

# Heat Treatment Effect on Multicomponent Nickel Alloys Structure

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**Abstract.** Superalloys are widely used in many industrial applications that require operating at elevated temperatures and pressures, applied static and dynamic stresses and aggressive environment due to their extraordinary mechanical properties and surface stability. Nickel-based superalloys have a face-centered cubic lattice, high values of Young's modulus and coefficient of diffusion that provide to Nickel-based superalloys excellent physical and mechanical properties. In this paper is analyzed Nickel-based superalloy Hastelloy S.

Mechanisms of strengthening are discussed as a function of chemical composition and vacuum heat treatments. Applied microscopic investigations were following the process of superalloy Hastelloy S structural degradation, with the main concern to observe the problem of cracking formation in material as well as structure ameliorisation after thermal processing in vacuum. The diffusion -interfacial mathematical model using Cahn-Hilliard equation that satisfactorily describes coarsening and phase-segregation kinetics is analysed in this paper.

**Keywords:** nickel superalloys, microstructure, desirable phases, undesirable phases, heat treatment.

## 1. INTRODUCTION

Nickel-based superalloys, among all other metallic materials, possess the most complex structure formed through advanced melting and refining technology, strengthening of the face-centered cubic (fcc) nickel matrix by a dozen alloying elements and post-heat treating. After solid-solution strengthening has been finished, saturated solution starts to form and during heat treatments precipitation starts to form  $\gamma'$  intermetallic compound, as well as various secondary phases: carbides, nitrides, borides, carbonitrides, oxides and topologically close-packed TCP undesirable phases. Thanks to their surface stability achieved by certain thermo mechanical processing, parts made of Nickel-based superalloys are creep, fatigue, temperature and corrosion resistant.

Nickel-based superalloys microstructure consists of:  $\gamma$  solid solution,  $\gamma'$  intermetallic compound, carbide participates and TCP phases (tetragonal close-packed crystal lattice).

Figure 1. shows schematic sketch of microstructure observed in some Ni-based superalloys that belong to Hastelloy series [1].

Nickel-based superalloys matrix is the *solid solution*  $\gamma$  with face centered cube lattice and a random distribution of the different species of atom. It contains a high percentage of dissolute elements such as: Fe, Cr, Co, Mo, Ti, W and others. In consequence of solution heat treatment,  $\gamma$  phase has good surface degradation

resistance even at very high temperatures and for a very long exposure time.

Intermetallic compound  $\gamma'$  is formed by adding Al and/or Ti. It has a face centered cube lattice. The Al and Ti atoms are distributed at the cube corners [1]. This atomic arrangement has the chemical formula  $\text{Ni}_3\text{Al}$ ,  $\text{Ni}_3\text{Ti}$  or  $\text{Ni}_3(\text{Al}, \text{Ti})$ . Phase  $\gamma'$  takes a high volume compared to its mass and is the result of the strong attractive bonds between various atoms and because of that it has specific mechanical and physical properties. Intermetallic compound  $\gamma'$  contributes to strengthening of the anti-phase grain boundary by interaction with dislocations. It is a main participated phase and is largely responsible for strength at elevated temperatures [2].

Besides  $\gamma'$  phase, carbides are significant for strengthening of nickel-based superalloys MC,  $\text{M}_{23}\text{C}_6$  and  $\text{MC}_6$ . Most alloying elements form primary stable metallic carbides (MC) with a tendency to their own degradation during heat treatments. They generate into carbides  $\text{M}_{23}\text{C}_6$  and/or  $\text{MC}_6$ , which segregate to the grain boundaries. Carbides at the grain boundaries have mostly positive influence on the rupture stress at high temperatures [3,4].

Carbides improve a superalloy's mechanical properties as they make grain boundaries stable and increase the strength at high temperatures. On the other hand they have unfavorable effects on deformability just because of precipitation at the grain boundary [5].

In some Ni-based superalloys rich in Cr, carbide phases  $\text{Cr}_7\text{C}_3$  are present and decrease  $\gamma'$  phase. If solution heat treatment is properly done, these carbides generate in  $\text{M}_{23}\text{C}_6$  carbides (M is mostly Cr) and precipitate at  $\gamma$  grain boundary. It is important to ensure during heat treatment to obtain fine particles  $\text{M}_{23}\text{C}_6$  at grain boundaries and have no continuous film.

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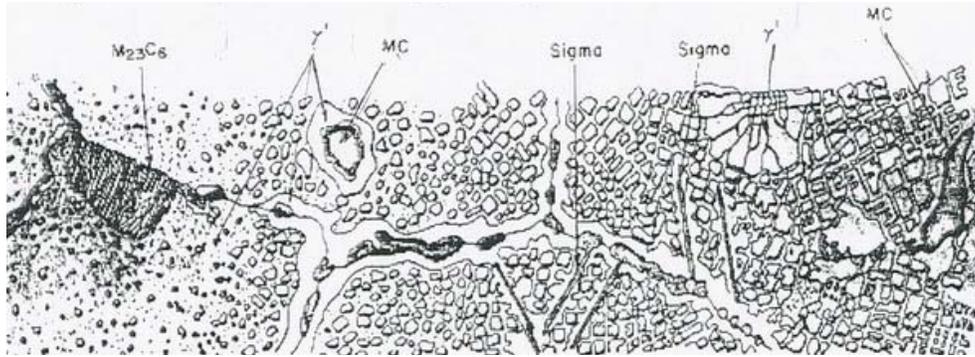


Figure 1. Schematic sketch of microstructure observed in superalloy from Hastelloy series [2].

If TCP phases are formed in superalloys they start to make nuclei on carbides by enriching themselves from  $\gamma$  phase. The most important TCP phases are: the phase with tetragonal lattice, the phase with orthorhombic lattice, Laves phases and  $\eta$  phase with hexagonal close-packed lattice.

The most typical representative is sigma phase with chemical formula  $(Fe,Mo)_x(Ni,Co)_y$ , where the value of  $x$  and  $y$  is between 1 and 7. This phase is formed after exposing at temperatures above 900°C or after a long time of exploitation [6].

Phase sigma has collar morphology, increases brittleness and has a bad effect on mechanical properties of superalloys. Presence of this phase leads to the early cracking formation in a base material. Phase sigma has unfavorable influence on the rupture stress and decreases ductility at elevated temperatures. It reduces  $\gamma$  matrix from fireproof materials that result by decreasing the yield strength and corrosion resistance at elevated temperatures and by an increase in brittleness [1].

### 1.1 Application of Cahn-Hilliard equation to a binary nickel alloy

Nickel-based superalloy Hastelloy S is a multicomponent alloy and due to the large effects of alloying elements and consequently, complex structural conditions, introducing the diffusion-interfacial mathematical model is a very complicated task.

This paper will present basic equations which describe an isostructural two-phase system, as it is a simplest phase-field description of two-phase microstructure. The two-phase microstructure is thermodynamically stable and we will apply the linear nonequilibrium thermodynamics – atom flux is linearly proportional to the chemical potential gradient.

Diffusion equation:

$$\frac{\partial C}{\partial t} = Nv\nabla \cdot M\nabla\mu \quad (1)$$

describes the temporal evolution of the composition where  $t$  is time,  $C(r,t)$  is a compositional field,  $Nv$  is number of atoms per unit volume and  $M$  is mobility. The term which describes coarsening is the local chemical potential field  $\mu$  and includes the contribution

of interfacial energy to the total free energy. Here, the interfacial energy is given through the gradient energy terms. The mobility in the Cahn-Hilliard equation does not depend on concentration field variable. The Cahn-Hilliard equation with constant mobility can be presented in a scaled form as [9]:

$$\frac{\partial C(r,t)}{\partial t} = \nabla^2 [-C + C^3 - \kappa\nabla^2 C]. \quad (2)$$

This equation can be solved by an efficient and accurate scheme, the semi-implicit Fourier spectral method.

This scheme provides excellent spatial accuracy, but it is only first-order accurate in time.

The coarsening of  $\gamma'$  precipitates in nickel-based superalloys and the control of  $\gamma + \gamma'$  two-phase microstructure is the answer for designing the superalloys with required high temperature properties. The precipitate volume fraction, morphology and distribution determine the mechanical properties. If a quantitative model can be developed that describes all physical, thermodynamic and kinetic factors for a given superalloy composition, it should be possible to make predictions for the corresponding microstructure and property at a given time [7].

### 3. EXPERIMENT

The main aim of experimental investigation of superalloy Hastelloy S demonstrated in this paper is to follow structural changes during heat treatment and also by applying the mechanical and microscopic examinations to contribute to the comprehension of cracking forming problem in testing material. This investigation continues investigations of superalloys Hastelloy X whose results are presented in papers [8].

Superalloy Hastelloy S is heat treated before its exploitation. Heat treatment consisted on the following stages:

- solution heat treatment at 1080°C for 1 hour and fast cooling to the room temperature,
- primary precipitation heat treatment at 840°C for 4 hours and cooling to the room temperature,
- secondary precipitation heat treatment at 760°C for 3 hours and air cooling to the room temperature,
- stress relief annealing at 700°C for 1 hour and air cooling to the room temperature.

Mentioned heat treatments were carried out in vacuum protected atmosphere in vacuum furnace VS 150/150 produced by Deguss. Technical investigations in vacuum are very important and require special techniques and equipment [9,10,11 ].

Vacuum in the furnace is ensured by vacuum pumps and by starting furnace heaters fed by particular transformer with specified thermal regime. After applied heat treatments, experimental investigations consisted of determination of following chemical composition, hardness measuring and microstructure.

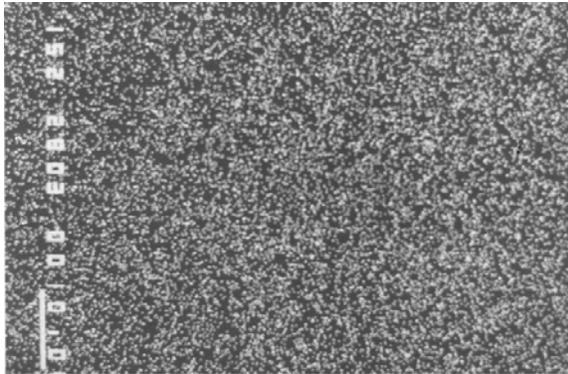


Figure 2. Chromium in solid solution and in carbides. Imaging surface with reflected electrons. Magnification 200X.

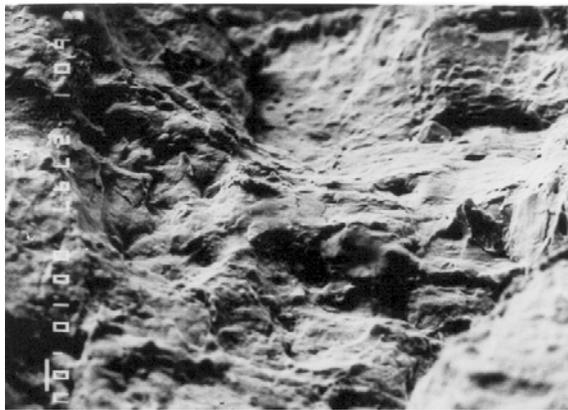


Figure 3. Ductile, intergranular fracture. Magnification 200X.

Table 1 shows obtained chemical composition results. This investigation has not confirmed the existing of La, and compared to the standard alloy, has obtained higher content of Fe, Si, Al and C. Table 2 shows mechanical properties of nickel-based superalloy Hastelloy S.

Chemical composition examination was done by quantometer and then by wet process, which is more accurate. Figure 2 shows scanning electron micrograph of superalloy's Hastelloy S microstructure. The results of identification of chemical elements by electron beam are presented in Figure 5.

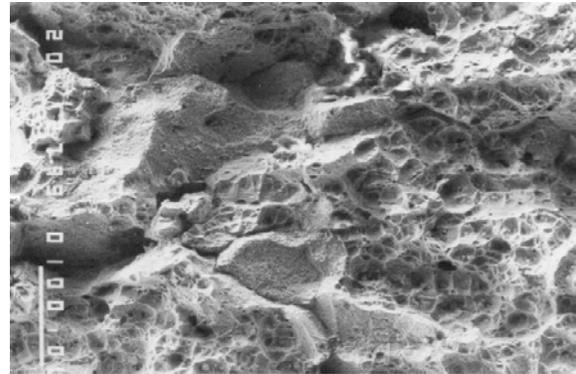


Figure 4. Fatigue failure surface. Magnification 600X.

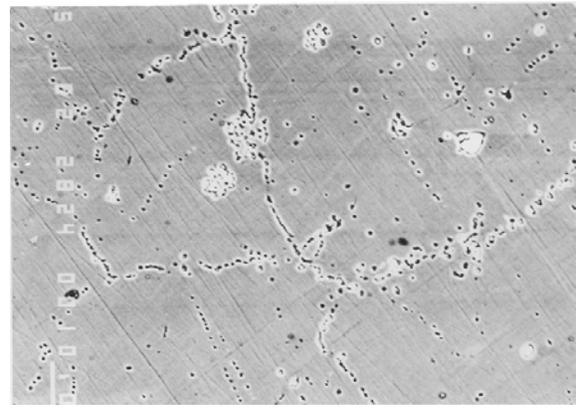


Figure 5. Molybdenum carbides segregated at the grain boundaries, as grains, arrays and clusters. Magnification 1000X.

Table 1. Results of chemical composition determination of superalloy Hastelloy S obtained by wet process

Chemical element	Ni	Cr	Mo	Mn	Si	Fe	C	Al	B	Others
% [wt]	67	15.3	14.4	0.5	0.5	1.34	0.3	0.3	0.01	0.05

Table 2. Mechanical properties of Nickel-based superalloy Hastelloy S [3]

Temperature	21°C	540°C	650°C	760°C	870°C	Condition of test material
Ultimate tensile strength, MPa	845	775	720	575	340	1065°C/AC
Yield strength at 0.2% offset, MPa	455	340	320	310	220	
Tensile elongation, %	49	50	57	70	47	
1000-h rupture strength, MPa	...	...	...	90	25	

#### 4. DISCUSSION

Analysis of strengthening mechanisms and structural degradation of superalloy Hastelloy S is a very complex process from the aspects of heterogenic chemical composition, multiphase heat treatment, and exploitation at evaporated temperatures and high pressures.

After solution heat treatment and primary precipitation heat treatment, solid solution  $\gamma$  (FCC) and intermetallic compound  $\text{Ni}_3\text{Al}$ , with compatible morphology and particles size, is in favorable orientation and leads to alloy strengthening. Figure 4. shows dominant presence of Chromium in  $\gamma$  matrix, detected by scanning microscope. Besides dissolving in  $\gamma$  lattice and contributing to strengthening of matrix, it also forms carbides  $\text{Cr}_{23}\text{C}_6$  and  $\text{Cr}_{21}\text{MoC}_6$ , which are characteristic for high concentration Chromium in alloy. Although carbides affect strengthening, in this stage heat treatment is the dominant influence of  $\text{Ni}_3\text{Al}$  phase that because of interaction with dislocations on antiphase boundaries contributes to the strengthening.

After secondary precipitation heat treatment at  $760^\circ\text{C}$  and relief stress annealing at  $700^\circ\text{C}$ , the measured hardness was the highest and this testifies that this regime gives the highest alloy's strengthening. Carbides  $\text{Mo}_{23}\text{C}_6$  and  $\text{Ni}_3\text{Mo}_3\text{C}$  most likely contributed mostly to alloy strengthening, which segregated to the grain boundaries in compatible orientation, shape and size.

These carbides serve as obstacles for the dislocation's motion, which segregate to the twin boundaries and stacking faults.

After longtime exploitation of superalloy in creep conditions, hardness of superalloy decreases. Also, by observing micrographs (Fig. 3.) on failure surface, micro-cracks can be noticed mostly on grain boundaries and in Fig. 4. fatigue surfaces. This structural condition is the result of various microstructural transformations that occur under creep conditions [10]. By forming films on the grain boundaries, molybdenum and chromium carbide grains grow, as shown in Fig. 5. The grain growth makes nuclei for TCP grain growth in first place sigma phase with complex chemical formula  $(\text{FeMo})_x(\text{NiCo})_y$ , discussed in reference 2.

Also, at the grain boundaries in Fig. 5, carbides can be noticed located in the nests and they enable sigma phase forming as well. Sigma phase forming is followed by creating multi-inter-phase surfaces where dislocations prearrangements are made by their rising and falling, by forming dislocation's fragments [1,4] and disclinations, as well as their movements to surface that contribute to cracks forming.

#### 5. CONCLUSION

Based on theoretical considerations and experimental investigations made on superalloy Hastelloy S, the following can be concluded:

- after solution heat treatment at  $1080^\circ\text{C}$  and primary precipitation heat treatment at  $840^\circ\text{C}$ , the main effect

of alloy strengthening has intermetallic compound  $\text{Ni}_3\text{Al}$ ,

- after solution heat treatment at  $1080^\circ\text{C}$  and primary precipitation heat treatment at  $840^\circ\text{C}$ , secondary precipitation at  $760^\circ\text{C}$  and relief stress heat treatment at  $700^\circ\text{C}$  the main effect on the structural degradation process forms a brittle sigma phase, which segregates at inter-phase carbides and other structures boundaries,
- applied heat treatments contributed to the alloy strengthening and prevention of crack formation and crack growth. This results in longer fatigue and exploitation life of superalloy,
- during exploitation of investigated superalloy Hastelloy S, formed chromium and molybdenum carbides have reached a critical size with additional forming of undesirable  $\sigma$  and  $\mu$  phases. Since alloy Hastelloy S has an increased content of chromium and molybdenum (Cr 15.5%, Mo 14.5%), the undesirable phases segregate at carbides grain boundaries. They are not coherent to the carbide particles and  $\gamma$  matrix, leading to an increase of stress concentration at interphase boundaries resulting with a crack initiation.

Due to investigations described in this paper, it was shown that the following of strengthening mechanism and structural degradation is a very complex process from the aspect of heterogeneous chemical composition, multiphase heat treatment and exploitation at elevated temperature and pressure.

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**ЕФЕКТИ ТЕРМИЧКЕ ОБРАДЕ НА  
СТРУКТУРУ ВИШЕКОМПОНЕНТНЕ  
ЛЕГУРЕ НИКЛА**

**Сања Петронић, Анђелка Милосављевић**

Суперлегури имају велику индустријску примену у областима, где се захтева рад на повишеним температурама и притисцима, при примењеним статичким и динамичким напонима и у агресивним срединама, због добрих механичких особина и површинске стабилности. Суперлегури никла имају површински центрирану кубну решетку, високе вредности модула еластичности и коефицијента дифузије, што им обезбеђује добре физичке и механичке особине. У овом раду је анализирана суперлегура никла Хастеллоу С. Механизам ојачавања је дискутован као функција хемијског састава и термичке обраде у вакууму. Примењена микроскопска истраживања су пратила процес структурне деградације суперлегури Хастеллоу С са циљем сагледавања проблема стварања прелина у материјалу, а такође и побољшања структуре после примењене термичке обраде у вакууму. У овом раду приказан је и дифузиони модел користећи Кан-Хилиардове једначине, које задовољавајуће описују окупљавање структуре и кинетику фазне сегрегације.

