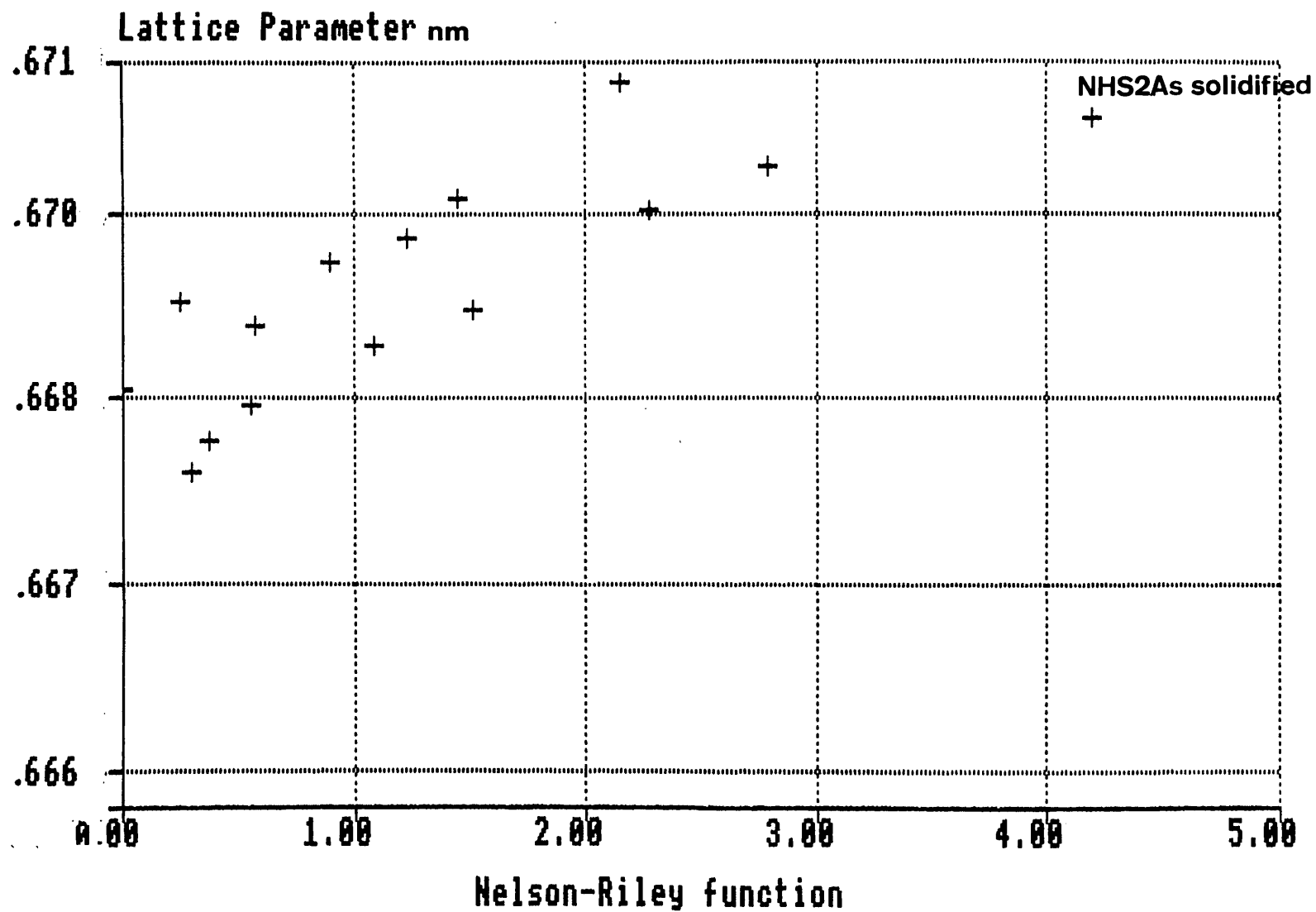


Fig.24. Lattice parameter versus Nelson-Riley function for the reflections attributed to Ni_5Hf in NHS2-as solidified.

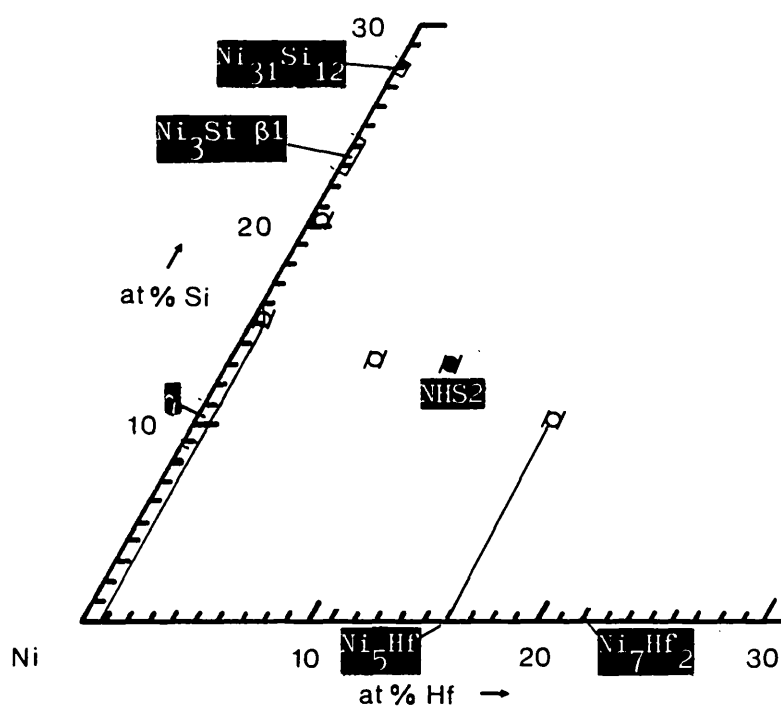


Fig.25. Ni-Hf-Si: EPMA data showing the compositions of eutectic Ni_5Hf , γ , and Ni_3Si in NHS2-as solidified. The alloy composition lay within these three points.

As-solidified	NHS1		NHS2		NHS3		NHS4		NHS5	
	a_o	r	a_o	r	a_o	r	a_o	r	a_o	r
γ solid soln.	0.352	0.6	0.356	0.7	0.352	0.4	0.353	0.7		
Ni ₅ Hf "	0.667	0.8	0.668	0.8	0.667	0.6	0.669	0.54	0.668	0.6
1125 °C										
γ solid soln.	0.352	0.8	0.352	0.7	0.352	0.4	0.353	0.5		
Ni ₅ Hf	0.668	0.2	0.668	0.5	0.667	0.2	0.666	0.24		
926 °C										
Ni ₃ Si β_1	-	-	-	-						
Ni ₅ Hf	0.668	0.3	0.668	0.8						

Table 25: Lattice parameters calculated from X-ray diffraction results for as-solidified and heat-treated Ni-Hf-Si alloys

a_o - lattice parameter as computed by Nelson-Riley function
r - correlation coefficient of data

b. Ni-9.9 at.% Hf-13.0 at.% Si (NHS2-As solidified)

The structure, as viewed by interference film microscopy, consisted of primary dendrites, which were surrounded by a white phase or phases and a small volume fraction of eutectic, (fig.21b).

The primary phase was identified by x-ray diffraction and EPMA to be Ni_5Hf . It contained 10.1 at.% Si according to energy dispersive analysis. The lattice parameter was calculated to be 0.668 nm using the Nelson Riley function (fig.24) (table 25).

Initially, the microstructure was interpreted as consisting of Ni_5Hf and a eutectic. The eutectic was identified as Ni_5Hf and γ . However, more detailed study of the as-solidified and heat treated microstructures using EPMA showed that the alloy was in fact three phase. The white area surrounding primary Ni_5Hf particles consisted of γ and $\text{Ni}_3\text{Si } \beta_1$. The compositions of the phases are given in table 24. The composition of γ agreed well with the literature (33). The composition of $\text{Ni}_3\text{Si } \beta_1$ did not (see section 4.2.1.b). By x-ray diffraction there was difficulty in distinguishing between $\text{Ni}(\gamma)$ and $\text{Ni}_3\text{Si } \beta_1$ (see section 4.1.2.c). The alloy composition lay inside a triangle of the measured compositions of the constituents of the non-primary phases (fig.25).

c. Ni-1.9 at.% Hf-22.8 at.% Si. (NHS3-As solidified).

The alloy, as viewed by interference film microscopy, consisted of large needles; small volume fractions of a darker phase which was usually associated with the needles;

areas containing large particles of grey and white phases, and finally; small volume fractions of eutectic dispersed throughout this area also (fig.21c).

Phases in this specimen were identified mainly by EPMA. X-ray diffraction data was confusing due to the large number of reflections observed. The primary phase in this alloy was $\text{Ni}_{31}\text{Si}_{12}$ which grew in the form of needles. The measured composition Ni-0.04 Hf-27.7 Si agreed well with data given in the literature (33). Other phases found in this alloy included Ni_5Hf , $\text{Ni}_3\text{Si } \beta 1$, $\text{Ni}_3\text{Si } \beta 2$ or $\beta 3$, and $\text{Ni}(\gamma)$ (table 24). The fact that there are 5 phases in this alloy clearly indicates a lack of equilibrium.

The $\text{Ni}_3\text{Si } \beta 2$ or $\beta 3$ phase was observed at the edges of the $\text{Ni}_{31}\text{Si}_{12}$ needles. This is the darker phase in the micrograph (fig.21c). By x-ray diffraction data it was not possible to identify whether the phase was $\beta 2$ or $\beta 3$ because of the large number of reflections observed and even when certain reflections had been attributed to other phases, i.e. Ni_5Hf , the remaining reflections could not be identified with those given in the literature for $\text{Ni}_3\text{Si } \beta 2$ or $\beta 3$ (45). In the areas surrounding the needles three phases were identified. These were Ni_5Hf , $\text{Ni}_3\text{Si } \beta 1$, and $\text{Ni}(\gamma)$. The compositions of the phases are given in table 24. Small eutectic regions were also observed. The composition of one area of eutectic was found to be Ni-7.4 at.% Hf-16.2 at.% Si and of another to be Ni-7.3 at.% Hf-18.9 at.% Si. Tie lines constructed between Ni_5Hf and $\text{Ni}_3\text{Si } \beta 1$ and Ni_5Hf and $\text{Ni}_3\text{Si } \beta 2$ or $\beta 3$ passed through the

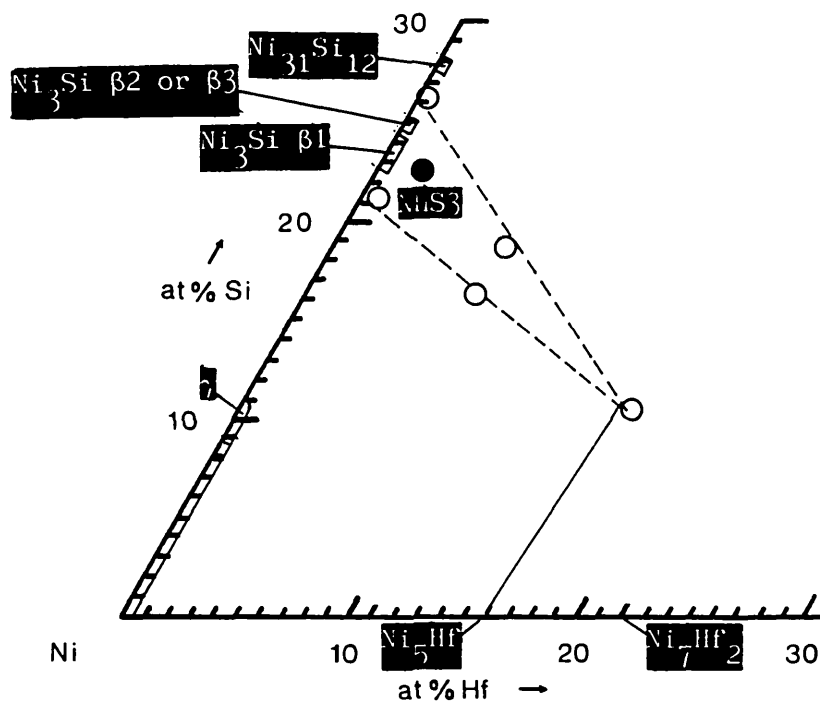


Fig.26. Ni-Hf-Si: Compositions of the phases, compounds and eutectics in NfS₃-as solidified, as determined by EPMA.

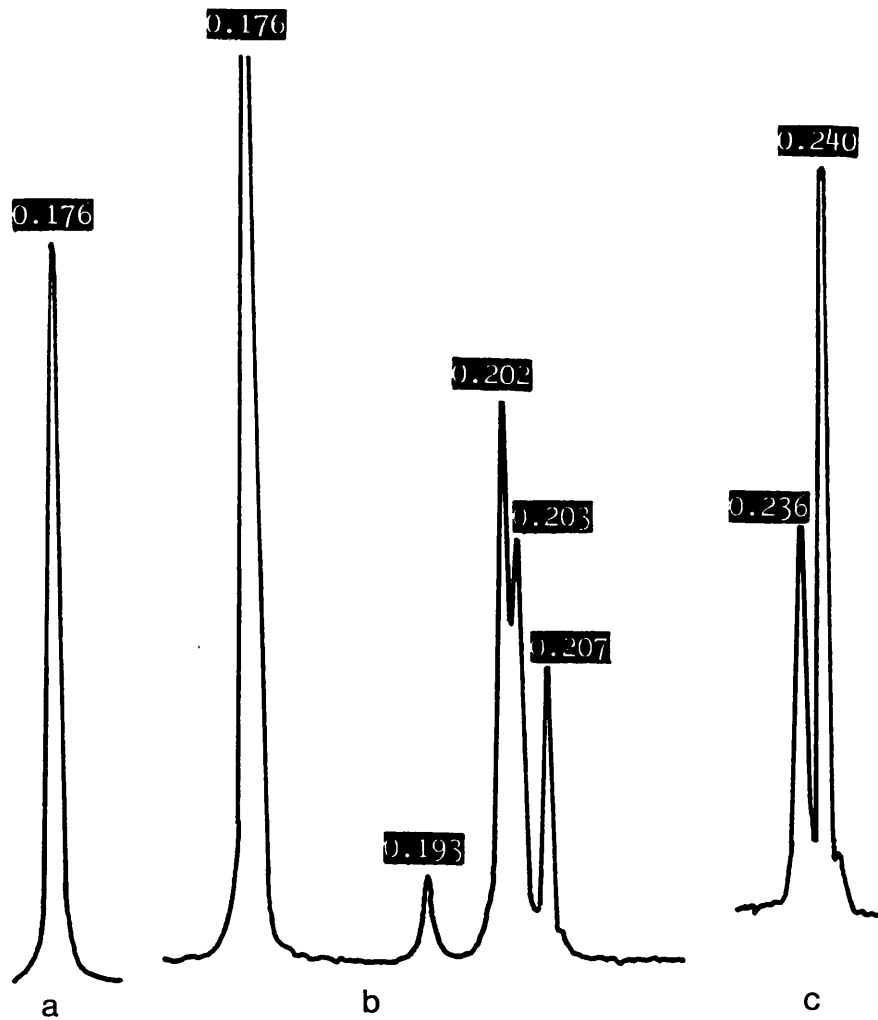


Fig.27 NHS4-as solidified: Reflections at 0.240 nm and 0.207 nm could not be indexed as γ or Ni_5Hf reflections. Reflections at 0.20156 nm and 0.176 were surprisingly more intense than at 0.203 nm which was expected to be the most intense γ reflection.

measured eutectic compositions (fig.26). Despite the large number of reflections observed by x-ray diffraction, it was possible to identify Ni_5Hf from other compounds or phases. The lattice parameter of Ni_5Hf was calculated to be 0.667 nm using the Nelson Riley function (table 25).

d. Ni-3.3 at.% Hf-5.2 at.% Si (NHS4 As-solidified).

This specimen consisted of a single primary phase and a eutectic (fig.21d).

By EPMA the primary phase was identified as $\text{Ni}(\gamma)$. The eutectic consisted of two phases, Ni_5Hf and $\text{Ni}(\gamma)$. The composition of the eutectic was obtained by EPMA and is given in table 24. However, certain reflections were observed by x-ray diffraction, ie. at 0.240 nm and 0.207 nm, which could not be indexed and were not reflections of Ni_5Hf or $\text{Ni}(\gamma)$ (fig.27). Also the relative intensities of some reflections were not found to be in the correct proportions. For example, the reflection at 0.088 nm (400) should only be 4% of the main peak at 0.203 nm (111) for $\text{Ni}(\gamma)$. This reflection was not observed in the corresponding Ni-Zr-Si alloy, i.e. NZS1-as solidified, which consisted of γ and Ni_5Zr . Also, since the volume fraction of the primary $\text{Ni}(\gamma)$ phase accounted for most of the microstructure then the reflection observed at 0.203 nm (111) should have been the most intense line. The reflections at 0.202 nm and 0.176 nm (200) were both more intense (fig.27). This could be accounted for by the presence of Ni_3Si . Ni_3Si β_2 has reflections at 0.245 nm (021), 0.212 nm (311), 0.201 nm (220), 0.174 nm (402).

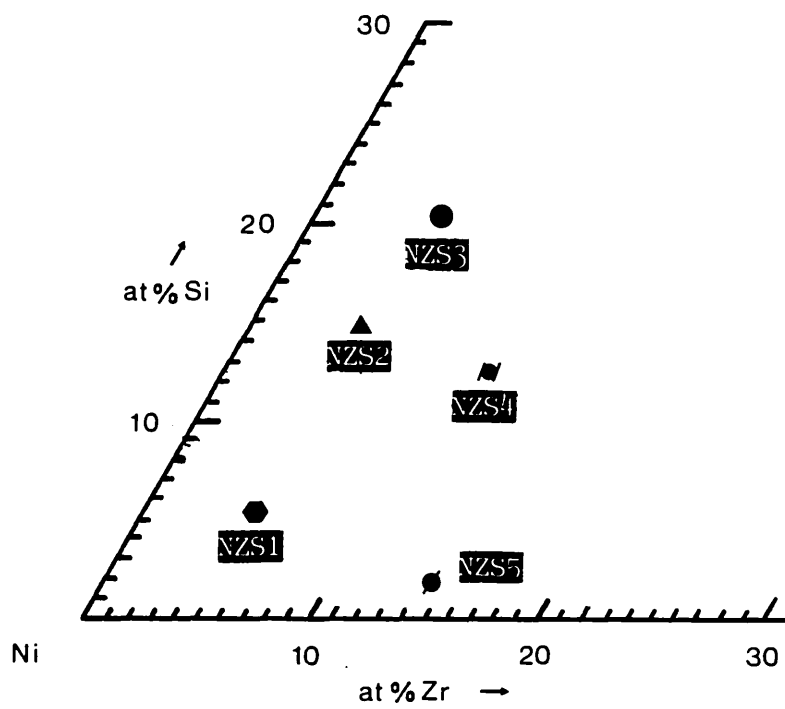


Fig.28. Schematic representation of the compositions of the model Ni-Zr-Si alloys.

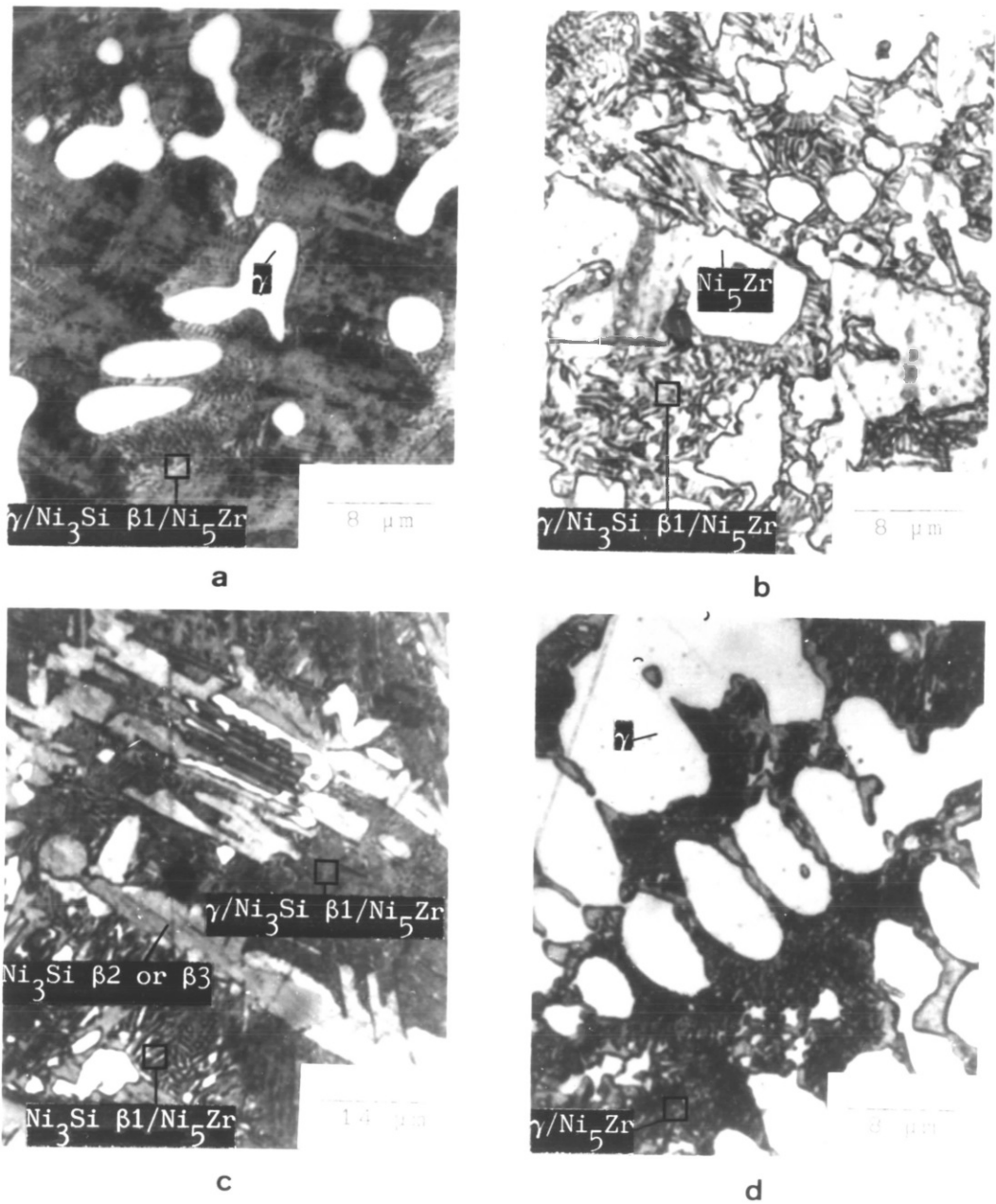


Fig 29

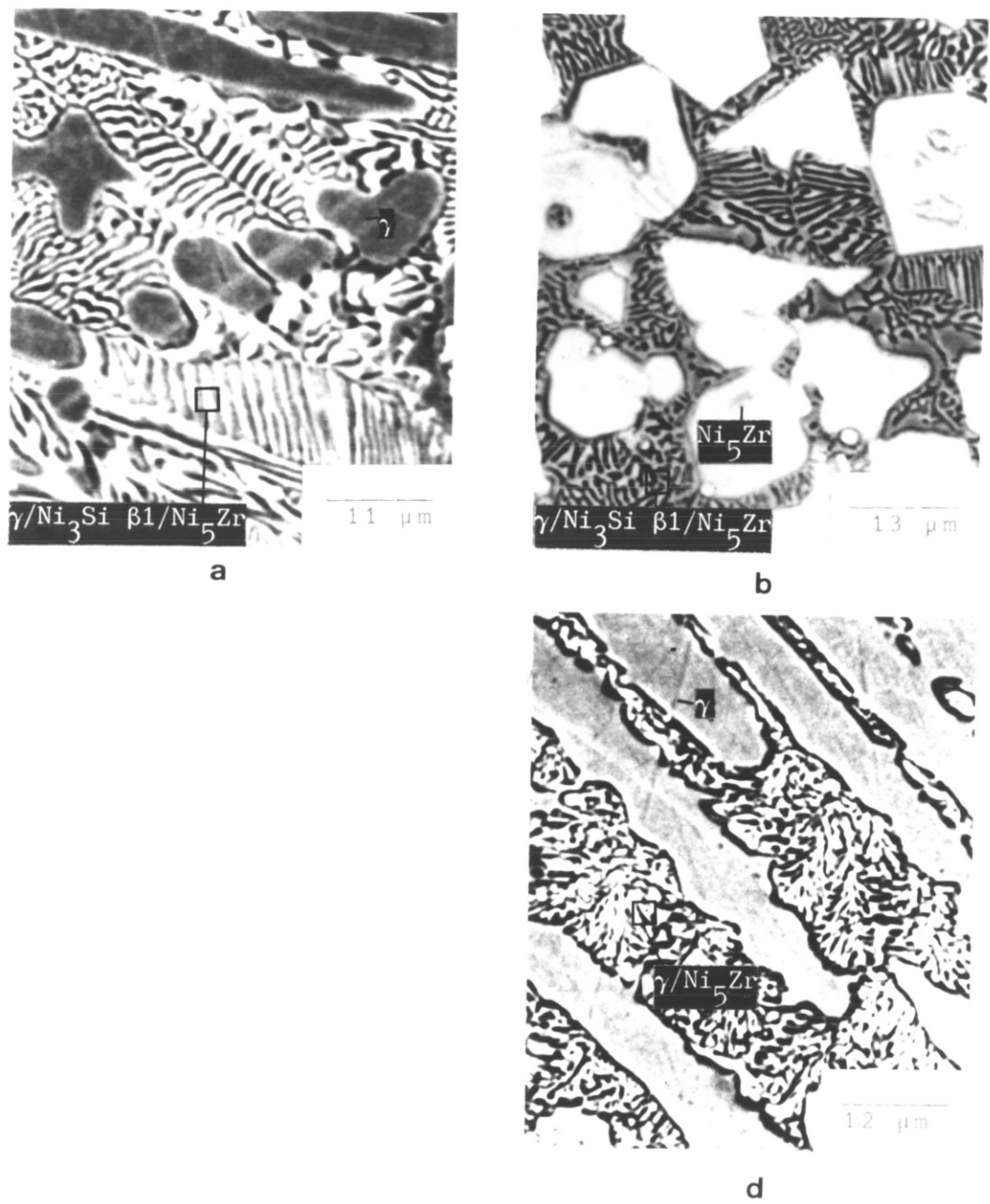
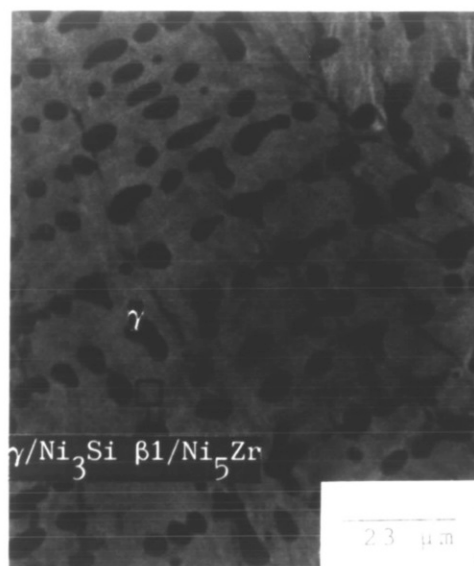
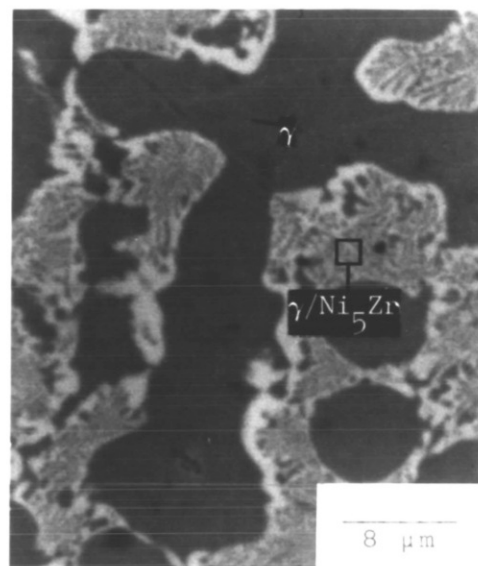


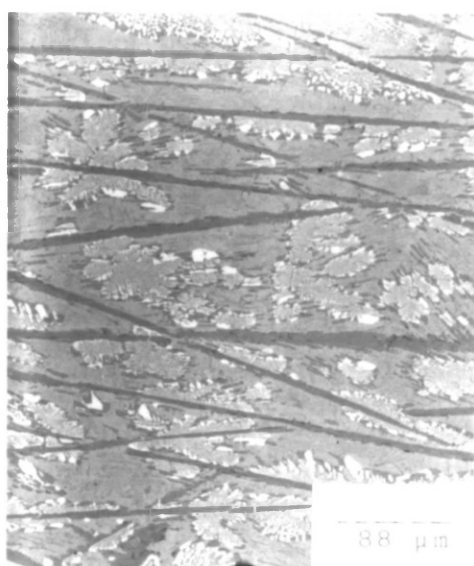
Fig 30



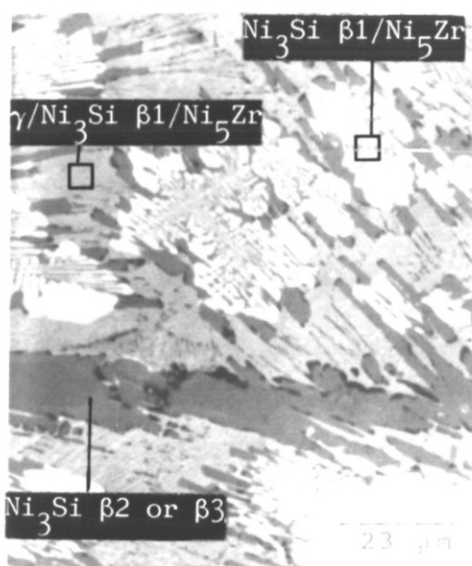
e



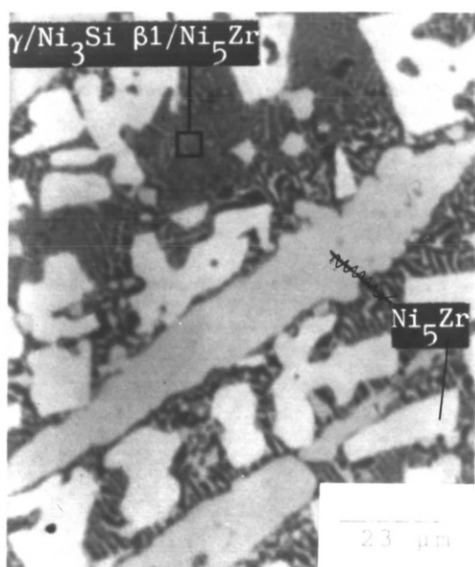
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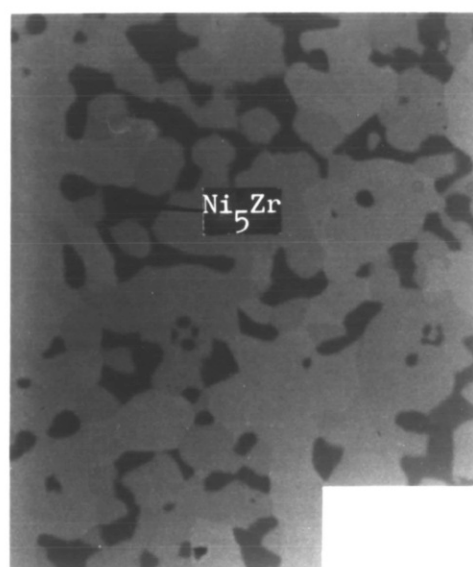
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h



i



j

Fig 30

Ni_3Si $\beta 1$ has a reflections at 0.202 (111) and at 0.175 nm (200).

e. Ni-14.6 at.% Hf-approx. 2.0-3.0 at.% Si. (NHS5-As solidified)

The composition of the alloy was uncertain with respect to the amount of silicon (See 4.1.2.e).

The structure, viewed by interference film microscopy, consisted of needles outlined with a second phase. The rest of the structure consisted of a eutectic (fig.21e).

The phases and compounds in the structure were identified by wavelength dispersive EPMA. The needle centres contained 21.5 at.% Hf and 0.8 at.% Si, which corresponded to Ni_7Hf_2 (31). The phase forms congruently at 1480°C (31). The compound was outlined with Ni_5Hf . Its composition was Ni- 16.1 at.% Hf- 0.9 at.% Si. A eutectic was also observed in this alloy and its composition was Ni-8.0 at.% Hf-4.6 at.% Si.

Three phases were identified by x-ray diffraction. These were Ni_7Hf_2 , Ni_5Hf and γ .

3.2 Ni-Zr-Si Alloys.

The compositions of the Ni-Zr-Si alloys are shown graphically in fig.28.

3.2.1 As-solidified alloys.

a. Ni-4.9 at.% Zr-15.0 at.% Si (NZS2 As-solidified)

The structure, as viewed by light microscopy and SEM, consisted of a primary phase and a eutectic (figs.29a,30a,30e).

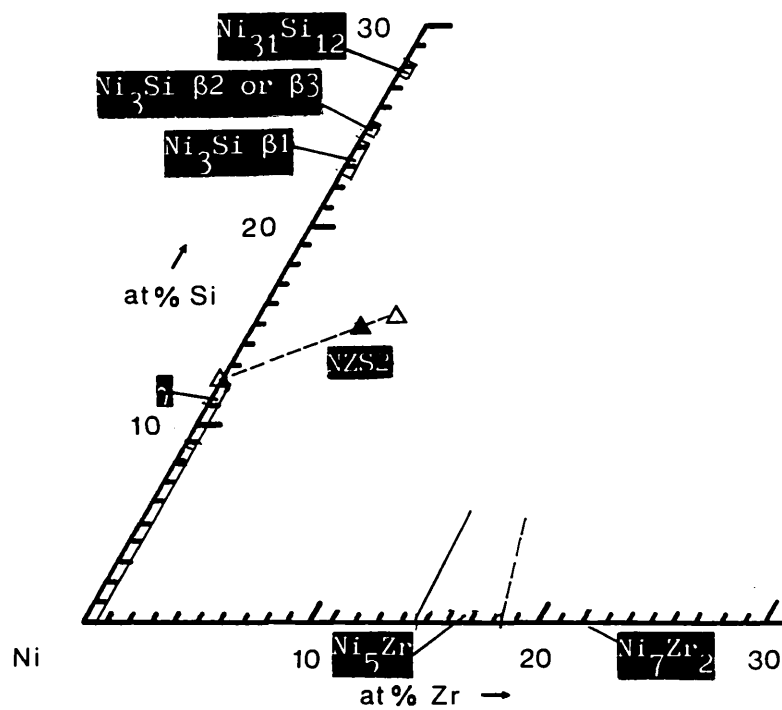


Fig.31. Ni-Zr-Si: The compositions of γ and the ternary eutectic, as determined by EPMA. The alloy composition lies in this line.

The composition of the primary phase, determined by EPMA, was Ni-0.0 at.% Zr-12.2 at.% Si. This corresponded to Ni(γ). A large volume fraction of the microstructure was eutectic. The composition of the eutectic was Ni-6.0 at.% Zr-15.6 at.% Si. A tie line could be drawn between the compositions of γ and eutectic and that line passed through the alloy composition (fig.31). A close study of the eutectic in the micrograph (fig.30a) showed that it could consist of 3 phases. The backscattered electron images in particular, revealed a very dark phase, a grey phase, similar in shade to the primary dendrites, and a white phase. Phases containing atoms of high atomic weight would be whiter the higher the atomic weight. This was observed in all these alloys where the Ni₅Hf or Ni₅Zr phase was white and phases like Ni₃Si were quite dark because elements like hafnium and zirconium exhibited very limited solubility in them. Therefore, the eutectic was interpreted as consisting of Ni₅Zr, Ni(γ) and Ni₃Si β 1, β 2 or β 3. X-ray diffraction results confirmed the presence of Ni₅Zr and Ni(γ). Many more reflections were also observed and these corresponded very well to reflections observed in NHS3 As-solidified and NHS4 As-solidified, but not particularly to Ni₃Si β 1, β 2 or β 3. It is suggested that the phase corresponding to these reflections may be related in some way to the high temperature forms of Ni₃Si or even, perhaps, to a combination of both, bearing in mind the large number of reflections which did not correspond to exactly one form or the other.

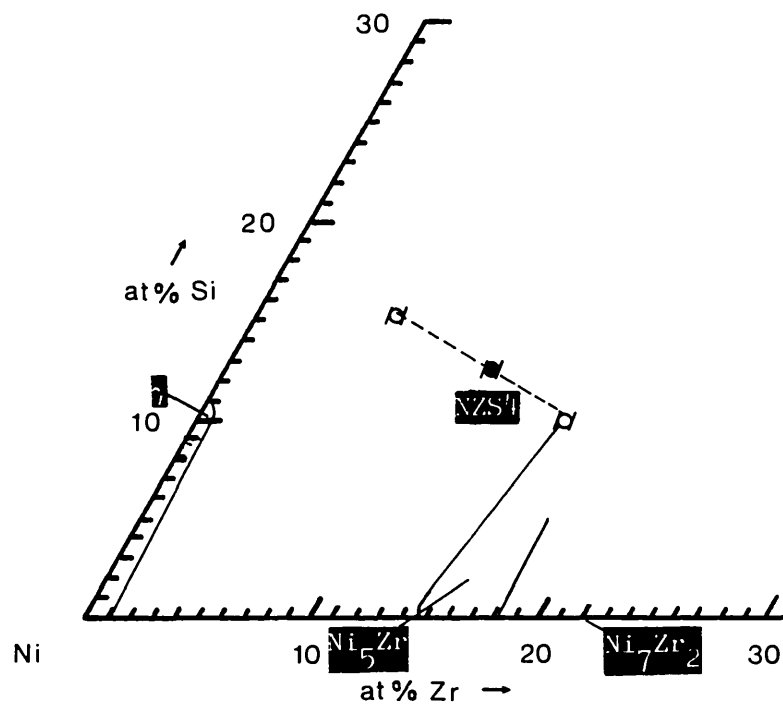


Fig.32. Ni-Zr-Si: Compositions of Ni_5Zr and a ternary eutectic, as determined⁵ by EPMA. The alloy composition lies on a line joining the two.

b. Ni-11.6 at.% Zr-12.8 at.% Si (NZS4 As-solidified)

The structure, viewed by interference film microscopy and SEM, consisted of a primary phase and a eutectic according to figs.29b & 30b. However, fig.30i shows that there were two phases and a eutectic in one area of the sample.

The composition of the primary phase, measured by EPMA, was Ni-16.2 at.% Zr-10.0 at.% Si, which was interpreted to be Ni_5Zr . The composition of the eutectic was Ni- 6.1 at.% Zr- 15.4 at.% Si. Comparison with the composition of the eutectic of NZS2 As solidified, showed that the eutectics were similar in both alloys. The eutectic is, therefore, also believed to be three phase. X-ray diffraction confirmed the existence of Ni_5Zr . Many of the reflections for $\text{Ni}(\gamma)$ overlap those for $\text{Ni}_3\text{Si } \beta 1$. This was seen in NZS2 As-solidified. Many other reflections were observed which also appeared in NZS3 As-solidified.

Again a tie line could be drawn between the Ni_5Zr and eutectic compositions which passed through the composition of the alloy (fig.32).

c. Ni-5.5 at.% Zr-20.7 at.% Si (NZS3 as-solidified)

The structure, viewed by light microscopy and SEM, consisted of a primary phase in needle form, particles of another white phase which was believed to be a constituent of a eutectic, and two eutectics, one with a coarse and one with a fine structure (figs.29c, 30g,30h).

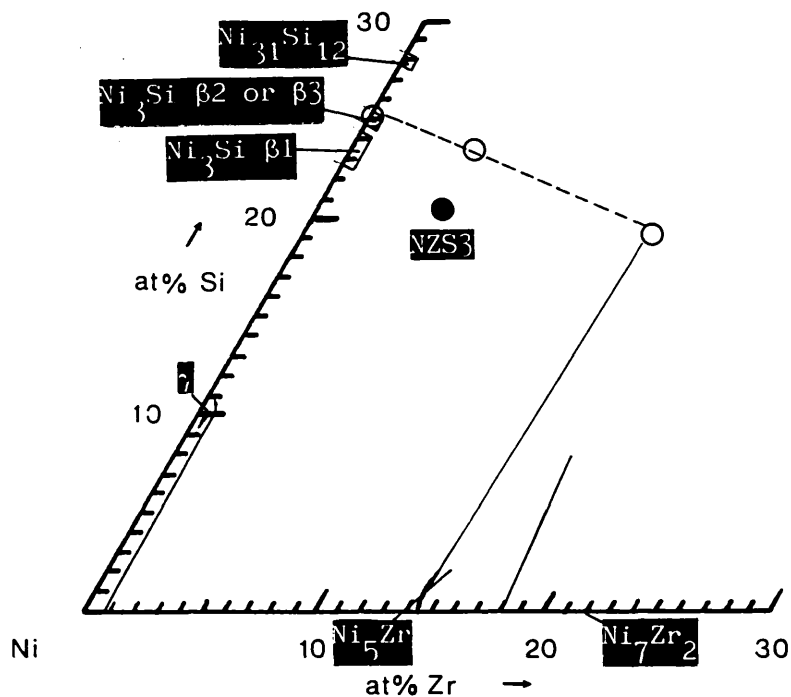


Fig.33. Ni-Zr-Si: Compositions of phases, compounds and eutectics in NZS3-as solidified. The composition of the binary eutectic lies on a line between Ni₅Zr and Ni₃Si β₂ or β₃.

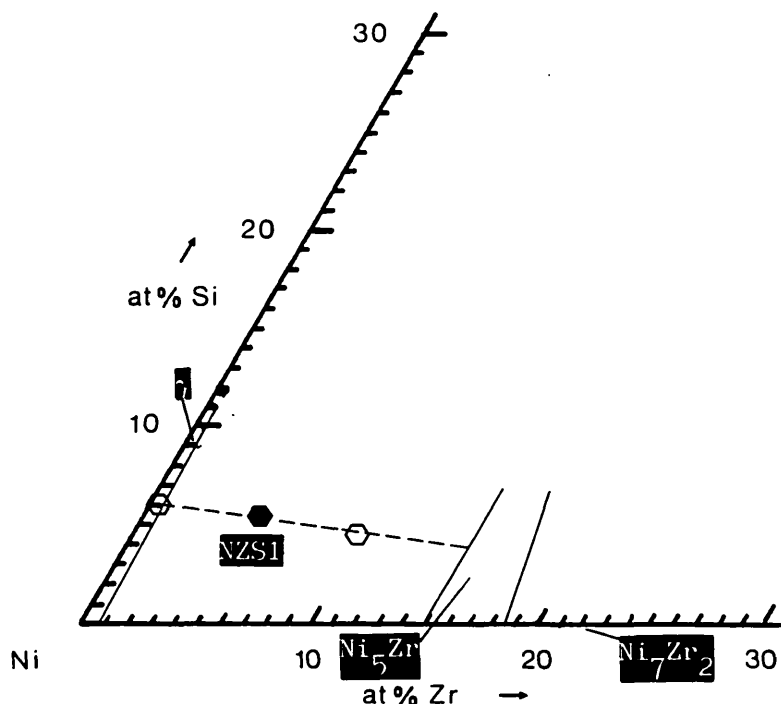


Fig. 34. NZS1 As solidified: Compositions of the phases and eutectics measured by EPMA.

Ni ₃₁ Si ₁₂ (nm)		CALC	NHS3AC	NHS3HT	NZS3AC
0.334	(110)				0.334
0.322	(111)				0.322
0.2931	(112)		0.294		0.293
0.2613	(202)	0.262			
0.2585	(113)	0.260	0.259	0.261	0.259
0.2260	(105)			0.226	
0.2184	(210)			0.219	0.217
0.2150	(211)	0.215	0.215	0.215	0.215
0.2103	(204)		0.211	0.210	0.210
0.2057	(212)				
0.1977	(115)		0.199		0.198
0.1924	(300)			0.194	0.193
0.1872	(205)				
0.1778	(214)			0.178	0.178
0.1742	(116)	0.175			
0.1669	(206)				
0.1631	(215)	0.164	0.163	0.163	0.163
0.1588	(311)	0.160	0.158		0.159
0.1543	(223)	0.156		0.155	

Table 26: Reflections attributed to Ni₃₁Si₁₂ in several specimens.

The composition of the primary phase which formed in the shape of needles was Ni-0.0 Zr-25.7 Si which corresponded to one of the high temperature forms of Ni_3Si i.e. β_2 or β_3 . Two eutectic compositions were measured in this alloy. One of these corresponded closely to the eutectic in NZS2 As-solidified and NZS4 As-solidified and contained Ni-4.2 Zr-15.3 Si. The composition of the other was Ni-5.4 Zr-23.8 Si. This composition point lay on a tie line joining Ni_3Si (β_2 or β_3) and Ni_5Zr (fig.33). The composition of Ni_5Zr in this eutectic was Ni-15.6 Zr-19.3 Si. The presence of Ni_5Zr in the specimen was confirmed from x-ray diffraction also. More reflections were observed in this alloy than in any other Ni-Zr-Si alloy. Many of the reflections observed in the other alloys were found to be more intense in this alloy. Some of these reflections were associated with $\text{Ni}_{31}\text{Si}_{12}$ (table 26) - $\text{Ni}_{31}\text{Si}_{12}$ reflections from NZS3 As-solidified).

d. Ni-5.0 at.% Zr-5.5 at.% Si (NZS1 As-solidified).

The structure of this alloy consisted of a primary phase and a eutectic (fig.29d,30d,30f).

The composition of the dendrites, by EPMA, was Ni- 0.3 Zr- 6.0 Si, which corresponded to γ . The composition of the eutectic was Ni- 9.8 Zr- 4.7 Si. Unlike NHS4-as solidified, all the x-ray diffraction reflections observed were indexed as corresponding to the phases $\text{Ni}(\gamma)$ or Ni_5Zr .

A tie line between γ and Ni_5Zr passed through the alloy composition (fig.34).

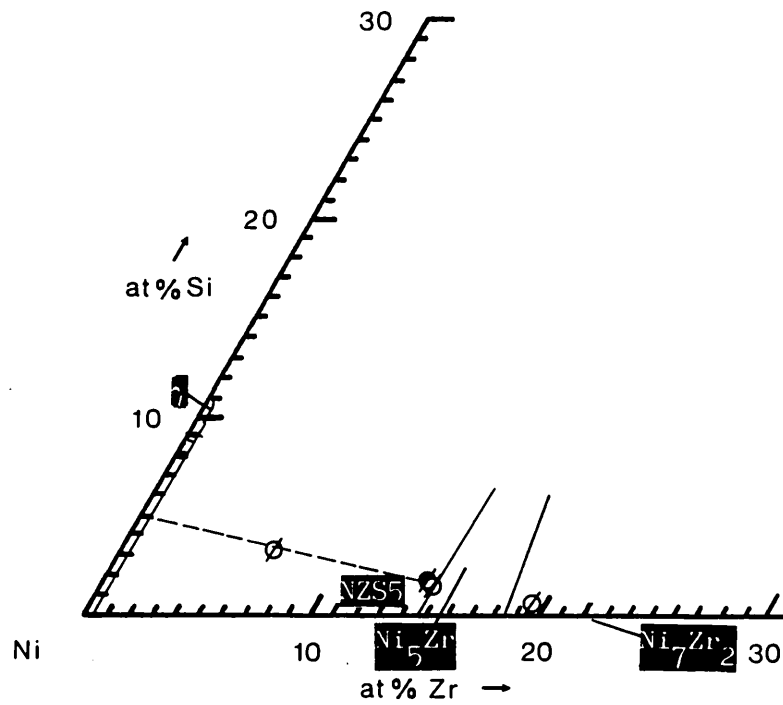


Fig.35 The compositions of the phases and compounds measured by EPMA in NZS5 as-solidified.

As-solidified	NZS2			NZS4			NZS3			NZS1			NZS5		
	Ni	Zr	Si	Ni	Zr	Si	Ni	Zr	Si	Ni	Zr	Si	Ni	Zr	Si
Composition	80.1	4.9	15.0	75.5	11.6	12.8	73.8	5.5	20.7	89.5	5.0	5.5	83.5	14.6	1.9
γ solid soln.	87.7	0.0	12.2							93.7	0.3	6.0			
Ni ₅ Zr				73.8	16.2	10.0	65.2	15.6	19.3				83.6	14.9	1.5
Ni ₇ Zr ₂													79.9	19.4	0.7
Ni ₃ Si β 1															
Ni ₃ Si β 2 or β 3							74.3	0.0	25.7						
Ni ₃₁ Si ₁₂															
Eutectic (1)	78.4	6.0	15.6	78.4	6.1	15.4	80.4	4.2	15.3	85.5	9.8	4.7	89.7	6.9	3.4
Eutectic (2)							70.8	5.4	23.8						

Table 27. EPMA results showing the compositions of the Ni-Zr-Si alloys in the as-solidified state, and of the phases and eutectics observed in them.

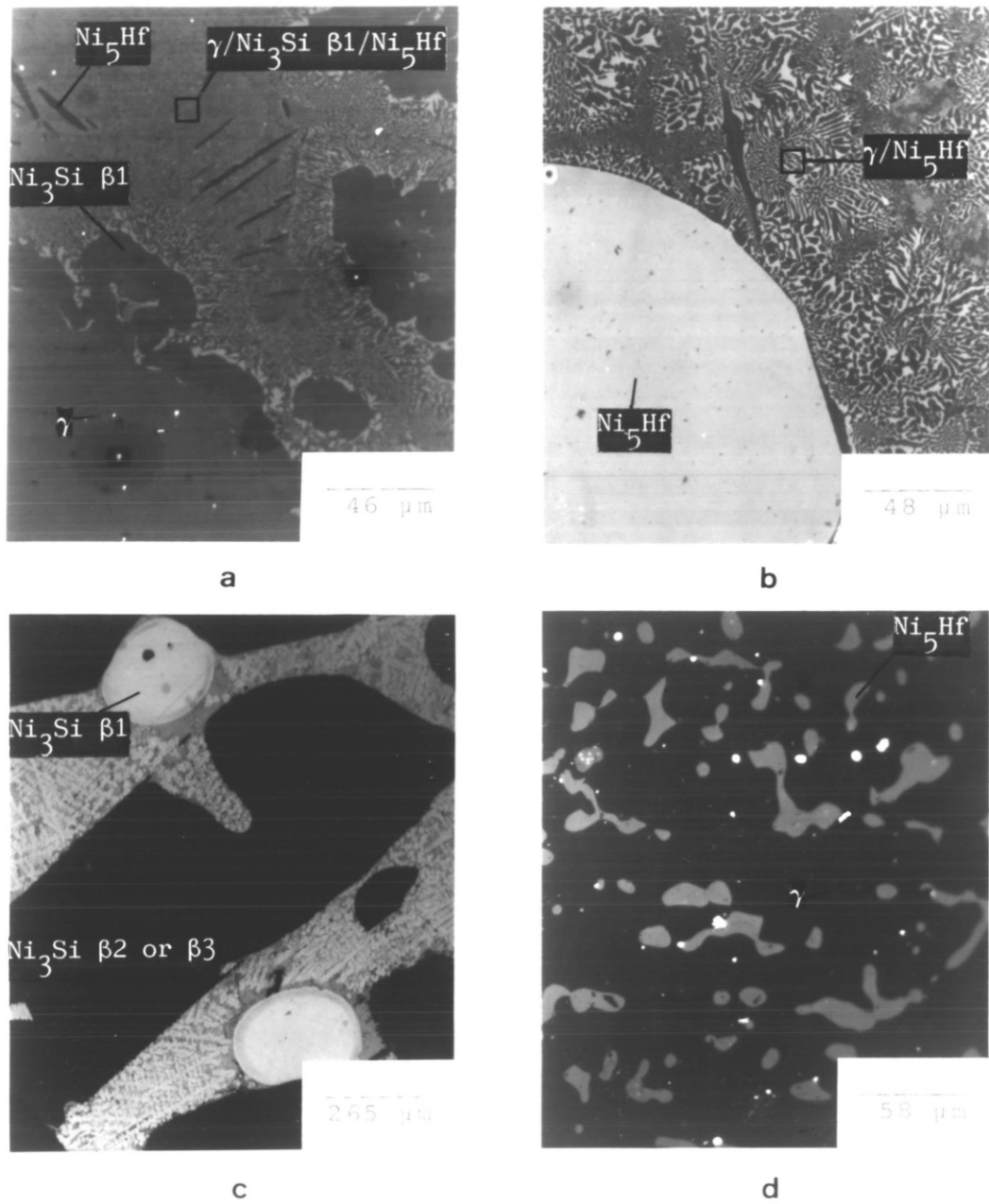
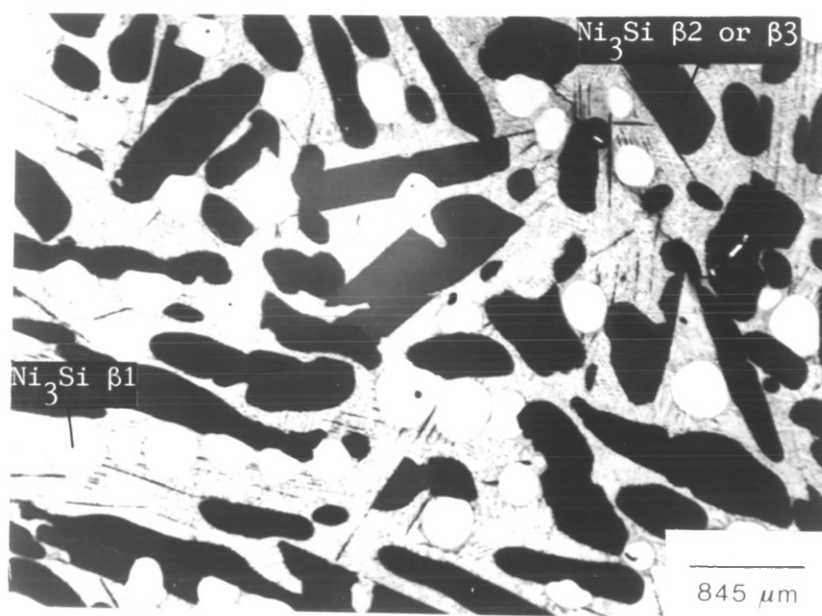
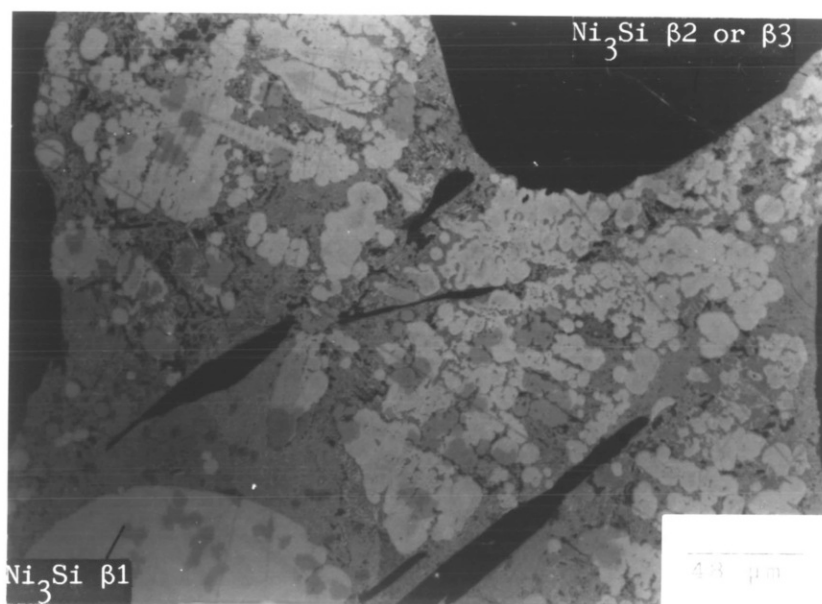


Fig 36



e



f

Fig 36

e. Ni- 16.0 Zr- 3.0 Si (NZS5-as solidified) (Nominal composition)

By EPMA the γ phase and two Ni-Zr intermetallic compounds were identified which were Ni_5Zr and Ni_7Zr_2 (table 27) (fig.35).

3.3 Ni-Hf-Si Alloys.

3.3.1 Heat treated alloys.

a(1). Ni-1.8 at.% Hf-15.5 at.% Si (NHS1-1125:1125°C for 163 hrs.)

The structure, viewed by interference film microscopy, consisted of a large volume fraction of γ , outlined by a second phase. This second phase in its own turn was outlined with small particles. A relatively coarse eutectic then came out from these particles and finally a very fine structure filled the rest of the area in which needles could be found (fig.36a).

A large volume fraction of the alloy was found to consist of $\text{Ni}(\gamma)$ by EPMA and x-ray diffraction. The γ phase was not in its original dendritic form, instead, there were large islands of it. The silicon content was determined to be 14.3 at.%. However, the specimen had partially melted. There was a substantial amount of a very fine eutectic, the composition of which was Ni-6.9 Hf-16.9 Si. The $\text{Ni}(\gamma)$ phase was surrounded by a phase whose composition was measured to be Ni-0.6 Hf-20.4 Si and this was interpreted as Ni_3Si β_1 . The particles around the edge of the islands were hafnium rich. The composition of these was determined

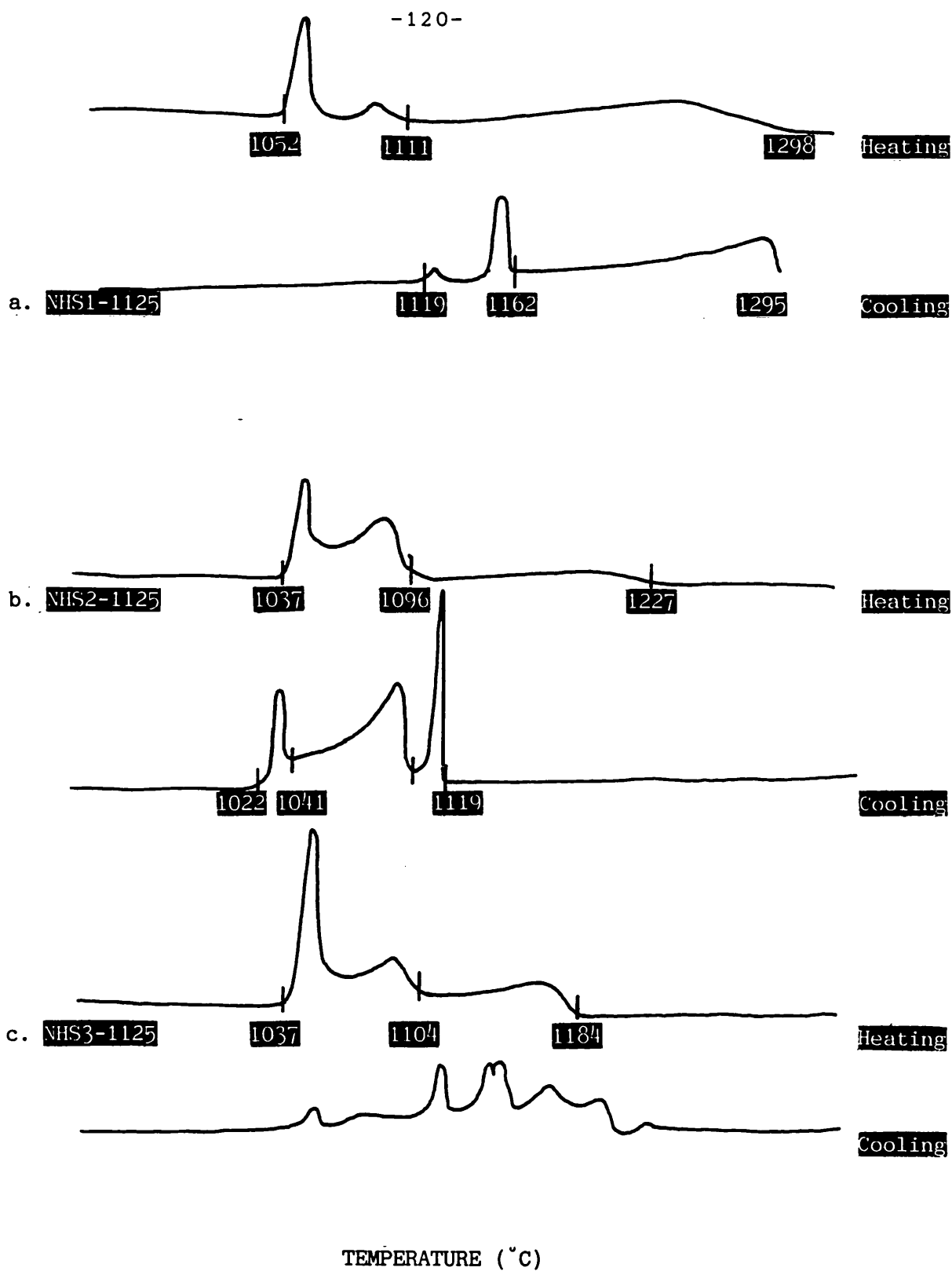
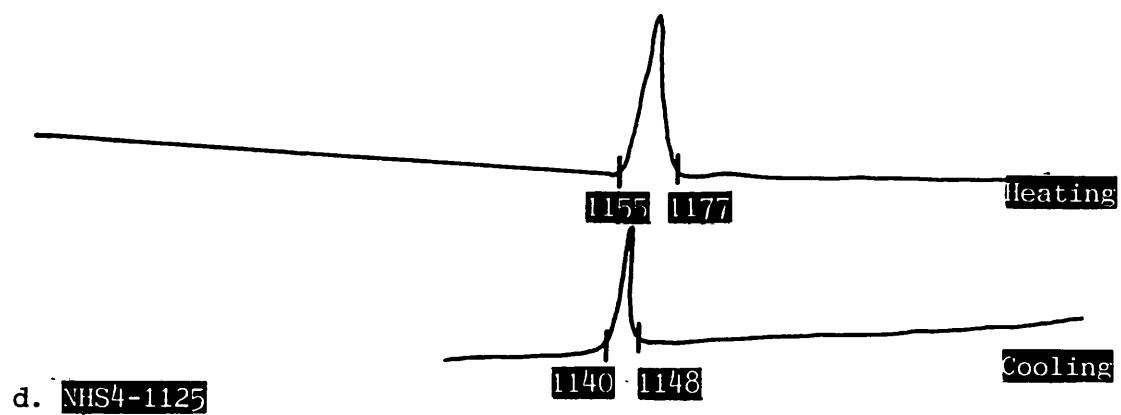


Fig 37a-Fig 37d. DTA curves for samples of the heat-treated NHS alloys, NHS1-NHS4.



TEMPERATURE (°C)

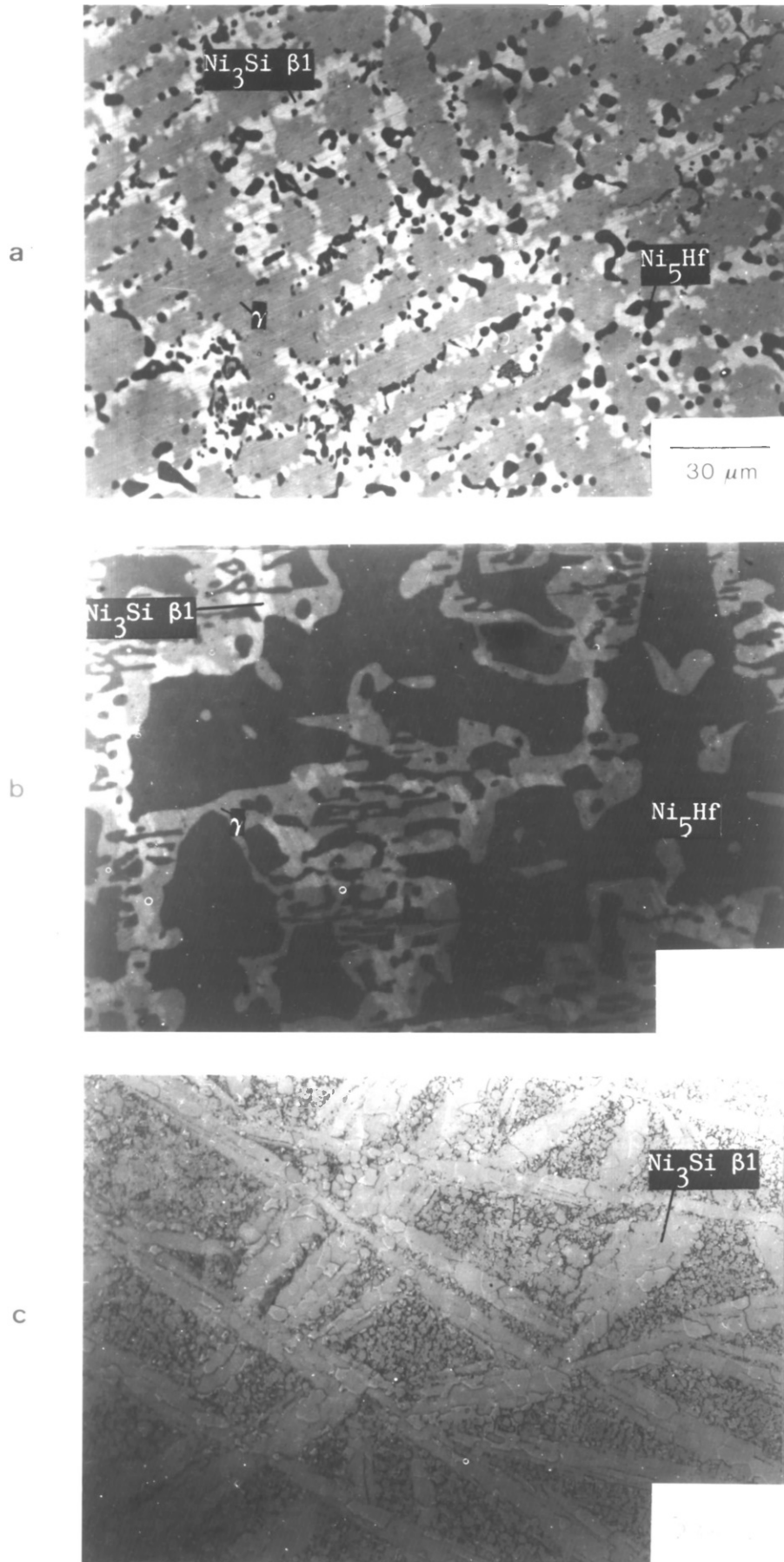


Fig 38

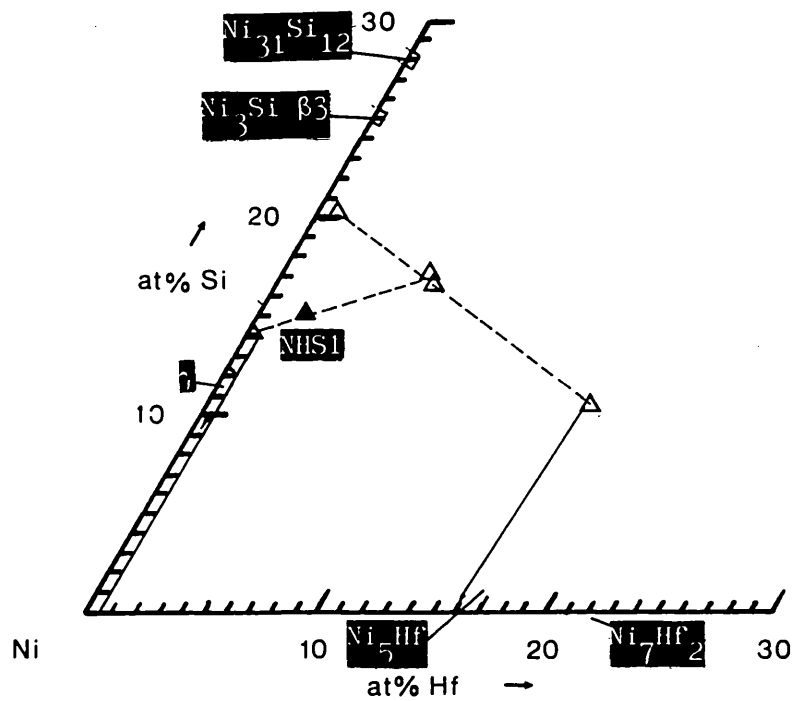


Fig.39 a

NfS1-1125: Schematic of the compositions of γ Ni_3Si β_3 , Ni_5Hf and the eutectics as measured by EPMA.

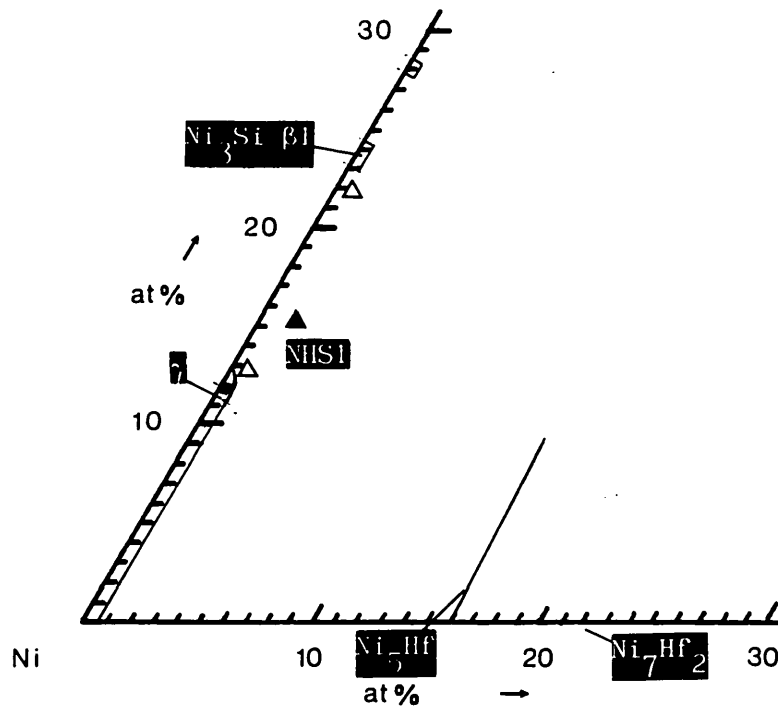


Fig.39 b

NfS1-926: Compositions of γ and Ni_3Si β_1 shown graphically.

926°C	NHS1			NHS2			NHS3		
	Ni	Hf	Si	Ni	Hf	Si	Ni	Hf	Si
Composition	83.0	1.8	15.2	77.0	9.9	13.0	79.6	1.9	18.6
γ solid soln.	86.4	0.6	13.0	83.6	1.1	15.4			
Ni ₅ Hf							77.4	15.8	6.8
Ni ₃ Si β 1	77.3	0.6	22.1	77.9	1.1	21.0	80.2	0.2	19.6

Table 28a: EPMA results showing the compositions of the Ni-Hf-Si alloys heat-treated at 926°C, and of the phases and eutectics observed in them.

1070°C	NHS3		
	Ni	Hf	Si
γ solid soln			
Ni ₅ Hf	72.8	14.4	13.5
Ni ₃ Si β 1	79.2	0.4	20.4
Ni ₃ Si β 2 or β 3	74.2	0.03	25.8
	86.1	18.4	25.5

Table 28b: EPMA results showing the composition of the Ni-Hf-Si alloy heat-treated at 1070°C, and of the phases and eutectics observed in it.

as Ni- 83.4 Hf- 0.8 Si. Some of the needles in the eutectic were found to be Ni_5Hf and the average composition of these was Ni-13 Hf-14.6 Si.

The DTA curve in fig.37a shows that the heat treatment temperature of the sample was above the first reaction observed between 1052°C & 1111°C. The largest peak would be the one for which there was a solid to liquid transformation.

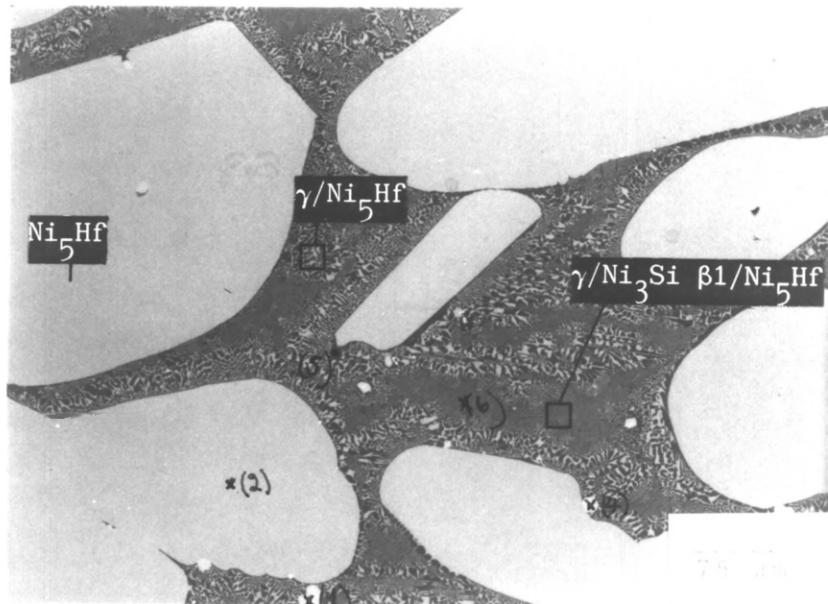
a(2). Ni- 1.8 at.% Hf- 15.2 at.% Si (NHS1-926: composition of as-solidified sample)

The structure, as viewed by interference film microscopy, consisted of three phases (fig.38a). By scanning electron microscopy only two phases could be clearly observed.

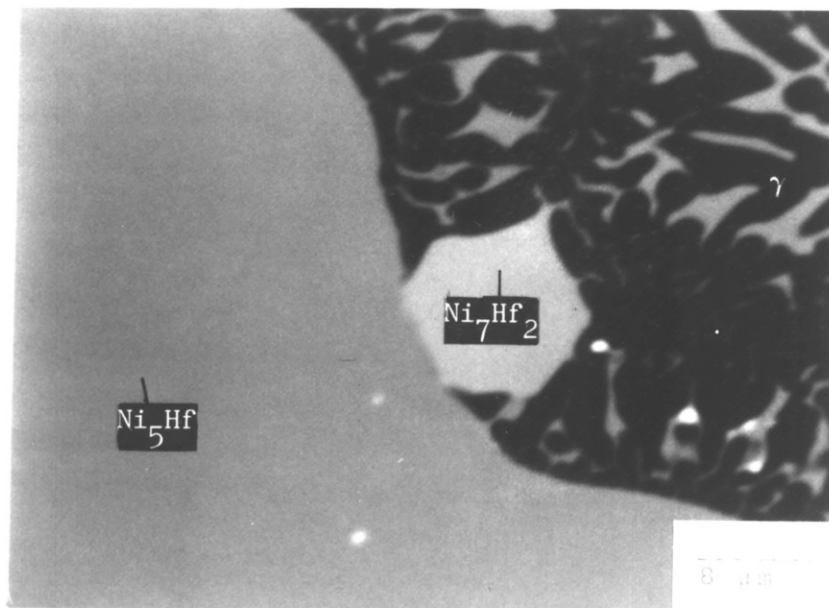
The composition of the dark constituent was not determined but the phase was interpreted to be Ni_5Hf by x-ray diffraction. The compositions of the other two phases were determined by EPMA and they were considered to be γ , with limited solubility of Si up to 13.0 at.%, and Ni_3Si $\beta 1$ (fig.39). The composition of Ni_3Si $\beta 1$ in this sample was found to be much closer to the observed composition (33) (table 28). The degree of solid solubility of Hf in γ and Ni_3Si $\beta 1$ was 0.6 at.%.

By x-ray diffraction γ , Ni_3Si and Ni_5Hf were identified (see section 4.1.2c in which the problem of identification of Ni_3Si $\beta 1$ in the presence of γ is discussed).

It was clear from the DTA results (fig.37a), that this



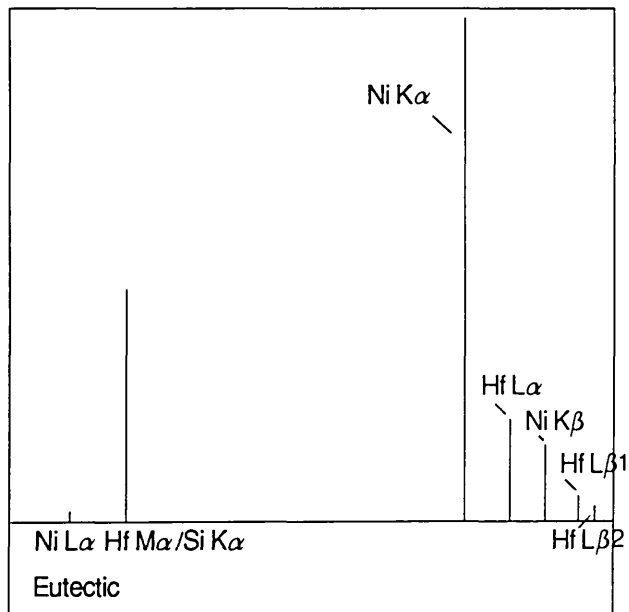
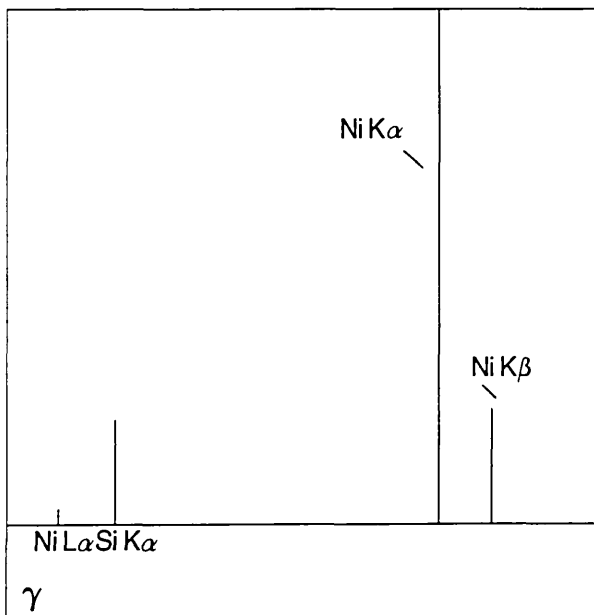
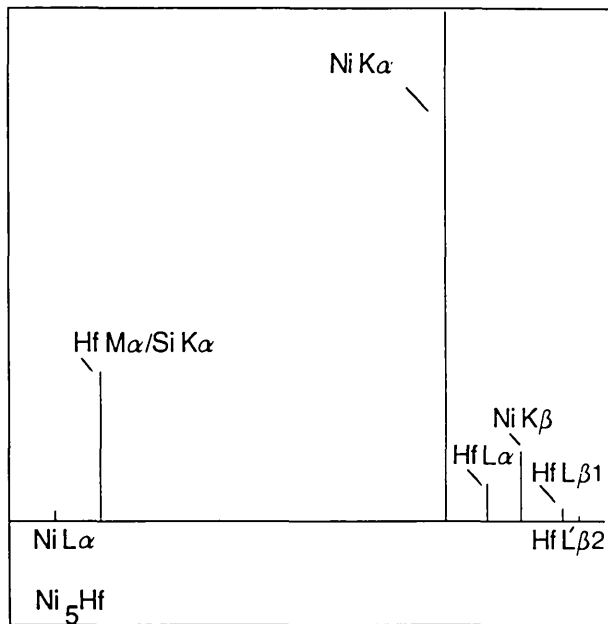
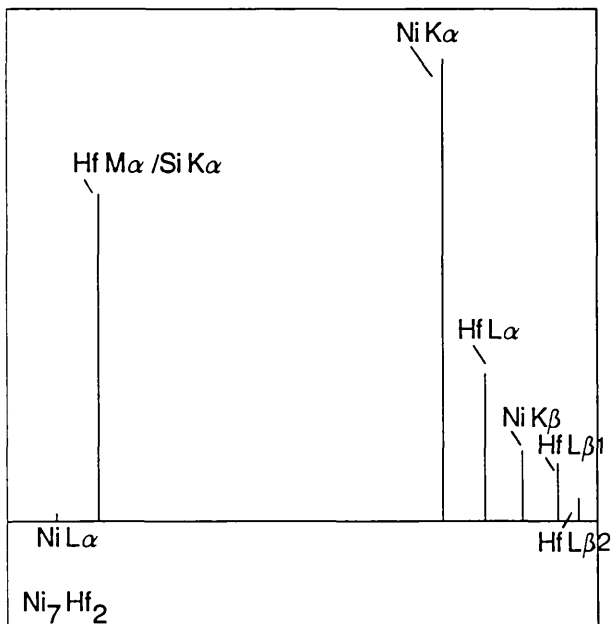
a

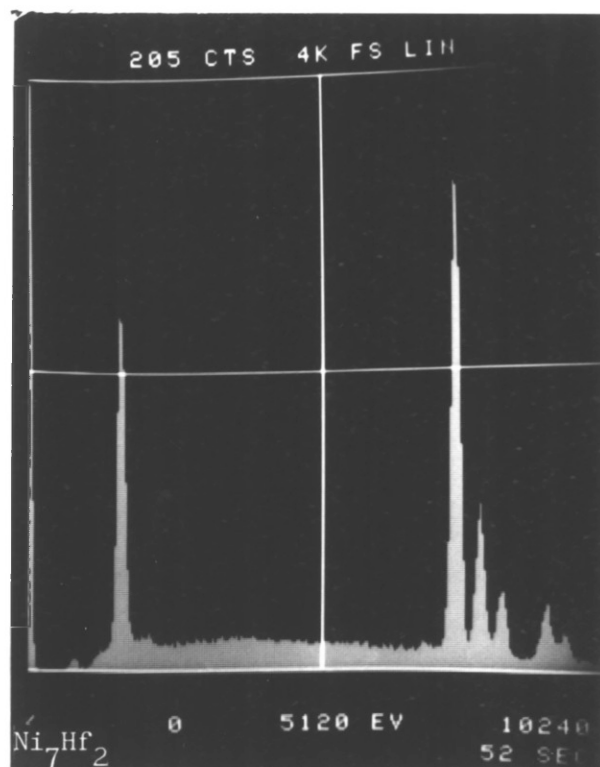


b

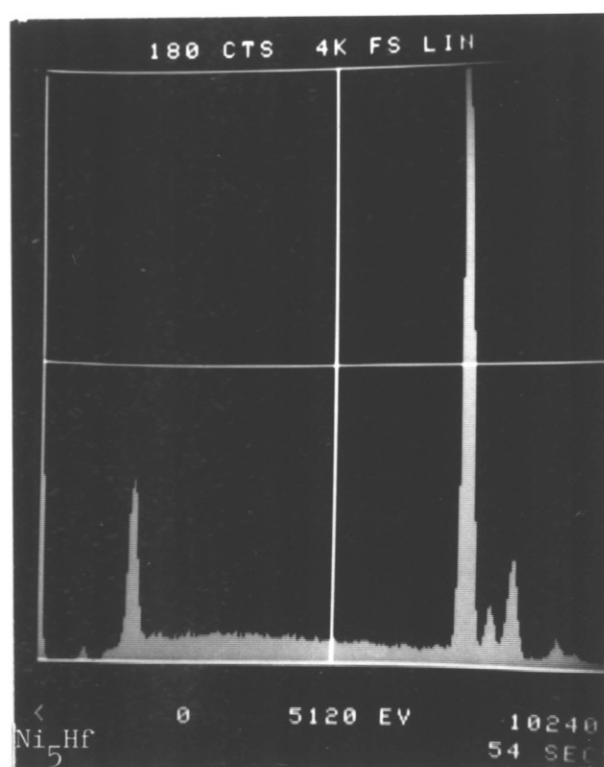
Fig 40

Fig.41 Schematic of the compositions of the phases and compound measured by EPMA in NHS2-1125.

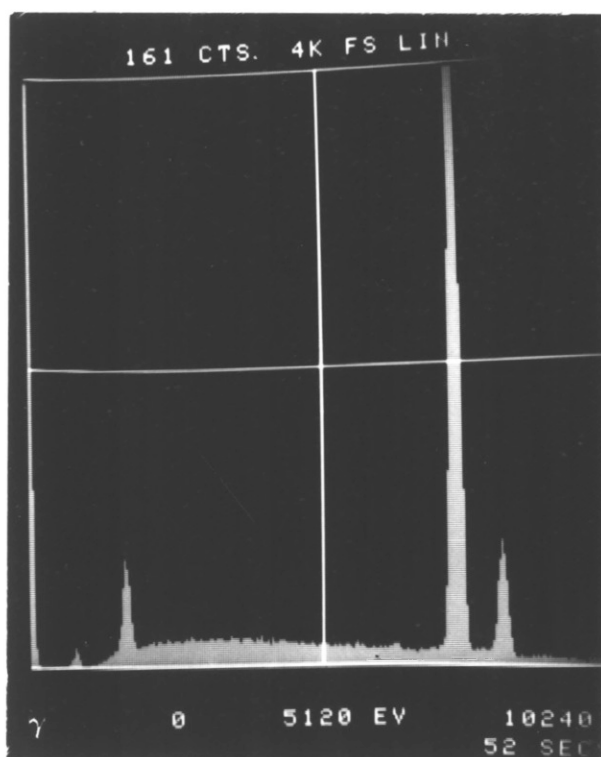




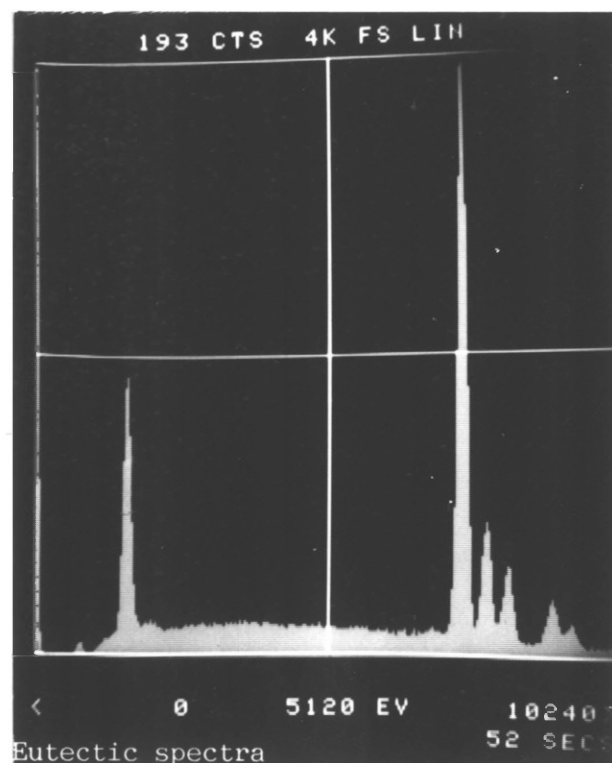
a



b



c



d

Fig 42

specimen was heat treated below the first peaks observed on heating (1052°C-1111°C and below the last observed on cooling (1119°C-1162°C). It is significant that no signs of melting were observed in this specimen. At 1125°C, however, signs of partial melting were evident. This suggests that a liquid phase was involved in the reaction between 1052°C-1111°C.

b(1). Ni-11.2 at.% Hf-12.3 at.% Si (NHS2-1125:1125°C for 163 hrs.)

The primary phase in this specimen was determined to be Ni_5Hf by EPMA and x-ray diffraction. The morphology of the phase had changed from the as-solidified dendritic structure to a structure consisting of large islands of Ni_5Hf (figs.36b,40a). The composition of the phase was Ni-15.4 Hf-10.3 Si. Two eutectics were observed. One had a coarse structure, the other a fine structure. The compositions of the two eutectics were found to be different. The composition of the coarse eutectic was Ni-6.6 Hf-12.6 Si. This was believed to consist of $\text{Ni}(\gamma)$ and Ni_5Hf and the composition of the fine structured eutectic was Ni-6.4 Hf-16.3 Si (fig.41). It was suspected that this alloy had also undergone incipient melting. A very small number of particles were also observed in the microstructure (fig.40b). The composition of these was determined as Ni- 18.8 Hf-18.2 Si by EDS and Ni- 21.4 Hf- 14.6 Si by WDS which were interpreted as being Ni_7Hf_2 . Figs.42a-42d show the spectra, obtained by EPMA, for Ni_7Hf_2 , Ni_5Hf , γ , and the fine-structured eutectic,

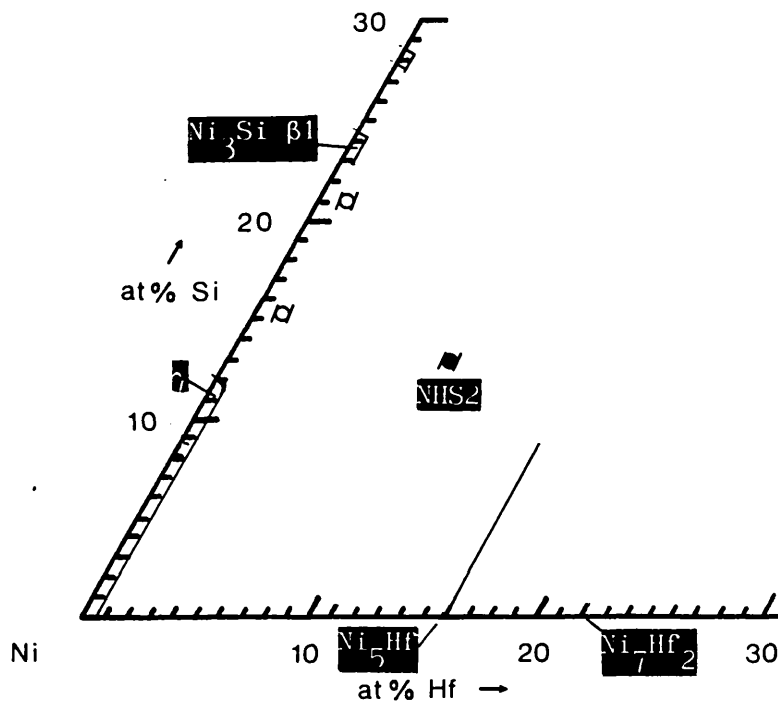


Fig.43 Schematic showing the compositions of γ and $\text{Ni}_3\text{Si } \beta 1$ in NHS2-926.

respectively, for this sample. In fig.42c the only peaks shown are those for nickel and silicon. The additional peaks acquired in figs.42a,42c & 42d were due to hafnium.

DTA results showed that at 1125°C the specimen was above the first peaks observed on heating (1037-1096) (fig.37b). Signs of partial melting were observed and this confirms the existence of a liquid phase in the reaction between 1037°C and 1096°C.

b(2) Ni-9.9 at.% Hf-13.0 at.% Si (NHS2-926: composition of as-solidified sample).

The structure, as viewed by interference film microscopy, consisted of three phases (fig.38b). By backscattered and scanning electron microscopy only two phases were observed clearly.

The composition of the phases, determined by EPMA, were very similar to NHS1-926 (table 28)(fig.43). The Si content of the γ phase was 15.4 at.% which is unusual compared with NHS1-926 because it should be the same at the same temperature. The average amount will obviously depend upon the number of particles analysed and if equilibrium had not been fully attained within the sample, then there would be compositional variations within particles. The Si content of $\text{Ni}_3\text{Si } \beta_1$ was 21.0 at.%.

From the DTA peak in fig.37b, it can be seen that the specimen was heat treated at a temperature lower than that for which the first reaction was observed on heating (1037°C - 1096°C) and no signs of partial melting were observed in the specimen.

By x-ray diffraction γ , Ni_3Si β_1 and Ni_5Hf were observed (see section 4.1.2c). It was noted that the relative peak heights of the reflections at 0.386 nm (Ni_5Hf - (111)) and 0.334 nm (Ni_5Hf - (220)) had changed in comparison to similar reflections observed in specimens of other alloys in which Ni_5Hf was observed.

The major difference between NHS1-926 and NHS2-926 was the volume fraction of constituents (figs.38a,38b). The primary phase in NHS1-926 was γ , whereas in NHS2-926 it was Ni_5Hf . The composition of the as-solidified samples lay within an area defined by the compositions of the constituent phases and compounds.

c(1). Ni-2.1 at.% Hf-22.5 at.% Si (NHS3-1125:1125°C for 163 hrs.)

The structure, as viewed by interference film microscopy, consisted of large islands of a black phase, a very circular white phase, and a large area containing small white dendrites and some needles (fig.36c,36e).

NHS3-1125 showed the most signs of incipient melting after heat treatment, because part of the specimen had changed its original shape. In a backscattered electron image of the microstructure the small dendrites were dark, similar to the most prominent single phase regions. They were believed to be dendrites of Ni_3Si although their composition was not measured. Dendrites of this type have been observed before in Ni-Si alloys (51). The presence of a liquid would explain the rounded shape of the white phase observed in the microstructure.

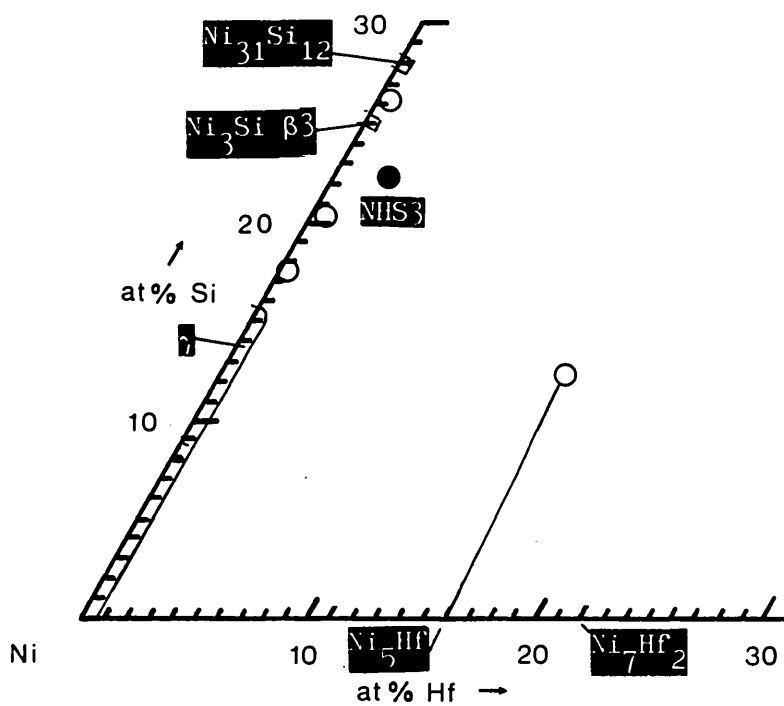


Fig.44 Schematic showing the compositions of the phases and eutectics, and compounds measured by EPMA in NHS3-1125.

- By DTA the heat treatment temperature of this specimen was above the first reaction observed on heating (1037°C - 1104°C), in which a liquid phase was involved (fig.37c). This is in accordance with observation made in other specimens. Indeed, most signs of melting were observed in this specimen. It was noted that at 1125°C this specimen was much closer to the temperature at which the specimens were envisaged to be completely molten - in this case at 1184°C .

The white phase was interpreted to be Ni_3Si $\beta 1$ which would be unstable at 1125°C according to the literature (33) and could thus have been dissolving in the liquid or undergoing transformation to Ni_3Si $\beta 2$ or $\beta 3$. This phase contained 0.6 at.% Hf and 20.4 at.% Si. In the electron backscattering micrograph this phase was black also. The large dark phase particles were Ni_3Si $\beta 2$ or $\beta 3$; EPMA showed that they contained 0.3 at.% Hf and 26.4 at.% Si. The $\text{Ni}_{31}\text{Si}_{12}$ phase that had been observed in the as-solidified specimen as needles was not observed in the heat treated specimen. The needles associated with the small dendrites were also measured by EPMA and their composition was found to be Ni-15.2 Hf-12.3 Si which corresponds to Ni_5Hf in which Si partially substitutes for Hf (fig.44). Results obtained from the x-ray diffractometer were complicated due to the large number of reflections. It was possible to distinguish reflections from Ni_5Hf and Ni_3Si $\beta 1$ (see section 4.1.2c) - γ was not expected in this alloy. The reflections given in the card index for Ni_3Si $\beta 2$ or $\beta 3$ could not be matched, but

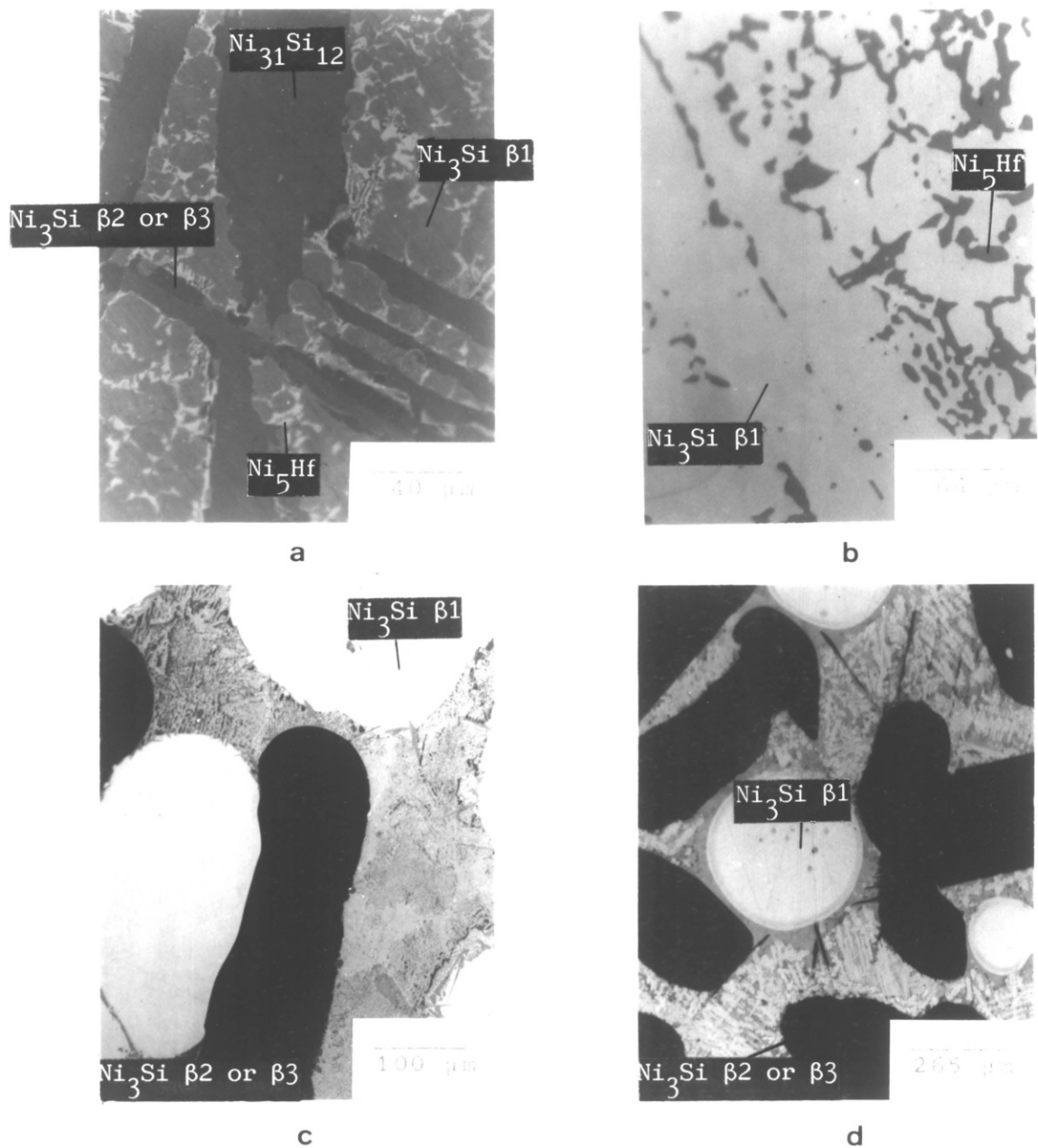


Fig 45

TABLE 29: INTERPLANAR SPACINGS FOR THE REFLECTIONS OBSERVED IN NHS3AC AND NHS3-1125
IN COMPARISON WITH THOSE FOR THE NZS AS SOLIDIFIED SPECIMENS

NZS2AC	NZS3AC	NZS4AC	NZS1AC	NHS31125	NHS3AC	NZS2AC	NZS3AC	NZS4AC	NZS1AC	NHS3-1125	NHS3AC
5.6196						1.9324	1.9275	1.9379	1.9371		1.9332
5.5760						1.9120	1.9166	1.9133			
4.1762	4.1780	4.1674					1.8845			1.8980	
4.0342							1.8697				
		3.8705	3.8740			1.8533	1.8549	1.8515			
3.4859	3.5059	3.4897				1.8100	1.8090	1.8115			
		3.3554	3.3560		3.3589	1.7811	1.7817	1.7829		1.7789	
3.3403	3.3449			3.3385		1.7581	1.7574	1.7591	1.7637	1.7572	1.7645
3.2097	3.2151	3.2200				1.6792	1.6703	1.6776		1.6824	
	3.1577			3.1595				1.6462	1.6530	1.6504	
	2.9302				2.9393		1.6331			1.6309	1.6338
2.8966		2.8993					1.6063				
	2.7458						1.5895	1.5886			
2.6320	2.6320	2.6360			2.6256	1.5679	1.5699	1.5721		1.5712	
2.5813	2.5862	2.5811			2.5941	1.5493				1.5460	
2.5104	2.5077	2.5107				1.4947	1.4945	1.4955	1.4997	1.4934	
	2.4836			2.4863	2.4887	1.4758	1.4776	1.4778			
	2.3873					1.4479	1.4482	1.4482			
		2.3730	2.3715		2.3671				1.4287		
	2.3556						1.3933			1.4016	
2.3227	2.3203	2.3251			2.3228	1.3864	1.3814	1.3873			
2.2342	2.2354	2.2385		2.2436		1.364	1.3749	1.3697	1.3694	1.3791	
2.1715	2.1745	2.1727		2.1853			1.3560	1.3540			
	2.1505			2.1453	2.1503	1.3207	1.3209	1.3221		1.3188	
	2.0996			2.0988	2.1102		1.3172				
	2.0914							1.2906	1.2901		
2.0859		2.0836					1.2679	1.2692			
	2.0283	2.0283				1.2428	1.2425	1.2426	1.2450	1.2426	1.2442
2.0296		2.0294	2.0293	2.0309	2.0319	1.2276	1.2167			1.2160	1.2177
2.0109	2.0118			2.0143		1.1892	1.1902	1.1906			
	1.9762			1.9759	1.9863			1.1861			
	1.9535										

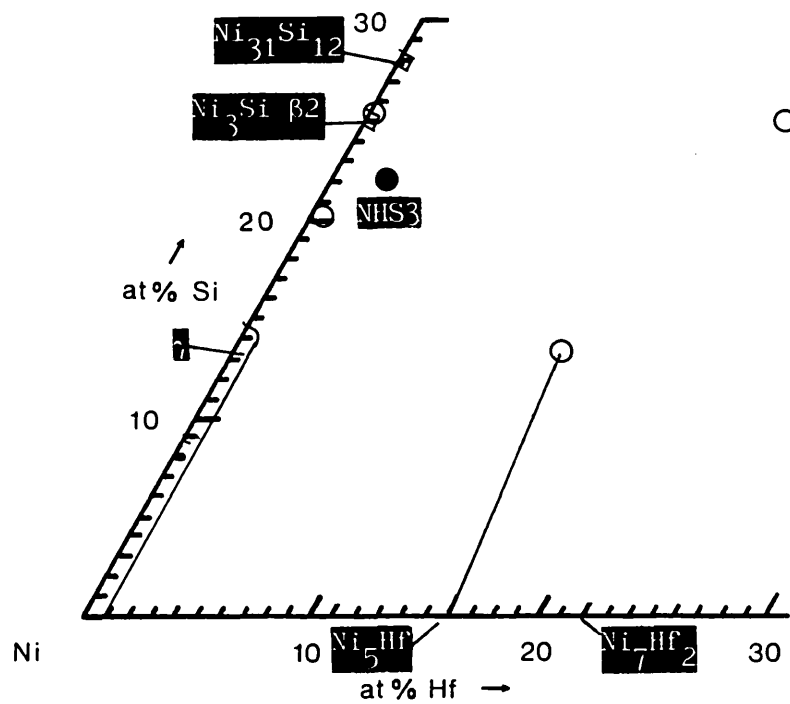


Fig.46 Schematic showing the compositions of the phases and eutectics, and compounds measured by EPMA in NHS3-1070.

the observed reflections did correspond very well with other unindexed reflections obtained from the other hafnium and zirconium containing alloys (table 29).

c(2). Ni-2.1 at.% Hf-22.5 at.% Si (NHS3-1071: NHS3-1125 given a subsequent heat treatment at 1071°C for 163 hrs).

The structure of this specimen was very similar to NHS3-1125, except for two features (fig.45c). The white round phases in NHS3-1125 were also observed in NHS3-1071 but they were not so rounded, and the area in which the dendrites had been observed in NHS3-1125 now consisted of a very fine eutectic structure. The needles which had been associated with the dendrites in NHS3-1125 were now associated with the eutectic structure.

The composition of the large dark particles was Ni-0.03 Hf-25.8 Si, which is vitually unchanged compared with the particles in NHS3-1125, therefore, the phase was interpreted as being $\text{Ni}_3\text{Si } \beta_2$ or β_3 (fig.46).

The large grey phase particles of composition Ni-0.4 Hf-20.4 Si were interpreted as being $\text{Ni}_3\text{Si } \beta_1$ as in NHS3-1125. The area in between the single phase regions which before had consisted of dendrites, now had a eutectic morphology. The composition of the eutectic was not measured, but the composition of the needles associated with it was Ni-14.4 Hf-13.5 Si which was interpreted to be Ni_5Hf in which Si partially substitutes for Hf. Small particles were also observed in this area. The composition

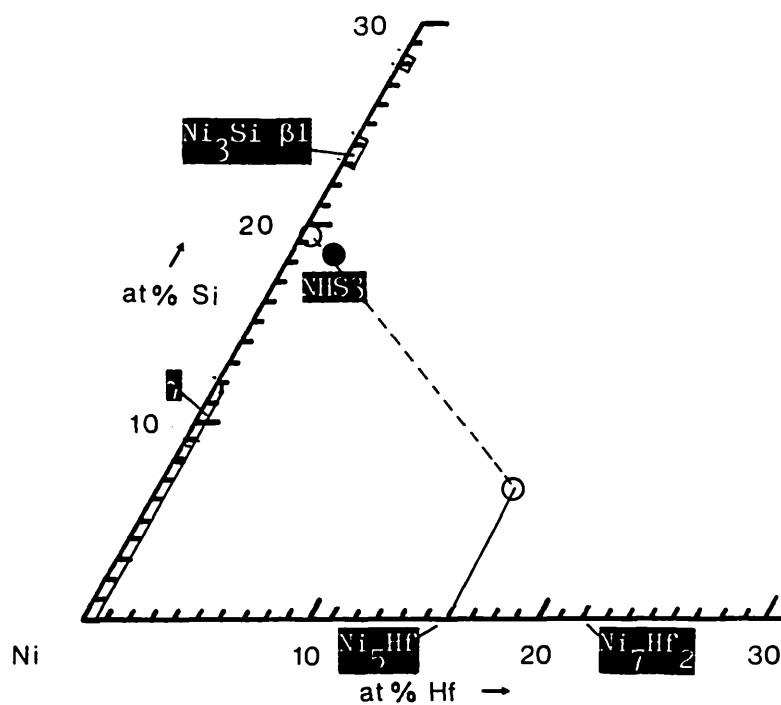


Fig.47 Schematic showing the compositions of the phases and eutectics, and compounds measured by EPMA in NHS3-926.

of these was determined to be Ni-18.4 Hf-25.5 Si and these were interpreted to be Ni_7Hf_2 .

The very fine-structured eutectic was due to the existence of liquid in the reaction observed between 1037°C and 1104°C by DTA. At 1070°C, the specimen was heat treated between these two temperatures.

c(3). Ni-1.9 at.% Hf-18.6 at.% Si (NHS3-926: NHS3-1071 subsequent heat treatment at 926°C for 163 hrs).

The alloy, as viewed by interference film microscopy and SEM, appeared to consist of two phases (fig.38c).

Following heat treatment for 163 hours at 1125°C and 163 hours at 1071°C, NHS3-1125 was kept at 926°C for 163 hours. The specimen was apparently two phase. The compositions of the phases as determined by EPMA were Ni-0.2 Hf-19.6 Si and Ni-15.8 Hf-6.8 Si and these were interpreted as being Ni_3Si $\beta 1$ and Ni_5Hf respectively. The overall composition of the sample was found to be Ni-1.9 Hf-18.6 Si which is significantly lower in Si content than the as-solidified or primary heat treated samples. The composition of the alloy lay on a tie line between the measured compositions of Ni_3Si $\beta 1$ and Ni_5Hf (fig.47). These two phases were also identified by x-ray diffraction, but reflections were observed which did not correspond to Ni_5Hf or Ni_3Si $\beta 1$. These were weak reflections in the low angle region of the pattern and were believed to be derived from the high temperature forms of Ni_3Si .

Consistent with the observations made from specimens NHS1-926 and NHS2-926 by DTA, no signs of melting were

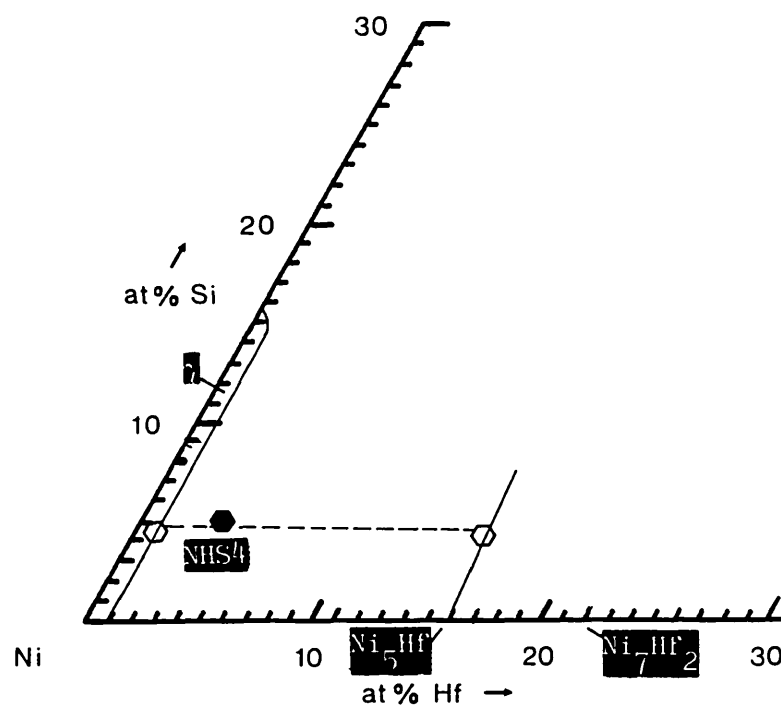
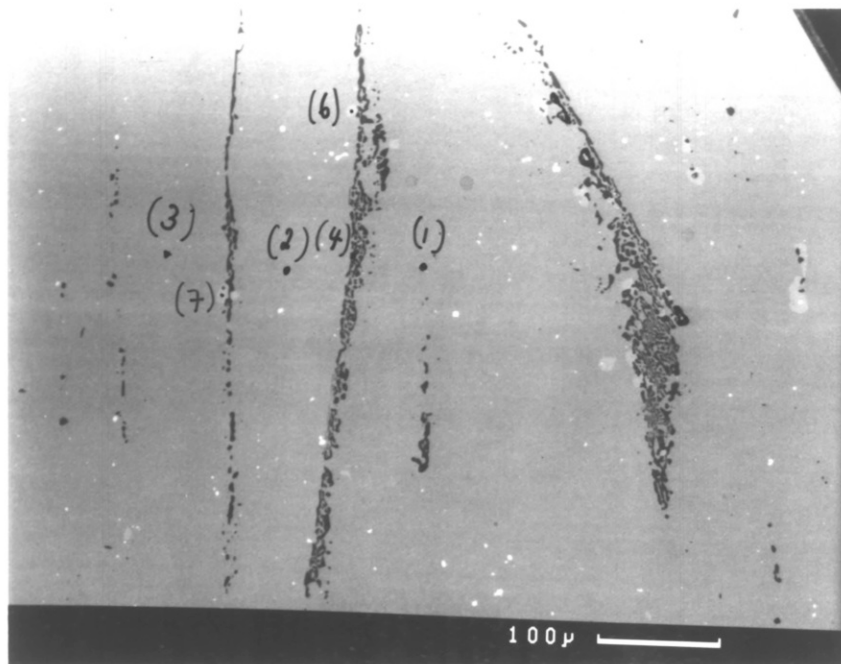
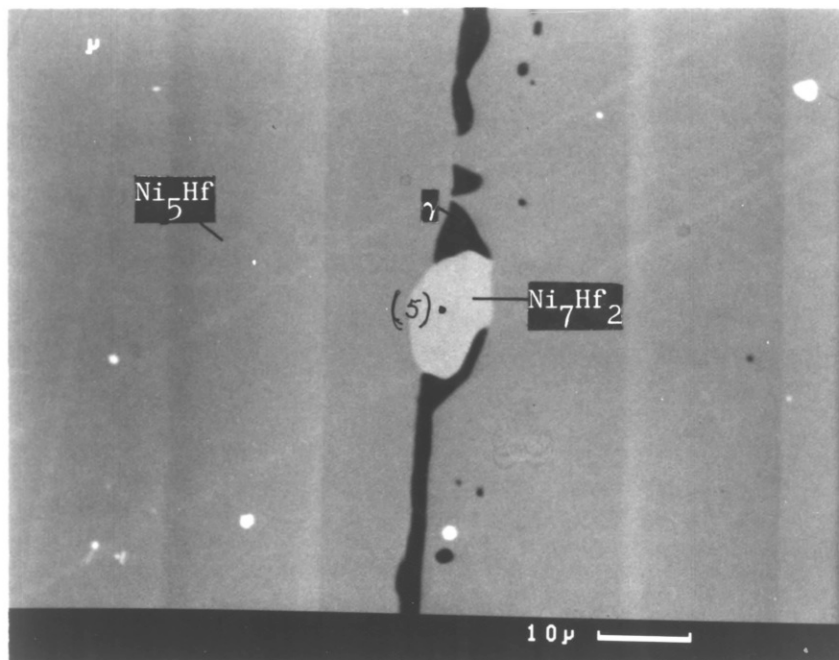


Fig.48 Schematic showing the compositions of the phases and eutectics, and compounds measured by EPMA in NHS4-1125.



a



b

Fig 49

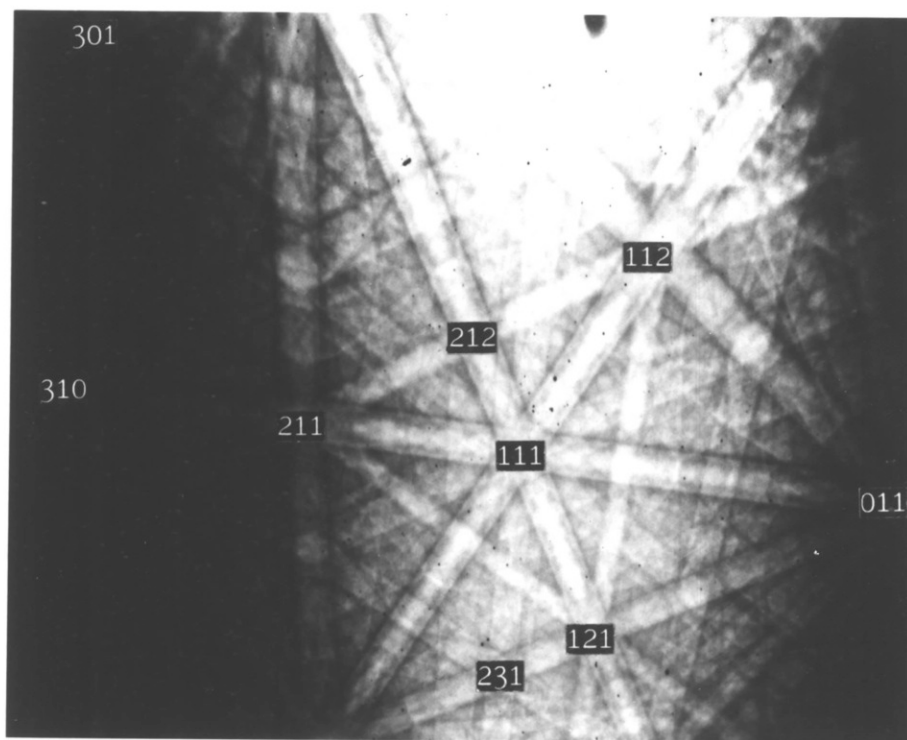


Fig 50

1050 °C	NHS5		NZS5	
	a_0	r	a_0	r
Ni ₅ Hf	0.668	0.9	-	-
Ni ₅ Zr	-	-	0.670	0.5

Table 30: Lattice parameters calculated from X-ray diffraction results for NHS5 and NZS5 heat-treated at 1050 °C.

a_0 - lattice parameter
r - correlation coefficient

observed in NHS3-926 either.

d. Ni-3.3 at.% Hf-5.2 at.% Si (NHS4-1125).

The structure was found to consist of two phases (fig.36d). The eutectic observed in NHS4-as solidified was not observed in this sample.

The compositions of the two phases, as determined by EPMA, were Ni- 15.2 Hf- 4.3 Si and Ni- 0.8 Hf- 4.8 Si which were interpreted as being Ni_5Hf and $\text{Ni}(\gamma)$ respectively (fig.48). These phases were also identified by x-ray diffraction. This specimen was one of the two hafnium containing specimens which did not show signs of partial melting above 1050°C. The other was NHS5-1050.

By DTA, the first peaks observed on heating a specimen were between 1155°C and 1177°C. No signs of partial melting were apparent (fig.37d).

e. Ni- 16.0 Hf- 3.0 Si (NHS5-1050) (Nominal composition).

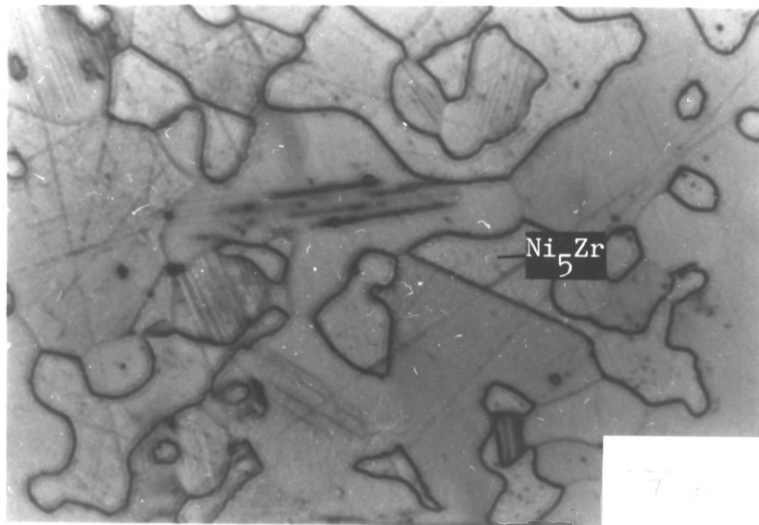
The structure, as viewed by interference film microscopy, was essentially single phase Ni_5Hf . There was a very small volume fraction of eutectic and a few small particles of Ni_7Hf_2 (fig.49).

By x-ray diffraction the alloy was shown to be predominantly single phase Ni_5Hf . The lattice parameter was calculated to be 0.668 nm (Table 30).

An electron back-scattering pattern was obtained from a freshly fractured surface of a sample of this alloy (fig.50). The face-centred cubic structure was identified and the lattice parameter calculated to be 0.66 nm. The accuracy of the result is only expected to be within 2% of



a



b

Fig 51

1070°C	NZS2			NZS4		
	Ni	Zr	Si	Ni	Zr	Si
Composition	Liquid			74.8	12.0	13.3
γ solid soln.				87.3	0.2	12.5
Ni ₅ Zr				76.0	16.0	8.1
				66.8	15.3	17.8

Table 31: EPMA results showing the compositions of the Ni-Zr-Si alloys heat-treated at 1070°C, and of the phases and eutectics observed in them.

1050°C	NZS5		
	Ni	Zr	Si
γ	94.1	0.1	5.8
Ni ₅ Zr	82.2	15.5	2.3

Table 32: EPMA results showing the compositions of the Ni-Zr-Si alloy heat-treated at 1050°C, and of the phases and eutectics observed in them.

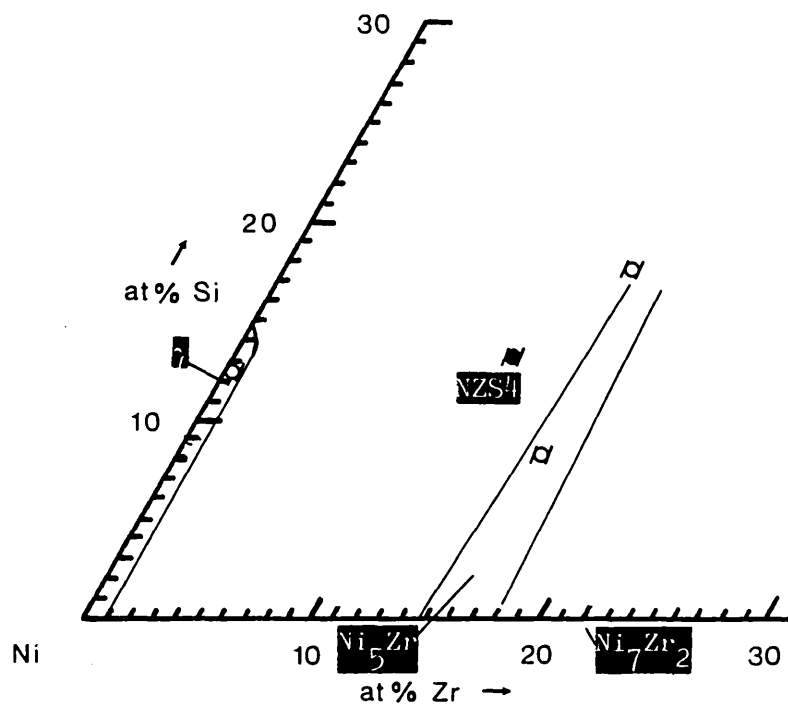


Fig.52 Schematic showing the compositions of the phases and eutectics, and compounds measured by EPMA in NVS4-1070.

the actual value because of the method of measuring the widths of the bands. Since the other phases present have very different lattice parameters from Ni_5Hf , the accuracy was sufficiently good to establish the identity of the phase.

3.4 Ni-Zr-Si Alloys

3.4.1 Heat Treated

a. Ni-4.9 at.% Zr-15.0 at.% Si (NZS2-1070: composition of as-solidified sample).

The sample was found to have melted completely after heat treatment. Therefore, no analysis of the microstructure was carried out.

b. Ni-11.6 at.% Zr-12.8 at.% Si (NZS4-1070: composition of as-solidified sample).

The structure, as viewed by optical light microscopy was apparently two phase (fig.51b). In one scanning electron micrograph three phases were clearly observed, however, in a third micrograph one area of the structure was apparently eutectic, which had a very fine morphology (fig.51a). Other than by TEM the constituent or constituents of this area could not be determined.

The compositions of the constituents, as determined by EPMA, are given in table 31 (fig.52).

c. Ni- 16.0 Zr- 3.0 Si (NZS5-1050) (nominal composition of alloy).

The structure, as determined by EPMA, was mainly single phase Ni_5Zr . The volume fraction of eutectic was

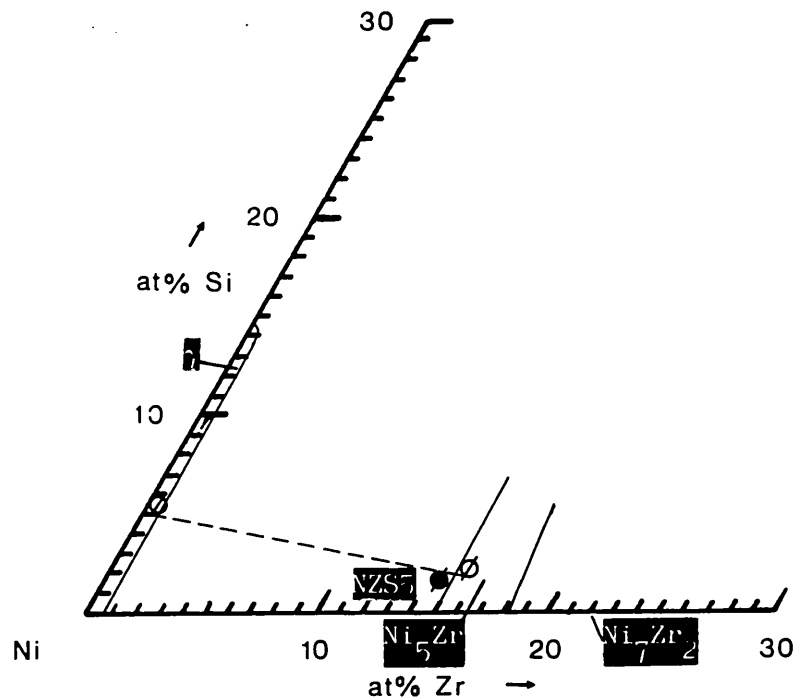


Fig.54 Schematic showing the compositions of the phases and eutectics, and compounds measured by EPMA in NZS5-1050.

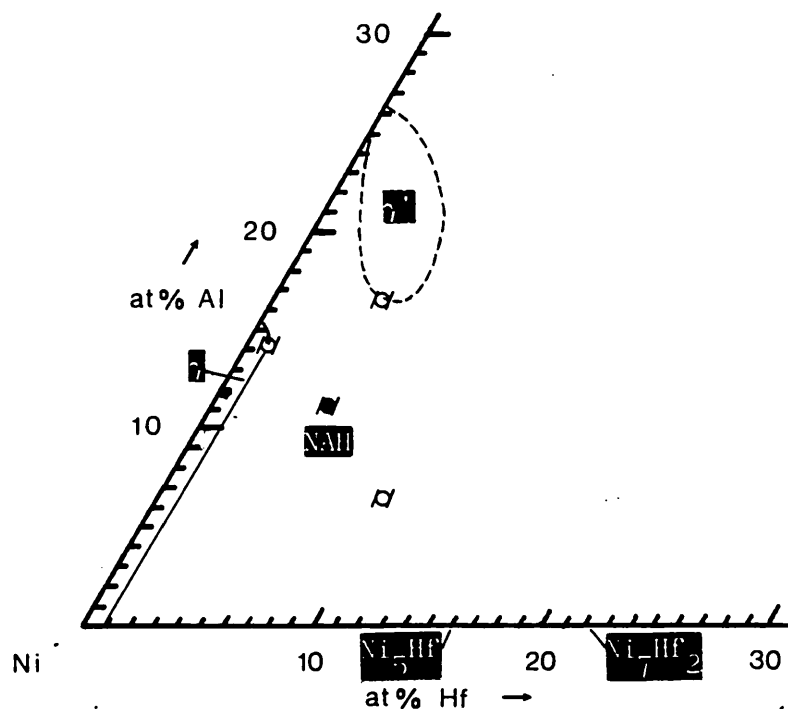


Fig.56 Schematic showing the compositions of the phases and eutectics, and compounds measured by EPMA in NAH as-solidified.

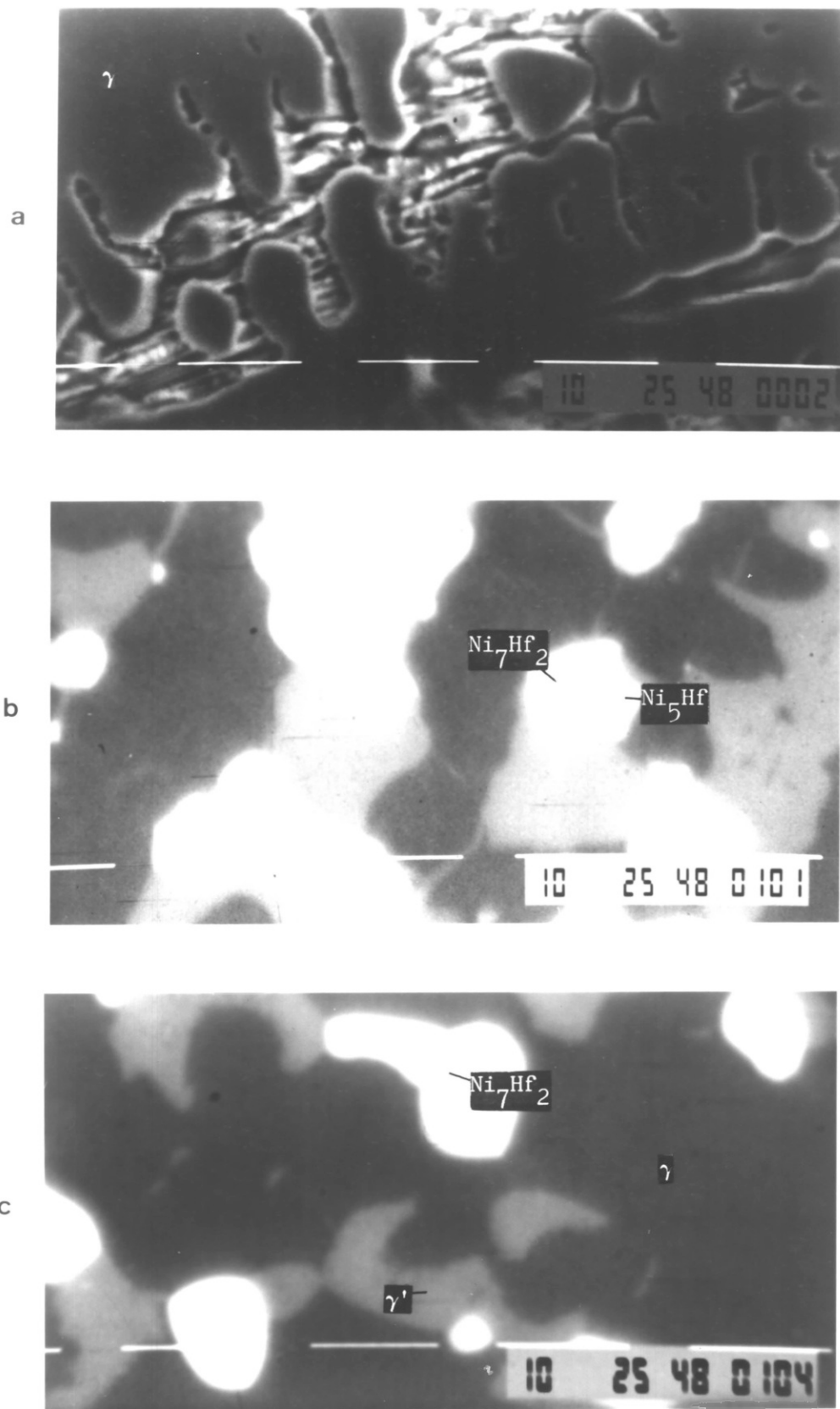


Fig 55

NAH	As-solidified			1000°C			1200°C		
	Ni	Al	Hf	Ni	Al	Hf	Ni	Al	Hf
Composition	83.8	5.0	11.2						
γ solid soln.	84.8	0.9	14.3	86.4	1.1	12.5	86.2	1.3	12.5
γ' solid soln.	78.7	4.7	16.7	77.7	5.6	16.7	75.5	6.2	16.3
Ni ₅ Hf				82.3	15.9	1.8			
Ni ₇ Hf ₂				77.9	21.0	1.1	78.2	20.7	1.1
Eutectic	83.7	9.9	6.4						

Table 33: EPMA results showing the overall composition, and the compositions of the phases and eutectics observed in the Ni-Al-Hf alloy in the as-solidified and heat-treated conditions (1000°C and 1200°C).

NAH	As-solidified		1000 °C		1200 °C	
	a_0	r	a_0	r	a_0	r
γ Solid Solution			0.355	0.5	0.355	0.5
γ'	0.361	0.1	0.361	0.4	0.360	0.4
Ni ₅ Hf	0.667	0.1	0.669	0.7	-	

Table 34; Lattice parameters calculated from X-ray diffraction results using the Nelson-Riley function for γ , γ' and Ni₅Hf in the as-solidified, and heat-treated Ni-Al-Hf alloy.

a_0 - lattice parameter
r - correlation coefficient

	Ni	Al	Hf	Si
Composition	83.3	6.5	5.1	5.0
γ	88.3	8.0	0.7	3.0
$\gamma/\text{Ni}_5\text{Hf}$	83.4	2.0	12.0	2.7

Table 35: EPMA results showing the compositon of the Ni-Al-Hf -Si alloy in the heat-treated condition, and of the phases and eutectics observed in it.

greater in this sample than in NHS5-1050. The compositions of the various constituents are given in table 32 (fig.54). The major phase contained 15 at.% Zr and was interpreted to be Ni_5Zr .

By x-ray diffraction the sample was shown to be predominantly Ni_5Zr . The strongest γ reflections were also observed, but these were relatively weak compared with the Ni_5Zr reflections.

3.5 Ni-Al-Hf Alloy.

a. Ni-11.2 at.% Al-5.0 at.% Hf (NAH-as solidified).

The alloy, consisted of dendrites and a eutectic (fig.55a).

The composition of the primary dendrites was determined to be Ni- 14.3 Al- 0.9 Hf by EPMA, which was interpreted to be $\text{Ni}(\gamma)$. The eutectic composition was Ni- 16.7 Al- 4.7 Hf (fig.56) (Table 33). The Ni_5Hf , $\text{Ni}(\gamma)$ and Ni_3Al compounds and phases were identified by x-ray diffraction (Table 34).

b. Ni-11.2 at.% Al-5.0 at.% Hf (NAH-1000: 1000°C for 144 hours)

The alloy, as viewed in the backscattering mode in the SEM, consisted of 4 phases (fig.55b). The sample had clearly not reached equilibrium. No eutectic was observed.

The compositions of the high hafnium containing phases-the white phases in the backscattered electron

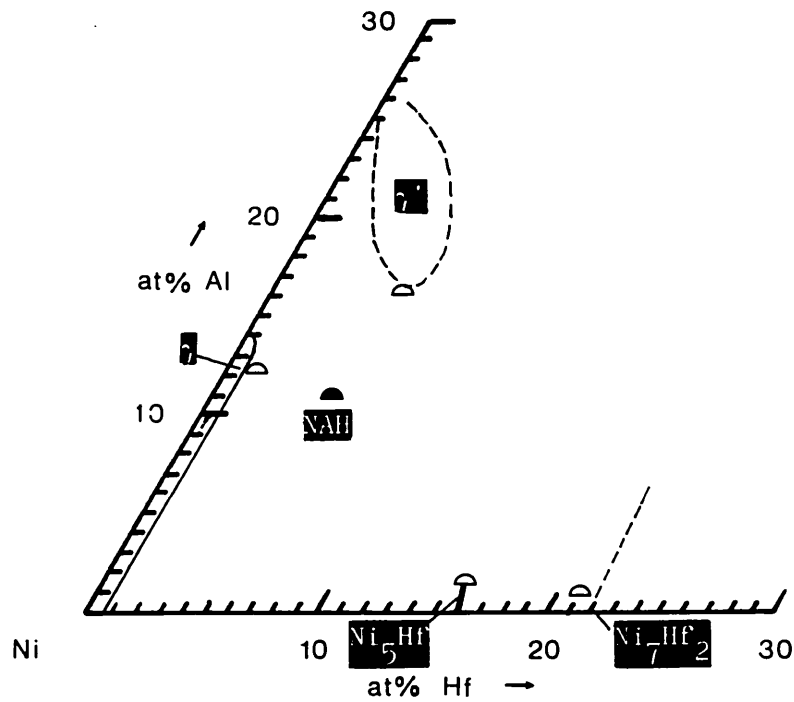


Fig.57 Schematic showing the compositions of the phases and eutectics, and compounds measured by EPMA in NAH-1000.

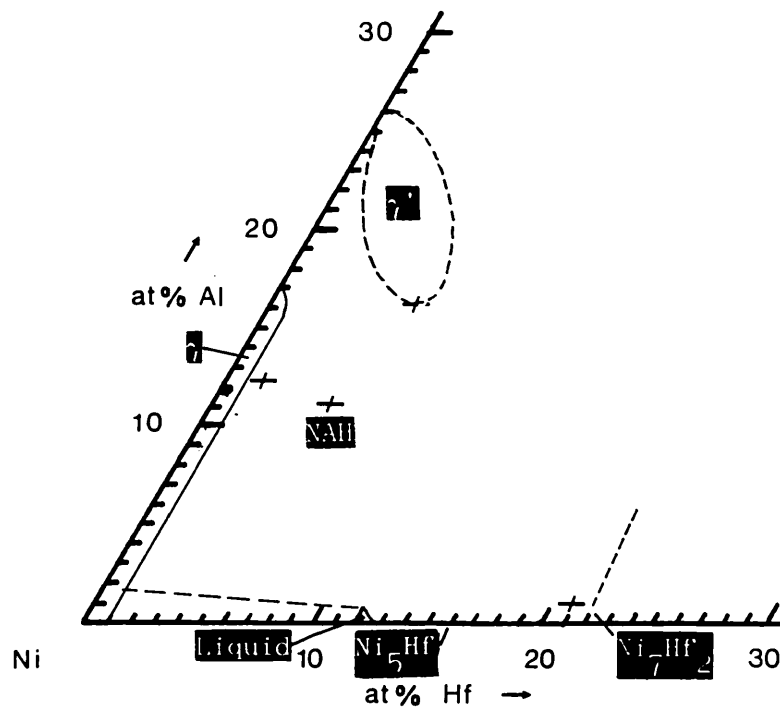


Fig.58 Schematic showing the compositions of the phases and eutectics, and compounds measured by EPMA in NAH-1200.

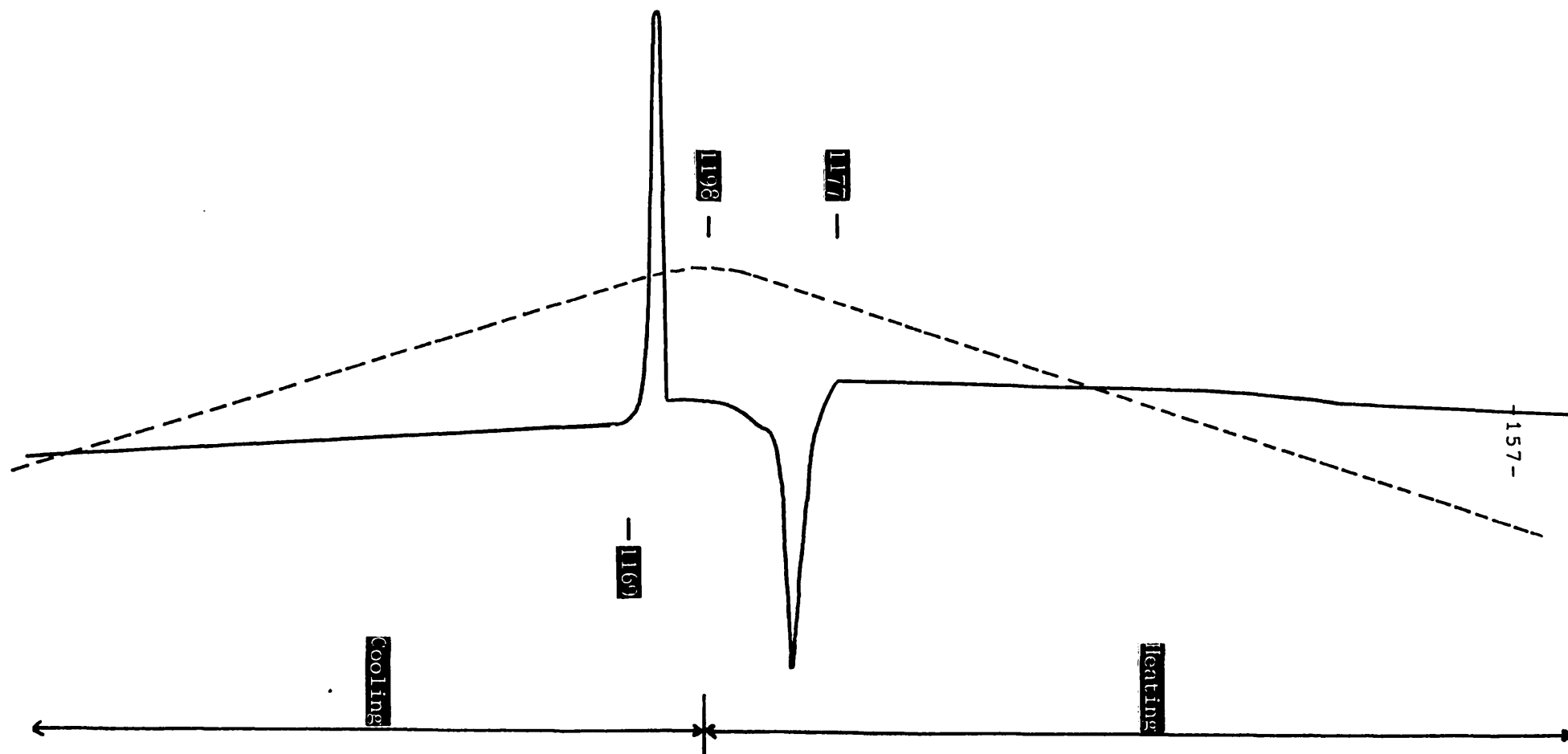


Fig.59 Differential thermal analysis curve for NAH-1000 heated between 1000°C and 1200°C and subsequently cooled.

images- were determined to be Ni- 1.8 Al- 15.9 Hf and Ni- 1.1 Al- 21.0 Hf by EPMA. These were interpreted to be Ni_5Hf and Ni_7Hf_2 respectively. The compositions of the other two phases are given in table 33. They were interpreted to be the γ and γ' phases. The hafnium content of the γ' solid solution was 5.6 at.% (fig.57).

By x-ray diffraction the major compounds and phases were determined to be $\text{Ni}(\gamma)$, Ni_3Al and Ni_5Hf . Some very weak reflections were attributed to Ni_7Hf_2 , which indicated that the volume fraction of this compound in the sample was very small.

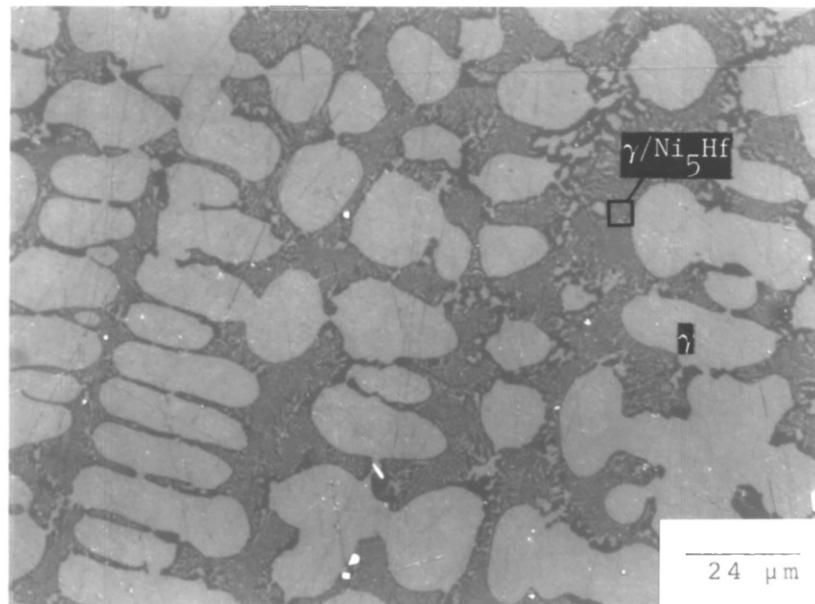
c. Ni-11.2 at.% Al-5.0 at.% Hf (NAH-1200: 1200°C for 168 hours).

The structure, consisted of 4 phases. As with NAH1000, the structure had not reached equilibrium. The backscattered electron image appeared to be very similar to NAH1000 (fig.55c).

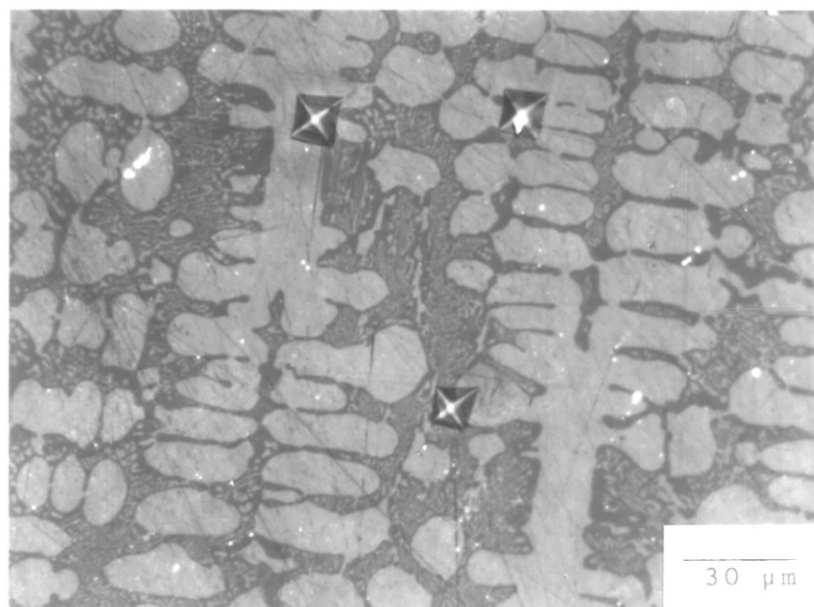
The compositions of the phases and compounds, determined by EPMA, are given in table 33. They were identified as γ , γ' , Ni_5Hf , and Ni_7Hf_2 (fig58).

By x-ray diffraction, however, the major phases in this sample were γ , γ' and Ni_7Hf_2 . Unlike NAH1000, only the very strong reflections for Ni_5Hf were observed. Therefore, between 1000°C and 1200°C the major Ni-Hf intermetallic compound in the samples had switched from Ni_5Hf to Ni_7Hf_2 .

By differential thermal analysis a peak was observed on heating and cooling between 1000°C and 1200°C (fig.59).



a



b

Fig 60

The temperature of the reaction is taken from the point at which the peak was first observed on heating, ie. 1177°C. The corresponding temperature from the cooling curve was 1169°C. On heating the reaction was observed very close to 1200°C and cooling had begun before the full peak had been completed (note the arrest on peak 1 in fig.59). Therefore, the reaction was interpreted as having only just reached completion at 1200°C.

3.6 Ni-Al-Hf-Si Alloy.

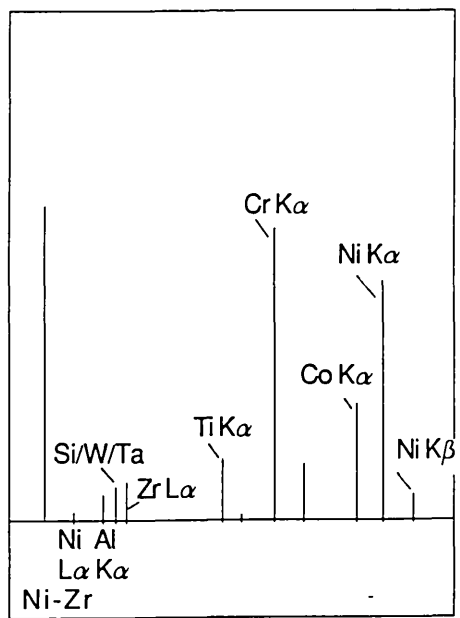
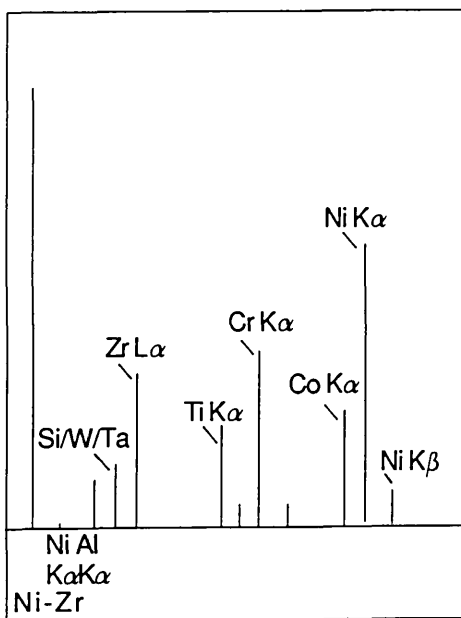
a. Ni-7 at.% Al-5 at.% Hf-5 at.% Si (NAHS as-solidified) (Nominal Composition).

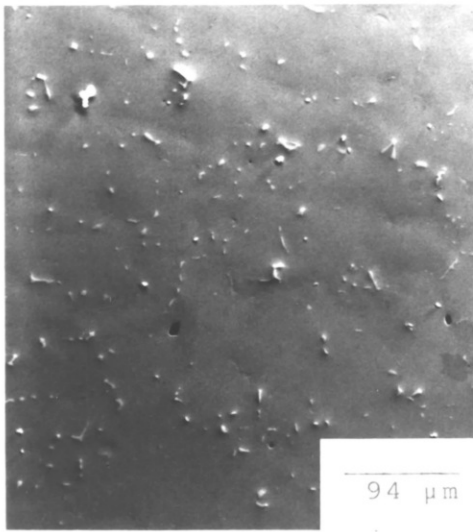
The structure, as viewed by interference film microscopy, consisted of dendrites and a eutectic (fig.60a).

A sample of NAHS-as solidified was heat-treated for 3 hours at 1000°C. In this short time very little diffusion was found to occur and the microstructure was very similar to that of the as-solidified specimen (fig. 60a, 60b).

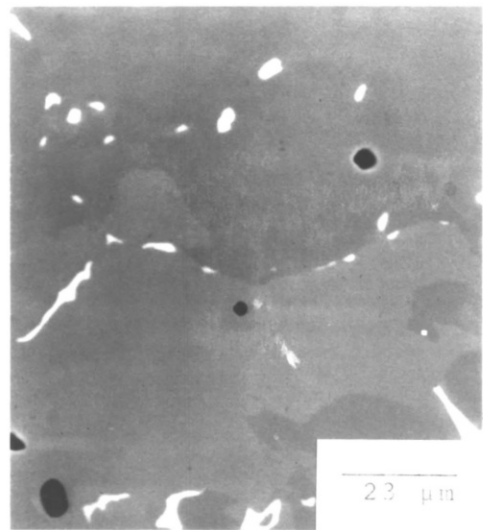
The overall composition of the alloy was obtained by EPMA from the heat-treated samples (Table 35). This was found to be in close agreement with the nominal composition of the alloy. The compositions of the dendrites and of the interdendritic areas were also measured by EPMA and interpreted to be γ dendrites and a $\gamma/\text{Ni}_5\text{Hf}$ eutectic.

By x-ray diffraction the presence of $\text{Ni}(\gamma)$ and Ni_5Hf was confirmed. The reflections observed for Ni_5Hf in this alloy were used to identify the compound in all the other samples.

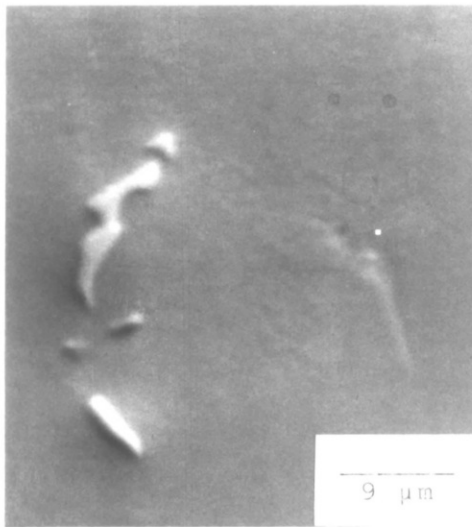




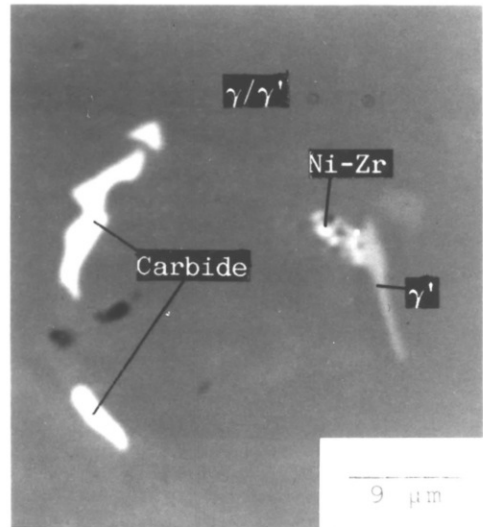
a



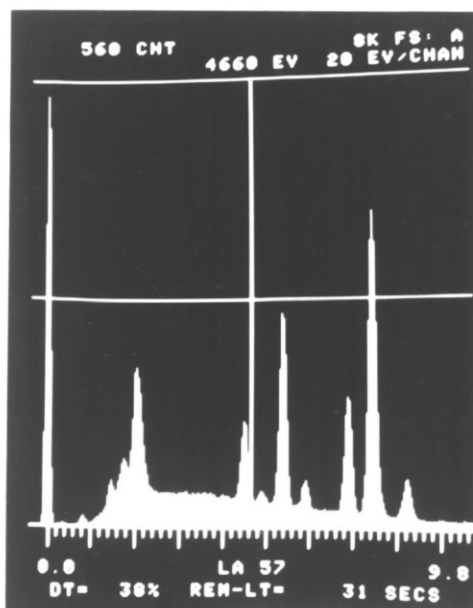
b



c

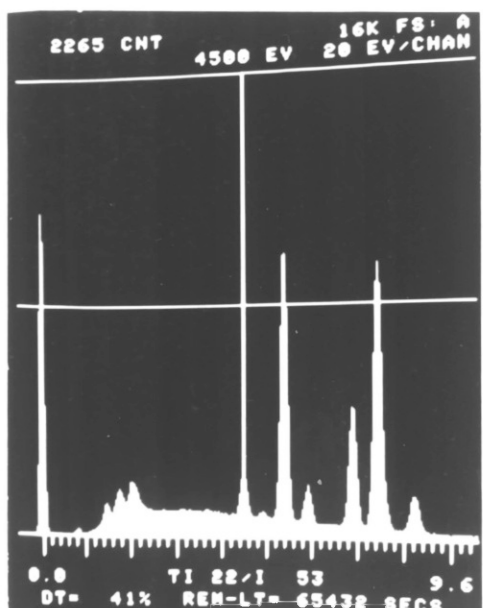


d



Ni-Zr spectra

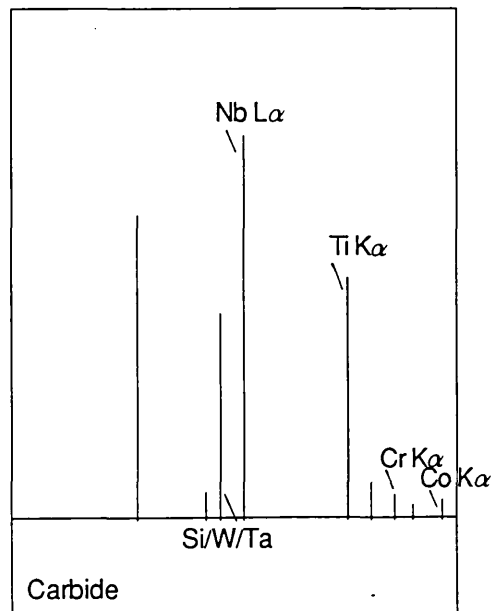
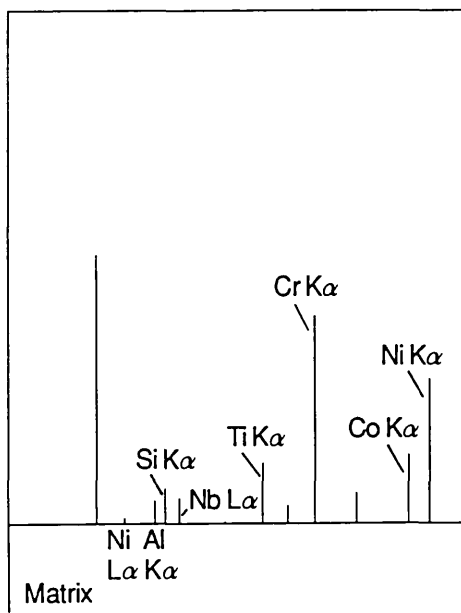
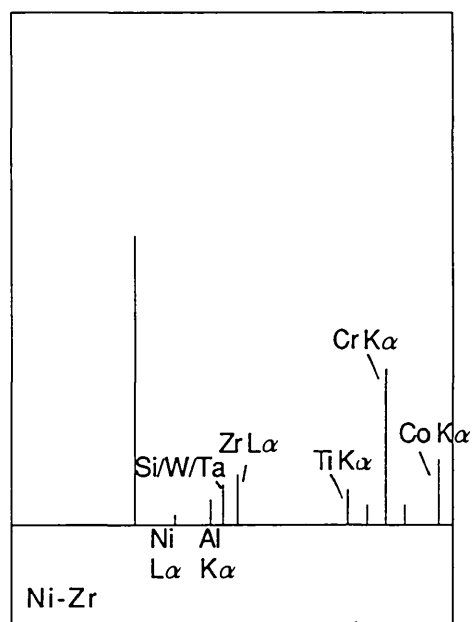
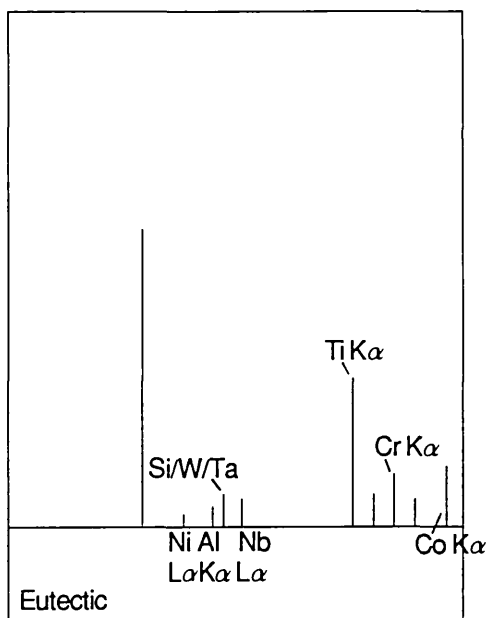
e



Ni-Zr spectra

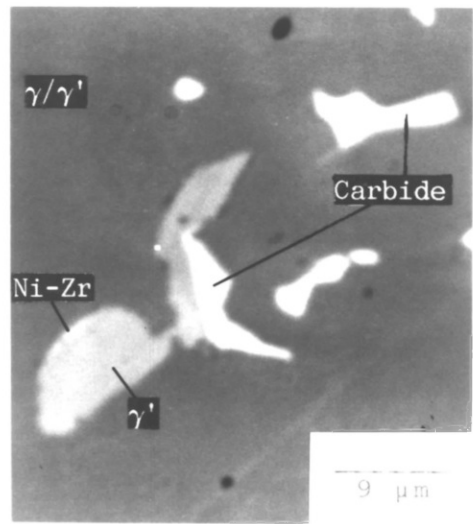
f

Fig 61

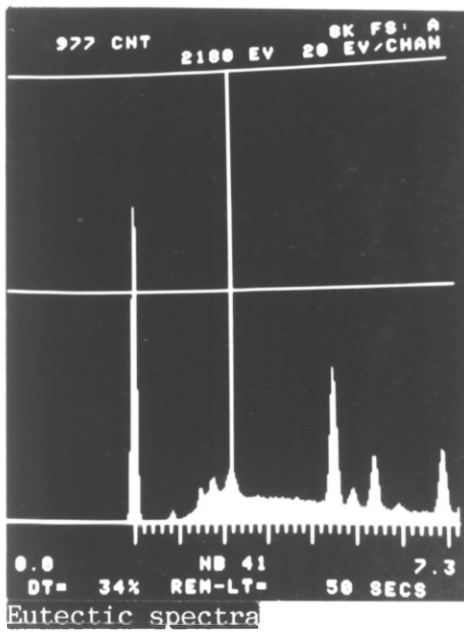




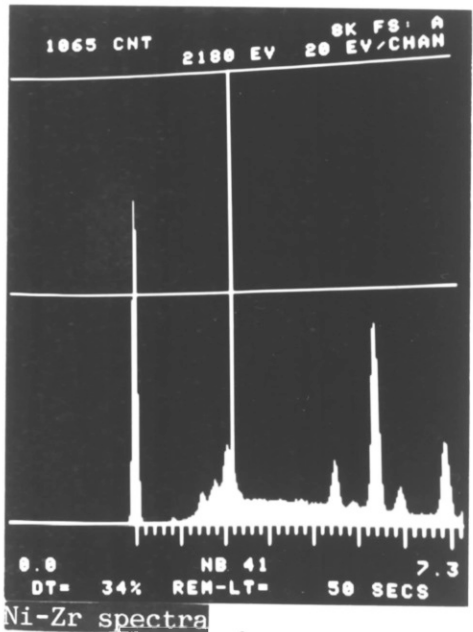
a



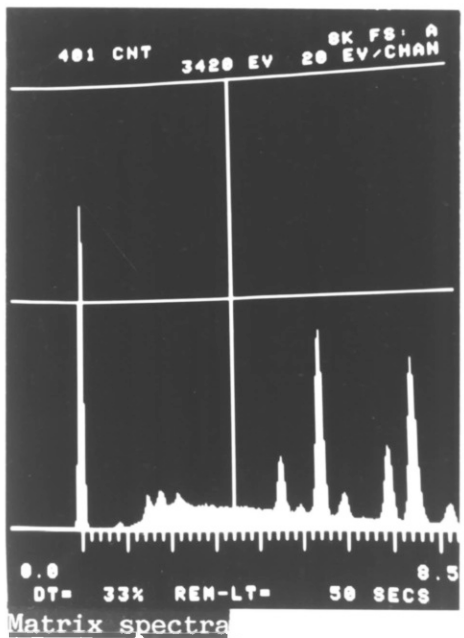
b



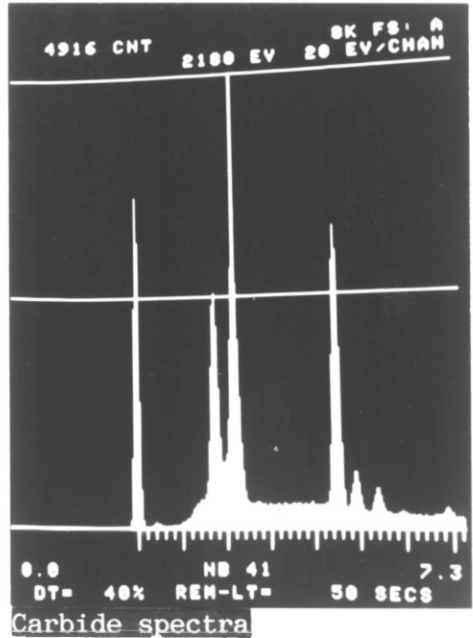
c



d

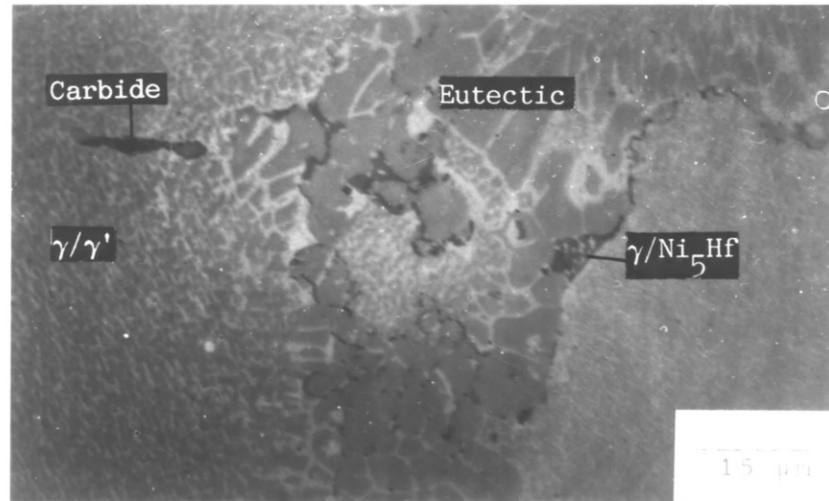


e

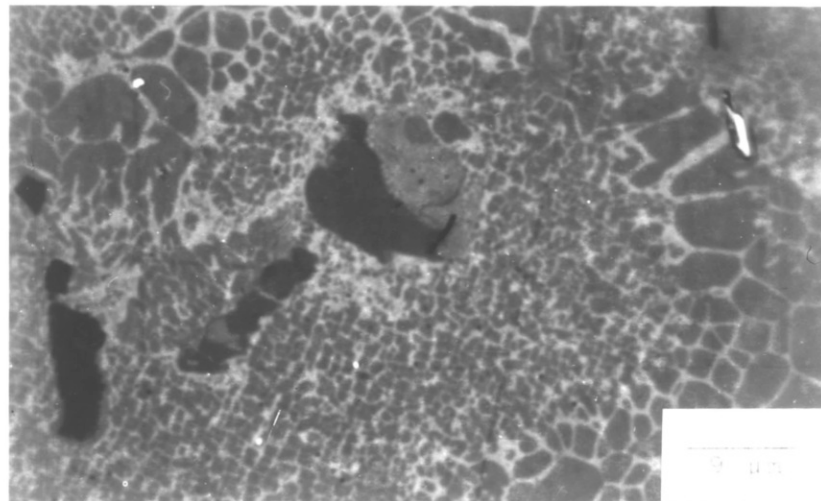


f

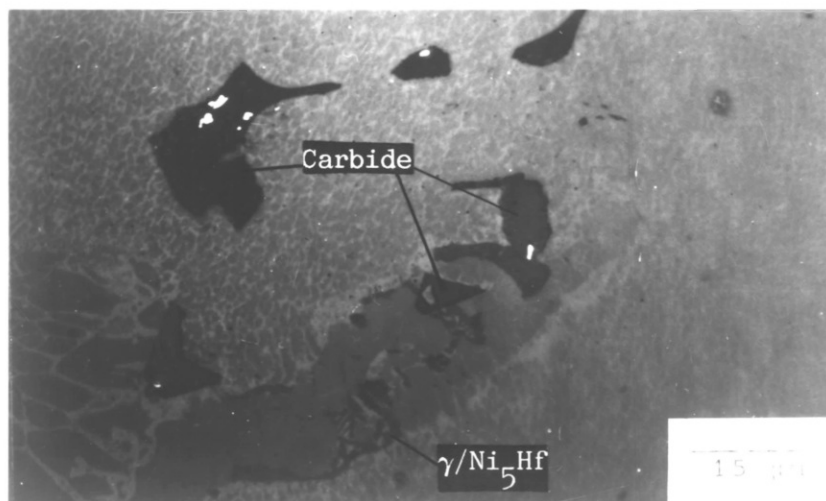
Fig 62



a



b



c

Fig 63

Ni-Hf and Ni-Zr intermetallic compounds in nickel-base superalloys.

Ni-Hf and Ni-Zr rich phases were identified, by a combination of different experimental and analytical techniques in IN939+0.2 wt.% Si (fig.63), IN939+0.2 wt.% Zr, MarM246 and MarM002+0.1 wt.% Si (fig.63) (The specimens were samples of commercial alloys to which additions of zirconium and silicon had been made). The techniques used were interference film microscopy, SEM (back-scattered images), and EPMA. There was also an attempt to obtain some electron back-scattering patterns too, but this was unsuccessful.

The compositions of Ni-Hf and Ni-Zr phases, obtained by EPMA, are given in table 7. The Hf and Si contents were determined by WDS analysis. The quantities of other phases were determined by EDS analysis. The results showed that the phases were Ni-Hf or Ni-Zr rich, and in most cases the amount of silicon in these phases was greater than in other phases or compounds observed in the structure (table 7). The size of the analysed particle was the limiting factor, however, and there was not believed to be sufficient evidence to determine the stoichiometry of the Ni-Hf or Ni-Zr phases.

Electron back-scattering patterns were obtained from the model alloy, NHS5 1050°C (fig.50). The face centred cubic structure was observed in NHS5-1050 and the lattice parameter calculated to be 0.66 nm. No patterns were obtained from the superalloy specimens due to various experimental difficulties (see experimental).

4. DISCUSSION

4.1 Introduction

4.1.1 Data Sources and Correlation

In contrast to the voluminous numbers of papers that have been written on the subject of nickel-base superalloys those that were available to study the alloy systems relevant to the present work were very limited. However, recent publications, mainly by Nash et al. (31-33), provided a basis. Thus, detailed reviews of the Ni-Hf, Ni-Zr, and Ni-Si binary phase diagrams were available which showed that the Ni-Hf and Ni-Zr diagrams have been confidently established in the regions of interest, i.e. between 0-25 at.% Hf and 0-25 at.% Zr (figs.7,9). However, it was apparent that considerable difficulties had been encountered in elucidating the region of the Ni-Si diagram between 20-30 at.% Si (fig.10). The primary problem related to Ni_3Si in its three forms β_1 , β_2 and β_3 .

The structures of the two high temperature forms of Ni_3Si are clearly in dispute (see literature survey) - β_2 has been reported to have a monoclinic structure (45) and a hexagonal structure (46), whilst β_3 has been said to have a monoclinic structure (45) and an orthorhombic structure (51).

Determination of the homogeneity range of $\text{Ni}_{31}\text{Si}_{12}$ is presenting difficulties in constructing the exact form of

the diagram. (It is important to note that in the present work γ is used to denote the nickel solid solution and not $\text{Ni}_{31}\text{Si}_{12}$ as it has been done by many other workers. Also, $\text{Ni}_{31}\text{Si}_{12}$ is referred to in some papers as Ni_5Si_2). One author reported a wide range of homogeneity in contrast to other observations (48). This was attributed to the existence of the phase in a metastable state. Considerable amounts of $\text{Ni}_{31}\text{Si}_{12}$ were observed in the as-solidified eutectic of an alloy with only 19.0 at.% Si (51), where it would not be expected according to evidence on which the phase diagram has been constructed (fig10). The eutectic was shown to consist of γ solid solution with some Ni_3Si β_1 coherent precipitates which formed during quenching and a second phase, indexed with the $\text{Ni}_{31}\text{Si}_{12}$ structure (51).

Other complications in the study of the Ni-Si binary system centred around the low temperature Ni_3Si β_1 form which had been found to precipitate from the γ phase on quenching and to form solid state dendrites on aging at temperatures < 1000°C in an alloy containing 19.0 at.% Si (51).

4.1.2 Problems of Interpretation.

In the present work several major complications arose in trying to interpret the data. These were;

- a. Partial melting of some of the Ni-Hf-Si alloys during heat treatment at 1125°C.
- b. The extent to which solid state changes occurred between the three forms of Ni_3Si on cooling.
- c. Identification of Ni_3Si β_1 in the presence of γ due

to the overlap of x-ray reflections.

d. In x-ray diffraction, measurement of the interplanar spacing of the (222) reflection of Ni_5Hf and Ni_5Zr . In the presence of $\text{Ni}_3\text{Si } \beta_2$, $\text{Ni}_3\text{Si } \beta_3$ and $\text{Ni}_{31}\text{Si}_{12}$, this measurement was difficult due to the overlap of x-ray reflections. This measurement was made in order to estimate the effect of silicon on the structure of Ni_5Hf and Ni_5Zr .

e. Reliability of EPMA in quantifying the hafnium and silicon content of phases and intermetallic compounds.

a. Partial Melting of the Ni-Hf-Si alloys.

On heat treatment of the alloys NHS1, NHS2, NHS3 at 1125°C, evidence was obtained of partial melting.

The NHS3-1125 sample was visibly changed in shape after quenching. No such change was observed with the other two specimens. Differential thermal analysis showed that on heat treatment at 1125°C the specimens were above the temperatures of the primary reactions observed on heating i.e. in NHS1-1125 the primary reaction(s) is between 1052°C and 1111°C (fig.37a). NHS3-1125 underwent most change in shape after heat treatment and at 1125°C the DTA sample of this alloy was closest to the termination of the final reaction observed at 1184°C (fig.37c).

These structures were, therefore, interpreted as representing the equilibria involving a liquid phase at 1125°C. Thus, data to construct a ternary isothermal

section at 1125°C was limited. The microscopical examination of NHS1-1125, NHS2-1125 and NHS3-1125 showed regions of very fine eutectic suggestive of rapid cooling from the liquid state; also certain phase particles adopted spherical shapes indicating their contact with liquid (fig.45d). Also, NHS3-926 was found to have a different overall composition from NHS3-1125 - NHS3-926 had been heat-treated at 1125°C and 1071°C prior to heat treatment at 926°C. NHS4-1125 was not found to have undergone any melting. The heat treatment of NHS4-1125 at 1125°C was below the reaction observed, between 1155°C and 1177°C, on heating the sample from 750°C during DTA experiments (fig.37d).

b. Ni_3Si and the extent to which solid state changes take place on cooling.

The most detailed paper on solid state transformations during cooling in the Ni-rich portion of the Ni-Si system is that of S. Lebaili and H. Thibault (51). It dealt with the precipitation of Ni_3Si β_1 from γ during quenching and with the existence of $\text{Ni}_{31}\text{Si}_{12}$ in the eutectic of an alloy containing 19.0 at.% Si. According to the assessed phase diagram (fig.10) $\text{Ni}_{31}\text{Si}_{12}$ would not be expected in an alloy of this composition which suggests that the compound existed in a metastable state.

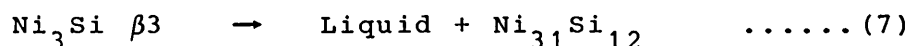
Ni_3Si β_1 has been found in the following Ni-Hf-Si alloys by EPMA:

	NHS1-1125		NHS1-926
NHS2 As-solidified			NHS2-926
NHS3 As-solidified	NHS3-1125	NHS3 1071	NHS3-926

Table 36. Specimens in which $\text{Ni}_3\text{Si } \beta_1$ was identified by EPMA.

The compound contained between 20.3-22.1 at.% Si. The hafnium content was typically 0.4 at.%. According to the phase diagram $\text{Ni}_3\text{Si } \beta_1$ should not be stable above 1035°C (fig.10). However, the phase was found in several alloys which had been heat-treated above that temperature, e.g. fig.45d. This could be due to precipitation of $\text{Ni}_3\text{Si } \beta_1$ on quenching or it could be that hafnium raises the temperature range of stability of the phase. However, it has already been shown that the solubility of hafnium in $\text{Ni}_3\text{Si } \beta_1$ was very limited i.e. 0.4 at.%. In NHS3-926 both of the high temperature forms of Ni_3Si had disappeared leaving an apparently two phase structure consisting of $\text{Ni}_3\text{Si } \beta_1$ and Ni_5Hf (fig.45b). Evidence from NHS1-926 and NHS2-926, in which three phases were observed, suggested that NHS3-926 also consisted of three phases. However, the γ phase could not be detected. The DTA results of NHS2-1125 and NHS3-1125 showed that, on heating, the first reaction to be observed was at 1037°C. In NHS1-1125, it was observed at 1057°C. The $\text{Ni}_3\text{Si } \beta_1$ to $\text{Ni}_3\text{Si } \beta_2$ transformation has been reported to occur at this temperature i.e. 1037°C (33). However, in comparison with a solid to liquid transformation the relative peak height observed for a solid to solid transformation would be significantly smaller. The $\text{Ni}_3\text{Si } \beta_2$ to $\text{Ni}_3\text{Si } \beta_3$ transformation was reported to occur at 1115°C (33). DTA results, from

NHS1-1125, NHS2-1125 and NHS3-1125, for heating, showed that the first reactions observed came to completion between 1096°C and 1111°C (fig.37a-37c). This first reaction could be envisaged to encompass the β_1 to β_2 and the β_2 to β_3 reactions. If this was the case then a third reaction, occurring at 1170°C in each specimen, would have been expected, signifying the reaction:



This would have been a relatively large peak because the reaction involves a solid to liquid transformation. However, it was not observed. Besides, the maximum temperature of the heating cycle in the DTA experiments was 1350°C. If $\text{Ni}_{31}\text{Si}_{12}$ had been present in the microstructure then a peak representing the congruent melting of $\text{Ni}_{31}\text{Si}_{12}$ would have been expected at 1242°C. This was not observed either. What can be stated is that below 926°C only $\text{Ni}_3\text{Si } \beta_1$ is present, and at 1070°C and above $\text{Ni}_3\text{Si } \beta_2$ or $\text{Ni}_3\text{Si } \beta_3$ do exist (figs.45b,45c,45d). $\text{Ni}_{31}\text{Si}_{12}$ was not observed.

c. Identification of $\text{Ni}_3\text{Si } \beta_1$ in the presence of γ .

$\text{Ni}_3\text{Si } \beta_1$ was first identified by EPMA. A phase containing approximately 20 at.% Si was observed in many of the as-solidified and heat-treated Ni-Hf-Si specimens (Table 36). There was difficulty in identifying this phase as $\text{Ni}_3\text{Si } \beta_1$ or γ because the homogeneity range of $\text{Ni}_3\text{Si } \beta_1$ has been given as 22.8-24.5 at.% and of γ as 0-15.8 at.% in Ni-Si binary alloys and the values obtained in this work lay in between these ranges. This suggested, of course, that the homogeneity range had been affected by the hafnium

addition, in which case the affect of only 0.4 at.% Hf on the homogeneity range of $\text{Ni}_3\text{Si } \beta 1$ is large. Another possible explanation is that $\text{Ni}_3\text{Si } \beta 1$ was precipitating from the γ phase on quenching. However, due to partitioning effects, when precipitation of $\text{Ni}_3\text{Si } \beta 1$ from γ occurs the amount of silicon measured by EPMA, from an area containing precipitates and matrix, should be the same as the silicon content of the original γ phase without precipitates, unless diffusion occurs from elsewhere in the structure i.e. from a liquid phase during heat treatment. As it was, a silicon content of 20.4 at.% in this phase is much closer to the expected composition of $\text{Ni}_3\text{Si } \beta 1$ on the nickel-rich side. The silicon content in this phase, measured in most samples in which it was found, was consistently about 2 at.% lower than the reported composition of $\text{Ni}_3\text{Si } \beta 1$. One exception was in alloy NHS1-926 where a silicon content of 22.1 at.% was observed. A silicon content less than that observed by other workers would be obtained if $\text{Ni}_3\text{Si } \beta 1$ and γ were in close proximity in the microstructure, not as a precipitate in a matrix, but as two distinct phases. The difficulty in measuring the silicon content of both phases occurs because they cannot be clearly distinguished in the SEM by BEI or SEI methods.

Difficulties in identification of the two phases were also encountered by x-ray diffraction. Below, in table 37, are the reflections observed for γ and $\text{Ni}_3\text{Si } \beta 1$, and those reflections that also correspond to Ni_5Hf and Ni_5Zr , which show that the only reflections unique to $\text{Ni}_3\text{Si } \beta 1$ in the

presence of either of these other phases are those at 0.350 nm and 0.2493 nm. (These values are all taken from the ASTM card index). It is understood that solid solutions have different lattice spacings depending on the percentage of element or elements present in solution. This fact, in itself, shows how even more difficult it could be to index reflections belonging to these phases when present in the same sample. If it was assumed that the degree of solid solution of hafnium in Ni_3Si $\beta 1$ was very limited, i.e. 0.4 at.%, then the lattice parameters of this phase would not be expected to change as much as they would for γ . The high temperature forms of Ni_3Si also have reflections occurring near to these, i.e. $\beta 2$ at 0.348 nm & 0.245 nm, and $\beta 3$ at 0.2475 nm. Slight distortions in the lattices of these phases due to small quantities, i.e. 0.3 at.%, of Hf in solution, could change the position of these reflections to further coincide with the reflections from Ni_3Si $\beta 1$.

γ		Ni_3Si $\beta 1$		Ni_5Hf		Ni_5Zr	
		0.350	30				
		0.2493	30				
0.2034	100	0.2020	100	0.2007	100	0.2024	100
0.1762	42	0.1751	70	0.1246	21	0.1234	70
0.10624	7	0.1055	70	0.1055	40	0.1060	60
0.10172	4	0.1011	50	0.1018	50	0.1021	60
				0.1007	40	0.1010	60
0.08810		0.0875	50	0.0870	80		

Table 37. Interplanar spacings for γ and Ni_3Si $\beta 1$.

The intensities of the Ni_3Si $\beta 1$ reflections at 0.350nm and 0.2493 nm are only 30% of the main reflection at 0.2020 nm. The presence of Ni_3Si $\beta 1$ could only be deduced from the relative intensities of all the other reflections observed.

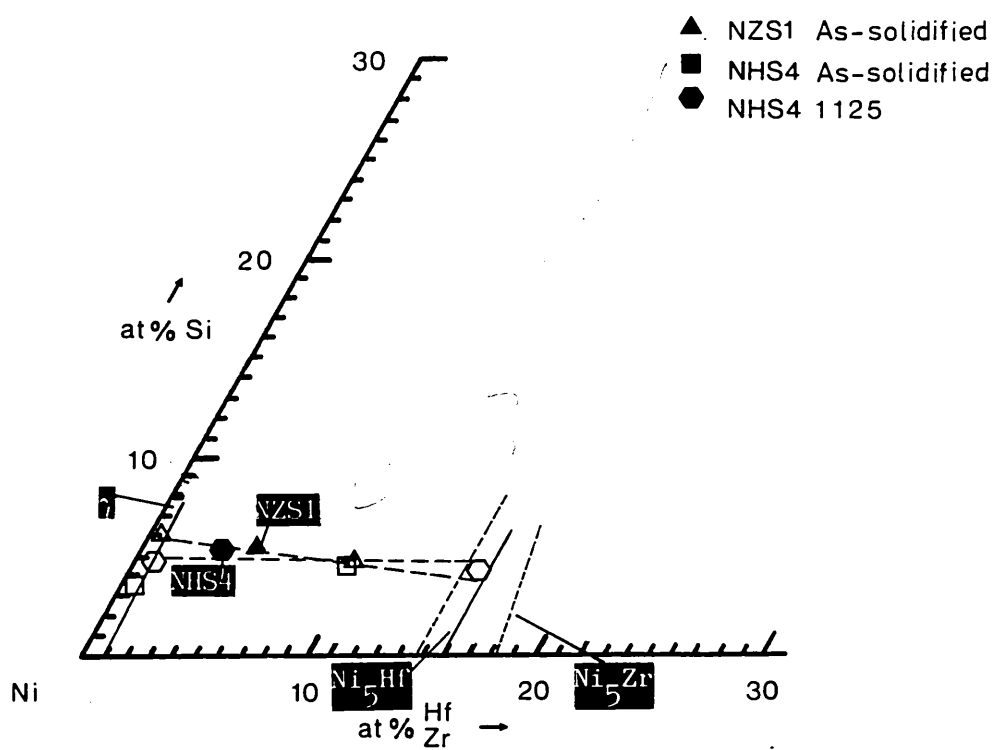


Fig.64 Tie lines between γ and Ni_5Hf as measured by EPMA.

This problem occurred in NHS4 as-solidified and NHS4-1125. The relative intensities of the peaks were inconsistent with the observation of two phases, γ and Ni_5Hf . The reflection at 0.176 nm in NHS-As-solidified, which would normally be 42 % of the main reflection was a little over 3 times the intensity of the main reflection at 0.203 nm and in NHS4-1125 it was just over twice as intense as the main reflection. Also, EPMA data from the two samples showed that the tie lines do not quite run through the composition of the alloy (fig.64). This is either due to the presence of a third phase, i.e. $\text{Ni}_3\text{Si } \beta_1$, or to the EPMA problem in analysing the composition of phases containing hafnium and silicon (section 4.2.1.e).

Reflections around 0.350 nm and 0.2493 nm were observed in other as-solidified and heat-treated alloys as listed below in table 38.

d. Measurement of the (222) reflection of Ni_5Hf and Ni_5Zr in x-ray diffraction.

In determining the effect of silicon on Ni_5Hf and Ni_5Zr , the problem of peak overlap was again encountered. The lattice spacing of the (222) reflection was required for Ni_5Hf and Ni_5Zr . Other phases in which a reflection with a similar lattice spacing would be observed are shown in table 39:

Specimen	(100)nm	(110)nm
NHS1 As-solidified	0.35304	0.24946
NHS2 As-solidified	not observed	
NHS3 As-solidified	0.35280	0.24887
NHS4 As-solidified	not observed	
NHS5 As-solidified	not observed	
NHS1 926	0.35261	0.24869
NHS2 926	0.35213	0.24860
NHS3 926	0.35215	0.24866
NHS3 1071	0.35310	0.24862
NHS1 1125	0.35161	0.24845
NHS2 1125	0.35232	0.24864
NHS3 1125	0.35196	0.24863
NHS4 1125	--	0.24859
NHS5 1050	not observed	
NZS2 As-solidified	0.34859	0.25104
NZS4 As-solidified	0.34897	0.25107
NZS3 As-solidified	0.35059	0.24836
NZS1 As-solidified	not observed	
NZS5 1050	not observed	

-coincides with $\text{Ni}_3\text{Si } \beta 2$.

Table 38. Reflections observed in specimens by x-ray diffraction at 0.352 nm and 0.249 nm.

Compound	Lattice Spacing	Relative Intensity
Ni_5Hf	0.1920 nm	(50)
Ni_5Zr	0.1928 nm	(80)
$\text{Ni}_3\text{Si } \beta 2$	0.1915 nm	(80)
$\text{Ni}_3\text{Si } \beta 3$	0.1915 nm	(20)
$\text{Ni}_{31}\text{Si}_{12}$	0.1924 nm	(100)
Ni_7Hf_2	0.1929 nm	(70)

Table 39. Interplanar spacings observed at 0.192 nm in the x-ray diffraction patterns of several intermetallic compounds.

e. Reliability of EPMA in quantifying the Hf and Si contents in phases.

Determination of the hafnium and silicon contents in phases by EDS analysis was found to be difficult when the silicon content was low. The problem arose in NHS4 As-solidified, NHS4-1125, NHS5 As-solidified and NHS5-1050. The hafnium and silicon contents in phases in these specimens were determined by WDS analysis. The problem was an important one because initial results suggested that silicon was soluble in Ni_5Hf which had not ^{been} expected because it had been reported that silicon was not soluble in Ni_5Zr (28). Ni_5Hf and Ni_5Zr have very similar structures. Results obtained from the as-solidified and heat-treated Ni-Zr-Si alloys were conclusive in showing that silicon was soluble in Ni_5Zr . The zirconium $M\alpha$ peak obtained during EPMA does not overlap the silicon $K\alpha$ peak as the hafnium $M\alpha$ one does.

EPMA results for the silicon contents of phases containing very small amounts of hafnium were accepted as correct, since, apart from $\text{Ni}_3\text{Si } \beta 1$, the silicon contents of the intermetallic phases found, $\text{Ni}_3\text{Si } \beta 3$ and Ni_5Si_2 , were in agreement with the literature (see EPMA results).

The errors associated with EPMA were calculated for all analyses. The maximum error for any given element in an analysis was 0.8 at.%.

4.2 Ni₅Hf and Ni₅Zr in the nickel-rich corners of the Ni-Hf-Si and Ni-Zr-Si systems.

4.2.1 The solubility of silicon in Ni₅Hf and Ni₅Zr.

The specimen which did not undergo partial melting during heat treatment in the Ni-Hf-Si system was NHS4-1125. Ni₅Hf was identified by EPMA and by x-ray diffraction and the silicon content in the phase was measured as 4.3 at.%. At first, the measurement was considered to be inaccurate (section 4.1.2.e) , but the position of a 'tie line' between the two phases in the alloy, based on the silicon content of the phase and the nominal composition of the alloy, supported the result (fig.64). Similarly, a 'tie line', based on EPMA results, was constructed for the NHS4 As-solidified sample. The 'tie line' passed through the eutectic and γ compositions and suggested that silicon did go into solution in Ni₅Hf. EPMA results obtained from NZS1 As-solidified supported this also. The 'tie line' drawn on the basis of the eutectic and γ compositions could be extended to the Ni₅Zr phase indicating that about 4-5 at.% Si was in solution in Ni₅Zr (fig64).

EPMA results obtained from NHS5 As-solidified and NHS5-1050 were confusing. By EDS analysis the silicon content of the alloy was three times higher than that expected (see section 4.1.2.e). However, EPMA results for NZS5 As-solidified and NZS5-1050 showed that silicon was in solid solution in Ni₅Zr up to 1.5 at.% and 2.3 at.% respectively. Further evidence was obtained after

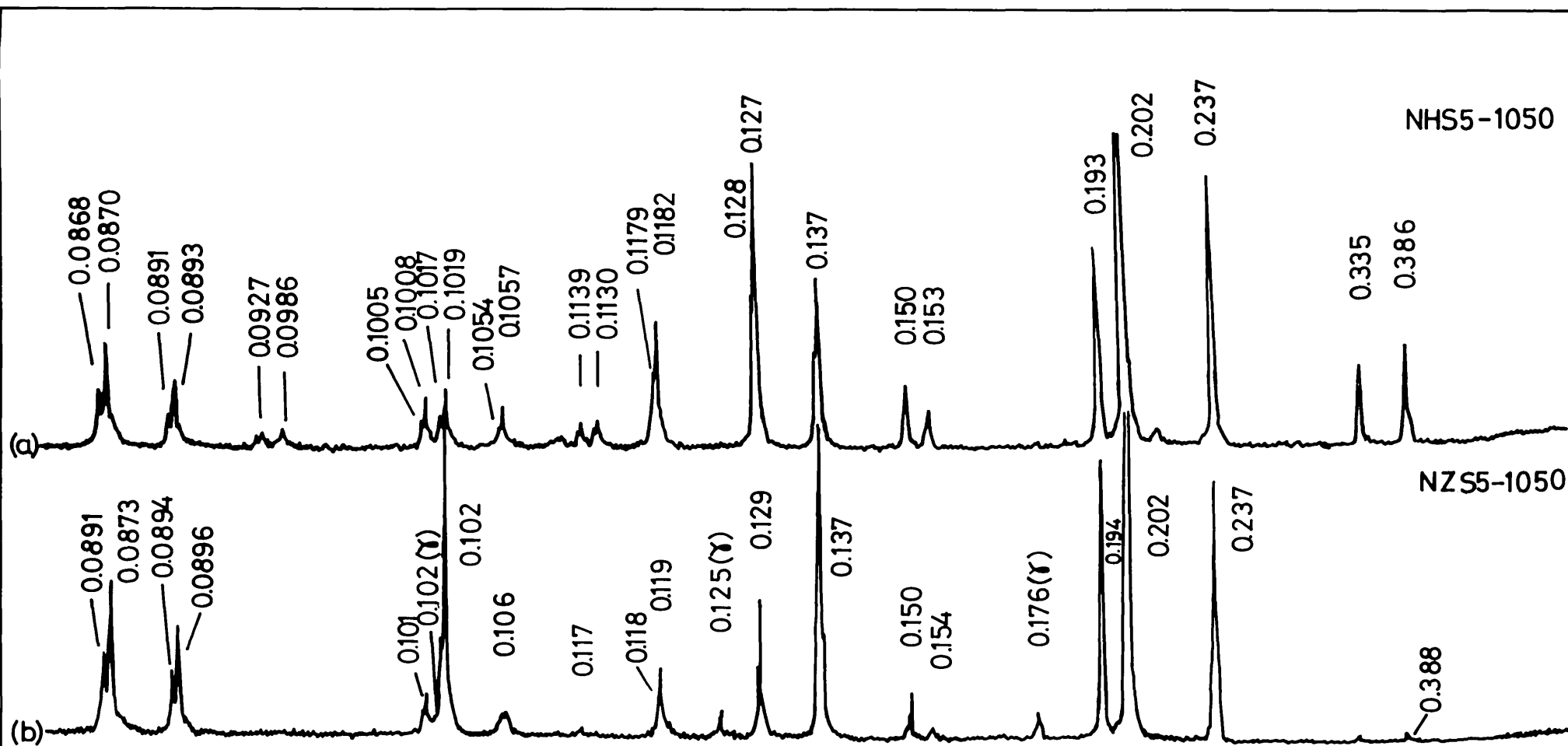


Fig 65 X-ray diffraction results showing the reflections obtained for specimens NHS5-1050 and NZS5-1050 (a) Ni₅Hf (b) Ni₅Zr + small reflections for γ.

heat-treatment of the as-solidified structures at 1050°C for 163 hours. NHS5-1050 was almost completely single phase apart from a very small volume fraction of eutectic and the presence a few particles of Ni_7Hf_2 which were identified by EPMA. NZS5-1050 was similar, although the volume fraction of eutectic was slightly greater. X-ray diffraction confirmed that both specimens were almost completely single phase Ni_5Hf and Ni_5Zr respectively (fig.65). (Extra reflections corresponding to γ were only observed in NZS5-1050 but these were extremely weak in comparison with the Ni_5Zr reflections).

The Electron Back Scattering Pattern shown in fig.50 was also obtained from NHS5-1050. This also showed the specimen to be Ni_5Hf and the lattice parameter was calculated to be 0.66 nm which agrees with the value obtained by x-ray diffraction although the method is only accurate to two decimal places.

Additional evidence for the solubility of silicon in Ni_5Hf and Ni_5Zr was found in other specimens also, especially in NHS2 As-solidified, NHS2-926, NHS2-1125, NZS4 As-solidified, NZS4-1070. In the as-solidified specimens of NHS2 and NZS4, the primary phase contained 10 at.% silicon. In the heat treated specimens the volume fraction of Ni_5Hf and Ni_5Zr was the greatest and the silicon content was found to be 10.1 at.% silicon in NHS2-1125 and 8.1 at.% silicon in NZS4-1070. In NHS3-926, 6.8 at.% silicon was found in solid solution in Ni_5Hf .

It has been shown here that silicon was soluble in

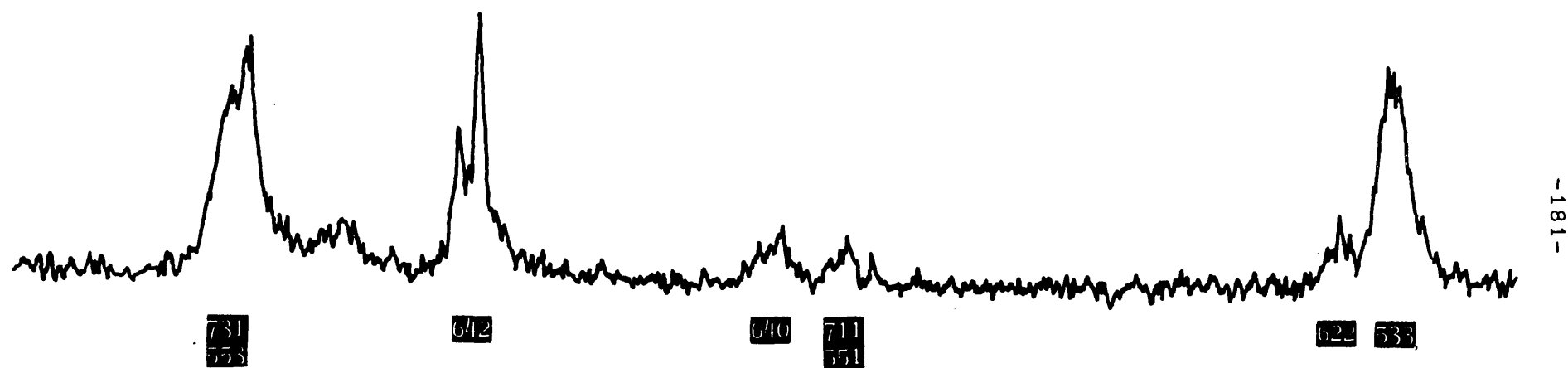


Fig.66 High angle x-ray diffraction reflections observed in NHS2-1125. The reflections can be seen to be splitting indicative of a changing crystal structure.

Ni_5Hf and Ni_5Zr up to at least 10.1 at.% silicon. A result obtained from NZS3 As-solidified suggested that the extent of solubility was in fact greater and Ni_5Zr , in the eutectic, was found to have 19.3 at.% silicon in solution.

4.2.2 Effect of the solubility of silicon in Ni_5Hf and Ni_5Zr .

Close observation of the high angle reflections obtained by x-ray diffraction, for Ni_5Hf and Ni_5Zr , but especially for Ni_5Hf in NHS2-1125, showed that if the silicon content in Ni_5Hf was high, i.e. 10 at.%, then the high angle reflections were splitting, indicative of a change in the crystal structure (fig.66). Even though the degree of splitting was fairly small, it was envisaged that the change in structure with silicon content could be detected by plotting the interplanar spacing for the (222) reflection against the silicon content of the phase (fig.67). This indicated that the effect of silicon content on the structure of Ni_5Hf and Ni_5Zr was minimal without more accurate measurements, at least. However, the interplanar spacings of the (222) reflections, in these compounds, were found to be consistently greater than the values given in the ASTM diffraction file for Ni_5Hf and Ni_5Zr .

4.2.3 Comparison of the solubility of silicon in Ni_5Hf and Ni_5Zr with the solubility of aluminium in Ni_7Hf_2 and Ni_7Zr_2 .

In NHS2-1125 and NZS4-1070, silicon was found to go

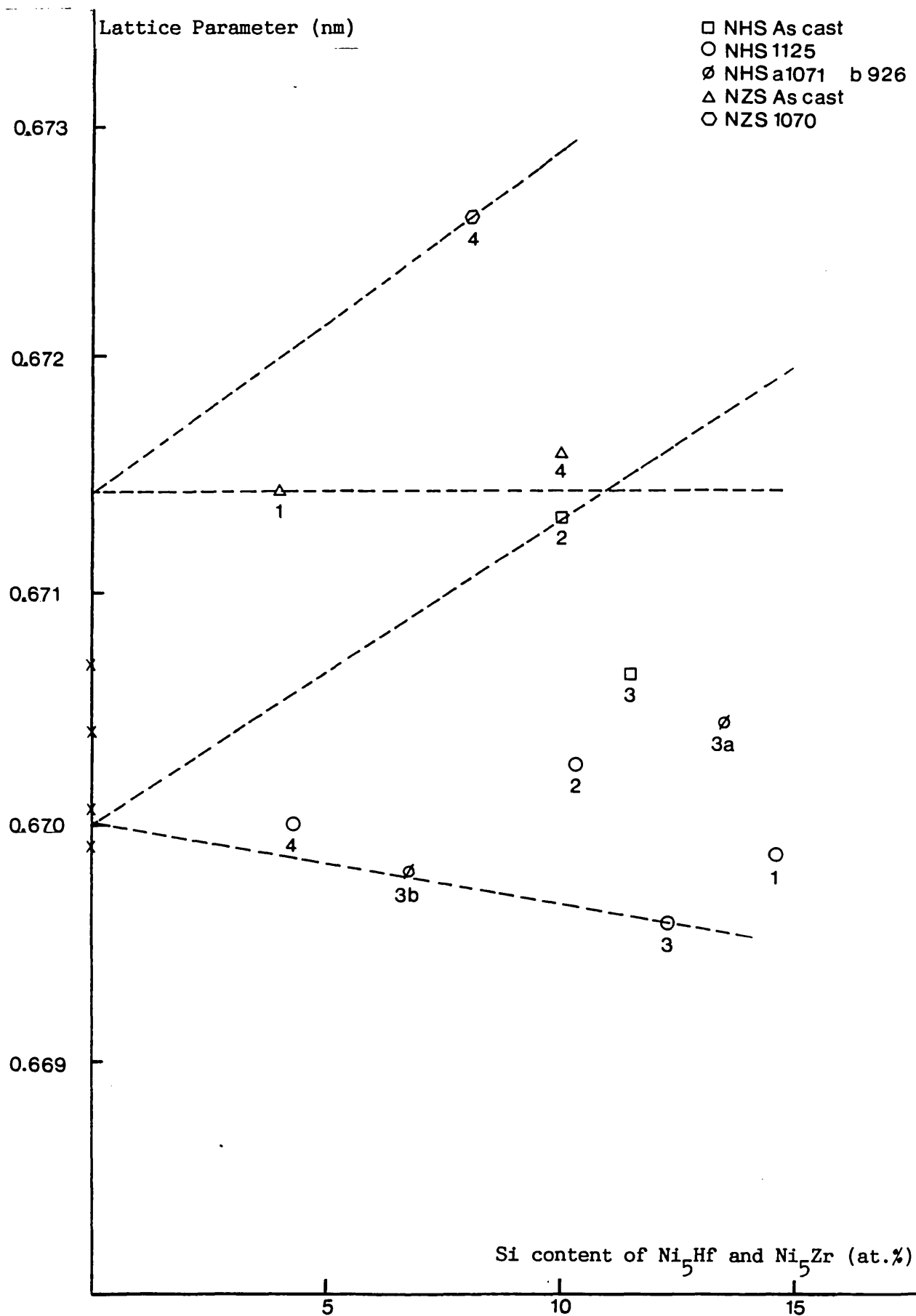


Fig.67 Plot of interplanar spacing for the (222) reflection in Ni_5Hf and Ni_5Zr against silicon content of the phase in various specimens.

into solution in Ni_5Hf and Ni_5Zr by 10 at.% and 8 at.% respectively. The phases have complex, cubic structures. The lattice parameters are 0.668 nm and 0.671 nm respectively. Ni_5Hf and Ni_5Zr are based on the AuBe_5 type structure. The positions of atoms in the unit cells are given in tables 12 & 14. Silicon was shown to replace nickel atoms in both crystals.

There are two types of nickel atom in the structure of Ni_5Hf and Ni_5Zr . If one of these types was replaced by silicon, then one could expect up to 16 at.% silicon to replace nickel in the structure. EPMA showed that one consistently replaced 10 at.% silicon in these phases. In NZS3 As-solidified, as much as 19.5 at.% silicon was measured in Ni_5Zr - but only one measurement was made. EPMA has shown that silicon did replace nickel atoms in the structure and the hafnium content always remained constant.

The nickel atoms are stacked in layers in Ni_5Hf and Ni_5Zr (fig.8). If these atoms were replaced with silicon atoms then the lattice would be expected to contract in the (111) direction because silicon atoms are smaller than hafnium or zirconium atoms. This theory supports the hypothesis of a change of structure in Ni_5Hf and Ni_5Zr with increasing silicon content.

In Ni-Al-Hf and Ni-Al-Zr systems limited solubility of aluminium in Ni_5Hf and Ni_5Zr has been reported, but extensive solubility in Ni_7Hf_2 and Ni_7Zr_2 was shown (27). The structure of Ni_7Hf_2 and Ni_7Zr_2 is monoclinic (31,32). The positions of the atoms in the unit cell are given in

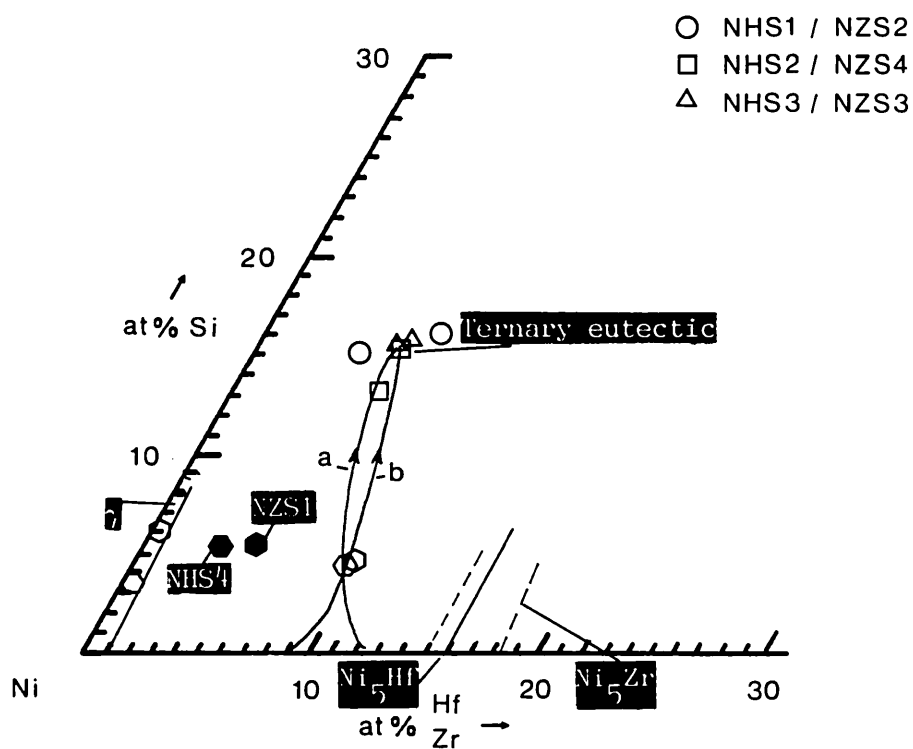


Fig.68 Approximate positions of the eutectic valleys for the reactions (a) $L \rightarrow \gamma + \text{Ni}_5\text{Hf}$ and (b) $L \rightarrow \gamma + \text{Ni}_5\text{Zr}$.

table 14 & 15. There is one set of nickel atoms which could be replaced with aluminium atoms such that the aluminium content of Ni_7Zr_2 would be 11 at.%. Nash has shown (27) that between 1000°C and 1200°C the aluminium content of Ni_7Hf_2 was 11-13 at.%, and the direction in which the solubility lobe extends shows that aluminium atoms replace nickel atoms.

4.3 The form of the liquidus in the nickel-rich regions of the Ni-Hf-Si and Ni-Zr-Si systems.

Fig.68 shows the approximate positions of the eutectic valley for the reactions:



and



There is a compositional difference in the binary systems but the curves lie quite close to one another in the ternary systems. It is suggested that the temperatures of these binary eutectic valleys in Ni-Hf-Si and Ni-Zr-Si decrease with increasing silicon content until such a temperature that any remaining liquid solidifies as a ternary eutectic. The evidence for this hypothesis is:

1. The eutectic compositions measured in the following specimens were all similar (Table 40).

2. Tie lines constructed from EPMA data indicated that the eutectic consisted of three phases, γ , Ni_5Hf and $\text{Ni}_3\text{Si} \beta_1$.

3. γ , Ni_5Hf , and $\text{Ni}_3\text{Si} \beta_1$ were identified by x-ray

diffraction after heat treatment of NHS2 and NHS1 at 926°C, and the structure, in each case, was shown to consist of three phases (figs.38a,38b).

4. Two eutectics were observed in some specimens. By EPMA, the one with the fine-structure was found to have the ternary eutectic composition.

Alloy	Eutectic composition		
	Ni	Hf	Si
NHS1-as-solidified	77.6	6.4	16.0
NHS2-as-solidified	80.4	6.2	13.4
NHS3-as-solidified	76.4	7.4	16.2
NZS2-as-solidified	78.4	6.0	15.6
NZS4-as-solidified	78.4	6.1	15.4
NZS3-as-solidified	80.4	4.2	15.3

Table 40. The postulated ternary eutectic composition in various specimens measured by EPMA.

The compositions of some of the as-solidified eutectics, measured by EPMA, are given in table 40. The compositions of these eutectics were found to be very similar. The small differences between some the results could be explained in terms of the area of eutectic chosen for analysis, the depth from which x-rays were emitted and the size of area chosen for analysis.

The compositions of the eutectics, which were away from the binary edges of the diagram and similar in these three alloys, were indicative of there being a ternary eutectic. As a result, the temperature at which the ternary eutectic forms should be the same for the three alloys. DTA results were interpreted as supporting this view. The Ni-Hf-Si specimens which had been heat treated at 1125°C

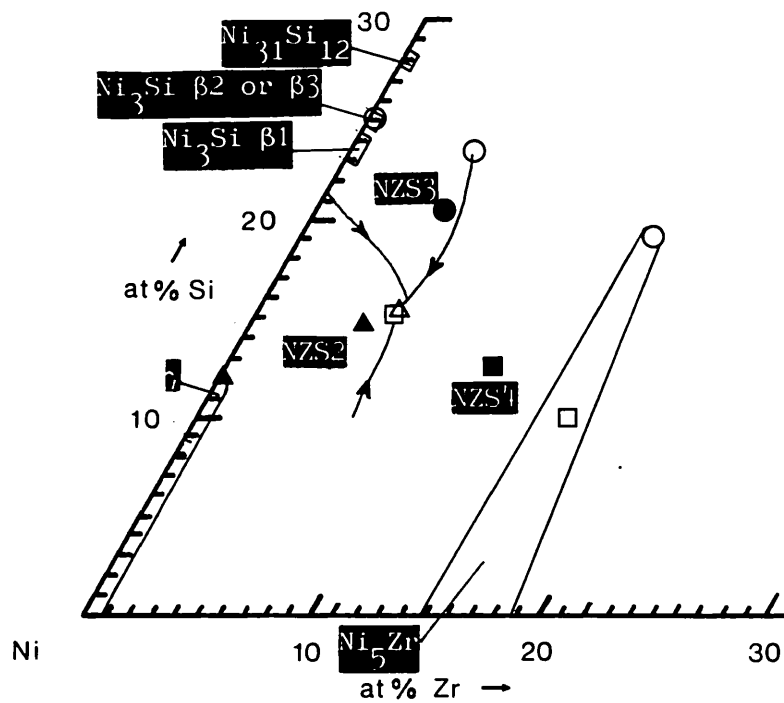


Fig.69 Ternary phase diagram in the Ni-rich corner of the Ni-Zr-Si system showing the position of the ternary eutectic, and of the primary phases in NZS2 as-solidified and NZS4 as-solidified. Positions of phases measured in NZS3 as-solidified are also shown.

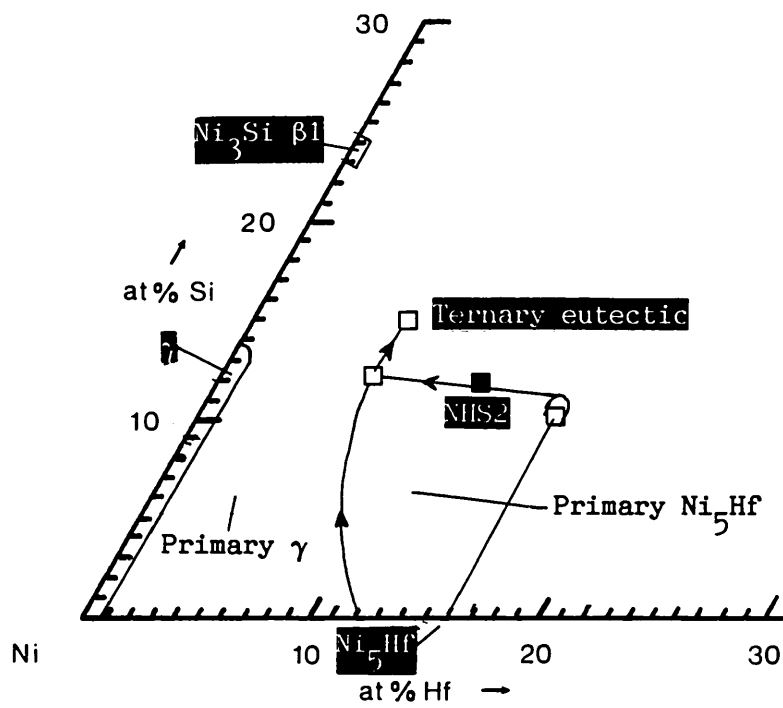
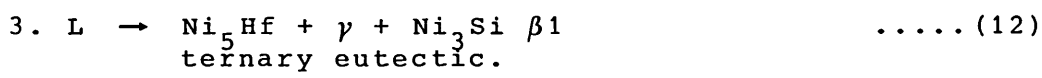


Fig.70 Postulated solidification sequence of NHS2 alloy showing liquidus.

were found to give very similar differential thermal analysis results below 1120°C. One explanation of this is that the ternary eutectic becomes liquid at about 1037°C. In which case the binary $\gamma/\text{Ni}_5\text{Hf}$ eutectic in the nickel-rich corner of the Ni-Hf system could run down from 1190°C into the ternary eutectic at 1037°C. The composition of the eutectic in NHS4-as-solidified and in NZS1-as-solidified would support this. Alloys 2 and 4 in the Ni-Zr-Si system lay directly on lines between the composition of the ternary eutectic and the compositions of their respective primary phases which was γ in NZS2-as-solidified and Ni_5Zr in NZS4-as-solidified (fig.69). The corresponding alloys in the nickel-hafnium-silicon system NHS1 and NHS2 showed a similar result, although the composition of what was considered to be a binary eutectic between γ and Ni_5Hf was also measured in NHS2-as-solidified. The solidification of NHS2 would, therefore, be expected to occur in the following way (fig.70):-



The binary eutectic, $\text{Ni}_3\text{Si} \beta 2$ or $\beta 3$ and Ni_5Zr , moving down into the ternary eutectic from the silicon rich part of the diagram was deduced from NZS3 (fig.69). A eutectic was observed which consisted of $\text{Ni}_3\text{Si} \beta 2$ or $\beta 3$ and Ni_5Zr .

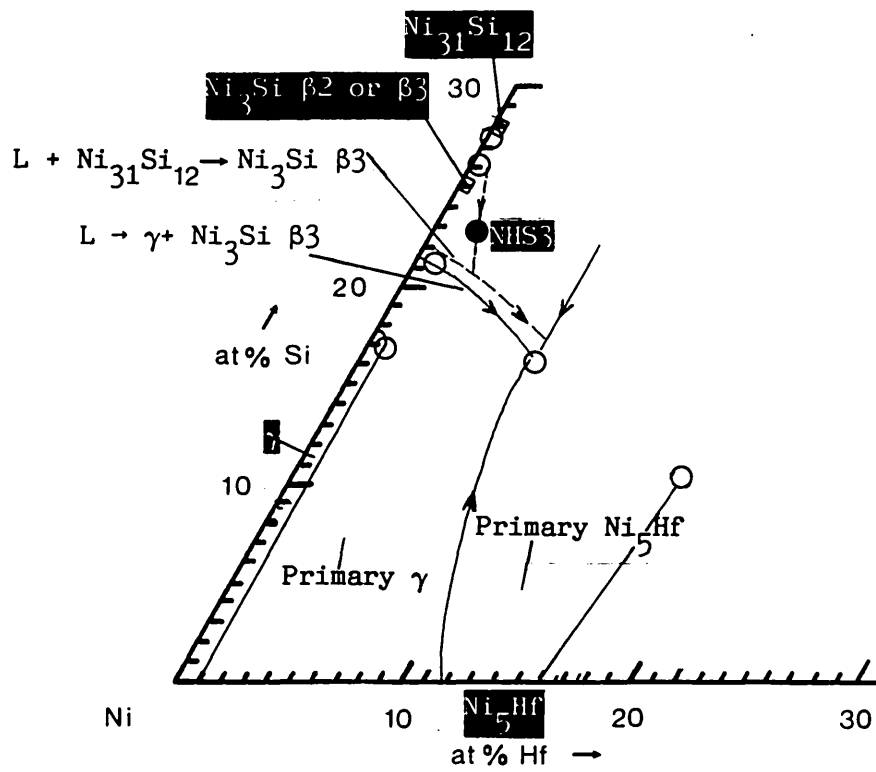


Fig.71 Solidification sequence of NBS3 as-solidified.

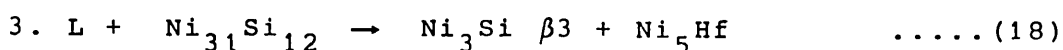
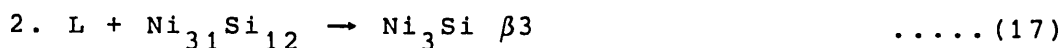
The eutectic composition is marked and lies midway between the compositions of the components of the eutectic.

NZS3 was interpreted to have solidified in the following manner.



The alloy finally consisted of needles of Ni_3Si $\beta 2$ or $\beta 3$, a binary eutectic of Ni_3Si $\beta 2$ or $\beta 3$ and Ni_5Zr and a ternary eutectic of Ni_3Si $\beta 1$, Ni_5Zr and γ .

The solidification sequence of the NHS alloy was interpreted to be different from NZS3-as-solidified because the composition of the alloy was different and in NHS3-as-solidified the first phase to solidify was $\text{Ni}_{31}\text{Si}_{12}$. The sequence was:-



$\text{Ni}_{31}\text{Si}_{12}$ at first formed from the melt congruently. The compound is considered to have limited solid solubility. The second reaction has to promote Ni_3Si in one of its forms, probably Ni_3Si $\beta 3$, so that the formation of

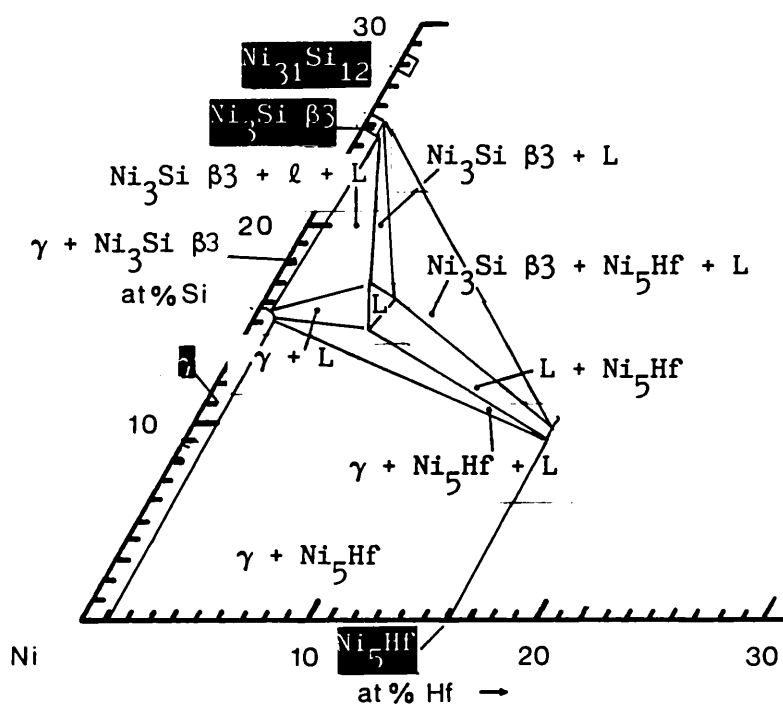


Fig.72 Postulated ternary isothermal section in the nickel-rich corner of the Ni-Hf-Si system at 1125°C.

$\text{Ni}_3\text{Si } \beta_3$ and Ni_5Hf is possible by a peritectic reaction. Equation 18 describes the formation of $\text{Ni}_3\text{Si } \beta_3$ and Ni_5Hf . The final reaction under non-equilibrium cooling would give rise to the formation of the ternary eutectic - equation 19.

Several reactions must occur in order to bring about the change from $\text{Ni}_3\text{Si } \beta_3$ to $\text{Ni}_3\text{Si } \beta_1$. This problem has not been addressed in this work as there is insufficient information to do so.

4.4 Isothermal sections at 1125°C and 926°C in the nickel-rich corner of the Ni-Hf-Si system.

4.4.1 Ternary isothermal section of the nickel-rich corner of the Ni-Hf-Si system at 1125°C.

The results indicated that at equilibrium at 1125°C there was liquid present in alloys NHS1, NHS2 and NHS3.

NHS4-1125 was the only alloy not to have undergone partial melting at this temperature. The two phases identified in the specimen were γ and Ni_5Hf . EPMA gave the compositions of both and a tie line was constructed between the two as in fig.64. This showed that silicon was soluble in Ni_5Hf and therefore, in conjunction with the EPMA results from NHS2-1125 i.e. the solubility of silicon in Ni_5Hf being 10 at.% at 1125°C, the two phase, $\gamma + \text{Ni}_5\text{Hf}$ region could be drawn (fig.72). On quenching from 1125°C the eutectics that formed in NHS1, NHS2 and NHS3 would provide the composition of the liquid that was present.

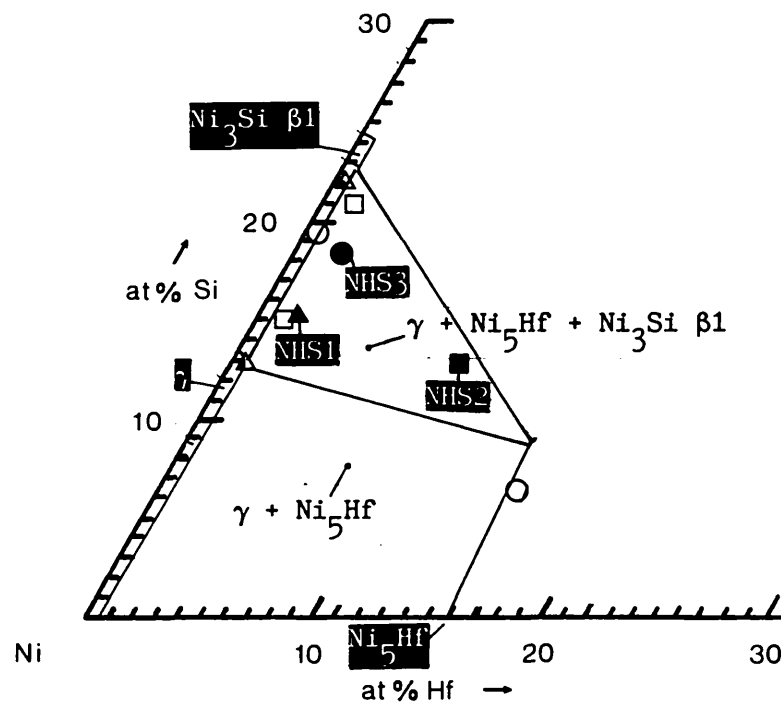


Fig.73 Postulated ternary isothermal section in the nickel-rich corner of the Ni-Hf-Si system at 926°C.

Three triangles have been drawn to show the equilibrium at this temperature. The equilibrium in the three specimens was as follows:

1. NHS1-1125 $\rightarrow \gamma + \text{Ni}_3\text{Si } \beta_2 + \text{liquid}$
2. NHS2-1125 $\rightarrow \text{Ni}_5\text{Hf} + \gamma + \text{liquid}$
3. NHS3-1125 $\rightarrow \text{Ni}_3\text{Si } \beta_2 + \gamma + \text{liquid}$

In NHS1-1125°C the agreement between this diagram and the microstructure was good. NHS2-1125 consisted primarily of Ni_5Hf , with only a small amount of liquid, which is represented by the parts of the microstructure with very fine structure. The binary eutectic contained the γ phase, together with Ni_5Hf . NHS3-1125 showed that $\text{Ni}_3\text{Si } \beta_1$ and $\text{Ni}_3\text{Si } \beta_2$ or β_3 were both present which was not expected according to the Ni-Si binary section. However, the composition of the alloy was such that on cooling the alloy could pass through the two phase $\text{Ni}_3\text{Si } \beta_1$, $\text{Ni}_3\text{Si } \beta_2$ phase field. At 1125°C only the $\text{Ni}_3\text{Si } \beta_3$ phase would be expected. The alloy has not had time to reach equilibrium.

4.4.2 Ternary isothermal section of the nickel-rich corner of the Ni-Hf-Si system at 926°C.

The ternary section is shown in fig.73. Only NHS1 and NHS2 were heat treated from the as-solidified state to 926°C. NHS3-926 was heat treated prior to this at 1125°C, followed by 168 hrs. at 1070°C. However, the results were in agreement and a three phase region consisting of γ , Ni_5Hf and $\text{Ni}_3\text{Si } \beta_1$ is postulated. NHS1 and NHS2 were three phase alloys containing γ , $\text{Ni}_3\text{Si } \beta_1$ and Ni_5Hf . The compositions of γ and $\text{Ni}_3\text{Si } \beta_1$ were established by EPMA.

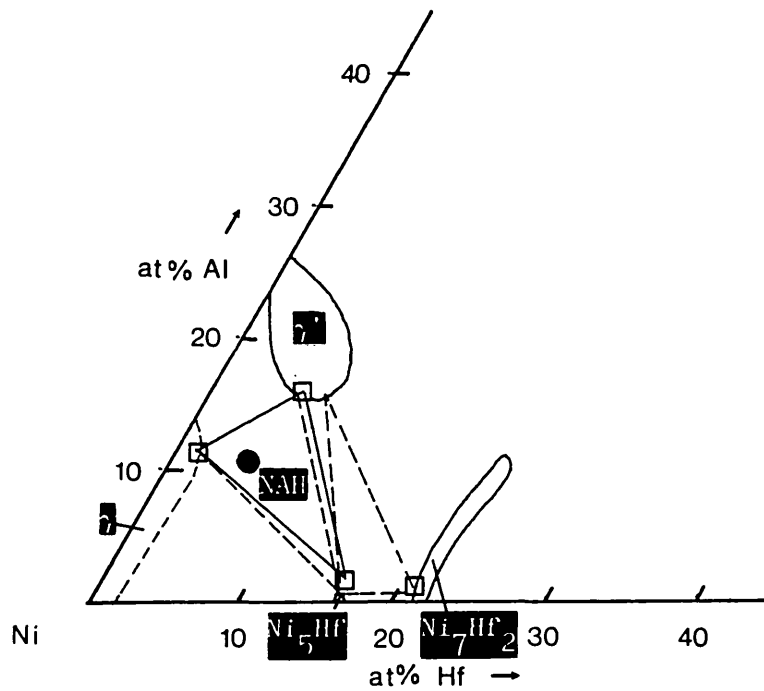


Fig.74a Ternary isothermal section in the nickel-rich corner of the Ni-Al-Hf system at 1000°C showing the alloy and the compositions of γ , γ' and Ni_5Hf .

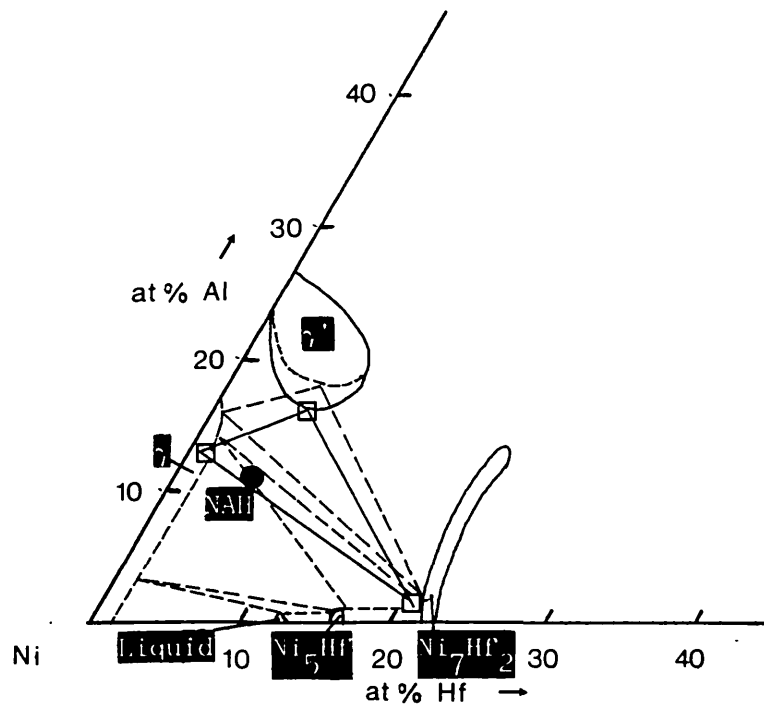


Fig.74b Ternary isothermal section in the nickel-rich corner of the Ni-Al-Hf system at 1200°C showing the alloy and the compositions of γ , γ' and Ni_7Hf_2 .

These results would be in agreement with the results obtained at 1125°C postulating a ternary eutectic. Ni_5Hf and Ni_3Si $\beta 1$ were identified in NHS3-926 by EPMA. γ was not detected, but this was not surprising since the composition of the specimen was almost directly on the two phase line joining the 2 phases.

4.5 The reaction occurring in Ni-12 at.% Hf-5 at.% Al between 1000°C and 1200°C.

The results were in basic agreement with the work of Nash and West (27), although the compositions of the phases in NAH1000 and NAH1200 from which the tie triangles in fig.74 were constructed were found to be more nickel-rich than those measured by Nash and West.

The intensities of reflections, obtained by x-ray diffraction, for Ni_7Hf_2 were very weak in NAH1000 compared with those for γ , γ' and Ni_5Hf , whereas, in NAH1200 the Ni_5Hf reflections observed were much weaker. This indicated that Ni_5Hf was the stable phase at 1000°C whereas, at 1200°C, the stable phase was Ni_7Hf_2 .

A reaction was also observed by DTA between 1000°C and 1200°C (fig.59) which was believed to be:



DTA detected the reaction 1177°C on heating. The temperature was required in order to be able to postulate the quaternary sections of the nickel-rich corners of the Ni-Al-Hf-Si system at 1000°C and 1100°C.

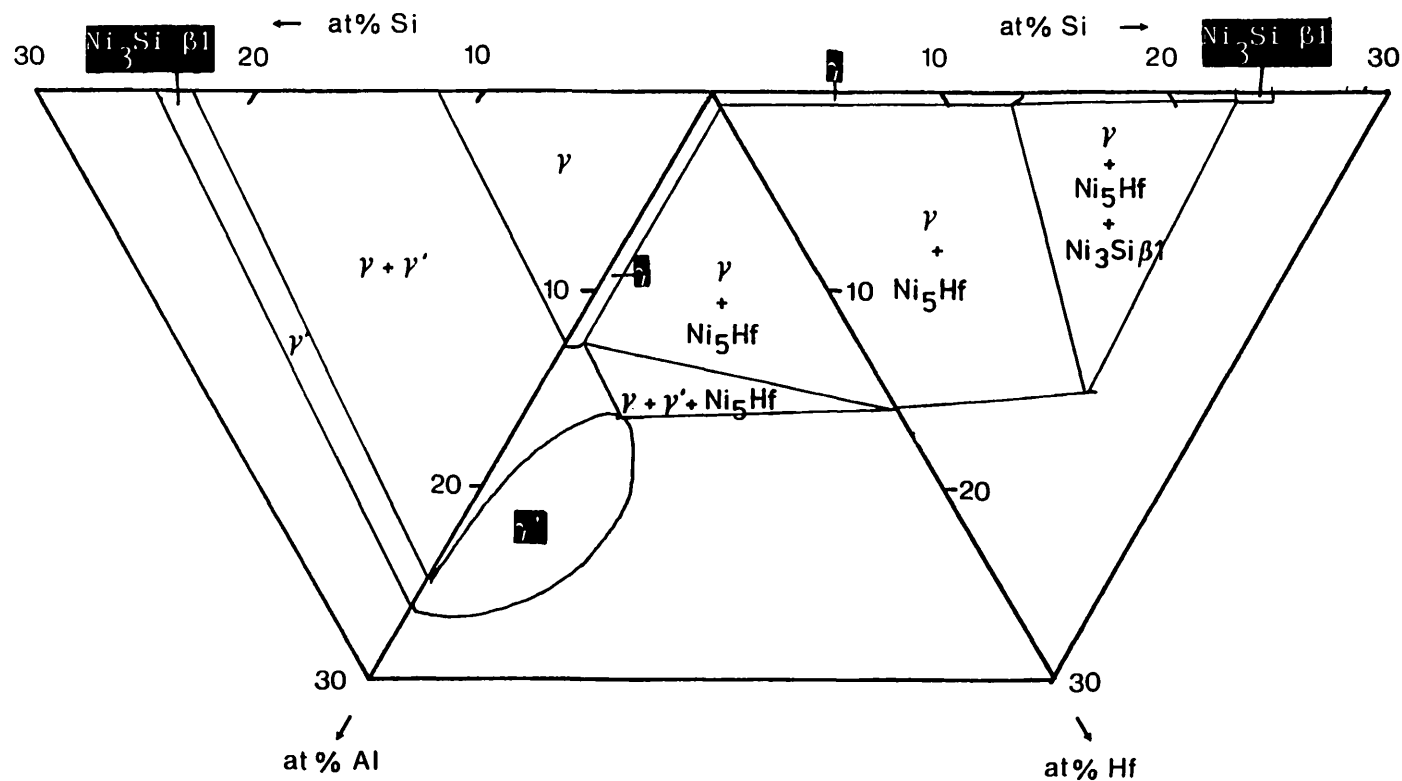


Fig.76 Isothermal sections of the 3 ternary alloy systems at 926°C which form the basis of the Ni-Al-Hf-Si section at this temperature. Note the continuous solid solution between $\text{Ni}_3\text{Si } \beta 1$ and Ni_3Al in the Ni-Al-Si ternary and the three phase $\gamma + \text{Ni}_3\text{Si } \beta 1 + \text{Ni}_5\text{Hf}$ region in the Ni-Hf-Si ternary.

4.6 Quarternary isothermal sections in the nickel-rich corner of the Ni-Al-Hf-Si system at 1000°C and at 1100°C.

The section shown in fig.75 is based on the following ternary sections:

1. Nickel-aluminium-hafnium 1000-1200°C. (Nash and West).
2. Nickel-aluminium-silicon at 1100°C. (Guard and Smith).
3. Nickel-hafnium-silicon at 1125°C. (This work).

The section shown in fig.76 is based on the following ternary sections:

1. Nickel-aluminium-hafnium 1000-1200°C. (Nash and West).
2. Nickel-hafnium-silicon at 926°C. (This work).

In the determination of the isothermal section of the ternary Ni-Al-Hf system at 1100°C Guard and Smith reported a limited solubility of Al in Ni_3Si . More recently, the β_3 forms of Ni_3Si have been postulated i.e. β_1 , β_2 and β_3 . It has been shown (30) that at 1100°C the high temperature forms of Ni_3Si would not accommodate ternary additions. In this work EPMA results for the amount of Hf in Ni_3Si showed that the total content of Hf in the high temperature form was only 0.3 at. %.

The limited amount of analysis carried out on the NAHS alloy was enough to show how extensive the $\gamma + \text{Ni}_5\text{Hf}$ two phase region was.

4.7 Ni-Hf and Ni-Zr rich phases in nickel-base superalloys

In comparison with the EDS spectra for the matrix, carbides and eutectic, the spectra obtained for the Ni-Zr-rich phases indicated that regions in these alloys

contained increased amounts of Ni and Zr in comparison with other phases. It is these regions that have been termed the Ni-Zr and Ni-Hf rich phases although the chromium content of these phases was also high. (The titanium content was always low). The amount of zirconium measured in the phase indicated that the phase could be Ni_5Zr i.e. Ni_5Zr would contain 16 at.% Zr (table 7). From the results obtained there was insufficient evidence to show that the phase was Ni_5Zr because of the limit in the EPMA technique of measuring the composition of a particle in the alloy whose size is less than $3\mu\text{m}$. Silicon was found to be associated with the Ni-Zr phase, however, and up to 4 at.% Si was measured in one alloy. The result was expected after having discovered that it was possible to replace 8 at.% nickel with silicon in Ni_5Zr in a model Ni-Zr-Si alloy.

The identity of the Ni-Zr or Ni-Hf phase was also sought by the EBSD method, by obtaining structural information about it. Unfortunately, although patterns were observed from the majority of phases in the superalloy, no pattern could be obtained from the Ni-Hf phase. The problem was due to the way in which the specimens had been prepared. A final polish with an OPS solution for a period of anything between $\frac{3}{4}$ hr. and 3 hrs. had proved an excellent method for preparing superalloy samples to be studied using the EBSD technique, but for Ni_5Hf it was found to give very poor results. A freshly fractured surface of Ni_5Hf proved to be the best method for obtaining patterns. However, it would have been very difficult to

identify the Ni-Hf phase in a freshly fractured specimen of MarM002.

CONCLUSIONS AND FURTHER WORK

1. Extensive two phase fields have been identified in the Ni-Hf-Si and Ni-Zr-Si systems at 1125°C and 1050°C respectively consisting of Ni (η)+Ni₅Hf and Ni (η)+Ni₅Zr.

2. Nickel atoms were replaced by silicon atoms in Ni₅Hf and in Ni₅Zr, and the results suggested that as the silicon content increased the structure was transforming from face centred cubic to tetragonal. In alloys NHS2 1125°C and NZS4 1070°C which contained the largest volume fractions of Ni₅Hf and Ni₅Zr, silicon was found to be soluble in these intermetallic compounds in amounts of up to 10 at. %.

3. A ternary eutectic in the nickel-rich corner of the Ni-Zr-Si system was postulated. This eutectic was believed to be of composition Ni-6.0 Zr-15.6 Si.

4. A ternary eutectic was also postulated in the nickel-rich corner of the Ni-Hf-Si system. The eutectic composition was also believed to be similar to that of the Ni-Zr-Si eutectic.

5. The phase relationships suggested by (28) in the Ni-Zr-Si system were not observed. The T phase at Ni-20.7 Zr-24.1 Si was not identified in the Ni-Zr-Si alloys either by x-ray

diffraction or by EPMA. Instead the Ni_5Zr phase was believed to extend out into the diagram, silicon atoms replacing nickel atoms, and the nickel rich corner of the diagram was thought to consist of 3 regions. These were:-

1. $\text{Ni}(\gamma) + \text{Ni}_5\text{Zr}$
2. $\text{Ni}(\gamma) + \text{Ni}_5\text{Zr} + \text{Ni}_3\text{Si}$ (below about $1100^\circ\text{C}.$)
3. $\text{Ni}_3\text{Si} + \text{Ni}_5\text{Zr}$

6. Silicon was also shown to be associated with a Ni-Zr phase believed to be Ni_5Zr in MarM246. The solubility of silicon in Ni_5Hf and Ni_5Zr lends support to the hypothesis that the Ni-Hf and Ni-Zr phases observed in certain nickel-base superalloys are indeed these compounds.

FURTHER WORK:

1. Alloys of the ternary eutectic composition be prepared by argon-arc melting. Heat treatments above and below 1037°C would confirm the existence of this eutectic. The eutectic could be examined in greater detail by preparation of thin foils for the TEM. DTA would also confirm the ternary eutectic. A peak should be observed at $1037^\circ\text{C}.$

2. A series of alloys, containing constant amounts of Hf or Zr of 16 at.% and increasing amounts of silicon up to 20 at.% should be prepared. The alloys should be essentially

single phase Ni_5Hf or Ni_5Zr after heat treatment at 1050°C for 168 hours. Accurate lattice parameter determination of the Ni_5Hf or Ni_5Zr phases should be obtained to observe the change in structure of the phases with increasing silicon content.

3. Alloys should be prepared to investigate the degree of solid solution of silicon in Ni_7Hf_2 and Ni_7Zr_2 .

4. Additional work to be done to establish the phase boundaries in Ni-Al-Hf-Si and the extent of solid solution of some of the phases.

5. Development of a suitable technique to obtain a suitable surface finish for Ni_5Hf and Ni_5Zr in order to be able to identify the Ni-Hf or Ni-Zr phase in various nickel-base superalloys by the electron back-scattering pattern method.

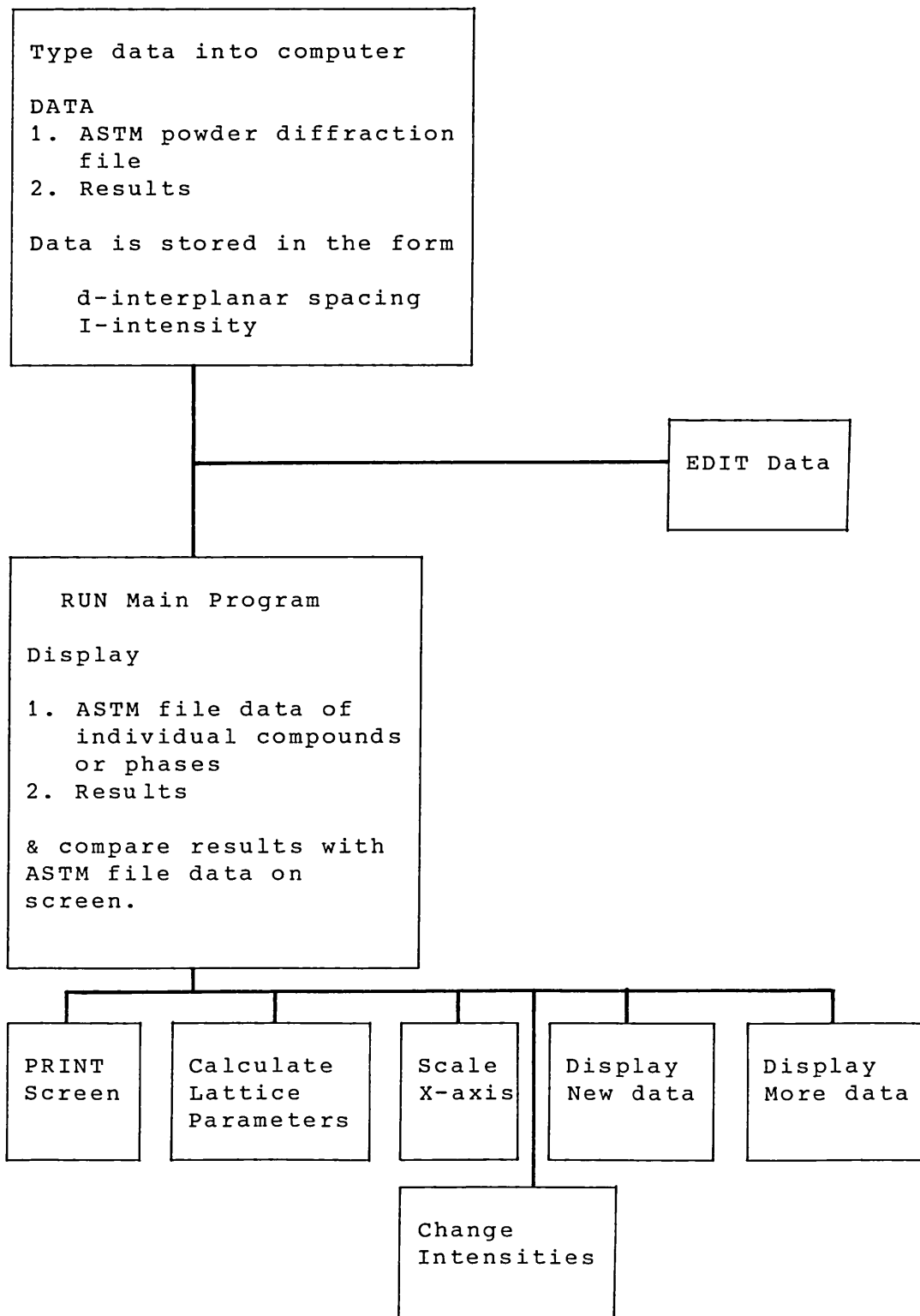
In all of the above the Ni-Zr system will prove to be the best system to work with because of the problems associated with EPMA when accurate silicon and hafnium compositions are required from the same specimen.

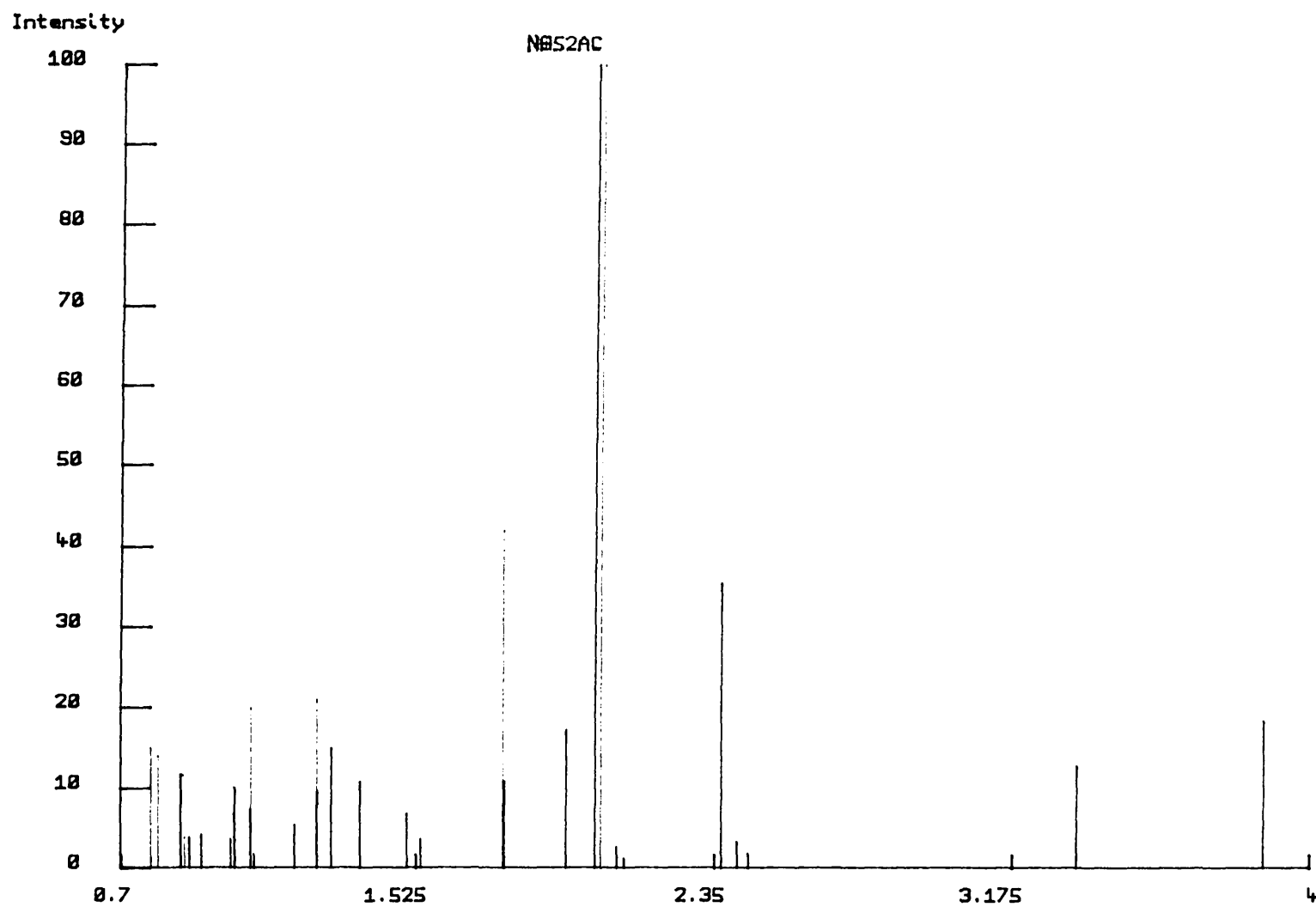
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APPENDIX 1 - X-RAY DIFFRACTION PROGRAM FOR COMPARING
RESULTS WITH KNOWN STANDARDS AND CALCULATING LATTICE
PARAMETERS FOR CUBIC CRYSTALS





INSTRUCTIONS FOR THE USE OF THE LINK "SPECTA PACKAGE"

1. Microscope on - stage to (32.5, 49.0)
(corresponds to 0, 0 position on Specta coordinates).
2. Spectrometer gate open.
3. WDX-2A computer 'on' - 'Element' mode (p.3).
Make a note of particulars (parameters) for all elements required.
4. Reset WDX-2A computer + put into 'external' mode.
5. SPECTA program in 'drive 0', if EDS analysis then ED files
or EDS/WDS analysis
required $\therefore$ ZAF⁴/FLS disc in drive 1.
6. Reset, Autoload.
7. Enter date in form - a / b / c eg. 5 / 4 / 89.
8. Change system parameters? for printer or screen output
- answer YES keeps the output as it was before.
9. LINK SYSTEMS - SPECTA WD/ED AUTOMATION.
Initialisation - very important to do this correctly.
(see example)

Answer as in example

except for:- (1) Co stage Position (this can be found later)
if not known already.

(2) Init. Dct. P.S Volts = (this can also be done later)

(3) Init. WDX 2A? Only answer YES if WDX 2A has been
switched to 'external' mode.

(4) Current crystal position / 1 (if just switched WDX 2A on)

(5) Stage Init. $\left. \begin{array}{l} x = 0 \\ y = 0 \\ z = 0 \end{array} \right\} \begin{array}{l} \text{if stage psn. on mechanical} \\ \text{readout} = (32.5, 49.0) \end{array}$

10. Switch on Red button (controls X, Y stage movement through SPECTA software).
11. See Command Modes List - different functions that can be performed within SPECTA.
12. R STAGE: check that stage limits have been set.
13. R SPMTR, " " Spectrometer " " "

All commands on the command modes list can be accessed in MAIN mode.

To get to another command one has to return to MAIN mode by typing MAIN. Alternatively one may go back to MAIN mode automatically.

Some command modes have their own set of commands

ie. see LSTAGE commands list.
EDIT commands list.

14. Obtain positions (x, y) of standards

- (1) Cobalt
- (2) WDS analysis standards.

'TSTAGE' - MAIN mode

the stage can be moved using key pad (orange keys on keyboard).
Move to standard positions - note X, Y coordinates displayed on monitor.

Also 'TSTAGE' can be used to set up a list of points (stage list)
(x, y positions) to be analysed on the sample.

Do this by pressing K on keyboard at each position where
analysis is required. Points are stored automatically.

ESC when finished.

15. Initialise Co standard co-ordinates

'IFLS' - MAIN mode.
Input co-ordinates of standard.

16. Set Up a FILE or FILES containing all elements to be analysed for

'Edit' - MAIN mode
'NEW' - EDIT mode.

Input information as it is requested.

Use (1) Example shown.

- (2) Standard positions noted in (14) if WDS analysis required.
- (3) Information obtained from WDX 2A initially in (3)

NB. if doing WDS analysis to begin with, for the following put
the values displayed in WDX 2A external mode.

PHA Th = 0.501 V
WIND = 9.25 V
Slit Size = 2.50 mm
Amp Gn = 40
Peak (time) = 10 s
Backgnd (time) = 100 s.

Also check that for the elements analysed the positions at
which backgnd counts will be measured do not coincide with
peaks from other elements.

- (4) For EDS analysis only the information required is found on the
ZAF4/FLS disc and can be obtained as a print out if required.

When finished putting all elements and information required into a file type after Elmt >.

+ you will have to input the file no. that this information will be stored in.

A listing of the file can be obtained using 'LIST'.

17. Analysis can now be carried out automatically.

SPECTA uses the file that has been created to do this.

'AN' - either MAIN
 EDIT
 LSTAGE } modes.

18. Option 3 for full stage list analysis.

ZAF4/FLS Option 1 for ZAF correction to be applied to result and result printed out.

Answer the remainder of questions - see book if necessary.

Analysis begins after answering YES or NO to final question - 'storage of result on disc?'

NB. WDS analysis

(1) Check result of analysis by performing an analysis on the standard itself, ie. choose one point for the stage list which is on the standard.

- if result poor answer NO to the question:-

Peak seek after crystal change only? NO

∴ a Peak seek will be carried out on std. psn. and sample psn.

(2) Also Counting times on Peak and background should correspond to the following relationship

$$\sqrt{\frac{\text{No of counts on Peak}}{\text{No of counts on Bckgnd}}} = \frac{\text{time on Bckgnd}}{\text{time on Peak}}$$

Can alter these times for each of the elements in a file by using

'MOD' - Edit mode.

enter Elmt , line , file no.

Use to keep parameter the same.

Alter any if necessary then press to go on.

At end

Elmt >

& 'LOAD' - Edit mode

- this loads the modified file into the memory of the computer

(3) The other parameters mentioned in (16) 3. (Again use 'MOD')
ie. PHA TL; WIND; SLIT SIZE; AMP GAIN;
(can be changed to optimise x-ray collection for a particular
element)

Brief Explanation of some of other commands

1. PEAK - Does not use WDX 2A peak seek routine.

Asks for

Chans - No of channels to be scanned

St. C - No of steps between channels

time - Counting time for each step.

∴ eg.

Chans = 100

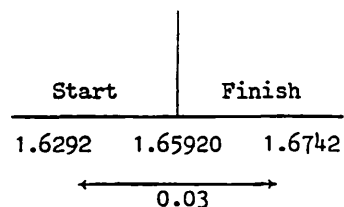
St. C = 3 Step = $0.0003 \overset{\circ}{\text{A}}$.

time = 1

Area scanned across = 100×0.0003

$= 0.03 \overset{\circ}{\text{A}}$

eg.



A peak in WDS system is 20 eV wide

Range of 20 eV $\equiv 0.00443 \overset{\circ}{\text{A}}$.

2. EDIT mode

- (a) EXT - Enter (Elmt, Line, file No)

Can extract any element from any file

+ can save these elements in a new file using SAVE.

- (b) LOAD - must load file required before automatic analysis done.

- (c) SAVE - ask which file to SAVE on. Enter file No. n.

- (d) 'UPDATE' - used whenever put a new specimen into the microscope
to check std. positions have not changed
+ if they have to enter the new std positions.

Asks, 'Go there?'

Answer (YES), stage moves to std psn.

if not correct then follow instructions and alter.

R CURTIS

June 1985

```
/Program: EDIT/ Mode *?*  
      EDIT COMMANDS LIST  
NEW -- Create New File  
EXT -- Extract Elmt Entries from Disk Files into System File  
MOD -- Modify Disk File Entries  
DEL -- Delete Disk File Entries  
LIST-- List Selected Disk File  
LOAD-- Multiple EXTRACT from All Disk File Entries  
SAVE-- Save System File on Disk  
ADD -- Add Entries to System or Disk Files  
COPY-- Copy All Elmt Disk Files to Second Disk  
LST -- Edit Stage-List  
EDIT-- Edit Elmt Data Files  
MAIN-- Return to Main Program  
AN  -- Proceed to Auto-Analysis  
UPDATE -- Update standard positions  
/Program: EDIT/ Mode *E
```

```
LSTAGE?  
/Program: EDIT/ Mode *LSTAGE*  
/Program: LSTAGE/Mode *?*  
      LSTAGE COMMANDS LIST  
NEW  -- Create new stage list  
MOD  -- Modify stage list  
ADD  -- Add to first vacant entry in stage list  
DEL  -- Delete entry in stage list  
CLEAR-- Delete all entries in stage list  
LIST -- List all entries in stage list  
SCAN -- Move stage through entries in stage list  
EDIT -- Edit elmt data files  
MAIN -- Return to main program  
AN   -- Proceed to auto analysis  
/Program: LSTAGE/Mode *
```

EDIT*

/Program: EDIT/ Mode *LIST*

File No.=2

Stds Data(0), Sample Data(1), or Both(2)= 2

ED/WD STDS FILE NO. 2 8/ 8/85

=====

No.	Elmt	KV	Tilt	Elev	Azim	ED/WD	Val	Conc%	FST	RST
1	Si:KA	20.00	.00	30.00	.00	/WD	4	100.00	1.0000	1.0000
2	Hf:MA	20.00	.00	30.00	.00	/WD	4	100.00	1.0000	1.0000
3	Al:KA	20.00	.00	30.00	.00	/WD	3	100.00	1.0000	1.0000
4	Ni:KA	20.00	.00	30.00	.00	/WD	2	100.00	1.0000	1.0000

ED Profiles :-

=====

No. Elmt Name

WD Data :-

=====

No.	Elmt	X	X-Off	Y	Y-Off	Z	Sp	Xtal	PKS--	Time	Chans	StC	NSm
1	Si:KA	13768	0	28335	5	0	1	PET	Cen	1.0000	50	10	0
2	Hf:MA	17515	0	33186	5	0	1	PET	Cen	1.0000	50	10	0
3	Al:KA	21051	0	37796	5	0	1	TAP	Cen	1.0000	50	10	0
4	Ni:KA	24341	0	42924	5	0	1	LIF	Cen	1.0000	50	10	0

No.	PHA-Th	Wind	Slit-Size	Posn	Amp.Gn	Det-Volt	Type
1	.501	9.25	2.50	-14	40	1535	FPC
2	.501	9.25	2.50	10	40	1535	FPC
3	.501	9.25	2.50	-28	40	1655	FPC
4	.501	9.25	2.50	42	40	1404	Both

-----Peak-----

-----Background-----

No.	Counts	Time	Posn.	Cnt.Rate	Counts	Time	Low	High	Cnt.Rate
1	0	5.0000	7.12080	2125.45	0	153.00	6.96800	7.21500	1.99267
2	0	10.000	7.53030	309.410	0	115.00	7.42300	7.70200	2.27897
3	0	5.0000	8.31260	6784.80	0	115.00	7.69800	8.98201	16.4275
4	0	10.000	1.65580	2252.01	0	130.00	1.62000	1.69000	13.9537

WD Data for Sample :- 8/ 8/85

=====

No.	Elmt	Counts	Time	Posn.	Cnt.Rate	Counts	Time	Cnt.Rate
1	Si:KA	0	5.0000	7.12620	.00000	0	153.00	.73452
2	Hf:MA	0	10.000	7.53900	22.8001	0	115.00	.65003
3	Al:KA	0	5.0000	8.34010	184.003	0	115.00	27.7527
4	Ni:KA	0	10.000	1.65920	1672.48	0	130.00	14.6265

/Program: EDIT/ Mode *

```

?x      COMMAND MODES LIST
SSTAGE -- Set Stage to (X,Y)
MSTAGE -- Move Stage by (X,Y)
GSTAGE -- Get Stage Posn.(X,Y)
ISTAGE -- Init Stage at (X,Y)
RSTAGE -- Set Stage Limits
LSCN   -- Stage Line-Scan Prog.
---
SSPMTR -- Set Spmtr (Absolute)
GSPMTR -- Get Spmtr Position in Input & Output Units
ISPMTR -- Init Spmtr Position in Either Input or Output Units
RSPMTR -- Set Spmtr Limits
SSCN   -- Spmtr Step-Scan Prog.
---
TSTAGE -- Track Stage
SSCA   -- Set SCA Counts/Time
GSCA   -- Get SCA Count Rate
---
IXTAL  -- Init Xtal Names and 2d-Spacings
SXTAL  -- Set/Change Xtal
---
PEAK   -- Peak-Seek Routine
CAL    -- Peak-Seek on Spec.Elmt
RATIO  -- Counts for Sample/Std.
---
EDS    -- Invoke EDS Analyser
LAB    -- Set Label for EDS
EDAN   -- Start EDS Analysis
PRINT  -- Print ED/WD Display
AN     -- Auto ED/WD Analysis
EDIT   -- Edit Element Data File
LSTAGE -- Stage-List Edit
MSCN   -- Create Grid Stage-List
FIN    -- Save Motor Positions
FLS    -- Manual ED-FLS/ZAF
ZAF    -- Manual ZAF Processing
MAC    -- MACRO option
---
STHRES -- Set PHA Threshold
GTHRES -- Get PHA Threshold
SWIND  -- Set PHA Window
GWIND  -- Get PHA Window
TSCN   -- PHA Threshold Scan
---
IFLS   -- Init FLS Std Co-ords
SFLS   -- Set Stage to FLS Std
ISAM   -- Init Sample Change Posn
SSAM   -- Set for Sample Change
---
SSLIT  -- Set Slit-Size
PSLIT  -- Set Slit Posn.
SAMP   -- Set Amp. Gain
SDET   -- Select Detector Type
SBIAS  -- Set Detector Volts
LOCAL  -- WDX-2A to Manual Mode
/Program: MAIN/ Mode *

```

8/8/85
Change System Parameters ? YES
Enter System Parameters
Change Output Configuration?NO
No. Spmtrs= 1/
Stage(X,Y) ? YES
Z Automation ? NO
Beam Current Monitor ? NO
LDOS(Filenames) ? YES
Input Units Of Spmtr Movement
Lambda ? YES
kV= 20.00/
eV/Ch= 20/
Calib. Elmt: C0/
Peak keV= 6.94200/
C0 Livetime= 100/
C0 Stage Position, X= 27790/
Y= 37288/
X-Offset(0- 255)= 0/
Y-Offset(0- 255)= 5/
Z= 0/
System Resolution, FWHM (eV) = $SN0+(SN1*10)+4=$ 115/
Cosine=1.000/
Tilt= .00/
Elevation=30.00/
Azimuthal Angle=39.40/
Xtal Spmtr 1 ,Elev=30.00/
Xtal Spmtr 1 ,Azim= .00/
Counter Dead-Time (Microsecs)= .100/
Init Spmtr/Stage Positions
Init Det.PS Volts= 0/
Init WDX-2A ? NO
Spmtr No. 1
Init Xtal Names ? ?YES
Xtal Changer Size(1-4)= 4/
Posn.1,Name= LIF /
Posn.1, 2D= 4.0267/
Posn.2,Name= PET /
Posn.2, 2D= 8.7420/
Posn.3,Name= TAP /
Posn.3, 2D= 25.7500/
Posn.4,Name= LOD /
Posn.4, 2D= 100.7000/
Current Xtal Posn(1-4)= 1/
Stage Init X= 0/
Init Y= 0/
Init Z= 0/

/Program: MAIN/ Mode *

Sr L 1	20.00	.00	30.00	39.40	SRL1	4	69.75	.8730	1.000
Sr K 1	20.00	.00	30.00	39.40	SRK1	4	69.75	.8820	-1.000
Y L 1	20.00	.00	30.00	39.40	YL1	2	100.00	1.0000	1.000
Y K 1	20.00	.00	30.00	39.40	YK1	2	100.00	1.0000	-1.000
Zr L 1	20.00	.00	30.00	39.40	ZRL1	4	100.00	1.0000	1.000
Nb L 1	20.00	.00	30.00	39.40	NBL1	5	100.00	1.0000	1.000
Mo L 1	20.00	.00	30.00	39.40	MOL1	6	100.00	1.0000	1.000
Rh L 1	20.00	.00	30.00	39.40	RHL1	3	100.00	1.0000	1.000
Pd L 1	20.00	.00	30.00	39.40	PDL1	2	100.00	1.0000	1.000
Ag L 1	20.00	.00	30.00	39.40	AGL1	1	100.00	1.0000	1.000
Ag L 2	20.00	.00	30.00	39.40	AGL1	2	100.00	1.0000	1.000
Cd L 1	20.00	.00	30.00	39.40	CDL1	2	100.00	1.0000	1.000
In L 1	20.00	.00	30.00	39.40	INL1	3	60.51	.8880	1.000
Sn L 1	20.00	.00	30.00	39.40	SNL1	2	100.00	1.0000	1.000
Sn L 2	20.00	.00	30.00	39.40	SNL1	4	100.00	1.0000	1.000
Sb L 1	20.00	.00	30.00	39.40	SBL1	3	100.00	1.0000	1.000
Sb L 2	20.00	.00	30.00	39.40	SBL1	4	100.00	1.0000	1.000
Te L 1	20.00	.00	30.00	39.40	TEL1	4	38.88	.7640	1.000
Ba L 1	20.00	.00	30.00	39.40	BAL1	2	78.33	.9120	1.000
La L 1	20.00	.00	30.00	39.40	LAL1	3	68.17	.9240	1.000
Ce L 1	20.00	.00	30.00	39.40	CEL1	4	72.20	.8780	1.000
Hf L 1	20.00	.00	30.00	39.40	HFL1	4	100.00	1.0000	1.000
Hf M 1	20.00	.00	30.00	39.40	HFM1	4	100.00	1.0000	-1.000
Ta M 1	20.00	.00	30.00	39.40	TAM1	4	100.00	1.0000	1.000
Ta L 1	20.00	.00	30.00	39.40	TAL1	4	100.00	1.0000	-1.000
W L 1	20.00	.00	30.00	39.40	WL1	4	100.00	1.0000	-1.000
W M 1	20.00	.00	30.00	39.40	WM1	4	100.00	1.0000	1.000
W M 2	20.00	.00	30.00	39.40	WM1	6	100.00	1.0000	1.000
Pt L 1	20.00	.00	30.00	39.40	PTL1	4	100.00	1.0000	-1.000
Pt M 1	20.00	.00	30.00	39.40	PTM1	4	100.00	1.0000	1.000
Au L 1	20.00	.00	30.00	39.40	AUL1	4	100.00	1.0000	-1.000
Au M 1	20.00	.00	30.00	39.40	AUM1	4	100.00	1.0000	1.000
Hg M 1	20.00	.00	30.00	39.40	HGM1	2	61.12	.8970	1.000
Hg L 1	20.00	.00	30.00	39.40	HGL1	2	61.12	.9580	-1.000
Pb L 1	20.00	.00	30.00	39.40	PBL1	2	61.90	.9550	-1.000
Pb L 2	20.00	.00	30.00	39.40	PBL1	4	61.90	.9550	-1.000
Pb M 1	20.00	.00	30.00	39.40	PBM1	2	61.90	.9150	1.000
Pb M 2	20.00	.00	30.00	39.40	PBM1	4	61.90	.9150	1.000
Bi M 1	20.00	.00	30.00	39.40	BIM1	4	100.00	1.0000	1.000
Bi L 1	20.00	.00	30.00	39.40	BIL1	4	100.00	1.0000	-1.000

EL	L	C	KV	TILT	ELEV	AZIM	PROFILE	VAL	CSTD%	FST	RST
C	K	1	20.00	.00	30.00	39.40		1	100.00	1.0000	1.000
O	K	1	20.00	.00	30.00	39.40		2	100.00	1.0000	1.000
F	K	1	20.00	.00	30.00	39.40		2	100.00	1.0000	1.000
Na	K	1	20.00	.00	30.00	39.40	NAK1	1	39.67	.6070	1.000
Mg	K	1	20.00	.00	30.00	39.40	MGK1	2	60.31	.6950	1.000
Al	K	1	20.00	.00	30.00	39.40	ALK1	3	27.80	.3410	1.000
Si	K	1	20.00	.00	30.00	39.40	SIK1	4	23.80	.7760	1.000
P	K	1	20.00	.00	30.00	39.40	PK1	5	30.76	.5340	1.000
S	K	1	20.00	.00	30.00	39.40	SK1	4	53.50	.8500	1.000
S	K	2	20.00	.00	30.00	39.40	SK1	6	53.50	.8500	1.000
Cl	K	1	20.00	.00	30.00	39.40	CLK1	1	60.33	.8700	1.000
K	K	1	20.00	.00	30.00	39.40	KK1	1	9.46	.8150	1.000
Ca	K	1	20.00	.00	30.00	39.40	CAK1	2	34.30	.9070	1.000
Ti	K	1	20.00	.00	30.00	39.40	TIK1	4	100.00	1.0000	1.000
V	K	1	20.00	.00	30.00	39.40	VK1	5	100.00	1.0000	1.000
Cr	K	1	20.00	.00	30.00	39.40	CRK1	3	100.00	1.0000	1.000
Cr	K	2	20.00	.00	30.00	39.40	CRK1	6	100.00	1.0000	1.000
Mn	K	1	20.00	.00	30.00	39.40	MNK1	4	100.00	1.0000	1.000
Fe	K	1	20.00	.00	30.00	39.40	FEK1	2	100.00	1.0000	1.000
Fe	K	2	20.00	.00	30.00	39.40	FEK1	3	100.00	1.0000	1.000
Co	K	1	20.00	.00	30.00	39.40	COK1	2	100.00	1.0000	1.000
Co	K	2	20.00	.00	30.00	39.40	COK1	3	100.00	1.0000	1.000
Co	K	3	20.00	.00	30.00	39.40	COK1	3	100.00	1.0000	1.000
Ni	K	1	20.00	.00	30.00	39.40	NIK1	2	100.00	1.0000	1.000
Ni	L	1	20.00	.00	30.00	39.40	NIL1	2	100.00	1.0000	-1.000
Cu	K	1	20.00	.00	30.00	39.40	CUK1	1	100.00	1.0000	1.000
Cu	L	1	20.00	.00	30.00	39.40	CUL1	1	100.00	1.0000	-1.000
Cu	K	2	20.00	.00	30.00	39.40	CUK1	2	100.00	1.0000	1.000
Cu	L	2	20.00	.00	30.00	39.40	CUL1	2	100.00	1.0000	1.000
Zn	K	1	20.00	.00	30.00	39.40	ZNK1	2	100.00	1.0000	1.000
Zn	L	1	20.00	.00	30.00	39.40	ZNL1	2	100.00	1.0000	-1.000
Ga	K	1	20.00	.00	30.00	39.40	GAK1	3	69.24	.9240	1.000
Ga	L	1	20.00	.00	30.00	39.40	GAL1	3	69.24	.9660	1.000
As	L	1	20.00	.00	30.00	39.40	ASL1	3	39.49	.5750	-1.000
As	K	1	20.00	.00	30.00	39.40	ASK1	3	39.49	1.0380	1.000
As	L	2	20.00	.00	30.00	39.40	ASL1	5	39.49	.5750	-1.000
As	K	2	20.00	.00	30.00	39.40	ASK1	5	39.49	1.0380	1.000
Se	K	1	20.00	.00	30.00	39.40	SEK1	2	100.00	1.0000	-1.000
Se	L	1	20.00	.00	30.00	39.40	SEL1	2	100.00	1.0000	1.000

APPENDIX 3.

DIFFERENTIAL THERMAL ANALYSIS Experimental Conditions

Ni-Al-Hf Alloy

Inert gas : Dried Argon, flow rate = 60
 DC amplifier range = 100 μ V
 start temperature = 1000°C
 Max. Temperature = 1200°C
 Finish temperature = 1000°C
 No. of heating cycles = 1
 Heating rate = 1000°C
 Chart speed = 5mm/min.
 Standard : Ni shot, vacuum arc melted to form an ingot,
 heat treated for 168 hrs. at 1200°C in a silica tube, under
 a partial pressure of argon. Weight Changes:

Sample

Before heating = 0.0720 g
 After heating = 0.0738 g
 Weight change = +0.0018 g

Standard

Before heating = 0.0750 g
 After heating = 0.0760 g
 Weight change = +0.0010 g

Crucible : recrystallized alumina

Ni-Hf-Si Alloys

Inert gas : Dried Argon, flow rate = 60
 DC amplifier range = 100 μ V
 start temperature = 750°C
 Max. Temperature = 1350°C
 Finish temperature = 750°C
 No. of heating cycles = 1
 Heating rate = 10°C/min.
 Chart speed = 5mm/min.
 Full scale deflection = 20 mV.
 Standard : Ni shot, vacuum arc melted to form an ingot,
 heat treated for 168 hrs. at 1200°C in a silica tube, under
 a partial pressure of argon.

Weight changes:

Samples

	1	2	3	4
Before heat =	0.0799 g	0.0723 g	0.0536 g	0.0723 g
After heat =	0.0777 g	0.0687 g	0.0525 g	0.0714 g
Wt. change =	-0.0022 g	-0.0036 g	-0.0011 g	-0.0009 g

Standards				
	1	2	3	4
Before heat =	0.0650 g	0.0828 g	0.0830 g	0.0783 g
After heat =	0.0639 g	0.0832 g	0.0830 g	0.0796 g
Wt. change =	-0.0011 g	+0.0004 g	0.0000 g	+0.0013 g

Crucible : recrystallized alumina