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Liquid-Solid Phase Equilibria of the (Ni-Cr-Co-W) - Al -Ta, Multiconstituent System. Type Superalloys.

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ABSTRACT -- Liquid-solid and solid-state phase equilibra have been studied in the S-Ni Al-Ni_3Ta triangle of the S-Al-Ta system where S is solution solid of (Ni-Cr-Co-W), in the S-rich corner, using a combination of several experimental techniques. Five primary phase occur in this region, including the ternary compound, π, S_6TaAl, which enters into equilibrium with each of the other four. Another compound S_8Ta, forms in the solid state by decomposition of the Ta-rich Ni solid-solutions and occurs in equilibrium with the γ, π and δ (S_3Ta) phase. The extent of these different phase fields has been determined at 1250°C and particular attention has been paid to the **γ- γ'** solvus surface which has been shown to be accurately described by a second-order polynomial function of the atomic concentration.
***Keywords**: Superalloys, turbine blades, ternary phase diagram, phase equilibria*

I. Introduction

The progressive improvement obtained over the last 40 years in the ability of the turbine blades to withstand high temperatures has been achieved to a large extent by a gradual increase in the volume fraction of the hardening phase **γ'** in the Ni-base superalloys ,together with processing innovations such as columnar-grain and single-crystal casting. The trend has been retarded by the associated rise in **γ'** solvus and the concomitant decrease in solidus temperature, rapidly leading to the appearance of eutectic **γ'.** In order to counteract this tendency, there has been a shift in composition: many recent high – performance blade alloys are largely based on the Ni-Al-Ta system, with further additions, of which the most frequently employed are chrome to increase corrosion resistance, Tungsten and Cobalt leads to higher solidus temperatures and Tantalum enables larger γ' volume fraction to be obtained without formation of eutectic.

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In spite of the practical importance, the (Ni-Cr-Co-W) - Al -Ta multi-constitute system has been relatively little investigated, especially in the liquidus- solidus region. Nash and west [1], who studied solid-state phase equilibra at 1000 and 1250°C in the region containing 50-100 at% Ni, have briefly reviewed previous work. The currently accepted version of the Ni-Al binary system is that given by Hansen and Anderko [2], and incorporates both a eutectic and a peritectic reaction close together, in the region of Ni3Al. After initial debate, these were found to be situated on the Ni-rich side of **γ',** following experiments carried by Floyd [3]. The Ni-Ta binary system given by Shunk [4], has been modified by Nash and west [5], who confirmed the formation in the solid state of Ni_8Ta first reported by Larson et al [6]. This face-centred tetragonal compound is stable up to 1300°C. In the three-compound system , a pseudo binary eutectic between Ni_3Al (**γ'**) and Ni_3Ta(**δ**) at 8-11at%Ta and 12.5 at% Al, has been reported ,together with a ternary eutectic between **γ , γ'** and δ at 11at %Ta and 9.5 at% Al [7]. However, this is not in agreement with the existence of a ternary compound Ni_6TaAl, first recorded by Giessen and grant [8] and subsequently confirmed by other workers [1, 9]. The melting

point of this phase has been reported to be 1530°C [9].
Apart from, a few isolated values [10]. Until recently little information was available concerning the liquidus and solidus temperatures within the ternary system.
Nickel-based superalloys are an unusual class of metallic materials with an exceptional combination of high temperature strength, toughness, and resistance to degradation in corrosive or oxidizing environments. These materials are widely used in aircraft and power-generation turbines, rocket engines, and other challenging environments, including nuclear power and chemical processing plants. Intensive alloy and process development activities during the past few decades have resulted in alloys that can tolerate average temperatures of 1200°C .The present authors have undertaken a more detailed study of this system and early results on the liquid-solid transformations have already been published [11]. These are briefly reviewed in the present paper, and the equilibria which occur in the solid state are described in detail. The present work was carried out as part of a more extensive programme whose ultimate aim is to calculate complex superalloy phase diagrams, and in particular to determine the limit of the primary γ solid-solution solidification field, together with liquidus, solidus and γ' solvus temperature in the multiconstituent system superalloy, were the composition of the solution solid S is: (79.3 at% Ni; 8at% Cr, 5.2at% Co and 7.5at%W)
Where W, Co and Cr are added to improve the characteristics of the matrix (raise the solvus, γ solid solution strengthening and improving the corrosion resistance in this new superalloy.
Although face-centered cubic (FCC) nickel is the major superalloy constituent, many alloys contain up to 40 wt% of a combination of five to ten other elements. The alloying elements present in Ni-based superalloys are γ former (Ni, Co, Cr, W, V, Mo, Ru), γ'former (Al,Ti, Nb,Ta). [12].
Formulation of the pseudo-binary system using a cellular automata (CA) model, was studied by [13]. The pseudo-binary system (A–B) is postulated to be between a hypothetical invariant pure γ (all γ - stabilizers grouped as A) and a stoichiometric pure γ' phase (all γ'-stabilizers are grouped as B) [13]. Let us consider an m-component Ni-based two-phase (γ + γ') alloy where I =1….m; I =1…k (Ni, Co, Cr, W etc.) are γ-stabilizers and k+1…m (Al, Ta, Nb etc.) are - γ' stabilizers.
Three multi-component Ni-base superalloys: Ni-Cr-Co-W whose compositions are given , were considered for pseudo-binary models It is seen that the multi-component phase equilibria determined through Thermo-calcs is well reproduced in the pseudo-binary phase diagram without the Loss of any information. Regions of single phase γ, γ' and liquid, two phase regions between these as well as the three-phase γ + γ' + liquid are delineated in these diagrams. It is to be noted that though the phase diagram information is generated for the complete range of composition (X_B from 0 to 1), the region of interest for microstructure modeling lies between the tie lines of the alloy composition. The two-phase γ / γ' alloys could be well represented through a novel pseudo-binary phase diagram. The use of the pseudo- binary phase diagram for solidification modeling using a cellular auto mata (CA) model has been demonstrated. The pseudo-binary Gibbs energies were used in phase field models to simulate a five-component. The phase field simulated phase fractions of γ and γ' matched very well with the phase fractions obtained from pseudo-binary phase diagram.

II. Experimental procedure

A number of master alloys were melted in a medium frequency induction furnace under inert atmosphere, using high-purity charge materials (≥ 99.9 %). Intermediate compositions were prepared from these in an arc melting furnace with cold copper crucible under inert atmosphere. In all about 60 alloys were studied.
In order to reduce segregations resulting from solidification, all the ingots were homogenized for 20h at 1200°C. For some specimens, additional isothermal annealing treatments were carried out for 40h at 850 and 1050°C. Transformation temperatures were determined by differential thermal analysis following a procedure which has been described in [14].

Solid –liquid transformations were studied on 200 mg specimens placed in alumina crucibles, heated, and cooled under helium at 5°C/mn. Solid-state transformations were studied using 400mg samples, taking care not to exceed the solidus temperature. The samples were previously annealed for 20h at 1200°C in order to reduce segregations. Fig.1 illustrates the types of thermogram observed. Thermogram 1 was obtained by heating the specimen beyond the liquidus. The γ' solvus corresponds to small and

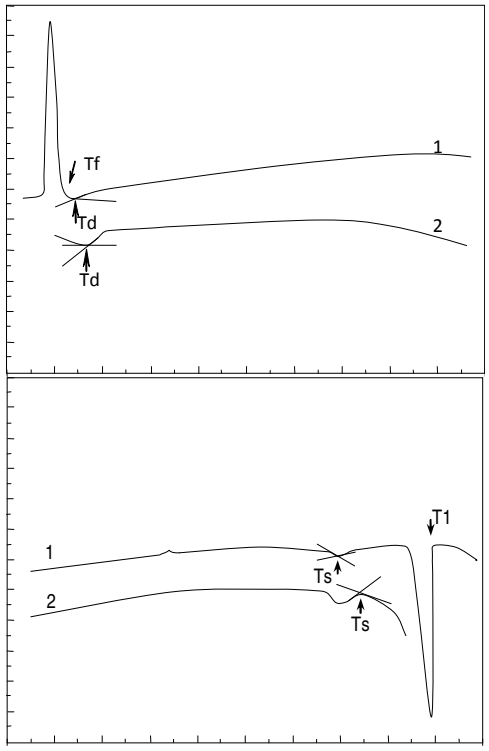

Fig. 1 Typical thermogram: 1-as cast; 2-homogenized. T_f – solidus temperature, T l- liquidus temperature. T_s- solvus temperature, Td-complete dissolution temperature.

poorly-defined peaks because of the heterogeneity of the as-solidified specimen. In contrast, thermogram 2 obtained from a larger, previously homogenized specimen, shows sharper, more readily exploitable peaks. Optical micrographic was carried out on polished sections etched in aqua-regia.

Phase analyses were characterized by scanning microscopy Philips XL30 microscope. The quantitative compositional microanalyses were conducted with an Electron dispersive spectrometer (EDS). Phases present in form of fine particles were analyzed.

X-ray diffraction was used to identify phases, mostly from massive specimens, while other samples were investigated using TEM on thin foils

III. Results

III. 1. Solid-liquid equilibria

Five phases have been identified within the triangle Ni-NiAl-Ni_3Ta: γ, γ', δ, β, (Ni can be replaced by S solution solid Ni-Cr-Co-W), and Ni_8TaAl, which has been designated as π. The crystal structures and lattice parameters are given in table 1 together with values from the literature.

Fig. 2 shows the projection of the liquidus surface for the S-S Al-S_3-Ta triangle, and gives the primary solidification fields for each phase. In the nickel (S)-rich corner an extensive γ solid solution region is bordered by three fields corresponding to the phases γ', π and δ.

Table 2 gives the ranges of composition determined for each of the primary phases and shows that the δ-phase dissolves very little Al, while solubility of Ta in the β-phase is also small. On the contrary γ, γ' and π. Phases have considerable solubility ranges in the solid-liquid region.

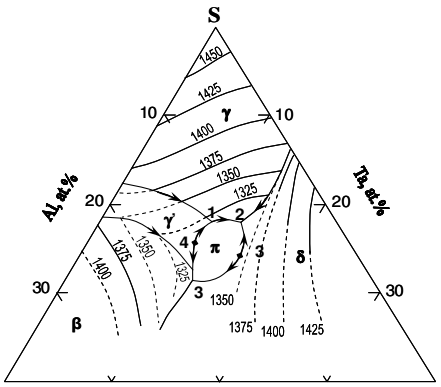

Fig 2: Liquidus surface and invariant lines in the S-Al- Ta system

The Ni_8-Ta compound does not exist up to the solidus temperature. In the Ni-Ta binary system, it forms by a peritectoid reaction between 1348°C and 1324°C [5].

Table 1. Crystal structures and lattice parameters (nm) of A_3B phases in S-Al-Ta

		Equivalent Ni base compound					
		Ni_3Al-	Ni_6TaAl	Ni_3Ta	Ni_3Ta	Ni_3Ta	Ni_3Ta
		Phase type					
		Cu_3Au	Ni_3Ti	Al_3Ti	Pt_3Nb	Cu_3Ti	βCu_3Ti
Composition at.%		Bravais lattice		Body-centred			face-centred
S(Ni,Cr,Co,W)bal.		Simple cubic	Hexagonal	Tetragonal	Monoclinic	Ortho.	Tetragonal
Al	Ta						
31.0	0	a=0.3573 (1)					
12.6	11.8	a=0.3607 (1)					
13.1	8.9	a=0.3608 (*)					
18	7	a=0.3609 (*)					
10.5	12		a=0.5114 (1) c=0.8360				
10.4	12.5		a=0.5114 (*) c=0.8362				
12.5	12.5		a=0.5112 (8) c=0.8340 (9)				
0	25			a=0.3627 (*) c=0.7465	a=0.512 b=0.452 c=2.537 α=90°50’	a=0.512(*) b=0.423(13) c=0.452	
0	25				a=0.511 b=0.454 (8) c=2.550 α=90°40’	a=0.514 b=0.425(13 c=0.454	
2.5	26			a=0.3571(*) b=0.7452		a=0.5117 b=0.4247(1) c=0.4527	
0	11.1						a=1.0754(6) b=0.3585

(*) Present result
(Numb.) references in the text

It was not always possible to determine with certainly the nature of the invariant lines. Most of them appear to be of the eutectic type. However, in Fig. 2, the line point 4 apparently maintains its peritectic character up to the invariant point 4, while the line e_3- 3 may possibly become peritectic before reaching the junction 3. The nature of the invariant reactions is likewise uncertain except for point 2 which is clearly a ternary eutectic. The eutectic line between β and δ falls away towards lower Ni contents and probably meets the S-Ta (Ni-Ta) field.

III. 2. Solid-state equilibria

The tie lines determined by analysis on about 30 alloys are shown in the form of a 1250°C isothermal section in Fig. 3, the phases identified are the same as the primary phases already described, but with the presence of the compound Ni_8Ta. This part of the diagram includes several two-phase fields with characteristic microstructures, examples of which are shown in Fig. 4.

Alloy A (15Ta, 25 Al) and alloy B (6.68Ta , 13.47Al) annealed for 40h at 1250°C (Fig 3),

was found to consist of two phases using EDS analysis. However, closer examination using transmission electron microscopy (TEM) of thin foils, revealed for alloy A, the presence of three phases (Fig 5, a), the laths consist δ phase, Ni_3TaAl. X-ray diffraction showed the structure to be orthorhombic with parameters; a=0,512, b=0,420; c=0.454 nm.

Table 2: Limiting compositions of phases, corresponding to maximum solubility for primary phases (all except Ni_8Ta)

Phase	Composition at %		
	Al	Ta	S(Ni-Cr-Co-W)
γ	0-16	0-14	70-100
γ'	18-22	0-11	70-80
β	23-50	0-10	40-75
δ	0-8	15-	85-86
π	9-15	11-16	70-80
Ni_8Ta	0-4	10-12	--

Between the laths, precipitates are observed in a γ-matrix (the alloy solidifies in the primary γ-field). These precipitates where identified by x-ray diffraction and where shown to have the face-centred tetragonal structure described by Larson et al [6], the lattice parameters being a=b=1.0937nm and c=0.366nm.

For alloy B it shown only two phase γ' in γ matrix (fig 5b), the typical microstructure of such superalloys is a high fraction of cuboidal *γ'* phase precipitates Coherently embedded in the *γ* matrix phase. It is the *γ'* phase that is largely responsible for the elevated-temperature strength of the material and its incredible resistance to creep deformation [15], where it identified as a face-centred cubic, type DO_{22} (CuAu), with the lattice parameters: a=0.361nm, as shown in Fig 5c.

Both the *γ* and *γ'* phase in superalloys have a fcc structures with very similar lattice parameters, which is 3.52 °A for fcc Ni and 3.573 °A for L12 Ni3Al [16]. The *γ* phase forms the matrix in which the *γ'* precipitates in a cube orientation relation with the *γ*. This means that both edges of the two phases are exactly parallel to each other.

In other words, when the precipitate size is small, the *γ'* phase is coherent with the *γ* in the [0 0 1] direction. The coherent structure of superalloys interface is important as it ensures a lower *γ/γ'* interfacial energy, the global minimization of which is the very mechanism of

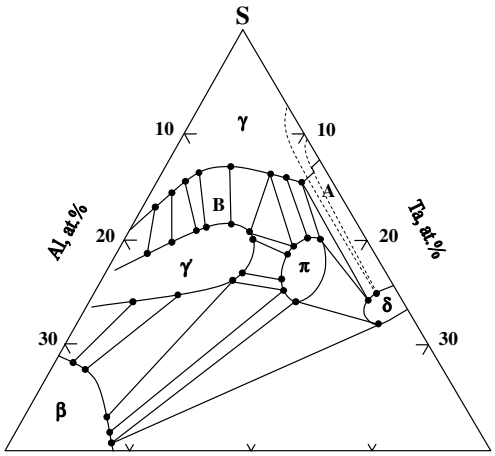

Fig 3: Isothermal section at 1250°C. Ni_8Ta phase, and γ + Ni_8Ta +δ phase fields broken lines estimated boundaries of of γ+ Ni_8Ta

precipitate coarsening. As a result, a coherent or semi-coherent interface makes the microstructure stable, a property which is useful for elevated temperature applications [17]. There are many methods available for characterization of the size and volume fraction of the **γ'** phase in Ni-based superalloys. The majority of these methods result in images that cannot be segmented in an automated manner.

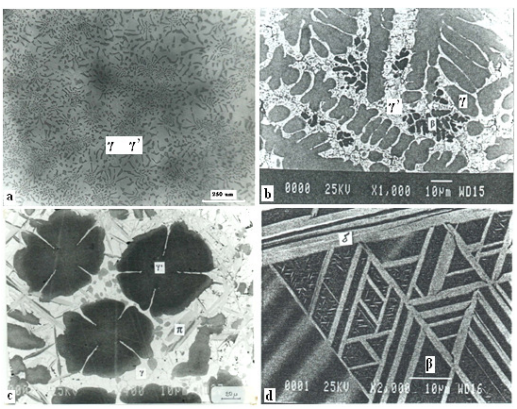

Fig. 4 : MEB (BSE)micrographs showing typical microstructures: a) γ'in γ;13.91Al-4.65Ta. b) γ in γ';17.28Al-4.09Ta . c) γ'and π in γ ;11.57Al-10.72Ta. d) Widmanstatten δ in β 28.12Al-9.45Ta (values in at%).

Semi-automated characterization of the γ'phase in Ni-based superalloys via high-resolution backscatter imaging [18].

Fig 5: TEM micrographs showing: a) Ni_3Ta laths (δ) surrounded by γ matrix containing Ni_8Ta Precipitates. b) γ' in γ matrix(γ- γ' equilibria). c) diffraction Patten of γ' phase Ni_3Al; [200] type DO_{22}

These various observations, together with the data published by Nash and west [5], for the Ni_8Ta phase have been used to delimit the different phase fields shown in fig. 3.

III. 3. γ' solvus surface

Information on the γ'solvus surface was obtained from two sources: the temperature at which γ' precipitates or it completely solutioned
and for a given temperature, the limiting compositions of alloys in the **γ + γ'** two phase field. Certain results are shown in table 3 in which a solvus temperature is given for each composition.
The solvus surface corresponding to the **γ** solid-solution phase field has been represented by a second order polynomial function of the atomic concentrations of each constituent element. The coefficients in this equation were determined by least squares fitting technique, using 30 experimentally determined values. The following expression was obtained:

$$T\,(°C) = -220 + 108.3X_{Al} + 157.9X_{Ta} - 1.52X^2_{Al} + 2.65X_{Al}X_{Ta} - 9.59\,X^2_{Ta}$$

The discrepancy between the experimental values and those calculated from the above relation is about 10°C, assuming that the uncertainly is largest at low temperatures.
Figures 6 and 7 show vertical and isothermal sections respectively, determined from the above equation.

IV. Discussion

The presence of π-phase has been reported by several workers [1, 8, and 9]. In a previous paper the authors show that this phase melts congruently at about 1442°C and establishes its extent on the liquidus surface [14]. The existence of the Ni_8Ta phase has been indicated by a number of authors [1, 5, and 6]. It does not occur at the solidus temperature but form by a peritectoid reaction at about 1332°C. The isothermal section presented in fig 3 is in good overall agreement with the data of Nash and west [1, 5]. The main difference are in the extent of solid solubility of the various phases, particularly that of γ' field, which was generally found to be greater [19, 20, 21, and 22].

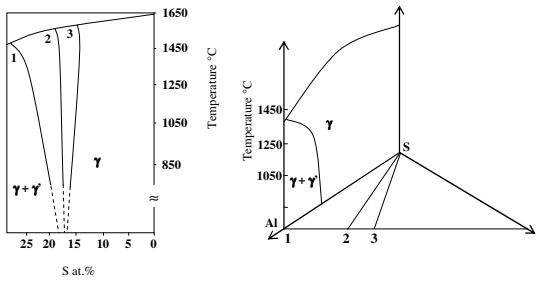

Fig 6 : Representation of γ' solvus surface along vertical sections with different Al/Ta ratio, upper curves represent liquidus surface along 0%Ta section

Compared with the stoichiometric binary γ' composition (Ni_3Al) the experimental observations in the ternary system indicate considerable substitution of Al by both Ni and Ta, with replacement of up to 60% of the Al atoms [12]. The total Ni content of the phase can thus attain 80 at%. Blavette and Bostel [23] have demonstrated this substitution of Al by Ni experimentally, using a time-of-flight atom probe in a study of γ' particles in an industrial superalloy. In contrast, the minimum Ni content of the γ' phase varies very little, with value of around 76 at%. This dissymmetry suggests that either the energy of formation of Ni vacancies is

too high, or that the insertion of Al atoms on Ni sites is too difficult, or both [22, 12].

The single phase field corresponding to the intermetallic compounds β and δ are also enlarged, indicating greater solubilities for Ta and Al, respectively. Finally the present results confirm the range of solubility of the Ni_8Ta phase at 1250°C.

It was not possible to determine the γ- π solvus temperature, nor the solubility limits at different temperatures. However, it is evident that the solubility decreases markedly with temperature, since copious precipitation is observed in the form of wide bands which grow along certain preferred crystallographic planes (fig. 4c).

Nash and west [1] identified three-phase regions γ- Ni_8Ta- π, γ - γ'- π, and Ni_8Ta- δ –π. The present work enabled three further three-phase fields to be defined γ - γ'- π ; γ- δ–π (including a ternary eutectic), and γ- δ – Ni_8Ta (specimen A).

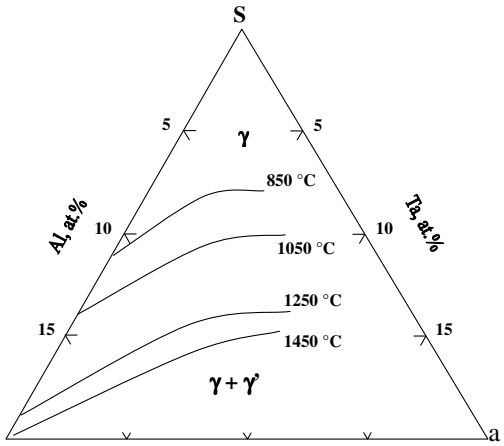

Fig 7: Projection of isothermal solvus lines

IV. Conclusions

The data obtained in the present work has confirmed the overall form of the 1250°C isothermal section determined by Nash and west with relatively few experimental alloys, and has enabled the phase boundaries to be defined more accurately. This should prove particularly useful for the calculation of more complex superalloy phase diagrams based on the multiconstituent (Ni-Cr-Co-W)-Al-Ta system.

Acknowledgements

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