# THE INFLUENCE OF HIGH TEMPERATURE ON THE MICROSTRUCTURE AND PROPERTIES OF A Ni-BASED SUPERALLOY

**N. Luptáková, P. Král, P. Dymáček**

***Abstract***
*The PM Ni-15Cr-18Co-4Al-3.5Ti-5Mo alloy is a high temperature resistant superalloy with high mechanical, chemical and thermal properties, ideal for high performance engine parts. This superalloy was used as grips of a creep machine. The material was exposed at 1100°C for about 10 days to a stress of 10 MPa. Unacceptable creep deformation of grips occurred, as well as severe surface oxidation with scales peeling off. Three types of PM samples were studied: initial, heat treated (annealing - 10 min/1200°C) and after creep in the machine. ($CoNi_2$)Ti particles were preferentially created at grain boundaries after creep testing. As a result of this process, grain boundaries are deprived of Ti. Moreover, its presence at grain boundaries caused reduction of the hardness of the material. The value of Vickers hardness after the creep test decreased by ~ 70 HV 5. On the basis of the obtained results, this material is not recommended to be used for grips of creep machines at temperatures above 1000°C.*
***Keywords: powder materials, Ni-based PM superalloy, grip of a creep machine, oxidation***

## INTRODUCTION

Production of the structural parts such as grips of a creep machine is closely connected with requirements for enhanced material quality, because these parts are exposed to heavy-duty in-service conditions. These requirements include high mechanical strength, phase stability, as well as oxidation and corrosion resistance of the Ni-based superalloy. One of the most important superalloy properties is high temperature creep resistance. Creep and oxidation resistance are the prime design criteria.

Ni-based superalloys have been developed more or less empirically over the past 60 years from a simple Ni-Cr matrix to the present multi element and phase systems, having a face centred cubic (*fcc*) structure which maintains mechanical properties superior at high temperatures to body centred cubic (*bcc*) alloys [1]. From the point of view of microstructure, Ni superalloys are complex. The *fcc* matrix, known as $\gamma$, mainly consists of nickel, cobalt, chromium and molybdenum. The strength of superalloys is conferred by the hardening precipitates known as $\gamma'$ ($Ni_3Al$ based $Ll_2$ structure) [5]. However, important phases are also the carbides of MC and $M_{23}C_6$ type, where M represents a metal [7].

Homogeneously distributed coherent hardening precipitates provide excellent tensile, creep and fatigue life properties at high temperatures. Their volume fraction is controlled by the nominal chemical composition. The size and the morphology are

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controlled by the production process and their crystallographic relations with $\gamma$ matrix. When the precipitates arise close to the solvus temperature, they grow larger, which subsequently restricts grain growth of pinning grain boundaries [5].

The mechanical and creep behaviour are closely related to the evolution of the microstructure [8-10]. Altering grain size results in various effects with regard to different mechanical properties. Tensile and fatigue life properties are optimized by a fine grain microstructure. On the other hand, good creep and fatigue crack growth properties at elevated temperatures are favoured by a coarse grain microstructure. The former is the result of grain orientation and stress concentration by dislocation movement along slip planes [4].

The aim of the present investigation is the microstructural evaluation and study of selected mechanical properties of the Ni-15Cr-18Co-4Al-3.5Ti-5Mo superalloy, of which material were creep machine grips that failed after a creep test at 1100°C.

## EXPERIMENTAL MATERIAL

Three samples of the commercially produced superalloy Ni-15Cr-18Co-4Al-3.5Ti-5Mo were investigated. The chemical composition and selected physical parameters of the material are given in Tables 1 and 2. Sample No. 1 was in the as received unexposed state, sample No. 2 heat treated (annealed) (10 min/1200°C) and sample No. 3 after the creep test as a part of the creep machine grips. The third specimen of the superalloy was exposed to a load of 365 N at temperature 1100°C for about 10 days. During the creep test unacceptable creep deformation of grips occurred, as well as severe surface oxidation with scales peeling off. Specimens were prepared metallographically and their microstructures were examined. In Figure 1 the corrosion of the surface in air impurities + Ar atmosphere at a high temperature is evident.


Fig.1. Image of damaged creep machine grips after the test.

In order to predict the possible failure of the components, it is necessary to pay attention to observations of microstructural changes and mechanical characteristics which can occur during the thermal and load exposure of the material. The prediction is related to the lifetime of the specific components and it is also connected with the selection of the right material for the specific conditions.

Tab.1. Chemical composition of Ni-based superalloy.

| Element | Chemical composition [wt. %] |
|---|---|
| Ni | 54.5 |
| Cr | 15.0 |
| Co | 18.0 |
| Al | 4.0 |
| Ti | 3.5 |
| Mo | 5.0 |

Tab.2. Selected physical parameters of Ni-based superalloy [6].

| | |
|---|---|
| Density | 7.95 [g·cm$^{-3}$] |
| T (solidus) | 1.315 [°C] |
| T (liquidus) | 1.351 [°C] |
| T (γ´ solvus) | 1.154 [°C] |

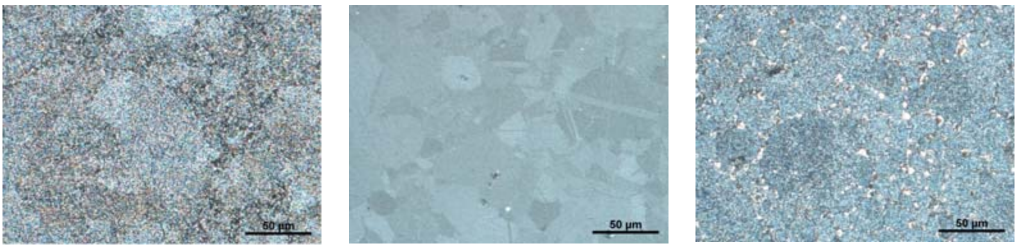
## TESTING METHODOLOGY

The phase composition and the microstructure were studied using optical microscopy (LOM), scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray analysis system (EDX) and transmission electron microscopy (TEM). The investigations were carried out using an optical microscope Zeiss Neophot 32,a scanning electron microscope LYRA 3 with EDX with detector X-MAX 80 (with resolution 124 eV at MnK$_\alpha$ line) and a transmission electron microscope TEM JEOL 2100F. The samples for optical microscopy were prepared by standard methods. A solution of $HNO_3$ (40 ml) + HF (30 ml) was used the etchant. Micrographs are shown in Figs.2 to 9 at various magnifications. Vickers hardness measurement was done using the Zwick Roell indentor ZHV30.

## RESULTS AND DISCUSSION

### Microstructure evaluation of samples by LOM

For the better understanding of the problem of unacceptable creep deformation of the grips, it is necessary to preliminary evaluate the samples by LOM (Fig.2).




a) b) c)

Fig.2. Microstucture of Ni-based superalloy at 500x magnification: a) No. 1 unexposed sample (initial state); b) No. 2 sample after annealing treatment at 1 200°C; c) No. 3 exposed sample after creep test.

During heat treatment and creep test microstructural changes occurred in the superalloy, as shown in Figs.2b and 2c, to be compared with the microstructure of the initial state (Fig.2a). It is visible that new precipitates are formed at the grain boundaries.

**Microstructure evaluation of samples by SEM**

Based on the microstructure observation by SEM (Figs.3 - 5), it can be pointed out that there is a different character of microstructure in relation to the exposure of the samples. Character of fine-grains of the unexposed sample is shown in Fig.3, where the occurrence of grain boundaries is better visible in the backscattered electron mode (BSE) than in secondary electron mode (SE).

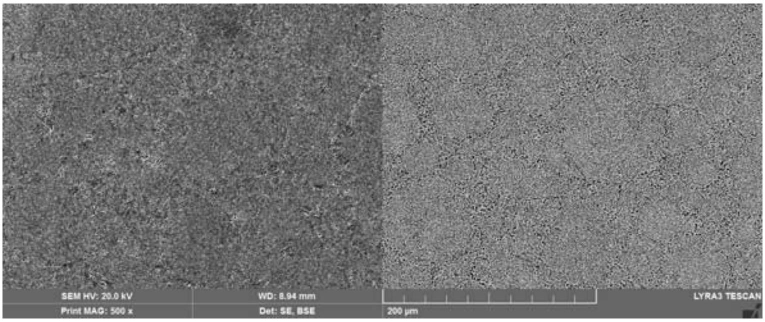



Fig.3. The unexposed sample No. 1, interface SE/BSE.

The microstructure shown in Fig.4 shows recrystallization of initial sample after heat treatment at 1200°C that formed austenitic-like structure with non-uniform grain size. Twins of different size were observed in the grains.

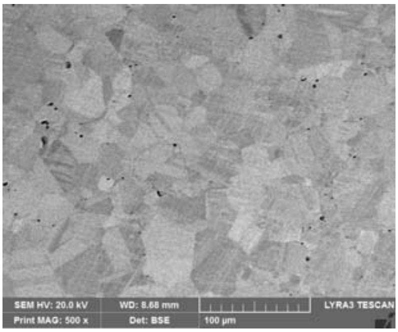



Fig.4. The sample No. 2 after annealing treatment.

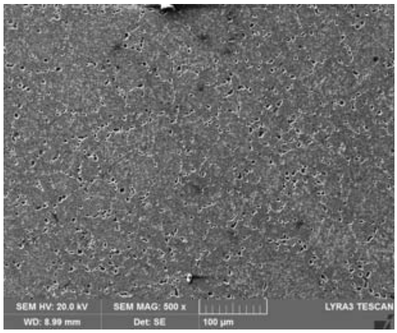



Fig.5. The sample No. 3 after creep test.

**EDX analysis**

Special attention was paid to the chemical composition of phases present. Superalloys with higher level of Cr (about 25 wt. %) exhibit superior corrosion resistance due to the more uniform distribution of Cr in the microstructure [2]. A higher content of $Cr_2O_3$ and $MoO_3$ in the passive layer could lead to higher resistance to metal ion transfer through the passive film. The homogeneous distribution of Cr is critical especially in low-Cr nickel-based alloys for better corrosion resistance. Compared with $Cr_2O_3$, the nickel oxide is more porous and has less protective ability to corrosion. Hence, the passive film zones, which are rich in NiO, will act as weak regions for localized corrosion, which can cause localized dissolution of Ni-rich phases [3].

SEM image and detailed EDX analysis are shown in Fig.6 for sample 3.The chemical composition of sample from grips after the creep test (Fig.6) is summarized in Table 3. From the EDX analysis, the composition of the sample was obtained - the new phase is formed by the majority of Ni (Spectrum 1 – 70.58 wt.%), and other elements, such as Co, Cr, Ti, Al and Mo. Ti percentage is about 3x increased in comparison with the nominal chemical composition. It is apparent that selected phases were rich in Ni and Ti.

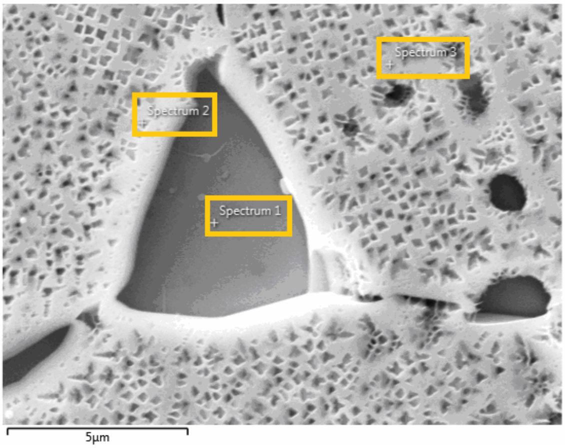



Fig.6. EDX point analysis of sample No. 3 after creep test.

Tab.3. Chemical composition of selected spectra [wt. %] in Fig.6.

| Element | Chemical composition [wt. %] | | |
|---|---|---|---|
| | Spectrum 1 | Spectrum 2 | Spectrum 3 |
| Ni | 70.58 | 50.02 | 44.64 |
| Co | 11.73 | 19.50 | 22.05 |
| Cr | 5.06 | 18.99 | 22.65 |
| Ti | 8.50 | 2.79 | 1.48 |
| Al | 3.05 | 2.64 | 2.05 |
| Mo | 1.08 | 6.07 | 7.14 |

**Microstructure analyzed by TEM**

The unidentified phases in the sample No. 3 after the creep test at 1100°C were investigated using TEM/STEM and are illustrated in Fig.7. Based on EDX analysis and the conventional TEM image, combining with the crystallographic analysis, we can assume that it is the $(CoNi_2)Ti$ phase. The chemical composition of the sample No.3 analysed by EDX is given in Table 4.

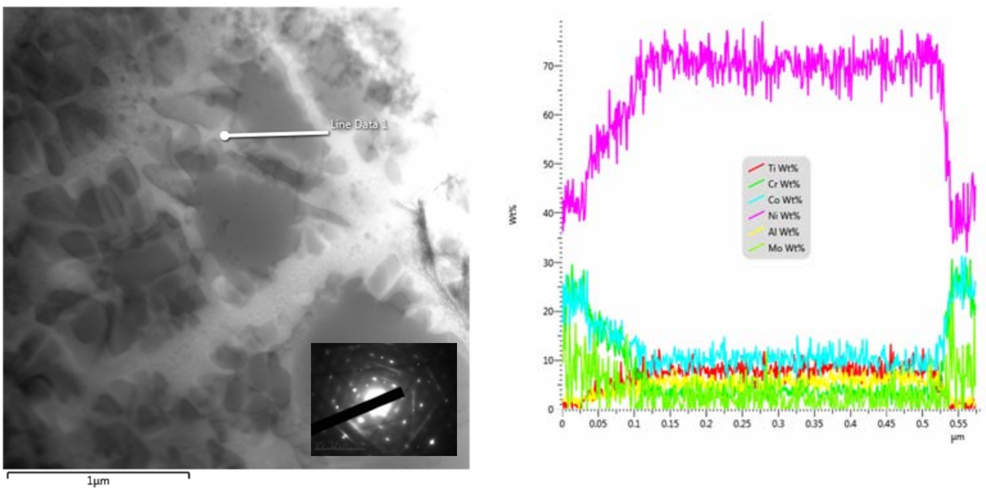



Fig.7. a) STEM bright field image of the phase (the thin line shows the length and the direction of the EDX line scan), b) STEM EDX line scan across the studied phase revealed enrichment by Ni, Al, Ti.

Tab.4. Chemical composition of the selected STEM EDX line [wt.%] from Fig.7.

| Element | Linescan Sum Spectrum [wt.%] |
|---|---|
| Ni | 66.2 |
| Co | 12.1 |
| Ti | 6.9 |
| Cr | 6.7 |
| Al | 5.0 |
| Mo | 3.1 |

It is shown that the content of Ni, Ti and Al into the identified phase has been increased. As a consequence, the zones around the coarsened phase $(CoNi_2)Ti$ (with $D0_{22}$ structure) precipitate have been depleted by these elements. The results obtained from EDX by both TEM and SEM methods are identical.

**Analysis of the oxidic layer**

Corrosion of the grips as a part of the machine has occurred during the creep test. Oxidic layer has formed at elevated temperature (1100°C). Corrosion damage was studied based on chemical analysis of the specimen No. 3 surface. During operation of the creep machine, continuous heat exposure may influence the microstructure and chemical composition. For that reason, it is of interest to see if chemical influence can have a significant effect on the material behaviour at elevated temperature (1100°C). EDX elemental mapping results (in Fig.8) show that the surface oxidic layer consists of $Cr_2O_3$. The analysis of internal oxide identified oxides of Ti and Ni.

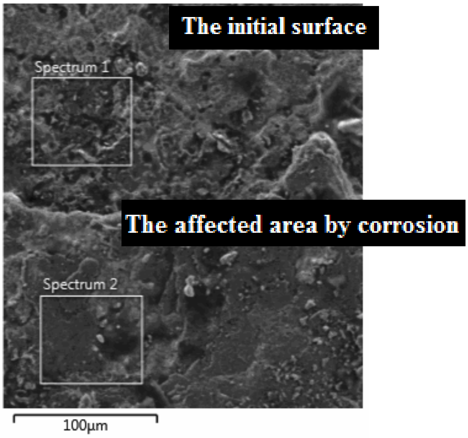



Fig.8. Interface of matrix of sample No. 3 and oxide layer after corrosion at 1100 °C in air + Ar conditions.

Oxygen has been observed to combine with Cr and Ti to form oxides, and C may combine with Mo and Cr to form carbides. Carbides are known grain boundary strengtheners that can precipitate on undesirable grain boundaries.

Tab.5. Chemical composition of selected spectra [wt. %] from Fig.8.

| Element | Chemical composition [wt. %] | |
|---|---|---|
| | Spectrum 1 | Spectrum 2 |
| Ni | 38.8 | 21.4 |
| Co | 13.6 | 8.6 |
| Cr | 13.5 | 27.5 |
| Ti | 9.4 | 11.7 |
| Al | 24.7 | 1.0 |
| O | - | 25.8 |
| Mo | - | 3.9 |

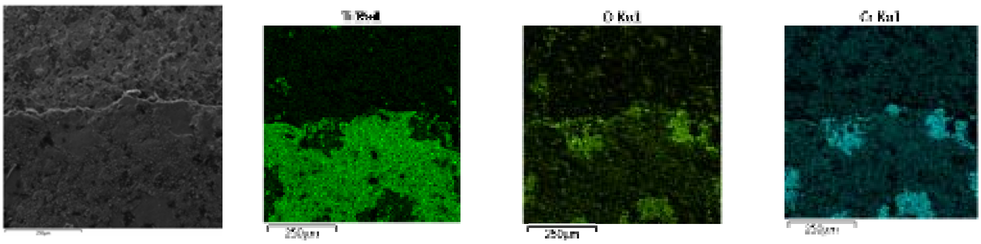


Fig.9. SEM image of the interface of matrix sample No. 3 and corroded surface and summary X-ray maps of elements.

Tab.6. Chemical composition of elemens [wt. %] from Fig.9.

| Element | Chemical composition [wt. %] |
|---|---|
| Ti | 21.74 |
| Cr | 25.72 |
| Co | 9.52 |
| Ni | 27.73 |
| Al | 11.69 |
| Mo | 3.60 |

The microscopic appearance with the representative chemical composition is shown in Fig.9. These results suggest that oxidic layers contain oxides of Cr and Ti.

The EDX area scan (Fig.8) and the EDX mapping (Fig.9) of oxides apparently show that the corroded surface is completely filled with oxides (oxygen map). There is a Cr and Ti rich oxide on the affected area. It is known than the limited energy resolution of EDX facility may lead to special cases when some pairs of peaks overlap so closely that it is necessary to recheck the results due to peaks overlapping. One of these cases is overlapping of $CrL_{\alpha}$ with $OK_{\alpha}$ lines. For this reason the results of numerous EDX analyses were examined in detail and the results showed that Cr and O are presented in the studied layer.

**Measurement of hardness**

The results of Vickers hardness measurements are presented in Table 7. The value decreased from unexposed 432 HV5 to approximately 362 HV5 after creep test. It is evident that hardness after thermal treatment (annealing), as well as after creep test, has notably decreased.

Tab.7. Measurement of hardness.

| Sample | HV 5 |
|---|---|
| The unexposed sample No. 1 | 432 |
| The annealed sample No. 2 | 418 |
| The sample after creep test No. 3 | 362 |

**CONCLUSIONS**

- As with all properties that are governed by plastic deformation processes, creep properties are sensitive to microstructure. Because superalloys experience extended periods under stress at high temperature, a high resistance to time-dependent creep deformation is essential. This is very important for superalloys, because they will experience temperatures up to 1200°C, whereas the studied Ni based PM superalloy should be limited to less than 1000°C.
- Depending on the chemical composition, we can conclude that there is a significant influence of temperature on the microstructure stability of the studied superalloy samples.
- Investigated samples were in the range of chemical concentrations specified by the producer.
- We can conclude that hardness of sample no.3 after the creep test decreased by more than 70 HV 5 to approximately 362 HV5.

- The temperature of the gamma phase solvus (phase transformation) is 1154°C. According to this, at temperatures 1100-1150°C this material has very low creep strength and it is not suitable for creep tests too much over 1000°C.
- As a solution, it is recommended to find a new suitable material of grips for creep machine for temperatures above 1000°C.
- The degradation (chemical oxidation) of the investigated material is possibly due to a chemical interaction between the device and the environment. The mechanism of the interaction was not fully analysed.
- It can be assumed that the degradation of material has been influenced by a contamination of furnace atmosphere, as well as the presence of other undesirable elements /compounds in the furnace.
- These results suggest that studied Ni-based superalloy, formed by PM as part of creep machine, is not suitable for long term use at temperatures over 1000°C.
- In this case, we recommend performing more consistent analysis of the used material as well as research of chemical interactions of the Ni based material with the other elements in the environment of furnace during creep tests.

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