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INTERMETALLIC PHASES – TCP AND Ni_3X PHASES IN CAST AND WROUGHT NICKEL SUPERALLOYS AND ITS INFLUENCE ON MECHANICAL PROPERTIES

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1.Introduction

Nickel- base superalloys are important construction materials used for the most stressed shafts of high-pressure turbine, exposed to high dynamic stress and various temperatures in dioxide-corrosion condition [1].

Superalloys are available in cast (usually heat treated or otherwise processed) or wrought (often heat treated or otherwise processed) forms. Cast products may include ingot for subsequent remelting or wrought processing (e.g., forging), or the products may be in the approximate shape of the component desired. Wrought products often are in an intermediate approximation of the shape desired or are mill products, including bar, sheet, wire, plate, and so on [2].

A wrought alloy generally is one that started from cast billets but has been deformed and reheated numerous times to reach its final state. Wrought alloys are more homogenous than cast alloys, which usually have segregation caused by the solidification process. Segregation is a natural consequence of solidification of alloys but may be more severe in some cases than in others. Wrought alloys generally are considered more ductile than cast alloys. Not all alloy compositions can be made in wrought form. Some alloys can only be fabricated and used in cast form. Some very difficult to work (wrought) alloys can be processed by powder metallurgy (P/M), usually to prepare them for final forging. In the intermediate-temperature application areas of gas turbines, where massive disks are frequently necessary, standard wrought or wrought P/M disks routinely are employed.

Cast alloys are found in the hot section areas of gas turbines, especially as airfoils, that is, blades and vanes. Most castings are polycrystalline (PC) equiaxed, but others are directionally solidified (DS). The PC castings contain many grains that may vary in size from one component to another. Directionally solidified castings may have a multiplicity of grains all aligned parallel to each other (usually parallel to the longitudinal or airfoil axis of a turbine blade or vane component) and are known as columnar grain directionally solidified (CGDS) parts. Castings are intrinsically stronger than forgings at elevated temperature. The coarse grain size of PC castings, as compared to finer-grained forgings, favors strength at high temperatures. In addition, casting compositions can be tailored effectively for high temperature strength, inasmuch as forgeability characteristics are not applicable. For example, the highest creep-rupture strength at elevated temperatures can be achieved in nickel-base superalloy castings for high stress, high-temperature turbine blade applications. The fine-grain structure of forgings, on the other hand, favors higher yield strengths and better low-cycle fatigue (LCF) strengths at low-to-intermediate temperatures, thus, the use of forgings in disk applications.

Superalloys consist of the austenitic fcc matrix phase γ plus a variety of secondary phases. Secondary phases of value in controlling properties are the fcc carbides MC, $M_{23}C_6$, M_6C, and M_7C_3 (rare) in virtually all superalloy types; gamma prime (γ') fcc ordered $Ni_3(Al,Ti)$; gamma double prime (γ'') bct ordered Ni_3Nb; eta (η) hexagonal ordered Ni_3Ti; and the delta (δ) orthorhombic Ni_3Nb intermetallic compounds in nickel- and iron-nickel-base superalloys. The γ', γ'', and η phases also are known as geometrically close-packed (GCP) phases. In addition to grain size and morphology, (plus occasional cold work) it is the production and control (manipulation) of the various phases that give superalloys their unique characteristics [3-5].

The superalloys derive their strength mostly from solid-solution hardeners and precipitated phases. Principal strengthening precipitate phases are γ' and γ'', which are found in iron-nickel- and nickel-base superalloys. Carbides may provide limited strengthening directly (e.g., through dispersion hardening) or, more commonly, indirectly (e.g., by stabilizing grain boundaries against excessive shear). Carbides are found in all three superalloy groups. The δ and η phases are useful (along with γ') in control of structure of wrought iron-nickel- and nickel-base superalloys during processing. The extent to which they contribute directly to strengthening depends on the alloy and its processing. In addition to those elements that produce solidsolution hardening and/or promote carbide and γ' formation, other elements (e.g., boron, zirconium, and hafnium) are added to enhance mechanical or chemical properties.

Detrimental phases also form in the superalloys. Topologically close-packed phases (TCP) are those such as σ, μ, and Laves (among others) that generally are brittle and detrimental to the mechanical properties of superalloys, particularly nickel-base superalloys. These phases can form in iron-nickel and cobalt-base superalloys as well. Based on early studies on stainless steels, these phases, and particularly σ phase, can be controlled by adjustments in alloy chemistry. Moreover, these phases are not always detrimental. Much evidence exists to show that very small amounts of σ may be beneficial to creep-rupture strength. There were attempts, at times, even to design alloys based on σ as a strengthening phase.

The detrimental effects of TCP phases depend to a large extent not only on TCP phase ductility shortcomings but also on:

• Phase morphology.

• Volume fraction of TCP phase.

• The extent to which the TCP phase may deplete the γ matrix of alloy elements required for γ or γ′ strengthening.

2.Experimental methods and materials

Semi – empirical models have been developed to predict the formation of TCP phases from the alloy composition. The first technique of this sort was the “PHACOMP” method (PHAse COMPutation), based on the number of unpaired electron vacancies for each element N_v. It is possible in this way to determine the average value of N_v for residual γ matrix, after precipitation of γ′, carbides and so. TCP phases can form when obtained value of N_v exceeds critical level, in the order of 2,45 – 2,5 for σ phase in a Ni – base matrix. These models, together with improved version (M_d model taking into account atomic size factors), are now regularly used by alloy designers, particularly in the case of turbine disk grades, which composition are generally more TCP prone than those for single crystal. Mentioned equation for N_v calculation is showed bellow (1) [3].

$$\boldsymbol{N_V} = \mathbf{4.66Cr} + \mathbf{2.66Fe} + \mathbf{1.71Co} + \mathbf{0.66Ni} + \mathbf{3.66Mn} + \mathbf{5.66V} + \mathbf{6.66Si} + \mathbf{9.66(W + Mo)} + \mathbf{7.66Al} + \mathbf{6.66Ti} + \mathbf{5.66(Ta + Nb)} + \mathbf{9.66Re} \quad (1)$$

As already mentioned, these relations are applied to the composition of residual matrix, expressed in atomic percentages. This composition is difficult to measure, due to the small dimensions of the spaces between γ′ precipitates. Based on microstructural evaluating is possible to separate superalloys into three groups according to the TCP distribution. Group 1 alloy contains no TCP phases. Group 2 contains less than 3 vol % TCP, which are formed exclusively at the grain boundaries. Group 3 contains between 3 and 17 vol % TCP, which are formed within grains as well as at grain boundaries. A regression model was developed to describe the presence of TCP phase in the microstructure of third – generation polycrystalline superalloy, on the basis of chemical content. The results of this analysis, in terms of atomic percent, follow (2) [6]:

$$\begin{aligned}(\boldsymbol{vol}\,\%\,\boldsymbol{TCP})^{1/2} = {} & \mathbf{16.344782 - 1.019587Al - 2.624322Cr - 3.821997Mo} \\ & \mathbf{+\ 1.109575Re - 3.207295Ta + 6.462984W - 2.271803Co} \\ & \mathbf{+\ 0.052884AlCo + 0.214059AlCr + 0.300698AlMo} \\ & \mathbf{+\ 0.80011CoRe + 0.257108CrMo - 5.081598ReW} \\ & \mathbf{+\ 1.824441TaW} \qquad (2)\end{aligned}$$

Polycrystalline cast Ni – base superalloys ŽS6K, INCONEL IN 713LC and INCONEL IN 738 were used as the experimental materials for TCP calculating and wrought INCONEL IN 718 alloy as well as previously mentioned alloys was used for GCP Ni_3X phase evaluation. Chemical composition of these alloys in wt % is in Tab. 1. For TCP calculation should be used an atomic percentage of all elements and then put to equations (1) and (2).

Tab. 1 *The chemical composition of experimental alloys (wt. %)*

Alloy	C	Cr	Al	Ti	Mo	Co	W	Fe	Mn	Ta	Nb
ŽS6K	0.2	12	6	3.2	4.8	5.5	5.5	2	0.4	-	-
IN 713LC	0.047	12.6	6.12	0.67	4.43	0.06	0.08	-	0.02	0.001	1.86
IN 738	0.17	16	3.4	3.4	1.7	8.5	2.6	-	-	1.7	0.9
IN 718	0.026	19.3	0.56	0.95	2.99	0.14	-	17.2	0.07	0.01	5.3

***Ni** *content is balance*

The samples were prepared by standard metallographic procedures (wet ground on SiC papers, DP polished with 3 μm diamond pastes followed by Struers Op-S and etched by standard etching reagent Marble) for SEM study of TCP phases and Ni_3X phases.

3.Results and discussion

After calculations we have obtained some results, which show probability of TCP intermetallic phases forming. The limit value of N_v factor for σ – phase forming is 2.45 – 2.5. Tab. 2 shows that only ŽS6K superalloy has tendency for σ – phase forming and falls into a 3 – rd group of alloys. This fact is also confirming with the microstructure analyses, Fig. 1, where σ-phase is formed after 850°C/24hrs. thermal loading at dendritic boundaries.

However, TCP phases are not only the one, which are forming during high temperature operation of alloys. Especially when the alloys are protected from high temperature effect with protective layers such as layers based on aluminium or aluminium and silicon mixture a β – phase (NiAl) is forming also very often. This β – phase is the reason of protective layer degradation and is presented as columnar shape morphology in underlayer area, Fig. 1. Because of Ni and Al elements diffusion is mentioned β – phase dissolving into γ′ - phase (Ni$_3$Al) and Al$_2$O$_3$ oxide with following dissolving γ′ - phase into Al$_2$O$_3$. This is the way in which the protective layer is loosing its heatproof properties.

Tab. 2 *Results of TCP calculation for superalloys*

Alloy	**N$_v$**	**% TCP**	**Alloy group**
ŽS6K	3.25	6.55	3-rd group
IN 713 LC	2.39	0.38	2-nd group
IN 738	2.31	3.37	3-rd group

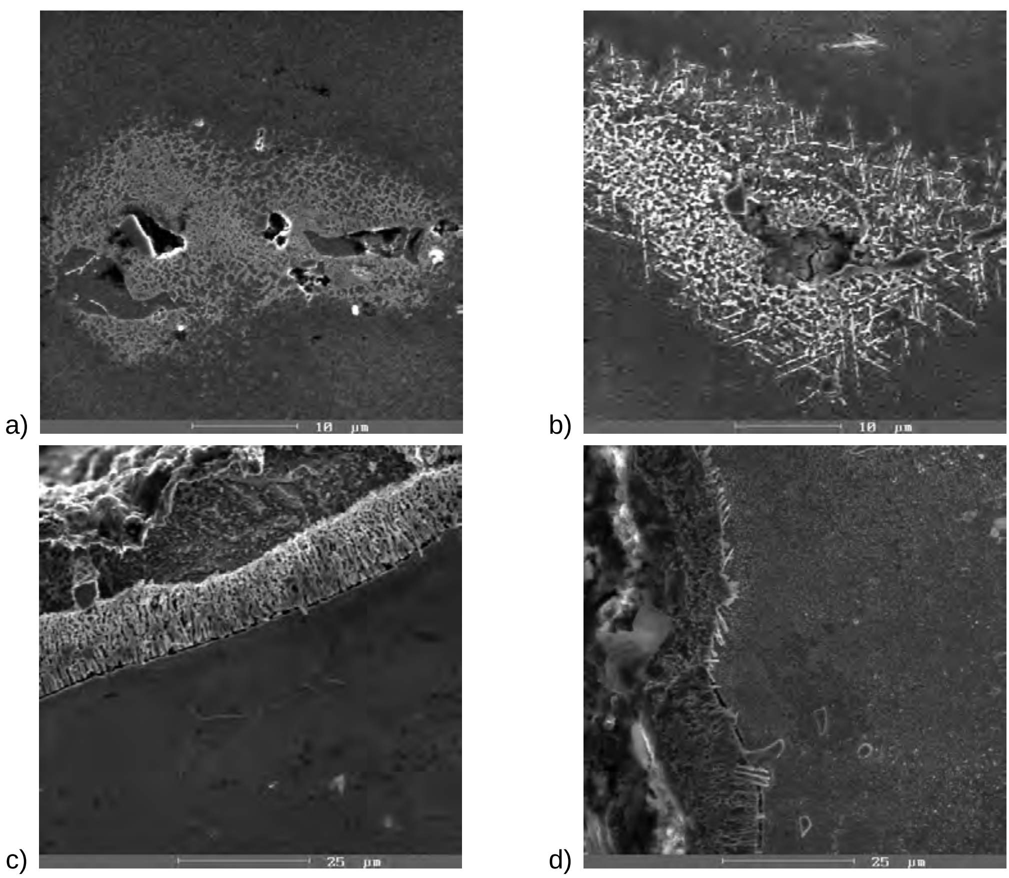
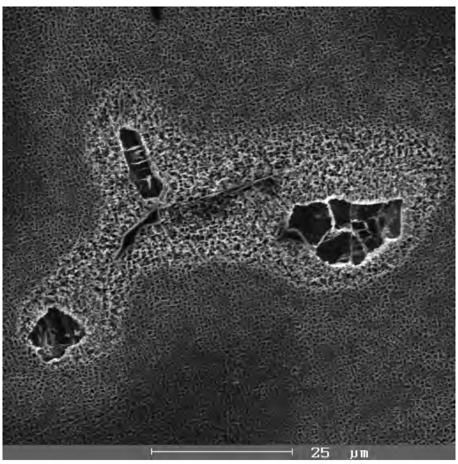


Fig. 1 *Microstructures of Ni – base superalloys, a) σ-phase forming in IN 738, b) σ-phase*

forming in ŽS6K; the β-phase columnar shape morphology in underlayer area, c) IN 713LC, d) IN 738, etch. Marble, SEM

Precipitation of the Ni_3X phases in Ni-base superalloys depends on chemical composition and applied stress or temperature loading. Figure 2 reports a principal strengthening phase γ'. It is fcc (ordered $L1_2$) generally Ni_3Al resp. Ni_3AlTi phase crystallised in cuboidal shape. Generally, shape may vary from spherical to cubic; size varies with exposure time and temperature. Experiments have shown that variations in molybdenum content and in the aluminum/titanium ratio can change the morphology of γ'. With increasing γ/γ' mismatch, the shape changes in the following order: spherical, globular, blocky, and cuboidal. When the γ/γ' lattice mismatch is high, extended exposure above 700°C causes undesirable η (Ni_3Ti) or δ (Ni_3Nb) phases to form.

a)

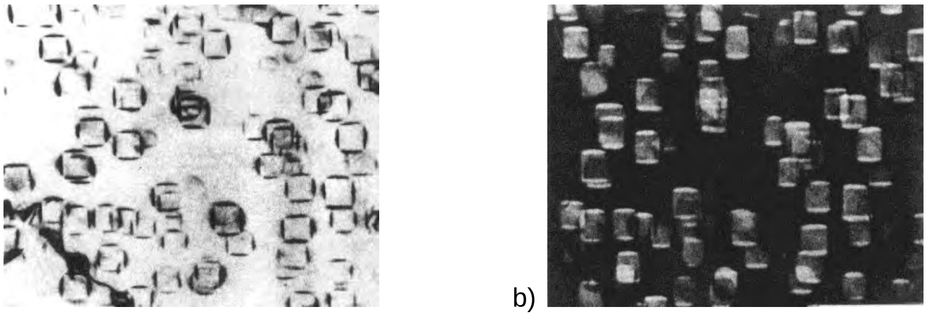


b)

***Fig. 2** Microstructure of principal strengthening phase γ' in Ni-base superalloys: a) ŽS6K, b) IN 738 with γ/γ' eutectic cells forming in interdendritic areas, etch. Marble, SEM*

Another important phase is gamma double prime γ'' bct (ordered $D0_{22}$). It is principal strengthening phase in Inconel 718; γ'' precipitates are coherent disk-shaped particles that form on the {100} planes (average diameter approximately 600 A˚, thickness approximately 50 to 90 A˚). The classic SEM or bright-field transmission electron microscopy (TEM) examination is unsatisfactory for resolving γ'' due to the high density of the precipitates and the strong contrast from the coherency strain field around the precipitates. However, dark-field TEM examination provides excellent imaging of the γ'' by selective imaging of precipitates that produce specific superlattice reflections. In addition, γ'' can be separated from γ' using the dark-field mode, because the γ'' dark-field image is substantially brighter than that of γ', Fig. 3.

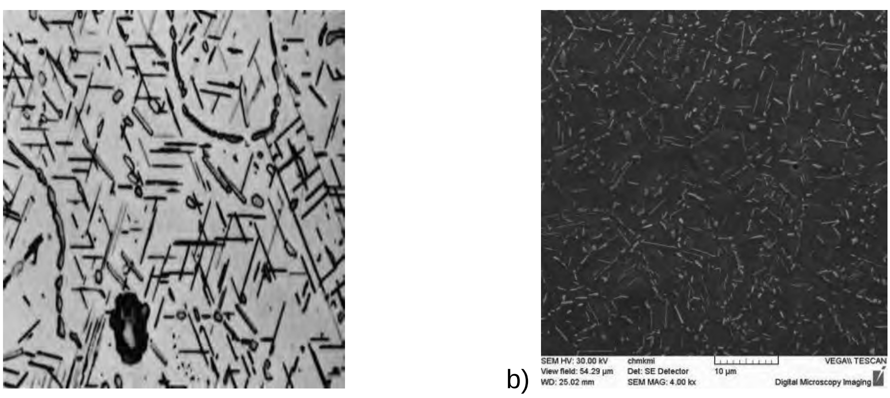
The η-phase Ni_3Ti (no solubility for other elements), hcp ($D0_{24}$), is Found in iron-nickel-, cobalt-, and nickel-base superalloys with high titanium/aluminium ratios after extended exposure; may form intergranularly in a cellular form or intragranularly as acicular platelets in a Widmanstätten pattern, Fig. 4a.



a) b)

Fig. 3 *TEM micrographs of a modified 718 alloy aged at 750°C for a) 64 hrs. (dark field image), b) 64 hrs. (bright field image) [7]*

The δ-phase Ni_3Nb, orthorhombic (ordered Cu_3Ti) is observed in overaged Inconel 718; has an acicular shape when formed between 815 and 980°C; forms by cellular reaction at low aging temperatures and by intergranular precipitation at high aging temperatures, Fig. 4b.



a) b)

Fig. 4 *Precipitation of a) η phase (needlelike) in A-286 wrought iron-nickel-base superalloy after 816°C for 546 h., etch. 15 ml HCl, 10 ml HNO_3, and 10 ml acetic acid. 1000x, [2]; b) δ phase (disc shape) in 718 type wrought iron-nickel-base superalloy [8], etch. Marble, SEM*

4.Conclusions

Tensile strength is not generally affected by TCP phase formation, but ductility and notch strength might be lowered. Creep strength may actually be increased in the early stages of TCP phase formation, but stress-rupture strength is soon degraded if significant TCP phase is formed. Topologically close-packed phases normally may not be constituents found in a given superalloy, but minor composition changes may initiate TCP formation.

About influence of γ'-phase on mechanical properties is well known fact, that size around 0.35-0.45 μm provides the best results for hot temperature application (creep). Generally, it is known, that temperature mainly affect morphology and size of delta phase, further cause coarsening of γ'' and force the transition γ'' to delta and finaly to γ' phase. The γ'' phase is least stable and at temperature above 650°C transform to delta phase, which is due to its morphology less desired. However, a small amout of delta phase situated at grain boundary, especially at wrought alloys, improve notch ductility and also control grain size.

5. Acknowledgements

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Summary

Intermetallic phases – TCP and Ni3X phases in cast and wrought nickel superalloys and its influence on mechanical properties

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The article deals with a Topologically Close Packed (TCP) intermetallic phases, which are presented during service operation of some Ni – base superalloys at high temperatures as well as Geometrically Close Packed (GCP) Ni_3X phases. Three cast Ni – base superalloys ŽS6K, IN 713 LC and IN 738 were used as experimental materials for TCP calculation and the same alloys including wrought IN 718 alloy for evaluation of Ni_3X phases. Influence of TCP and GCP phases on mechanical properties is briefly disscussed as well.