

The alloying behaviour and mechanical properties of polycrystalline Ni₃Al (γ' phase) with ternary additions

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A survey of the results from a variety of techniques has shown that the substitution behaviour of alloying additions is primarily determined by electronic considerations. Thus, Si, Ti, V, Mn, Nb, Hf and Ta substitute for aluminium; Co and Cu substitute for nickel and Cr, Fe, W, and Mo substitute for both species.

A number of conclusions have been drawn from an analysis of compression test data, the most significant of which was that the mechanical properties of γ' depended on both the substitution behaviour of the alloying addition and the degree of non-stoichiometry. Considerable strengthening is only obtained when (1) the alloying addition substitutes for aluminium and has a large size misfit parameter, and (2) the alloy is aluminium-rich or stoichiometric.

1. Introduction

The compound Ni₃Al (the γ' phase) has an *L1₂* crystal structure. It is known to retain an ordered structure up to 1320°C [1] and may well be ordered up to its melting point. The binary phase field extends over a narrow compositional range on either side of the stoichiometric composition Ni₃Al and is approximately 3 at. % wide at 1200°C. Many elements show considerable solubility in γ' , substituting either exclusively for aluminium atoms or exclusively for nickel atoms or for both species.

The mechanical behaviour of Ni₃Al is unusual in that the flow stress increases with increasing temperature to a maximum value, which occurs at a temperature in the range 550 to 750°C [2-6]. Both the temperature and the stress level of the peak are affected by the degree of non-stoichiometry and ternary additions. Typical flow stress versus temperature plots are shown in Fig. 1.

Guard and Westbrook [7] carried out an extensive investigation of the alloying characteristics and mechanical properties of γ' . From an analysis of ternary phase diagram data they were able to deduce the substitution behaviour of a number of elements, namely that Co and Cu substitute for nickel, Si, Ti, V and Mn for

aluminium and Cr and Fe for both species. In addition, hardness values were determined for these ternary alloys as a function of temperature.

Since this early authoritative paper binary and ternary γ' alloys have been studied by a number of workers using a variety of experimental techniques. In particular, the compression test, which is more sensitive than the hot-hardness test used by Guard and Westbrook, has been employed to study the plastic deformation of γ' . The peaks in the hardness versus temperature curves of Guard and Westbrook were extremely broad and generally the peak hardness was only 50% greater than the room temperature hardness. In contrast, the peaks in the flow stress versus temperature plots discussed in this paper were well defined and the peak flow stress was two to five times greater than the room temperature flow stress. This meant that values for the temperature of the peak, T_p , and the parameter ΔYS_p , where $\Delta YS_p = (\text{peak flow stress} - \text{room temperature flow stress})$ could be easily determined and comparison made between the various γ' alloys. Flow stress measurements have a further advantage over hardness measurements in that they give a better indication of strengthening due to alloying additions. The maximum increment in room temperature hardness due to

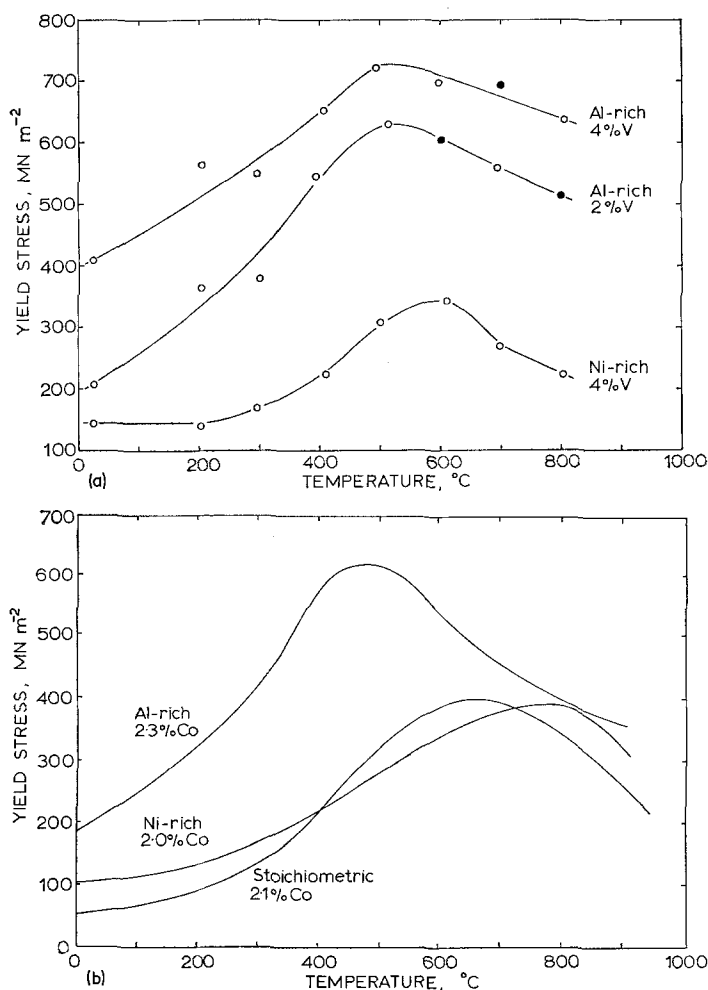


Figure 1 The unusual temperature dependence of the yield stress for γ' alloys: (a) vanadium additions (full points indicate average of two tests) (b) cobalt additions [3].

alloying additions was less than a factor of 2.5 compared with an order of magnitude increase that has been observed in the flow stress. It is apparent from the above considerations that a more thorough analysis of the mechanical properties of γ' alloys is possible using flow stress data rather than hardness results.

Each individual investigation of the flow stress of γ' has concentrated on a narrow range of alloying additions, but taking all the investigations together the amount of information available is considerable. This, coupled with the fact that much of the forementioned data on γ' has not yet been published in recognized scientific journals, makes a concise survey of this field opportune. New experimental data have

been determined where it was considered there was a lack of information from previous investigations.

2. Experimental procedure

The ternary alloys for the present work were prepared from binary Ni_3Al (kindly provided by International Nickel Ltd) and the appropriate alloying elements, using an argon arc furnace. The alloys were homogenised for 72 h at 1250 °C in an argon atmosphere. Compression specimens, $2.4 \times 2.4 \times 6.0 \text{ mm}^3$ were tested on an Instron machine, converted for compression by means of a rig attached to the underside of the moving cross-head. A furnace attachment was used for

TABLE I Substitution behaviour of ternary additions in γ' alloys

Species substituted				
Ni	Al	Ni + Al	Ref.	Technique
Co, Cu	Si, Ti, V, Mn	Cr, Fe	[7]	Phase diagrams
	Hf		[8]	Phase diagrams
	Nb		[9]	Phase diagrams
Co	Ti, Cr*	W	[12]	X-ray
	Ti, V, Nb, Ta		[13]	X-ray
	Nb		[15]	Analysis of γ' precipitate
Co, Fe*	Ti, V, Nb, Mo*,	Cr	[16]	Analysis of γ' precipitate
	Ta, W*			
			Fe	[14]

*Evidence would tend to favour the substitution for Ni and Al.

tests above room temperature. A strain rate of $3.3 \times 10^{-4} \text{ sec}^{-1}$ was employed throughout.

3. Results of survey

3.1. Alloying behaviour

A number of ternary phase diagrams have been published since Guard and Westbrook's analysis, e.g. Ni-Al-Hf [8], Ni-Al-Nb [9], Ni-Al-W [10]. A possible form for the Ni-rich corner of the Ni-Al-Zr phase diagram has also been proposed [11]. However, because of the low solid solubility of Zr in Ni₃Al (2.7 at. % Zr), it does not provide a clear indication of substitution behaviour.

In the context of this paper the Ni-Al-Hf diagram is the most significant as it supplies the only information available on the substitution behaviour of hafnium. In this diagram the γ' phase field is extended towards Ni₃Hf, indicating that hafnium substitutes for aluminium.

X-ray diffraction has also been used to determine the substitution behaviour of certain elements in Ni₃Al [12, 13], since substitution sites may be deduced from the relative intensities of fundamental and superlattice lines in X-ray diffraction patterns. The results from the X-ray work are given in Table I together with all other available information, such as that obtained from the chemical analysis of γ' precipitates in nickel-based alloys [15, 16], on the alloying characteristics of γ' . There is good agreement between the data from the various sources, the only exceptions being for Cr, Fe, Mo and W. However, from the evidence presented in Table I there is little doubt that all these elements substitute for both aluminium and nickel.

The Mössbauer investigation by Nicholls [14]

produced an interesting result. The proportion of Fe atoms on aluminium and nickel sites was found to be a function of Fe concentration. At low concentrations (2.5 at. %) approximately three-quarters of the Fe atoms were on aluminium sites, whereas at high concentrations (10 at. % Fe) there were approximately equal numbers of Fe atoms on aluminium and nickel sites.

The data of Table I and the atomic diameters of the relevant elements (d) are presented in Fig. 2, which is a part of the Periodic Table. It is clear from this figure that, as first suggested by Guard and Westbrook, the substitution behaviour is determined by electronic rather than size factor considerations. This point is best illustrated by considering the substitution sites of silicon and tungsten. From size factor considerations one would expect the large tungsten atoms ($d = 2.823 \text{ \AA}$) to substitute for aluminium and the smaller silicon atoms ($d = 2.638 \text{ \AA}$) to substitute for nickel. In fact, tungsten is found to occupy both aluminium and nickel sites and silicon substitutes only for aluminium.

3.2. Mechanical properties

In the present analysis of polycrystalline γ' alloys the term yield stress, YS , will be used even though the original researchers may have quoted the proportional limit or a proof stress. In addition, no allowance has been made for variation in grain size. However, the degree of non-stoichiometry, which is the most important factor affecting the flow stress, has been taken into account; any alloy having an aluminium (or aluminium plus ternary atoms substituting for aluminium) content in the range 24.7 to 25.3

Period ↓	Group →										IIIB	IVB
	IVA	VA	VIA	VIIA	VIII				IB	IIB	13	14
3											Al 2.864	Si 2.638
4	22 Ti 2.896	23 V 2.697	24 Cr 2.573	25 Mn 2.731*	26 Fe 2.557	27 Co 2.505	28 Ni 2.492	29 Cu 2.556				
5		41 Nb 2.944	42 Mo 2.807									
6	72 Hf 3.127	73 Ta 2.941	74 W 2.823									




KEY		ELEMENTS SUBSTITUTING FOR Al
		" " " Ni
		" " " Al+Ni

Figure 2 Section of the Periodic Table showing the effect of electronic configuration on element substitution behaviour. (The Goldschmidt $CN = 12$ radius in Å is shown below each symbol. * γ Mn at 1095°C.)

at. % has been designated as stoichiometric. The results of the survey are presented in Table II.

3.2.1. The effect of ternary additions on the room temperature yield stress

The room temperature yield stress of binary Ni_3Al is a function of the degree of non-stoichiometry, aluminium-rich alloys being stronger than stoichiometric and nickel-rich alloys. A similar trend is shown by the γ' ternary alloys.

In Table II, the dependence of the YS of γ' on the concentration of ternary addition, $\Delta YS/\Delta C$, has been tabulated for different alloying elements directly and in terms of the shear modulus. The shear modulus $G = 6.5 \times 10^4$ MN m^{-2} was calculated from the elastic constant data of Ono and Stern [20].

Elements substituting for Al show a low concentration dependence of the YS , with values of $\Delta YS/\Delta C$ in the range ($G/130$) (Ti) to ($G/4$) (Hf). These values are typical of the gradual hardening produced by spherically symmetrical atomic defects. (Rapid hardening, which is produced by tetragonal defects results in values of $\Delta YS/\Delta C$ of the order of G to $10G$).

The elements Co and Cu which substitute for Ni have a much smaller strengthening effect and in some cases appear to cause softening, values for $\Delta YS/\Delta C$ lying in the range $-G/31$ through zero to $+G/43$. Negative and zero values for $\Delta YS/\Delta C$ were also obtained for Fe and Cr, which substitute for both Ni and Al, the range of

values in this case being from $-G/28$ to $G/14$. It therefore appears that there are at least two different hardening mechanisms depending on the substitution site of the ternary addition.

There are thought to be three types of dislocation/solute atom interaction which cause strengthening of metals: elastic, electrical and chemical. Of these the most important is the elastic interaction. In his work on the solid solution strengthening of Cu [21] Fleischer estimated that the elastic interaction was three to six times greater than the electrical interaction. Experimental evidence for the chemical interaction, which may be thought of as the pinning of dissociated dislocations by "Suzuki atmospheres", has yet to be observed, which suggests that it is weak.

A theory has been developed for the elastic interaction between dislocations and symmetrical defects [22]. The interaction may be divided into two parts: a hydrostatic interaction resulting from the size difference of the solute atom and a shear interaction resulting from the different shear modulus of the solute atom. The relative importance of these two interactions depends on both the solute element and the dislocation Burgers vector. The shear interaction is dominant for a screw dislocation because, to the first order, it has no hydrostatic stress field.

In order to calculate the shear force between a dislocation and a solute atom it is necessary to know the rate of change of the shear modulus with solute concentration, dG/dC . Unfortunately,

TABLE II The mechanical properties of γ' alloys

Alloying addition X (at. %)	Degree of non-stoichiometry* (at. %)	Substitution behaviour	Room temperature yield stress (MN m ⁻²)	ΔYS per at. % X	$\frac{\Delta YS}{\Delta C}$ in terms of the shear modulus $G\ddagger$	Yield stress at peak YS_p (MN m ⁻²)	ΔYS_p (MN m ⁻²)	Temperature of peak (°C)	Ref.
Binary	A (26.80%)	different grain sizes	[195 245			615 660	420 415	550 600	[2] [2]
Binary	A (26.42%)		180			600	420	650	[3]
Binary	A (25.63%)		90			340	250	600	[3]
Binary	S		90			410	320	650	[4]
Binary	S	different grain sizes	[90 125			415 460	325 335	600 600	[2] [2]
Binary	S		95			445	350	600	[5]
Binary	S	DS	160			660	500	750	[6]
Binary	N		90			330	240	700	[3]
Binary	N		70			390	220	650	[2]
5.0 Si	A (26.63%)	Al†	690	97	$G/7$	1050	360	350	[3]
5.1 Si	N	Al	145	11	$G/59$	620	475	500	[3]
4.0 Ti	A (26.97%)	Al	335	23	$G/28$	665	330	450	[2]
4.0 Ti	A (25.84%)	Al	135	5	$G/130$	475	340	500	[2]
4.0 Ti	S	Al	120	8	$G/81$	380	260	500	[2]
10.5 Ti	S	Al, DS	315	15	$G/43$	1100	785	850	[6]
11.0 Ti	S	Al	460	34	$G/24$	650	190	350	[2]
4.0 V	A (27.00%)	Al	412	42	$G/15$	720	308	510	Present work
2.0 V	A (25.70%)	Al	201	50	$G/13$	635	434	510	Present work
4.0 V	N	Al	143	13	$G/50$	310	167	610	Present work
6.0 Nb	S	Al, DS	615	76	$G/9$	1140	525	700	[6]
2.0 Hf	A (26.50%)	Al	524	167	$G/4$	—	—	—	Present work
2.5 Hf	S	Al	360	108	$G/6$	895	535	700	[4]
2.5 Hf	S	Al, DS	325	66	$G/10$	960	635	750	[6]
2.7 Hf	S	Al, DS	480	119	$G/6$	1140	660	700	[17]
5.0 Hf	S	Al	1000	182	$G/4$	1350	350	550	[4]
2.0 Hf	N	Al	172	41	$G/16$	—	—	—	Present work
2.0 Hf	N	Al	186	48	$G/14$	—	—	—	Present work
2.2 Ta	A (27.30%)	Al	396	53	$G/12$	—	—	—	Present work
1.0 Ta	S	Al	185	95	$G/7$	670	485	750	[4]
2.5 Ta	S	Al	215	50	$G/13$	645	430	600	[4]
2.5 Ta	S	Al, DS	285	50	$G/13$	960	675	700	[4]
5.0 Ta	S	Al	335	49	$G/13$	590	255	600	[4]
2.0 Cr	A (25.5%)	Al + Ni	180	45	$G/14$	—	—	—	Present work
2.0 Cr	S	Al + Ni	162	36	$G/18$	—	—	—	Present work
2.0 Cr	S	Al + Ni, DS	130	-15	$-G/43$	690	550	900	[6]
2.0 Cr	N	Al + Ni	64	-13	$-G/50$	—	—	—	Present work
2.2 Fe	A (26.98%)	Al + Ni	195	-23	$-G/28$	640	445	600	[3]
10.7 Fe	A (26.47%)	Al + Ni	180	0		555	375	650	[14]
2.1 Fe	A (25.91%)	Al + Ni	80	-21	$-G/31$	445	365	700	[3]
2.4 Fe	S	Al + Ni	100	4	$G/162$	420	320	600	[3]
2.1 Fe	S	Al + Ni	135	21	$G/31$	420	285	800	[3]
9.9 Fe	S	Al + Ni	160	7	$G/93$	500	340	600	[3]
10.0 Fe	S	Al + Ni	225	14	$G/46$	540	315	600	[18]
2.1 Fe	N	Al + Ni	140	24	$G/27$	365	215	800	[3]
2.3 Co	A (26.54%)	Ni	195	0		620	425	500	[3]
2.0 Co	S	Ni	120	15	$G/43$	485	365	700	[3]
2.1 Co	S	Ni	60	-14	$-G/46$	395	335	650	[3]
10.0 Co	S	Ni	75	-2	$-G/32$	425	350	650	[3]
2.0 Co	N	Ni	105	8	$G/81$	375	270	800	[3]
2.0 Cu	A (26.50%)	Ni	148	-21	$-G/31$	—	—	—	Present work
2.0 Cu	S	Ni	59	-15	$-G/43$	—	—	—	Present work
2.0 Cu	N	Ni	72	-9	$-G/72$	—	—	—	Present work

DS = Directionally solidified.

*A = Al-rich; S = stoichiometric; N = Ni-rich. The aluminium (or aluminium plus tertiary addition on aluminium sites) contents are given for aluminium-rich alloys.

†Al = substitutes for Al, Ni = substitutes for Ni; Al + Ni = substitutes for Al and Ni.

‡ $G = 6.5 \times 10^4$ MN m⁻² calculated from the elastic constant data of Ono and Stern [20].

C = atomic fraction.

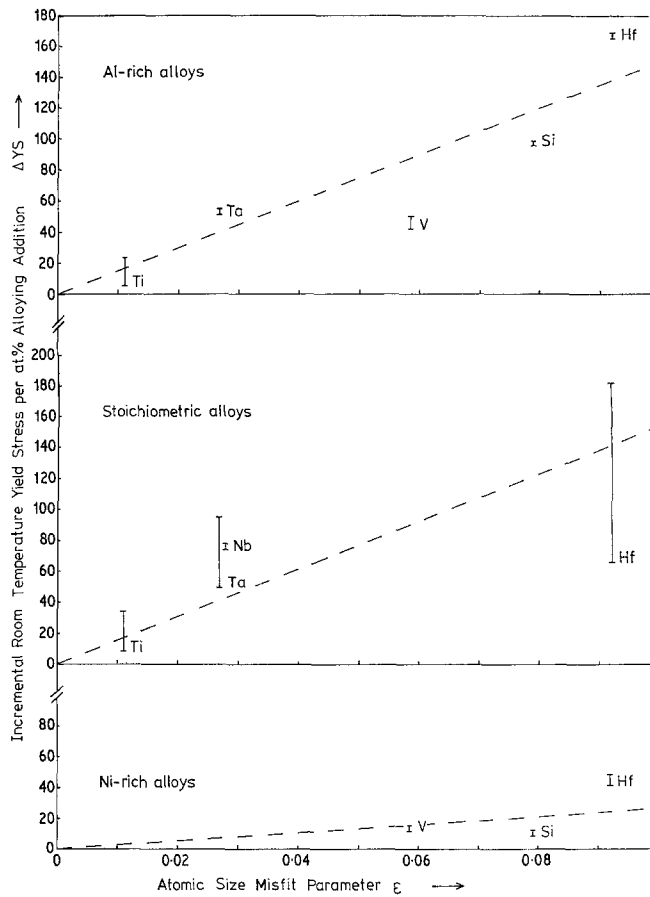


Figure 3 The room temperature strengthening associated with elements which substitute for aluminium.

this has not been measured for the alloys of Ni_3Al , so that a quantitative analysis is not practicable. On the other hand, it is possible, to look for a correlation between strengthening and the solute misfit parameter, not forgetting that the shear modulus is also a contributing factor.

In Figs. 3 and 4 the incremental room temperature yield stress per atomic percentage alloying addition, ΔYS , is plotted as a function of the atomic size misfit parameter ϵ , where ΔYS and ϵ are defined as follows:

$\Delta YS = (YS \text{ of ternary } \gamma' \text{ alloy} - YS \text{ of binary } \text{Ni}_3\text{Al} \text{ having the same degree of non-stoichiometry}) / \text{Atomic percentage of alloying addition}$

$$\epsilon = \frac{d_A - d_I}{d_I}$$

d_A is the diameter of the alloying atom and d_I is the diameter of the atom for which it substitutes. In the case of Fe and Cr, which sub-

stitute for both Ni and Al, ΔYS has been plotted against the average misfit parameter. ΔYS was calculated using the results of Lopez and Hancock [2] for the binary. The exceptions to this were the directionally solidified (DS) alloys for which ΔYS was determined using the room temperature yield stress value for DS Ni_3Al reported by Thornton *et al.* [6].

The results will be discussed in three groups, according to the substitution site of the alloying element.

3.2.1.1. Elements which substitute for Al (Si, Ti, V, Nb, Hf, Ta). Fig. 3 clearly demonstrates that ΔYS is a strong function of the misfit parameter of elements substituting for Al, in both stoichiometric and aluminium-rich alloys. Furthermore, from these figures it can be seen that the strength increment due to ternary additions for aluminium-rich and stoichiometric alloys is approximately the same.

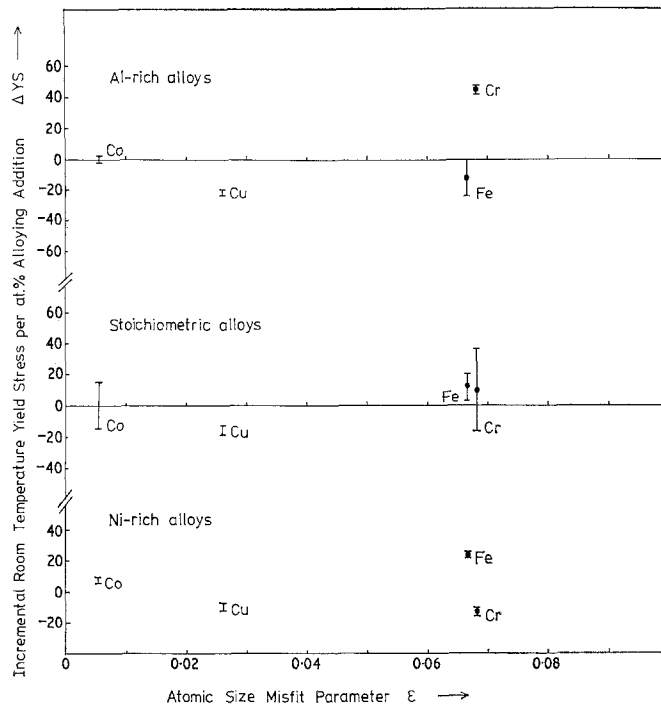


Figure 4 The room temperature strengthening associated with elements which substitute for nickel, or for both nickel and aluminium. (Full circles indicate substitution for both species.)

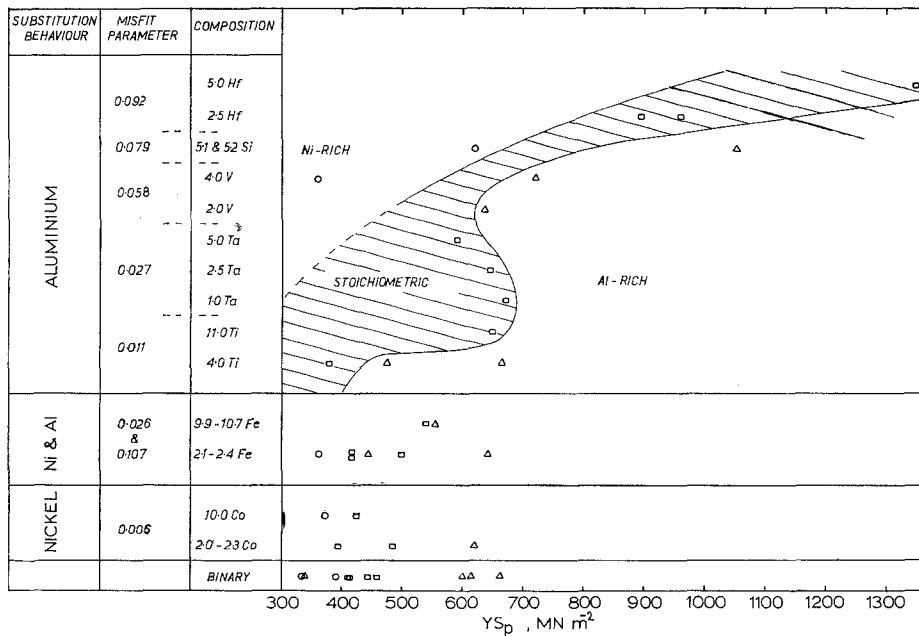


Figure 5 The effect of the degree of non-stoichiometry and misfit parameter on the peak yield stress of γ' alloys (DS alloys not included). $\circ \equiv$ Ni-rich; $\square \equiv$ stoichiometric; $\triangle \equiv$ Al-rich.

In contrast there is very little strengthening associated with the same ternary additions in Ni-rich alloys. This is so, even when the misfit parameters are as large as $\epsilon = 0.079$ (Si) and $\epsilon = 0.092$ (Hf). This suggests that the strain fields introduced into the material by the solute atoms are in some way cancelled out in the presence of excess Ni atoms.

3.2.1.2. Elements which substitute for Nickel (Co, Cu) or for both species (Fe, Cr). Fig. 4 shows that elements that substitute for Ni or Ni and Al produce no significant hardening irrespective of either the misfit parameter or the degree of non-stoichiometry. Thus the analysis of the room temperature data indicates that ternary addition *per se* only lead to strengthening if they substitute for aluminium and the composition of the material is aluminium-rich or stoichiometric.

3.2.2. The effect of the degree of non-stoichiometry on the mechanical properties of γ'

It has already been shown that the solid solution strengthening of γ' is strongly dependent on the degree of non-stoichiometry. From Table II it is apparent that other mechanical properties, and in particular the magnitude and temperature of the peak flow stress, are also functions of the degree of non-stoichiometry. From the results it is possible to make certain generalizations.

For a γ' alloy containing a given concentration of a given solute, changing the composition from Ni-rich to aluminium-rich has the following effects on the mechanical properties:

(a) the room temperature yield stress YS_R is increased;

(b) the peak yield stress YS_p is increased;

(c) the value of $\Delta YS_p = YS_p - YS_R$ is increased;

(d) the peak yield stress temperature T_p is decreased.

The last three effects may be seen most clearly in Figs. 5 to 7. In addition these figures show that the misfit parameters influence YS_p for those elements which substitute for Al, but not ΔYS_p or T_p .

Generally, the behaviour of the stoichiometric alloys is intermediate between that of the aluminium- and nickel-rich alloys. Therefore, for simplicity, in the following discussion a comparison will only be made between the two extremes of behaviour exhibited by the nickel-rich and aluminium-rich alloys.

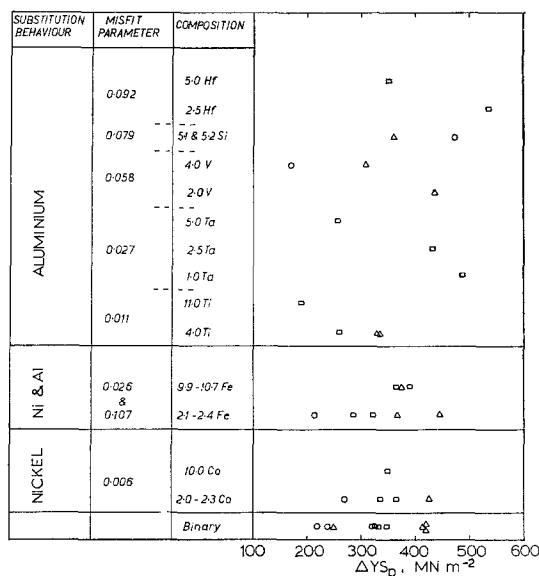


Figure 6 The effect of the degree of non-stoichiometry and the misfit parameter on the magnitude of ΔYS_p where $\Delta YS_p = (\text{peak yield stress}) - (\text{room temperature yield stress})$. (DS alloys are not included.) $\circ \equiv$ Ni-rich; $\square \equiv$ stoichiometric; $\triangle \equiv$ Al-rich.

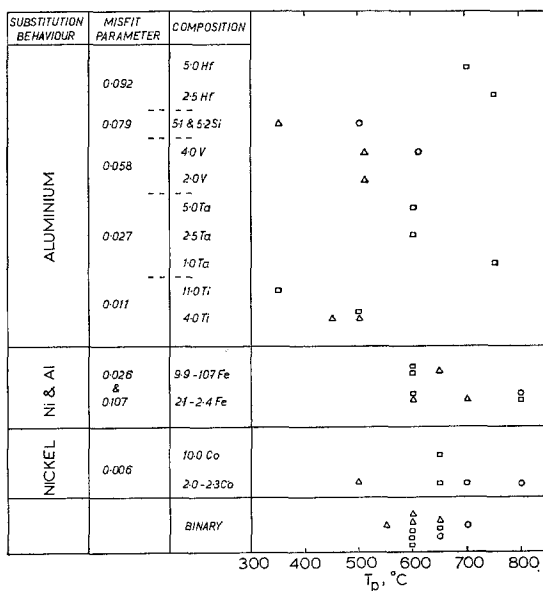


Figure 7 The effect of the degree of non-stoichiometry and misfit parameter on the temperature of the peak in the yield stress (DS alloys not included). $\circ \equiv$ Ni-rich; $\square \equiv$ stoichiometric; $\triangle \equiv$ Al-rich.

From generalizations a to d it follows that the average gradient of the YS versus temperature plot below T_p is greater for Al-rich than for

Ni-rich alloys. It is difficult to comment on the temperature dependence of the yield stress at temperatures in excess of T_p since grain-boundary cracking occurs which introduces uncertainty into the YS values. However, if it is assumed that above the peak the gradients are similar for Al-rich and Ni-rich alloys, the schematic plots shown in Fig. 8 are obtained. This assumption is reasonable since the plots approximate to the experimental curves. The degree of non-stoichiometry, therefore, appears to affect dYS/dT only at temperatures below T_p .

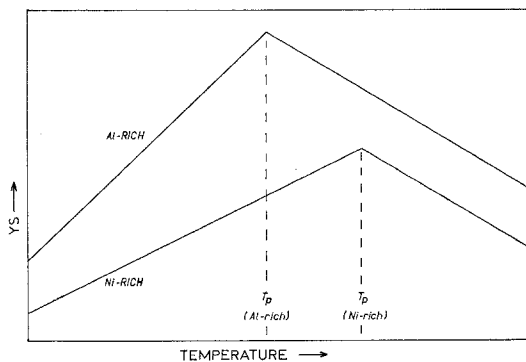


Figure 8 Schematic yield stress versus temperature plots to illustrate the effects of deviations from stoichiometry.

It has been shown conclusively [19] that in γ' crystals primary slip only occurs on $\{111\}\langle 110\rangle$ systems up to the yield stress peak, and that $\{100\}\langle 110\rangle$ slip predominates above T_p . There is no evidence to suggest that the slip behaviour of polycrystalline γ' should differ greatly from this and consequently the change in dYS/dT with the degree of non-stoichiometry must be associated with $\{111\}\langle 110\rangle$ slip. Since γ' has an ordered fcc structure, $(a/2)\langle 110\rangle$ dislocations lying on $\{111\}$ planes may dissociate into partial dislocations of the $(a/6)\langle 112\rangle$ type. The degree of dissociation, which depends on the stacking fault energy, would undoubtedly affect the motion of the dislocations and hence dYS/dT . In contrast $\{100\}\langle 110\rangle$ slip, which occurs above T_p , would be unaffected, since dissociation does not occur on $\{100\}$ planes. Thus, a change in stacking fault energy with the degree of non-stoichiometry would account for the observed behaviour. There is no information available on the relationship between stacking fault energy and degree of non-stoichiometry; however, there

is evidence from recrystallization twin counts that the stacking fault energy is dependent upon composition [2] which could be significant.

3.2.3. Effect of directional solidification

From Table II it can be seen that directional solidification (DS) increases YS_p , ΔYS_p and T_p . The growth axis of DS γ' is $\langle 100\rangle$, hence specimens prepared with the compression axis parallel to the growth axis, as is the general practice, are not favourably orientated for $\{100\}$ slip. It has been shown [19] that the fall-off in strength above T_p is due to the onset of slip on the $\{100\}$ planes. Therefore, it follows that specimens orientated to hinder $\{100\}$ slip would exhibit high values for YS_p , ΔYS_p and T_p , as found for DS γ' .

4. Conclusions

(1) The substitution behaviour in γ' alloys is determined by electronic considerations. Si, Ti, V, Mn, Nb, Hf and Ta substitute for aluminium; Co and Cu substitute for nickel; Cr, Fe, Mo and W substitute for both species.

(2) For elements which substitute for Al, the strengthening is a function of the atomic misfit parameter. Strengthening is also dependent on the degree of non-stoichiometry of the alloy. Considerable strengthening occurs for Al-rich and stoichiometric alloys but only a small amount for Ni-rich alloys.

(3) Elements which substitute for Ni or Ni and Al produce no significant strengthening irrespective of the misfit parameter or the degree of non-stoichiometry.

(4) The peak temperature is lower, and the peak stress greater for aluminium-rich alloys than for nickel-rich alloys. It was tentatively suggested that this behaviour is the result of change in the stacking fault energy with the degree of non-stoichiometry.

(5) YS_p , ΔYS_p and T_p are greater for directionally solidified γ' due to the suppression of $\{100\}$ slip.

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