Potential Nb Base Superalloys

F. Saint-Antonin and A. Mitchell

Department of Metals and Materials Engineering,
University of British Columbia, Vancouver, B.C., Canada V6T 1Z4

ABSTRACT

From a) the Hume-Rothery rules about inter-solubility and compound formation, b) binary phase diagrams, c) physical properties of atoms and d) the reasons of the effects of the different constitutional elements in Ni base superalloys, we point out which parameters are necessary: for the precipitation of an ordered phase, or intermetallic, in the Nb matrix to create a two-phase alloy; for the solid-solution strengthening of the matrix and for the precipitation of a strengthening phase in the grain boundaries. Effects of interstitials are described regarding the parameters necessary to create a structure similar in Nb-base alloys to that found in the γ/γ' Ni base superalloys.

INTRODUCTION

The current technology for both gas turbines and aeroengine turbines relies heavily on the nickel-base superalloys for construction materials in the high temperature regions /1/. These alloys are generally limited to working temperatures below 1150C, although the use of coatings and cooling systems permits turbine inlet temperatures above the melting point of nickel itself (1453C). Although there is a general advantage in using higher temperatures in the engine operation, and the search for such systems is ongoing, the requirements of reliability, cost and emission control impose some quite severe limits on practical progress /2/. In conventional air-breathing engines the turbine inlet temperature is theoretically limited by the adiabatic stoichiometric combustion temperature, in the range of 1800 to 2100C depending on the fuel used. In practice, however, even the present sophisticated combustor designs are likely to be limited to an inlet temperature of around 1650C because of the requirement to control NOX emissions. This limit then sets the goal for the use-temperature of un-cooled components in the high temperature region.

It has been suggested by many sources that the logical solution to this problem is the application of ceramics, or ceramic-based composites, and these materials certainly have many attractive properties in this temperature range. However, from the designer's standpoint, it is not yet clear how the materials might be used and there would be a great advantage in fulfilling the temperature requirements with a metallic alloy possessing familiar fatigue and fracture properties, particularly in respect of crack-growth rates. Niobium-based alloys are potential candidates for this application because of their high melting points, and densities which are close to, or less than, those of the nickel-base alloys.

Generally, niobium-base alloys show a poor oxidation resistance compared with the superalloys, although some progress has been made through additions of Al, Ti, Cr, V and Si, which give superior oxidation resistance as compared with the conventional commercial alloys such as C103 or FS85 /3,4/. It has been suggested that this approach could lead to the development of "layered" components in which the oxidation-resistant alloy would be a substrate on the principal alloy, serving as the base for a true oxidation-resistant coating /5/.

Niobium alloys are generally strengthened by solid-solution additions of Hf, W or Zr /6/. Strengthening by precipitate or dispersoid particles of carbides, oxides, nitrides or borides /7/, has generally been found to be defeated by the rapid coarsening of the precipitate at high temperatures due to the low stability of the precipitate compounds and the high mobility of the metalloid in the niobium base /7/. Niobium alloy development including the potential for composite structures has been reviewed in the literature /2,3,5, and 8-12/.

The present study covers the theoretical definition of the direction of development which should be followed in the search for the niobium equivalent of the nickel-base superalloys, at least in terms of mechanical behavior. That is, a structure which contains an ordered second phase precipitate, stable at high temperature, within a matrix strengthened by solid solution, with the addition of grain-boundary phases to inhibit grain sliding. The problem of oxidation resistance is probably best addressed by coating techniques, but some suggestions are made as to how the proposed alloy systems might be best optimized from this aspect also.

First Considerations

Oxidation resistance and a lower density for Nb base alloys can be improved by additions of Ti and Al. In particular, Ti addition to the binary Nb-Al increases the oxidation resistance between 600°C and 1000°C /5/. The system Nb-Ti-Al has been studied by several authors /13-16/. These studies have shown that an ordered BCC phase (B2) exists, but this phase is metastable /17/. The phase diagram Nb-Ti-Al shows that the Nb-Ti BCC solid-solution has a large Al solubility, because of the large solubility of Al in Ti(β). In the binary Nb-Al, the Al solubility is about 7 at% at room temperature and the maximum Al solubility is about 20 at% at 2000°C. For a composition above 40 at% Nb, the Nb-Ti is a continuous β (BCC) isomorphous structure.

Solubility and Compounds: Choice of Elements for a Possible Precipitation of a Second Phase within the Matrix

The Hume-Rothery's Rules, Application to Niobium

First Rule: If the difference of atomic radius between the solvent and the solute is less than ± 15%, extended solubility (more than 5%) may occur. As noted in /18/, this is a negative rule: if the difference is more than ± 15%, it will be unlikely that extended solubility will occur. If the difference is more than ± 15%, there will be formation of compounds. Figure 1 gives the atomic radius of the elements versus the atomic number and situates elements for a favorable extensive solid solubility in Nb /19/. The ratio (radius of X) / (radius of Nb) for the more common metals are:

X	R_X/R_{Nb}	X	R_X/R_{Nb}	X	R_X/R_{Nb}
Al	0.974	Ni	0.847	Hf	1.075
Ti	0.994	Zr	1.09	Ta	1.001
V	0.916	Nb	1	W	0.959
Cr	0.874	Mo	0.954	Re	0.936
Fe	0.868	Ru	0.911	Os	0.920
Co	0.851	Rh	0.914		

(The atomic radii are from reference /20/). Ti, V, Zr, Mo, Hf and W form complete solid-solutions with Nb, with an atomic radius difference of less than ± 10%. These elements have a very large solubility in the binary Nb-Ti. No compounds seem to exist in the systems Nb-Ti-X, where X = V, Zr, Mo, Hf or W. Systems based on elements with a low solubility in Nb present ordered structures. Cr, Fe, Co and Ni are close to or higher than the ± 15% limit, so these elements should produce a low solubility in niobium. The maximum solubility of X in Nb is:

X	Cr	Fe	Co	Ni
at%	15	6.6	4	4.6

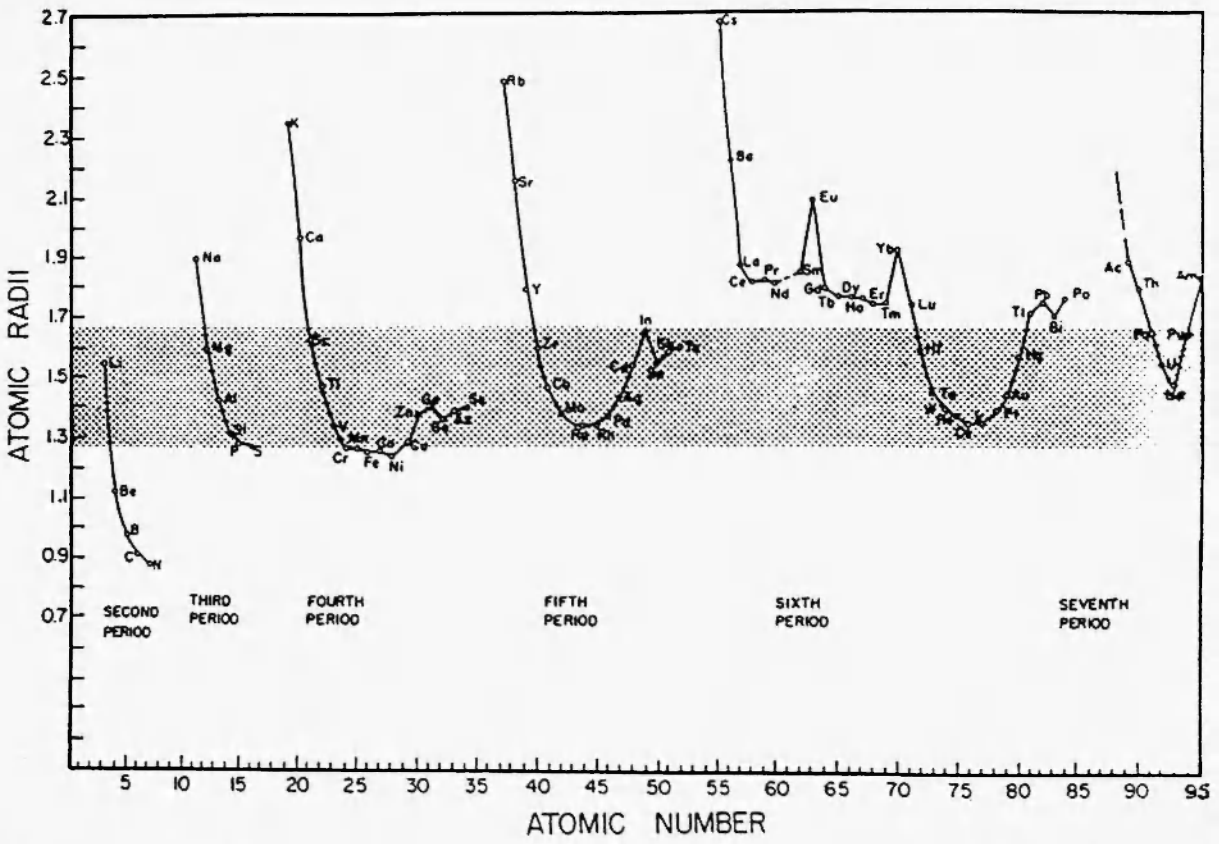

Fig. 1: Atomic radius for the various elements. The shaded band gives the range (± 15%) of radius favorable for extensive solid solubility in Nb (Cb) /19/.

Chromium has a relatively large solubility in Nb with an atomic radius difference of 12.6%. The solubility at room temperature is very low (less than 1 at%). The binary is characterized by a Laves phase Cr_2Nb which has a phase transformation at about 1600°C. The binary diagrams with Fe and Co present a μ phase near the Nb side.

In the previous list, Ni is the only element with an atomic radius difference higher than ± 15%. For the purpose of homogenization during heat treatment, a certain amount of solubility is necessary at high temperature. We can also note that the maximum solubility of Nb in X, where X = Cr, Fe, Co or Ni, is largest for Ni (about 12.7 at%), and significantly less for Cr, Fe and Co, at 6 at%, about 1 at% and 4 at% respectively.

Second Rule: If the difference in electronegativity between the two components of a binary alloy is large, there is a strong tendency to form compounds with a great stability. The electronegativity of Nb is 1.6 and for Cr, Fe, Co and Ni, it is 1.66, 1.83, 1.88 and 1.91 respectively. Nickel has the highest electronegativity difference with Nb (0.31). Chromium has an electronegativity close to that of Nb.

It should also be noted that between Al and Nb, the atomic radius difference is 2.6% and the electronegativity difference is only 0.01. This could perhaps explain the instability of the phase B2 during aging in the ternary Nb-Ti-Al /17/.

Comparison with the Ni Base Superalloys

In Ni base superalloys, Al and Ti are necessary for the precipitation of the second phase γ'in the Ni matrix. The atomic radius difference with Ni is almost 15% for Al and 17.3% for Ti. The difference with Ni is 0.3 for Al and 0.37 for Ti. These numbers are almost the same for both the atomic radius and electronegativity difference between Ni and Nb.

The Nb-Ni System (Fig. 2) and the Ta-Ni System

In the Nb-Ni system, there are three intermediate phases Ni_8Nb, Ni_3Nb and Ni_6Nb_7. The solubility decreases with the temperature: about 5 at% at 1290°C and less than 1 at% at 400°C. A fourth phase has been reported as Nb_5Ni (16.7 at% Ni) /22-24/. This phase appears in alloys with 1.86 at% and 2.78 at% Ni after an annealing time of 1000 h at 800°C. These alloys contain both Nb_xNi and Nb, i.e. a two-phase domain. Between 6.37 at% and 20 at%, this phase coexists with Nb and a μ phase. Nash *et al.* /24/ report that this phase is "doubtfully an equilibrium phase", but no tests have been performed to verify the stability.

Niobium and tantalum have almost the same atomic radius and the difference in electronegativity is very small, so they have the same kind of properties towards other elements. In the Ta-Ni system /23,25/, the compound $NiTa_2$ is in an equilibrium state, in an alloy with 13.9 at% Ni, after an annealing time of 1000 h at 800°C, it is also a two-phase domain of $NiTa_2$ + (Ta). Substitution of Nb by Ta could stabilize the phase Nb_5Ni, if this phase is not stable. The structure of Nb_5Ni is FCC, type $NiTi_2$, with a = 1.164 nm, or in Pearson symbol cF96. The structure of $NiTa_2$ is tetragonal, or in Pearson symbol tI12 (Al_2Cu type). From /23/, the limit of Ni addition in Nb is about 6 at% to avoid the μ phase.

The solubility of Ni in Ta is about 20 at% at 1788°C and decreases very quickly with a decrease in temperature to 9 at% at 1700°C, 4 at% at 1600°C and 2 at% at 1200°C.

BACKGROUND

Only one published work was found in regard to Nb base alloys containing elements from group VIII /26/. The Widmanstätten structure of the precipitate for the alloy was given and a hardness curve showing almost no decrease of the hardness until 830°C is shown (Fig. 3). There is no indication about the alloy composition or which element of the group VIII was used.

Interest of Tantalum Addition in Nb Base Alloys

The Ta-Nb binary forms a complete BCC solid-solution. In related systems, addition of less than 5 at% Ta in Ti retains the BCC structure of Ti. The solubility of Al in Ta is between 4 at% and 10 at% at about 2200°C, 1 at% at 1000°C and almost 0 at% at room temperature (two phase diagrams exist /27/). Aluminium must be in solid-solution to avoid the creation of brittle phases. The Al solubility at room temperature in Nb is about 7 at%, the Al content should be decreased as the Ta content is increased.

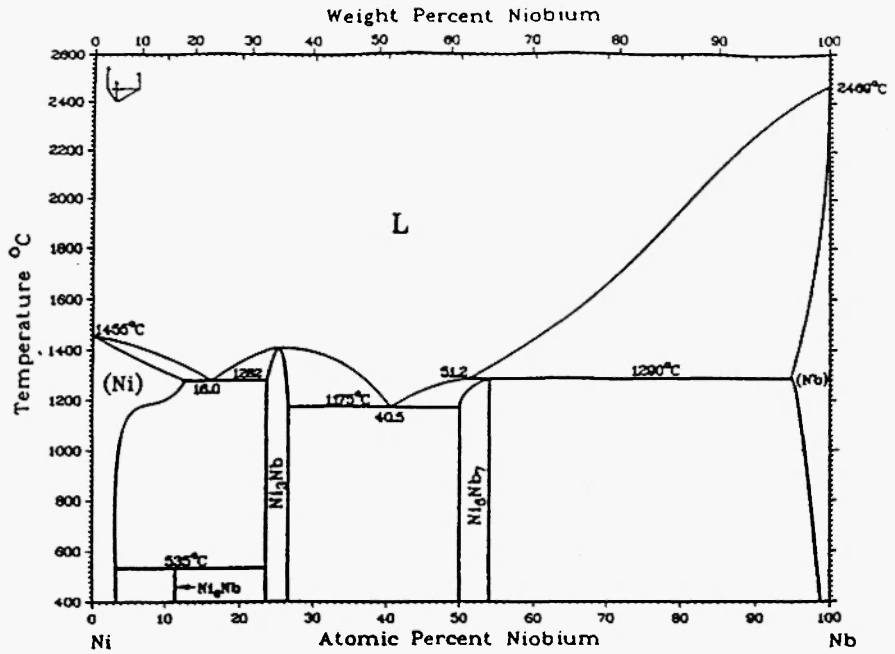

Fig. 2: The Nb-Ni phase diagram /21/.

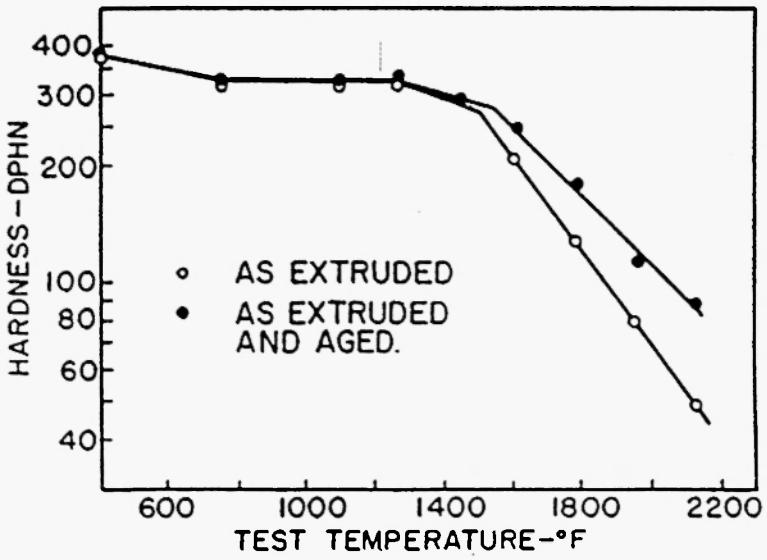

Fig. 3: Hardness versus temperature in a Nb base alloy "with group VIII elements" (Fig. 12 in /26/).

Addition of Ta in Nb base alloys increases the oxidation resistance /28/ as well as the melting temperature and, above all, should increase the solubility of Ni at high temperature and so the volume fraction of the precipitates may be increased. The high density of Ta is compensated by additions of low density elements like Ti and Al.

Choice of Elements for the Precipitation of Phases Within the Grain Boundaries

The precipitation of a strengthening phase in the grain boundaries occurs if elements which induce the precipitation have a very low solubility in the matrix of the alloys or form an unstable phase with the matrix. The idea that the "insoluble impurities partition preferentially to grain boundaries" was clearly expressed in /29/.

Example of the Ni Base Superalloys

The intergranular phases in the Ni base superalloys are borides, carbides and nitrides. The atomic ratio between for B, C and N with Ni is respectively 0.595, 0.559 and 0.545, i.e., more than the limit of ± 15%. The maximum solubility for B, C and N is respectively 2.7 at%, 0.03 at% and 0.3 at%. The solubility of C is relatively large compared to the solubility of B and N, but there are no stable carbides with Ni.

In the Nb Base Alloys

The atomic ratio between B, C and N with Nb is respectively 0.505, 0.474 and 0.461. These numbers are far above the limit of ± 15%, but because of the large size of the Nb atom, B, C and N form an interstitial solution with Nb. Different compounds can be formed and can precipitate within the grains, so these elements cannot be used for the precipitation of intergranular phases. Moreover, carbon promotes the formation of unstable niobium carbides (Nb_2C).

The atomic radius difference between Nb and the rare earth metals is higher than +15% (except Sc). The rare earth metals are immiscible with Nb (when the binary phase diagram is known /21/), therefore these elements must segregate to the grain boundaries.

Rare earth elements with a) a melting point higher than 1000°C, b) a boiling point higher than 2500°C and c) no phase transformation near the Nb rich side of the binary phase diagram Nb-X (where X is a rare earth element), are erbium, holmium, lutetium and yttrium (rare earth elements for which no phase diagram with Nb is currently available have been eliminated /21/). In general, rare earth elements form compounds with Ni. For holmium and lutetium, there is no information in regard to the structure of the compounds formed with

Ni. Between erbium and yttrium, the latter is the more currently available, having the lowest density (4.46). Yttrium is also immiscible with Ta and forms compounds with Al.

Generally, in the Ni base superalloys, there is less than 0.1 at% of C. As Y is very reactive with oxygen, a Nb base alloy free of oxygen is necessary for the formation of compounds with Y. Compounds formed between Ni and rare elements are brittle, but carbides, which are in the grain boundaries in Ni base superalloys, are also brittle.

We can note that Cu is also immiscible in Nb, but the melting point (1084°C) is very low compared to Y. Copper forms a complete solid-solution with Ni. Moreover, Cu forms compounds with Y. As the electronegativity difference between Cu and Y is larger than between Y and Ni, Y should be associated with Cu instead of Ni. If Cu is added, it would be better to use erbium instead of yttrium, because compounds Cu-Er are seen to have a higher melting point than compounds Cu-Y (the phase diagram Cu-Er is not known completely /21/).

Solid-Solution Strengthening of the Matrix

For the solid-solution strengthening of the matrix, the main parameters for the selection of elements to add to a matrix are: the difference in atomic size between the solvent and the solute, and the diffusion of the solute in the solvent which controls the dislocation motion at high temperature /30/.

Example of the Ni Base Superalloys

In these alloys, the solute elements in the matrix γ are Co, Cr, Fe, Mo, W and Re, with an atomic radius difference to Ni being +0.5%, +3.1%, +2.5%, +12.6%, +13.1% and +10.5%, respectively. Because of the high density and cost, W and Re are not often used. The main strengthening element is Mo because of its large atomic difference with Ni and a lower diffusion coefficient in Ni compared to the self-diffusion coefficient of Ni for the same temperature (Table 1, calculation from /31/).

It should be noted that Co, Cr and Fe have a higher diffusion coefficient in Ni than the self-diffusion coefficient of Ni, and furthermore, that W and Mo have a lower diffusion coefficient in Ni compared to the self-diffusion coefficient of Ni.

Strengthening Elements for the Nb Base Alloys

The atomic radius difference, with Nb, for the elements within the range ± 15% are:

Zr	+9%	Mo	-4.6%	V	-8.4%
Hf	+7.5%	Re	-6.4%	Rh	-8.6%
Ta	+0.1%	Os	-8%	Ru	-8.9%
W	-4.1%				

The diffusion coefficient of (Table II, calculation from /31/):

- Zr and V, in Nb, are higher than the self-diffusion coefficient of Nb,
- Ta in Nb is the same order of magnitude compared to the self-diffusion coefficient of Nb,
- Mo and W are respectively two and three orders of magnitude lower compared to the self-diffusion coefficient of Nb.

No data was found with respect to the diffusion of Hf, Re, Os, Rh and Ru in Nb, but it is believed that a

Table 1

Self-diffusion coefficient (cm^2/s) of Ni and diffusion coefficients of some elements in Ni at 1000°C /31/. Some coefficients are extrapolated for the temperature of 1000°C.

	Ni Self-diffusion	Cr	Co	Fe	Mo	W
1000°C	$3.7\ 10^{-12}$	$7.3\ 10^{-12}$	$5.2\ 10^{-12}$	$9.4\ 10^{-12}$	$2.8\ 10^{-12}$	$1.0\ 10^{-12}$

Table 2
Self-diffusion coefficient (cm^2/s) of Nb and diffusion coefficients of some elements in Nb at 1400°C /31/. Some coefficients are extrapolated for the temperature of 1400°C.

	Nb self-diffusion	Mo	Zr	Ta	W	V
1400°C	$1.2\ 10^{-13}$	$3.5\ 10^{-15}$	$2.0\ 10^{-12}$	$1.0\ 10^{-13}$	$5.2\ 10^{-16}$	$1.7\ 10^{-11}$

correlation exists between the melting point and the diffusion coefficient /32/. For a given temperature, the higher the melting point, the lower the diffusion coefficient. The melting points of the preceding elements are:

Zr	1852°C	Mo	2617°C	V	1900°C
Hf	2227°C	Re	3180°C	Rh	1963°C
Ta	3014°C	Os	3030°C	Ru	2250°C
W	3417°C				

Among elements with no diffusion data, only Re and Os have a higher melting point than Nb (2468°C). The diffusion coefficient of these two elements should be lower than the self diffusion coefficient of Nb. The elements which can strengthen the Nb alloys should be W, Mo, Re and Os. Rhenium is reported as the most effective solid-solution strengthener /33/. Moreover, W, Mo, Re and Os have a higher number of bonding electrons than Zr and Hf and the addition of elements such as Re or Os should decrease the oxygen solubility in Nb.

Interstitials, Internal Oxidation and Nitriding in Nb Base Alloys

The ductile brittle transition temperature (DBTT) in Nb base alloys increases with the oxygen and nitrogen content /6/. The oxygen and nitrogen content must be very low: this goal can be reached by a good process control and by adjusting the alloy chemistry to decrease their solubilities.

Moreover, in oxidation resistance studies, the relationship between "the distribution of oxygen in the scale and that dissolved in the substrate" is not taken into account /3/. It seems there is a link between the external and internal oxidation for Al /5/. Rhines /34/ has reported the formation of a sub-scale by internal oxidation, especially when some of the alloy components have a high reactivity with oxygen.

BCC Structures and Interstices

The BCC structure is less closely packed (68%) than the FCC structure (74%) and contains two types of interstices /20,35/. If atoms are taken as rigid spheres, the radius of the sphere which can be inserted in octahedral interstices is 0.067a and in the tetrahedral interstices is 0.127a, where a is the lattice parameter. Insertion of an atom with a radius larger than 0.127a (tetrahedral interstice) causes the displacement of 4 atoms, whereas an insertion of an atom in an octahedral interstice moves only two atoms parallel to the cube edge. The shape of the octahedral interstice is an ellipsoid with a small radius of 0.067 and a large radius of 0.273a. The lattice parameter of Nb is 0.33007 nm, the size of the tetrahedral interstice is 0.0419 nm and the size of the octahedral ellipsoid interstice is 0.02 nm for the small radius and 0.090 for the large radius. The atomic radius of the possible interstitials are (in nm):

H	B	C	N	O
0.030	0.087	0.07	0.071	0.065

So, all the possible interstitials can be in the octahedral interstice but must elastically displace two atoms. The group IVA elements have a large atomic size associated with a large compressibility (Fig. 4) /36/. For the 2nd and 3rd long period of the transition elements, the compressibility decreases with atomic size.

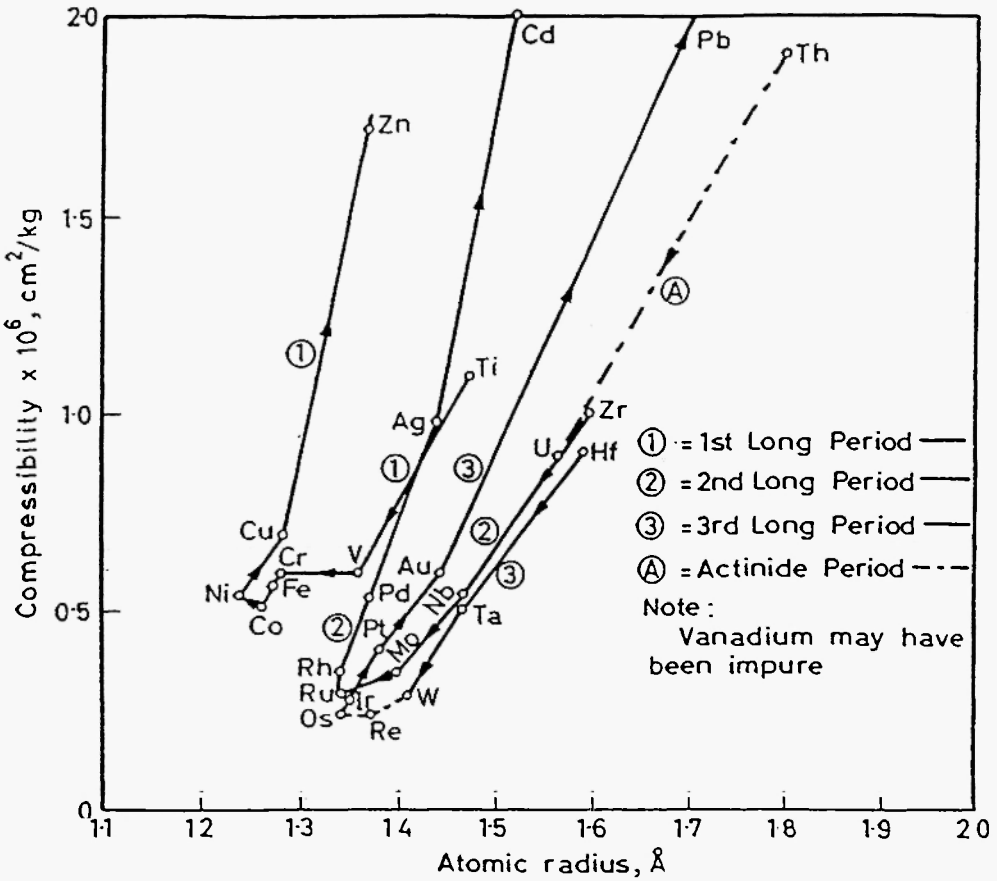

Fig. 4: Compressibility of metals as function of the atomic radius /36/.

(The previous description is based on the assumption that atoms are considered to be hard spheres, therefore interstice sites are voids. Actually, interstices can be described as regions with a very low electron density).

Coordination Number and Number of Bonding Electrons: Evolution of the Oxygen and Nitrogen Solubility with the Increase of Bonding Electrons

The maximum stability of a crystal is reached when the number of bonding electrons per atom is half the coordination number. In a BCC structure, the number of first nearest neighbors is 8 at a distance of 0.866a and the number is 12 in the FCC structure. In the BCC structure, the coordination number should be 8, but because of the slightly greater distance of the 6 second nearest neighbors, the coordination number is taken higher than 8. The bonding process is essentially supported by the 8 nearest neighbors and partly by the 6 second nearest neighbors. This implies that the coordination number is between 8 and 14 /37/. A coordination number of 11.8 has been proposed, so the maximum stability of the BCC structure should be reached for bonding electrons per atom of 5.9 (Ref. No. 8 in /37/).

Group VIA elements have 6 bonding electrons per atom. For group VIA and group VA, there is a deficit of bonding electrons per atom to reach the maximum stability, so the elements of these two groups will tend to accept electrons to approach the number of 5.9.

The solubility of the interstitial elements decreases from group IV elements to group VIA elements (Fig. 5) /38/. From group IVA elements to group VIA elements, the number of bonding electrons increases from 4 to 6.

Boron, carbon, nitrogen and oxygen can be seen as electron donors where some electron transfer is taking place from the non-metal atoms to the metal atoms

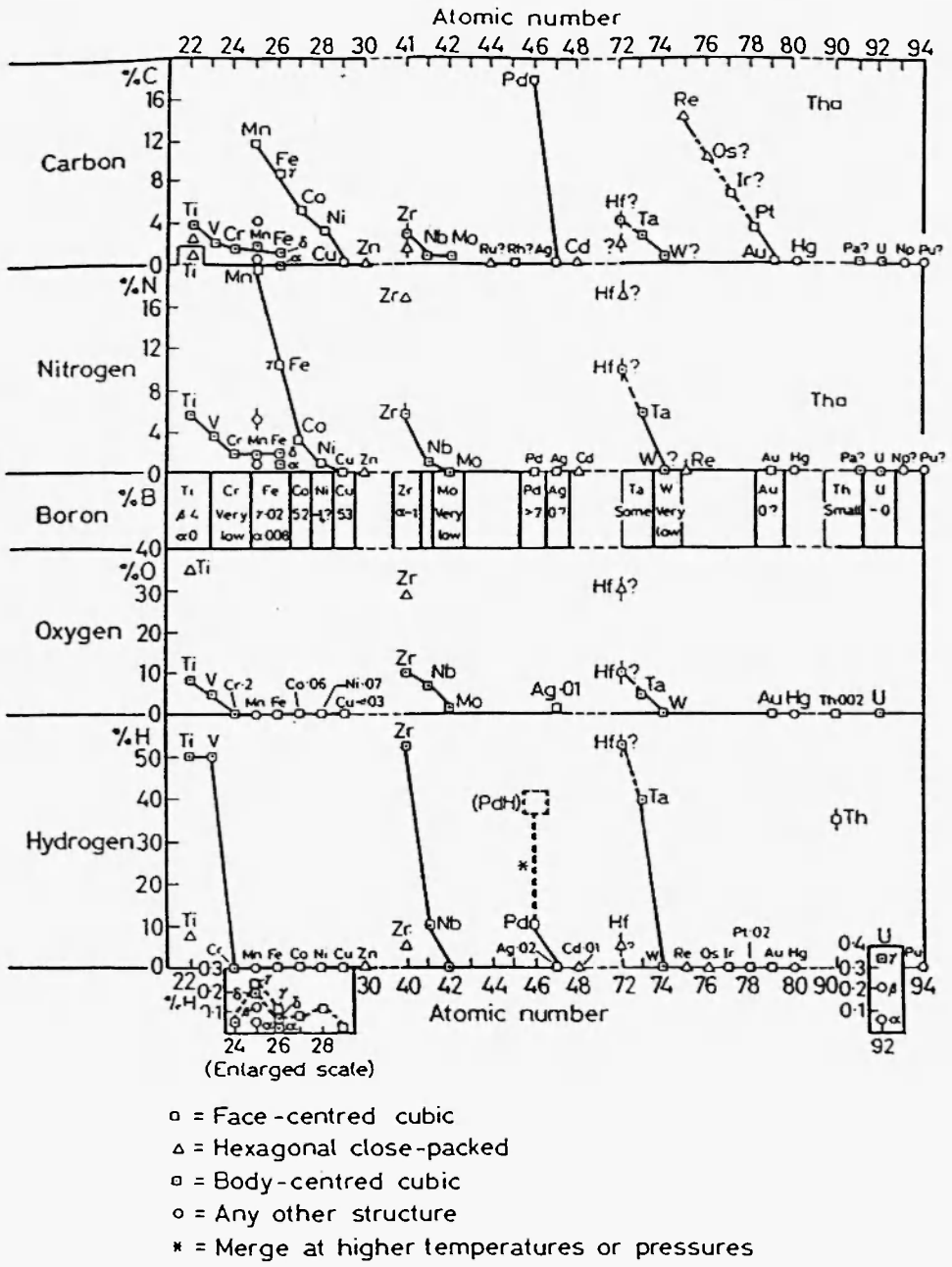

Fig. 5: Maximum solid solubility of interstitial elements in transition metals (at%) as function of atomic number and crystal structure /38/.

/37/. this lack in bonding electrons and the large interstices explain the high solubility of interstitial elements in group IVA and group VA elements.

The oxygen and nitrogen solubility, and hence internal oxidation, can be reduced by increasing the number of bonding electrons per atom. The oxygen solubility is almost zero for a number of bonding electrons per atom beginning at 5.6 /39/ or between 5.7 and 5.8 /37/. Therefore, the addition of elements such as Mo, W, Re and Os should decrease the oxygen and nitrogen solubility. The addition of these elements will also decrease the coordination number because their

atomic size is smaller than Nb /37/. But the addition of these elements could increase the possibility of brittle phases forming during aging.

Chromium in Nb Alloys

Addition of Cr is in general interesting to improve the oxidation resistance of alloys. Thus, Cr must be in solid-solution regardless of the temperature. The Cr solubility in Nb is less than 2 at% at 1000°C. Addition of Ti and Ta should reduce the Cr solubility in Nb at low temperature because the Cr solubility is less than 1 at% in Ti at 600°C and in Ta at 1000°C. In the three systems Nb-Cr, Ta-Cr and Ti-Cr, Cr forms Laves phase. This is why small additions of Cr should reduce the ductility of Nb alloys. For these reasons, chromium addition should be less than 1 at% for a homogeneous repartition in the alloy.

Nb Base Alloys and Intermediate Phases

Figure 6 (from /40/) gives the occurrence of intermediate phases in binary systems. The intermediate phases with a variable stoichiometry are σ, μ and χ. Two other families of intermediate phases with variable compositions, the P and R phases, appear in ternary systems. The σ phase forms with elements of almost equal atom size. The μ phase forms with elements of different atom size. When an element of group IVA, VA or VIA is mixed with an element from group VIIA or VIIIIA, alloys often show the following sequence /41/:

$$BCC \rightarrow Cr_3 \rightarrow \sigma \rightarrow \mu \rightarrow \chi \rightarrow CPH \rightarrow FCC$$

On the left side of the transition elements (group IVA and VA), the structure is BCC. On the right side of the transition elements (elements to the right of group VIIIA and group IB), the structure is FCC.

The σ, μ and χ phases appear for a specific range of the electron/atom ratio (e/a). This electronic criterion is not the only one for the occurrence of these phases, but a schematic arrangement of these phases has been proposed as a function of the e/a ratio (Fig. 7, from /40/).

Topologically Close-Packed (TCP) Phases in Ni Base Superalloys

Cr and Mo are two common elements added in Ni base superalloys but the e/a ratio is above 7 for the

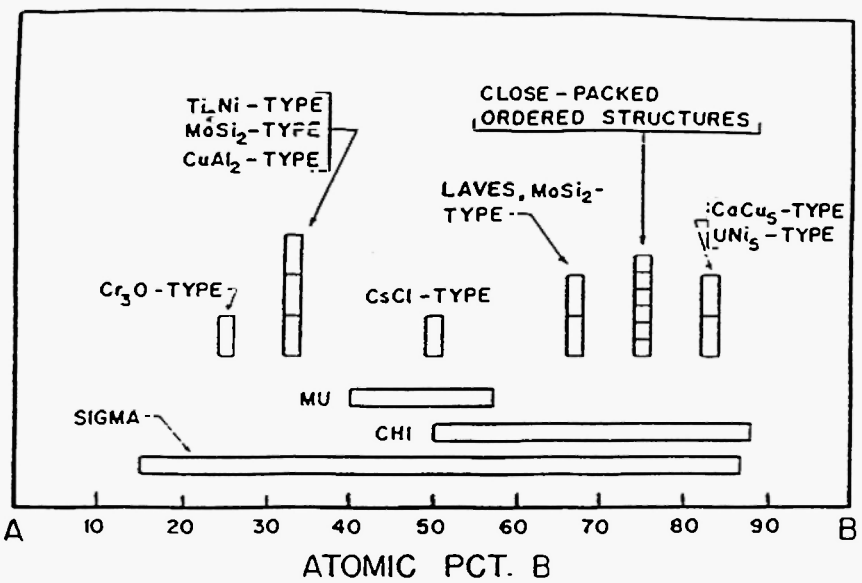

Fig. 6: Simplified summary of the occurrence of intermediate phases in binary systems of transition elements. The A component is an element of the Sc, Ti, V or Cr group; the B component is an element of the Mn, Fe, Co, Ni or Cu group /40/.

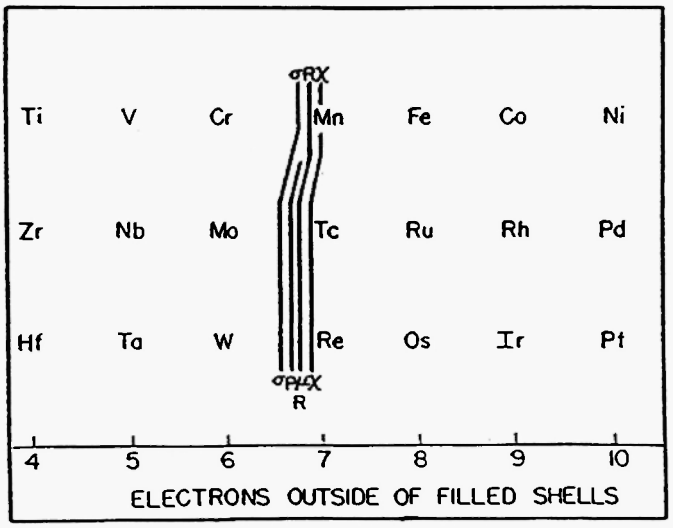

Fig. 7: Schematic arrangement of σ, P, μ, R and χ phases in order of increasing electron concentration /40/.

different alloys. However, after aging, these phases can appear in the alloy. Typical composition for σ and μ appear. Hence, locally in the material, the e/a ratio can be reached.

Occurrence of Intermediate Phases in Nb Base Alloys

In Nb base alloys intermediate phases might occur if Re or Os are added as solid-solution strengtheners. Ni is also on the right side of the line where the intermediate phases appear. The presence of a μ phase has been reported in Nb alloys for contents of Ni higher than 6 at% /23/. We should also notice that intermediate phases exist in the binary systems of Nb-Al and Ta-Al for an e/a ratio lower than in the other binary system where these phases exist.

Strengthening of the Second Phase

In Ni base superalloys, the strengthening elements of the γ phase $Ni_3(Al, Ti)$ are Nb and Ta. These two elements take the place of Al and Ti in this phase. These elements have almost the same atomic size and a very close electronegativity number compared to Al and Ti, but they have a higher melting point. In Ni base superalloys, these elements do not replace the base element (Ni).

For Nb base alloys, the elements with the same atomic size and a very close electronegativity compared to Ni are Co and Cu. But these two elements have a similar or a lower melting point than Ni. This is why for Nb base alloy Nb should be substituted in the second phase.

Zirconium and hafnium have a higher reactivity with Ni than Nb, so they should be associated with Ni in a Nb base alloy. These two elements form a complete solid-solution with Nb. The Ni solubility in both Zr and Hf is smaller than in Nb. The melting point of Hf is higher than for Zr, but the atomic difference with Nb is higher for Zr than for Hf. Zirconium and hafnium should take the place of Nb in the second phase.

CONCLUSIONS

In this study, parameters necessary for the creation of Nb base superalloys with a microstructure similar to that found in Ni base superalloys γ/γ' are emphasized: the different elements for this purpose are given. Niobium base alloys must be completely free of interstitials to avoid the formation of carbides, nitrides and oxides with the different elements in the alloys within the grain. These phases are unstable and/or a rapid coarsening occurs at high temperature.

A parallel and a comparison can be made between

Ni base superalloys and Nb base alloys:

		Ni Base Alloys	Ni Base Alloys
1	Elements necessary for phase precipitation in the grain boundaries	C, B, (N)*	Rare earth metals: Y, Er – and (Cu)*
2	Base element	Ni	Nb
3	Solid-solution strengtheners and oxidation resistance elements	Cr, Co, Fe, Mo, W, Re	Mo, W, Re, Al, Ta, Ti, Os (Cr^{O})*
4	Elements for precipitation of a second phase	Al, Ti	Ni, (Co)*

*In brackets, possible elements.

^{O}Less than 1 at%, for an homogeneous repartition in the alloy.

In Ni base superalloys, the atomic size increases from row 1 to 4, in Nb base alloys, the atomic size increases from row 4 to 1.

In Ni base superalloys, Nb and Ta strengthen the second phase γ. In Nb base alloys, the structure and the chemical composition of the second phase is unknown: but Zr and Hf form a complete solid-solution with Nb and are more reactive with Ni than Nb, so these elements should strengthen the second phase. Hafnium has a higher melting point than Zr.

REFERENCES

1. C.T. Sims, N.S. Stoloff and W.C. Hagel (eds.), Superalloys II. J. Wiley & Sons, 1987.
2. R.H. Titran, *Adv. Mater. & Process. J.*, **II**, 34 (1992).
3. E. Loria, *J. Metals*, **39**(7), 22 (1987).
4. J.J. Stephens, *J. Metals*, **42**(8), 22 (1990).
5. R.A. Perkins and G.H. Meier, *J. Metals*, 42(8), 17 (1990).
6. C. English, in: Niobium, H. Stuart (ed.), TMS-AIME, Warrendale, PA, 1981, p. 239.
7. D.L. Anton, D.B. Snow and A.F. Giamei, in: High Temperature Niobium Alloys, J.J. Stephens and I. Ahmad (eds.), TMS-AIME, Warrendale, PA, 1991, p. 49.
8. H.M. Yun and E.N. Sheftel, in: High Temperature Niobium Alloys, J.J. Stephens and I. Ahmad (eds.), TMS-AIME, Warrendale, PA, 1991, p. 83.
9. A.K. Misra, in: High Temperature Niobium Alloys, J.J. Stephens and I. Ahmad (eds.), TMS-AIME, Warrendale, PA, 1991, p. 135.
10. J.S. Lee, J.J. Stephens and T.G. Nieh, in: High Temperature Niobium Alloys, J.J. Stephens and I. Ahmad (eds.), TMS-AIME, Warrendale, PA, 1991, p. 143.
11. H. Stuart (ed.), Niobium, TMS-AIME, Warrendale, PA, 1981.
12. J.J. Stephens and I. Ahmad (eds.), High Temperature Niobium Alloys, TMS-AIME, Warrendale, PA, 1991.
13. J.H. Perepezko, Y.A. Chang, L.E. Seltzman, J.C. Lin, N.R. Bonda, T.J. Jewett and J.C. Mishurda, in: S.H. Whang, C.T. Liu and D.P. Pope (eds.), High Temperature Aluminides & Intermetallics, TMS-AIME, Warrendale, PA, 1990, p. 19.
14. L.A. Bendersky and W.J. Boettinger, *Mat. Res. Soc. Symp. Proc.*, **133**, 45 (1989).
15. T.J. Jewett, J.C. Lin, N.R. Bonda, L.E. Seltzman, K.C. Hsien and Y.A. Chang, *Mat. Res. Soc. Symp. Proc.*, **133**, 69 (1989).
16. D.T. Hoelzer and F. Ebrahimi, in: High Temperature Niobium Alloys, J.J. Stephens and I. Ahmad (eds.), TMS-AIME, Warrendale, PA, 1991, p. 105.
17. R. Strichor, J.C. Williams and W.A. Sofa, *Met. Trans.*, **19A**, 225 (1988).
18. W.B. Pearson, The Crystal Chemistry and Physics of Metals and Alloys, J. Wiley & Sons, 1972, p. 76.
19. A.E. Dwight, in D.L. Douglass and F.W. Kunz (eds.), Columbium Metallurgy, Met. Soc. of AIME, Interscience Publishers, 1961, p. 383.
20. H.W. King, in: R.W. Cahn and P. Haasen, Physical Metallurgy, North-Holland Physics Publishing, 1983, p. 38.
21. T.B. Massalski (ed.), Binary Alloy Phase Diagrams, ASM, 1986.
22. I.I. Kornilov and E.N. Pylaeva, *Russian Metallurgy* (metally), English translation, **5**, 69 (1966).
23. P.I. Kripyakevich and E.N. Pylaeva, *Soviet*

Physics Crystallography, **12**(2), 294 (1967).
24. P. Nash and A. Nash, *Bull. Alloy Phase Diagrams*, 7(2), 124 (1986).
25. A. Nash and P. Nash, *Bull. Alloy Phase Diagrams*, **5**(3), 259 (1984).
26. F.J. Anders, in: M. Semchysen and J.J. Harwood, Refractory Metals and Alloys, Met. Soc. of AIME, Interscience Publishers, 1961, p. 219.
27. C. McCullough, J.J. Valencia, C.G. Levi, R. Mehrabian, M. Maloney and R. Hecht, *Acta Metall. Mater.*, 39(11), 2745 (1991).
28. A.B. Michael, in: W.R. Clough, Reactive Metals, Met. Soc. of AIME, Interscience Publishers, 1959, p. 487.
29. F. Garofalo, Fundamentals of Creep and Creep-Rupture in Metals. The Macmillan Company, 1965, p. 135.
30. J.P. Hirth and J. Lothe (eds.), Theory of Dislocations, 2nd edition, John Wiley & Sons, 1982, p. 639.
31. E.A.A.A. Brandes (ed.), Smithells Metals Reference Book, 6th edition. Butterworth & Co., London, Chapter 13, 1983.
32. A.M. Brown and M.F. Ashby, *Acta Met.*, 28, 1085 (1980).
33. J. Maltz, in: I. Machlin, R.T. Begley and E.D. Weisert, Refractory Metal Alloys, Met. Soc. of AIME, Plenum Press, 1968, p. 451.
34. F.N. Rhines, *Atom. Movements, Trans. ASM*, 34A, 174 (1951).
35. J. Benart, A. Michel, J. Philibert and J. Talbot, *Métallurgie Générale*, Masson & Co., 1969, p. 32.
36. W. Hume-Rothery and B.R. Coles, *Phil. Mag.*, suppl. 3, 149 (1954).
37. D.A. Robins, *J. Less-Comm. Met.*, **1**, 396 (1959).
38. H.J. Goldschmidt, Interstitial Alloys, Butterworth & Co., Publishers, 1967, p. 61.
39. W.D. Wilkinson, Properties of Refractory Metals, Gordon and Breach Science Publishers, 1969, p. 11.
40. M.V. Nevitt, in: P.E. Beck (ed.), Electronic Structure and Alloy Chemistry of the Transition Elements, Met. Soc. of AIME, Interscience Publishers, J. Wiley & Sons, 1963, p. 101.
41. W. Hume-Rothery, R.E. Smallman and C.W. Haworth, The Structure of Metals and Alloys, The Metals and Metallurgy Trust, London, 1969.