Abstract

Model alloy systems were chosen for their ability to illustrate competing elements involved in the formation of A3B phases, i.e., aluminium and titanium, aluminium and tantalum. A solid solution was substituted for nickel in the pseudoternary systems "S"-Al-Ti and "S"-Al-Ta. The range of compositions of the primary solidification phases was determined in order to observe the changes due to the elements present in the solid solution.

The different solubility ranges were studied on the basis of our experimental results on specimens annealed at 1250°C and analyzed in the light of the numerous data concerning ternary systems obtained from the literature.

Particular attention was focused on high temperature reactions and transformations involving the liquid phase. A correlation was established between certain microstructures obtained and the peritectic transformations occurring between the \( \gamma \), \( \gamma' \) and liquid phases.
Introduction

The continually increasing demands on the creep resistance of turbine blade materials has led to a marked evolution in their composition in recent years, corresponding in particular to larger volume fractions of the $\gamma'$ (Ni$_3$Al) strengthening phase. Alloy chemistries have moved gradually closer to eutectic compositions, with a tendency toward higher solvus and lower solidus temperatures.

In order to overcome this disadvantage, there has been a "shift" in the latest single-crystal superalloy compositions, in which tantalum is used in preference to titanium and niobium. Even if the total range of elements can now be considered to be relatively stable, there remains considerable scope for obtaining improved creep properties by the optimization of compositions. This involves the close control of phase equilibria, both in the solid state, in particular the precipitation of $\gamma'$ in $\gamma$, and between liquid and solid, in order to facilitate homogenization and solutioning of $\gamma'$ without incipient melting and to enhance the aptitude for single crystal solidification. However, currently available phase diagrams are not sufficiently accurate or complete to achieve this goal.

Since modern industrial single-crystal blade alloys such as CMSX 2 or PWA 1480 contain at least 8 elements, it is essential in such studies to adopt a clearly defined strategy. For this reason, the pseudoternary model systems "S"-Al-Ti or "S"-Al-Ta were chosen to represent the real complex alloys. The symbol "S" here represents the matrix solid solution, which was taken as Ni-8Cr-5Co-8W (weight %), which is typical of the composition of numerous commercial alloys such as CMSX 2. The compositions ("S", 30%Al,30%Ti or Ta) were chosen to ensure the presence of all the main phases and to compare the contribution of aluminium and titanium/tantalum to their formation. The approach adopted was to compare compositions in these complex materials with alloys of similar Al, Ti and Ta contents in the Ni-Al-Ti and Ni-Al-Ta previously determined nickel rich corner (1,2).

The main basic ternary systems Ni-Cr-Ti (3), Ni-Ti-Al (4,5), Ni-Al-X (6) were investigated in the fifties. More recently, further developments or new investigations have concerned both these systems, Al-Cr-Ni (7), Cr-Ni-Ti (8), Ni-Or-Ta (9), and pseudoquaternary systems Ni$_3$Al-Ni$_3$Cr-Ni$_3$Ta (10), Ni$_3$Al-Ni$_3$Cr-Ni$_3$Mo (11) or even more complex systems (12,13), but in this case limited to phase equilibria between $\gamma$ and $\gamma'$. Our investigation differs from these studies, aimed chiefly at determining solid phase equilibria, in that it focuses on equilibria involving a liquid phase.

Experimental method

The experimental method (14) consists in a characterization of the structures of alloys solidified under controlled conditions. Freezing was monitored in a differential thermal analysis (DTA) furnace and a rapid quench was operated in order to interrupt the solidification process at different stages, particularly when the first crystal was formed at the liquidus temperature. This method, used in conjunction with electron beam analysis, enables the determination of the liquid-solid tie-lines. In addition, the observation of the so-quenched structure also allows the specification of the crystallization sequences.

The liquidus surfaces are determined from the transformation temperatures. The liquidus temperature range is found to be rather narrow for alloys in the $\gamma'$ field and in the $\gamma'/\gamma$ border line case. Temperatures alone are not sufficient to discriminate the different fields for each primary phase.
Consequently the investigation has to be completed by morphological examination, careful phase identification and microanalysis. All the usual characterization methods are employed: TEM, STEM, electron probe and X-ray diffraction.

Some sixty compositions were prepared for each "S"-Al-Ti or Ta system, as well as a few compositions with 0 and 4 wt% tungsten content.

The "S"-Al-Ti system

Figure 1 shows for a pseudoternary system "S"-Al-Ti, the projection of the liquidus surfacess superimposed on the corresponding projection in the Ni-Al-Ti ternary system. The primary phase within these limits will be examined with respect to their ability to generate precipitations at lower temperatures. To better illustrate chemical interactions, all the results are given in atoms per cent or in atomic concentration.

The γ phase field is shown to be reduced, shifted towards the high nickel contents. This result reflects the marked tendency of Cr and Co, and to a lesser degree of W, to become part of the γ' phase. The γ liquidus hypersurface can be represented by a polynomial, after smoothing the experimental values, and expressed as a function of the atomic concentration in Al, Ti and also W. Overall precision is of the order of 4°C.

\[
T + C = 1447 - 606 \times_Ti - 151 \times_{Al} + 193 \times_W - 3256 \times_Ti^2 - 8661 \times_{Ti} \times_{Al} + 74 \times_{Ti} \times_W + 1774 \times_{Ti} \times_W - 1774 \times_{Al} + 2021 \times_{Ti} \times_W + 8945 \times_W^2
\]

Tungsten raises the liquidus temperature and this influence is enhanced for low aluminium contents and even more so for low titanium contents.

The η(Ni3Ti) primary phase has significant solubility for alloying elements: cobalt (6%), tungsten (1.3%), aluminium (4%) or chromium (3.4%). The η field is not reduced to a point in the compositional space as could be previously assumed (6). However at 1250°C tungsten becomes totally insoluble.
Figure 2 - Projection of the tie-lines at the liquidus temperature a) in the 
"S"-Al-Ti plane b) in the (Ni, Co, W)-Cr-Ti plane.

while the solubility of chromium is greatly reduced. Small very rounded 
precipitates are formed, composed almost exclusively of tungsten (5%Ni, 
5%Cr, 1%Ti).

The β(NiAl) primary phase has also a significant solubility for alloying 
elements: cobalt (3.5%), tungsten (0.7%), titanium (7.7%) or chromium 
(7%). Various precipitates are formed at 1250°C: γ', αW and αCr, depending 
on the respective Al, Cr and Ti contents. These γ, γ' and αCr precipitations 
can be interpreted by referring to the Ni-Al-Cr phase diagram (7). Tungsten 
is totally eliminated in the form of αW precipitates. Similar precipitations 
have been observed in the Ni-Al-Ta-Cr-W system (15).

The γ' phase covers a wide solid solution range, in particular in the case 
of titanium which can be contained in contents five times greater than that 
of aluminium. Comparing the systems Ni-Al-Ti and "S"-Al-Ti, the solubility 
of Al and Ti in the pseudoternary system is found to be reduced in a 
proportion of up to 30%. Interactions between Cr and Ti, and also between 
Cr and W, are observed. In the solid phase, chromium diminishes the 
solubility of W in the γ' phase (16) and also that of titanium.

Tie-lines and crystallizations paths

The experimental method can be used to determine the tie-lines of complex 
alloys; this is of practical interest in that at the liquidus temperature 
the tie-line indicates both the direction of the crystallization path, to 
which it is tangent, and the extent of segregations. Figure 2a shows that 
the respective Al and Ti contents of the liquid and solid phases are 
equivalent for low titanium contents, as is the case for similar Ni-Al-Ti 
ternary compositions. Tungsten is concentrated in the initial solid, as shown 
on the electronic image of Figure 3a where the centre of the dendrite 
appears quite white because a heavy element is present. For titanium 
contents exceeding 5% a strong interaction between Cr and Ti is noticeable. 
There is much less segregation of Cr when the Ti content increases (Fig. 
2b). All in all, for alloys pertaining to the γ liquidus surface, the 
crystallization paths can be interpreted by referring to the ternary system 
and result in the formation of γ'.

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On the contrary, when the primary phases are \( \eta \) and \( \beta \), tungsten is strongly segregated in the liquid. For titanium rich alloys with primary phase \( \eta \), chromium is segregated in the interdendritic liquid. After solidification, different binary or ternary eutectic structures are observed, implying the presence of \( \eta \), \( \gamma' \), \( \gamma \), \( \alpha\text{Cr} \) and \( \text{H} \) (Ni2AlTi) phases. The \( \gamma \) phase has the most extensive solubility range, accommodating up to 30 %Cr. The \( \alpha\text{W} \) phase is also found next to the eutectic zones, in the form of coarse blocks formed from the tungsten-enriched liquid where they have been trapped in the interdendritic groove. Such structures can be detrimental since they comprise zones with elements that diffuse poorly, intermetallic compounds not readily resoluble in the solid solution, eutectics of relatively low melting point, and, last but not least, contain all the elements capable of forming the \( \sigma \) phase.

**Morphologies and nature of three-phase equilibria**

In a earlier publication (2) we showed that the nature of the equilibria between \( \gamma-\gamma' \)-liquid changes along the monovariant line. For Ti contents of over 5 % the \( \gamma-\gamma' \) liquid equilibria are peritectic in nature whereas \( \gamma'-\beta \) liquid equilibria become eutectic. The same effect is observed with tantalum (1). In the case of our complex alloys, such changes are practically impossible to prove by means of the insufficiently precise conodes and it is necessary to rely on morphology similarities with the ternary system. The electron micrograph of Figure 3 show \( \gamma \) phase dendrites completely surrounded by a \( \gamma' \) phase fringe of peritectic origin. A eutectic zone is observed in the interdendritic groove. Temperature variations along a section such as "S"-Al (Fig. 4) confirm this observation. On the other hand the alloys on the border of the \( \beta-\gamma' \) regions have a typically eutectic morphology. This means that solidification of alloys with compositions lying in the primary \( \gamma \) field can result in the formation of \( \beta \) phase since the solidification path can cross the peritectic region.

![Figure 3](image1.png)

**Figure 3** - (Left hand) Electron micrograph of alloy "S"-10Al-7,5Ti showing \( \gamma \) dendrites surrounded by a \( \gamma' \) fringe and a eutectic structure in the interdendritic groove with Ni2AlTi (dark phase).

![Figure 4](image2.png)

**Figure 4** - (Right hand) Vertical section for the system "S"-Al and Ni-Al.
Figure 7 – Projection of the liquidus surface "S"-Al-Ta. Full lines, the boundaries of the primary fields, dotted lines, the monovariant lines for the system Ni-Al-Ta.

In the Ni-Al-Ti system, for titanium-rich alloys with compositions close to the monovariant line, the microstructure change markedly during high temperature exposure, the variations being more complex than a simple precipitation reaction. This change is illustrated by the example of an alloy containing 8 at%Al and 12 at%Ti. Samples were quenched at different stages of 300°C/h programmed cooling cycle. Figure 5a shows that, when quenching is carried out at the liquidus temperature, the primary γ' dendrites are perfectly homogenous. Figures 5b and 5c correspond to the same alloy respectively quenched from 20°C solubility of nickel and especially titanium, the γ' has undergone a transformation with rejection of γ phase. This transformation ultimately leads to the formation of spherical pockets whose appearance suggests partial remelting. These pockets appear (Fig. 5b) in the magnified area, to contain a dense precipitation of hyperfine γ' particles, whereas the latter have a coarser dendritic morphology in the slowly cooled specimens. Similar remelted pockets surrounded by a fine network of γ precipitation can be observed in alloys of the "S"-Al-Ti system (Fig. 6). In this case the remelted pocket, enriched in nickel, titanium and also in chromium and tungsten results in more complex phases on solidification.

Such structures are not recommended for industrial alloys. Consequently the formation of titanium-enriched primary γ' should be avoided. On the contrary, the presence of a peritectic γ phase ensures a high proportion of this phase in the ultimate alloy. Alloy AM1, for instance, solidifies in the primary γ phase thereby avoiding interdendritic segregation of tungsten, but also contains a good proportion of peritectic γ'.

Comparison with the "S"-Al-Ta system

In this system the primary phase π(Ni6AlTa) is present as in the Ni-Al-Ta system (1). It also takes the same type of morphology i.e. relatively coarse primary phases and platelike precipitations along preferred planes. Figure 8 shows the projection of the liquidus surfaces in a "S"-Al-Ta pseudoternary...
Figure 5 - Electron micrograph for alloy Ni-Al8-Ti12 a) specimen quenched at the liquidus temperature; b) specimen quenched 20°C below the liquidus temperature; a magnified area shows the remelted zone; c) specimen cooled at a rate of 5°C/mn.

Figure 6 - Electron micrograph of alloy "S"-7,5Al-11,5Ti cooled at a rate of 5°C/mn.
system according to (17). Again, as in the Ni-Al-Ta ternary system, tantalum diminishes the solubility of W, Cr and Co in the γ' phase. In the presence of tantalum instead of titanium, the liquidus temperature of the alloy is lowered, but the drop is much less marked, more than halved, than in the case of titanium. As for the crystallization paths of the primary γ alloy, they are characterized by less segregation of tantalum in the interdendritic liquid and the formation of the γ' phase. For Ta contents exceeding 10 %, annealing of the γ matrix at 1250°C precipitated intermingled γ', δ (Ni3Ta) and π phases.

Stability of the Ni3X type phases

Various approaches can be adopted to study the stability of A3B compounds. A thermodynamics approach at macroscopic level is not easy to realize due to the small differences in free enthalpy of the compounds that make it difficult to predict the formation of one or other of these compounds. This remains true even when using models extended to the ternary system such as the sub-lattice model which takes into account the distribution of atoms in the lattice (18). In terms of crystal structure, Ni3Al can be described as two cubic sublattices containing respectively nickel atoms and aluminium atoms. However, the location of the other elements is not so clearly established; they are disposed on either sublattice according to their bonding characteristics. Assumptions can be made considering the extent of the γ' field illustrated in Figure 8. The nickel content appears to be limited, thus indicating that nickel cannot be replaced on both lattices. This limitation no longer applies in the case of the Al-Cr-Ni system (7). Time-of-flight atom probe experiments (19) give more precise information: aluminium can be easily replaced by titanium and tantalum and also nickel, whereas chromium can substitute on either sublattice and tungsten can only substitute nickel.

These A3B compounds are also similar in their crystallographic structure. They are composed of stacks of compact planes called T or R planes depending on whether they have 3-fold or 4-fold symmetry. These planes are closely stacked with spacings of between 0.2059 and 0.2126 nm. The differences in crystallographic structure correspond to stacking sequences involving several tiers of planes.

Table I: Compositions and crystal structures of A3B phases in the Ni3Al-Ni3Ti-Ni3Ta system. * present study.

<table>
<thead>
<tr>
<th>Spatial group</th>
<th>Phases</th>
<th>Composition</th>
<th>Type of planes</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>P m3m</td>
<td>γ'</td>
<td>Ni3Al</td>
<td>T</td>
<td>(21)*</td>
</tr>
<tr>
<td>P63/mmc</td>
<td>π</td>
<td>Ni3(Al0.5Ta0.5)</td>
<td>T</td>
<td>(22)*</td>
</tr>
<tr>
<td>P mmm</td>
<td>γ</td>
<td>Ni3Ta</td>
<td>R</td>
<td>(23)*</td>
</tr>
<tr>
<td>undefined</td>
<td></td>
<td>Ni3(Ti0.33Ta0.67)</td>
<td>R</td>
<td>(24)*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni3(Ti0.5Ta0.5)</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>P 63/mmc</td>
<td></td>
<td>Ni3(Ti0.67Ta0.33)</td>
<td>T</td>
<td>(24)*</td>
</tr>
<tr>
<td>R 3m</td>
<td></td>
<td>Ni3(Ti0.83Ta0.17)</td>
<td>T</td>
<td>(24)*</td>
</tr>
<tr>
<td>undefined</td>
<td></td>
<td>Ni3(Ti0.96Ta0.04)</td>
<td>T</td>
<td>(24)</td>
</tr>
<tr>
<td>P 63/mmc</td>
<td>n</td>
<td>Ni3Ti</td>
<td>T</td>
<td>(21)*</td>
</tr>
</tbody>
</table>
Electron entropy is a valuable means of characterizing these transition metal compounds due to the diversity of hybridized orbitals associated with the transition metals. Sinha (20) showed that, depending on the e/a ratio, i.e. average number per atom of electrons of the outer shell participating in the bond, it was possible to predict the formation of phases with R planes ($8.65 < e/a < 8.75$) or phases with T planes ($7.75 < e/a < 8.65$). Unfortunately, this criterion does not help to predict the stacking sequence and therefore the crystallographic structure and resulting differences in energy.

We studied the Ni$_3$Ti-Ni$_3$Ta system experimentally. In addition to the $\eta$ and $\delta$ extreme phases, four known intermediate phases and one new phase were identified in specimens annealed at 1250°C (Table I) (2,21,23,24). This section therefore comprises seven phases with A3B stoichiometry - a fair measure of the complexity of the problem.

Conclusion

The strategy for this investigation was based on the model systems method. The model systems chosen clearly illustrated the competition between, first, titanium and aluminium, secondly, tantalum and aluminium, in forming A3B type phases with nickel. The great similarity of $"S"$-Al-Ti and $"S"$-Al-Ta systems with their corresponding ternary system is adequate evidence that additional cobalt, chromium and tungsten elements have little influence on the outcome of this competition. Chromium and tungsten principally affect the crystallization paths since the $\eta$, $\beta$, $\tau$, $\delta$ primary phases, and to a lesser degree the $\gamma'$ phase, segregate these elements in the interdendritic liquid. By a more thorough investigation of these reference systems we established that the specific morphologies where linked with the peritectic or even metatectic nature of the $\gamma$-$\gamma'$ liquid reactions. Finally we point out that thermodynamic models can hardly be used to represent the competing reactions in these A3B systems because of the small differences in their energies due to their overall similarity.

Acknowledgments

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