HIGH TEMPERATURE DEGRADATION OF POWDER-PROCESSED Ni-BASED SUPERALLOY

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Resume

The aim of present work is to study the high temperature degradation of the powder-processed polycrystalline superalloy Ni-15Cr-18Co-4Al-3.5Ti-5Mo. This superalloy has been applied as material for grips of a creep machine. The material was exposed at 1100 °C for about 10 days at 10 MPa stress. During the creep test occurred unacceptable creep deformation of grips as well as severe surface oxidation with scales peeling off. Three types of the microstructure were observed in the studied alloy: (i) unexposed state; (ii) heat treated (annealing – 10 min/ 1200 °C) and (iii) after using as a part of the equipment of the creep machine during the creep test. It is shown that the microstructure degradation resulting from the revealed γ´ phase fcc $Ni_3(Al,Ti)$ particles preferentially created at the grain boundaries of the samples after performing creep tests affects mechanical properties of the alloy and represents a significant contribution to all degradation processes affecting performance and service life of the creep machine grips. Based on investigation and obtained results, the given material is not recommended to be used for grips of creep machine at temperatures above 1000 °C.

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1. Introduction

Production of the structural parts such as grips of 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. Ni-based superalloys meet these requirements including the high temperature creep resistance.

A typical microstructure of Ni based superalloys usually contains $L1_2$-ordered γ´ ($Ni_3(Al,Ti)$) precipitates in γ (Ni-based solid solution) matrix with face-centered cubic crystal structure [1]. From the point of view of microstructure, Ni superalloys are complex. The fcc matrix (γ), mainly consists of nickel, cobalt, chromium and molybdenum. The strength of superalloys is conferred by the hardening precipitates γ´ phase. 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 controlled by the production process and their crystallographic relations with γ matrix. When the precipitates arise close to the solvus temperature they grow larger which subsequently restrict the grain growth pinning grain boundaries [2 - 5].

The deformation mechanism of the polycrystalline Ni-base superalloys during heat treatment and creep includes twinning, dislocations by-passing or shearing into the γ´ phase [6, 7]. Actually, the mechanical

properties of the Ni-based superalloy are related to the quantities, morphology and distribution of γ' phase [8, 9]. Because the various microstructures in the alloy may be obtained by different heat treatment regimes, it is very important to understand the influence of heat treatment regimes on the microstructure of the studied superalloy.

The aim of present investigation is the microstructural evaluation and study of selected mechanical properties of Ni-based superalloy
that represented material of creep machine grips that failed after the creep test at 1100 °C.

2. Experimental material and testing methodology

We have examined three samples of the superalloy Ni-15Cr-18Co-4Al-3.5Ti-5Mo, sample (i) in as received unexposed state (see Fig. 1), sample (ii) after heat treatment (annealing) and sample (iii) (see Fig. 2) made of a part of failed grips after the creep test. The condition of annealed sample (ii) approximates thermal conditions in the creep machine (without loading). Sample (ii) was subjected to heat treatment consisting of annealing at 1200 °C for 10 min., cooling on air to room temperature at pressure 1 atm. The tested samples of Ni-based commercially produced superalloy were prepared metallographically and their microstructure was evaluated. The third specimen of the superalloy was exposed to load of 365 N at temperature 1100 °C of about 10 day duration. During the creep test occurred unacceptable creep deformation of grips as well as severe surface oxidation with scales peeling off. In Fig. 2 you can see the corrosion of surface performed in argon atmosphere with air humidity and air impurities at 1100 °C. The presence of impurities and air humidity was caused by the improper design of the creep furnace. In this case, the furnace is enclosed in a sealed chamber. This design of creep machine prevents dehydration of furnace lining, therefore air humidity remains in the chamber. The chemical composition and selected physical parameters of the material is given in Tables 1 and 2.

Fig. 1. Photograph of grips as received state in the creep machine.
(full colour version available online)

Fig. 2. Photograph of damaged creep machine grips after the creep test.
(full colour version available online)

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

exposition in the material. The mentioned 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.

Table 1
Chemical composition of Ni-15Cr-18Co-4Al-3.5Ti-5Mo superalloy (wt. %).

Element	Chemical composition
Ni	54.5
Cr	15.0
Co	18.0
Al	4.0
Ti	3.5
Mo	5.0

Table 2
Selected physical parameters of Ni-15Cr-18Co-4Al-3.5Ti-5Mo superalloy [10].

Physical parameter	Value
Density	7.95 (g.cm^{-3})
T (solidus)	1 315 (°C)
T (liquidus)	1 351 (°C)
T (γ' solvus)	1 154 (°C)

The phase composition and the microstructure were studied using light optical microscopy (LOM), scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray analysis system (EDX) and transmission electron microscopy (TEM).

The measurements were carried out using the light optical microscope Zeiss Neophot 32, the scanning electron microscope Tescan LYRA 3 XMU with EDX and the transmission electron microscope JEOL 2100F. Specimens were mechanically polished and finished with 0.05 µm colloidal silica in a vibratory polisher Buehler VibroMet 2 and etched. The etchants (a solution of 20 ml HCl + 20 ml C_2H_5OH + 4 g $CuSO_4$ and a solution of 30 ml HF + 40 ml HNO_3) were selected depending on preferential attack of γ' phase. The TEM samples were sectioned as discs of 3 mm diameter and 1 mm thickness, mechanically lapped to 100 µm and dimpled to 30 µm. X-Ray diffraction (XRD) analyses were performed by Rigaku diffractometer SmartLab operating in Bragg-Brentano geometry with a CuK$\alpha_{1,2}$ radiation and equipped with a linear detector D-Tex and β-filter in diffracted path was used for the XRD data acquisition at ambient temperature. The qualitative analyses were made by High Score Plus software accompanied by pdf-4 database. Vickers hardness measurement was done on the samples of Ni-based superalloy using the Zwick Roell indentor ZHV30.

3. Results and discussion

Following study was carried out to examine the microstructural changes of Ni-based superalloy, common chemical impact between the furnace environment and superalloy in the creep machine as well as corrosion behaviour of grips after creep test.

3.1 Microstructure evaluation of samples by LOM

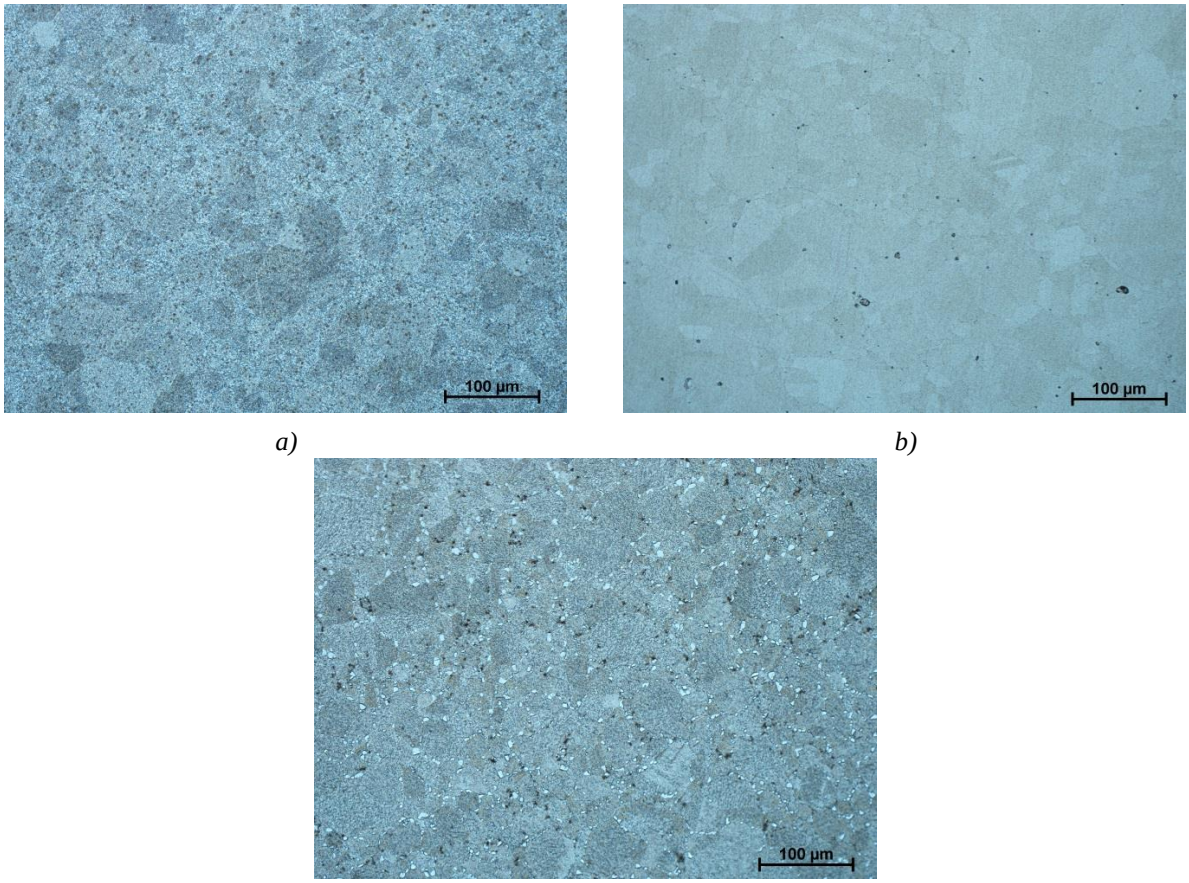
As a first step for better understanding of grips unacceptable creep deformation the samples were evaluated by LOM (see Fig. 3).

The microstructure of the studied alloy is cosiderably heterogeneous in terms of size and morphology of γ' precipitates (see Fig. 3a). During the heat treatment and creep test the microstructural changes occurred in the superalloy as shown in Figs. 3b and 3c in comparison with the microstructure initial state (see Fig. 3a). It is visible that new precipitates are formed at the grain boundaries. Based on the microstructure observation, it can be pointed out that there is a different character of microstructure in relation to the exposition of the samples. The microstructure in Fig. 3b shows recrystallization of initial sample after heat treatment at 1200 °C that formed austenitic-like structure with the non-uniform

grain size. The twins of different sizes were observed in the grains [11].

3.2 Microstructure evaluation of sample (iii) by SEM

The composition of the sample (iii) was obtained from the EDX analysis based on the microstructure observation by SEM. New phase is formed by the majority of Ni (Spectrum 1 – 70.58 wt. % is available in Table 3),and other elements, such as Co, Cr, Ti, Al and Mo. Titanium content (in wt. %) is about 3x increased compare to nominal chemical composition. Based on the investigation using EDX it is apparent, that selected phases were rich in Ni and Ti. (see Fig. 4).



a) *b)* *c)*

Fig. 3. LOM micrograph of Ni-based superalloy at 200x magnification: a) (i) unexposed sample (initial state); b) (ii) sample after annealing treatment 10 min. at 1 200 °C; c) (iii) exposed sample after creep test, etch. 20 ml HCl + 20 ml C_2H_5OH + 4 g $CuSO_4$.
(full colour version available online)

Table 3

Chemical composition of selected spectrums (wt. %) in Fig. 4.

Element	Spectrum 1	Spectrum 2	Spectrum 3
Ni	70.58	50.02	44.64
Cr	11.73	19.50	22.05
Co	5.06	18.99	22.65
Al	8.50	2.79	1.48
Ti	3.05	2.64	2.05
Mo	1.08	6.07	7.14

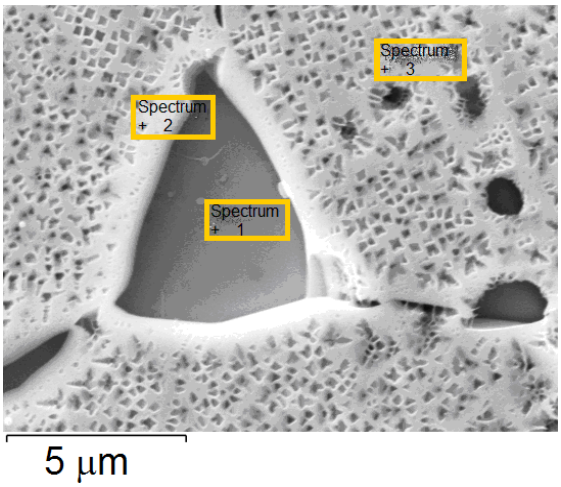


Fig. 4. EDX point analysis of sample (iii) after creep test, SEM, etch. 40 ml HNO_3 + 30 ml HF.
(full colour version available online)

High-temperature corrosion of the grips as a part of the machine has occurred during the creep test at the 1100 °C. Studied sample (iii) was subjected to a hot atmosphere containing argon with air humidity and air impurities. A passivation oxide layer has formed at elevated temperature. Corrosion damage was studied based on chemical analysis of surface of the specimen (iii).

During operation of the creep machine, continuous heat exposure may influence the microstructure. For that reason, it is of interest to see if chemical impact can have a considerable effect on the material behaviour at elevated temperature (1100 °C). EDX elemental mapping results (see Fig. 5 and Table 4), show that the passivation oxide layer consists of minority oxide (Cr_2O_3) and majority matrix Ni-Co-Ti.

The same result was obtained by XRD analysis. The X-ray pattern contains 59 wt. % of Ni-Co-Cr matrix, 21 wt. % Cr_2O_3 and 20 wt. % Al_2O_3. The occurrence of Al_2O_3 can be explained the contamination of the sample during collection of the sample from the surface.

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

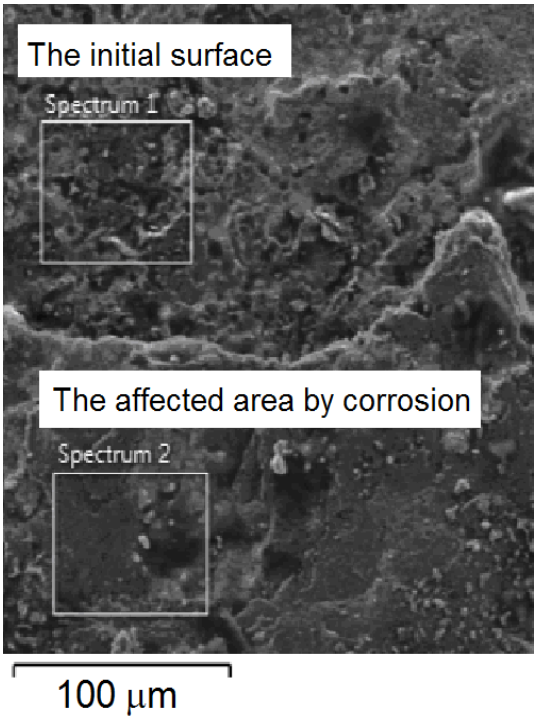


Fig. 5. SEM micrograph of sample (iii) and passivation oxide layer after corrosion at 1100 °C in Ar + air mixt.
(full colour version available online)

The microscopic appearance with the representative chemical composition is shown in Fig. 6. These results suggest that the passivation oxide layer contain oxides of Cr and Ti. The EDX area scan available in Fig. 5 and the EDX mapping (for more details see Fig. 6) of oxides apparently show that the passivation oxide layer is completely filled with oxides (oxygen map). There is a Cr and Ti rich oxide on the affected area. Detailed analysis of EDX results that focused on the overlapping and the flank of peaks confirmed that oxides are presented in the studied layer.

3.3 Microstructure evaluation of samples by TEM

Transmission electron microscopy investigation was undertaken in order to try to understand the differences between the precipitates in the different states of superalloy.

Table 4

Chemical composition of selected spectrums (wt. %) in Fig. 5.

Element	Spectrum 1 (initial surface)	Spectrum 2 (affected area by corrosion)
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

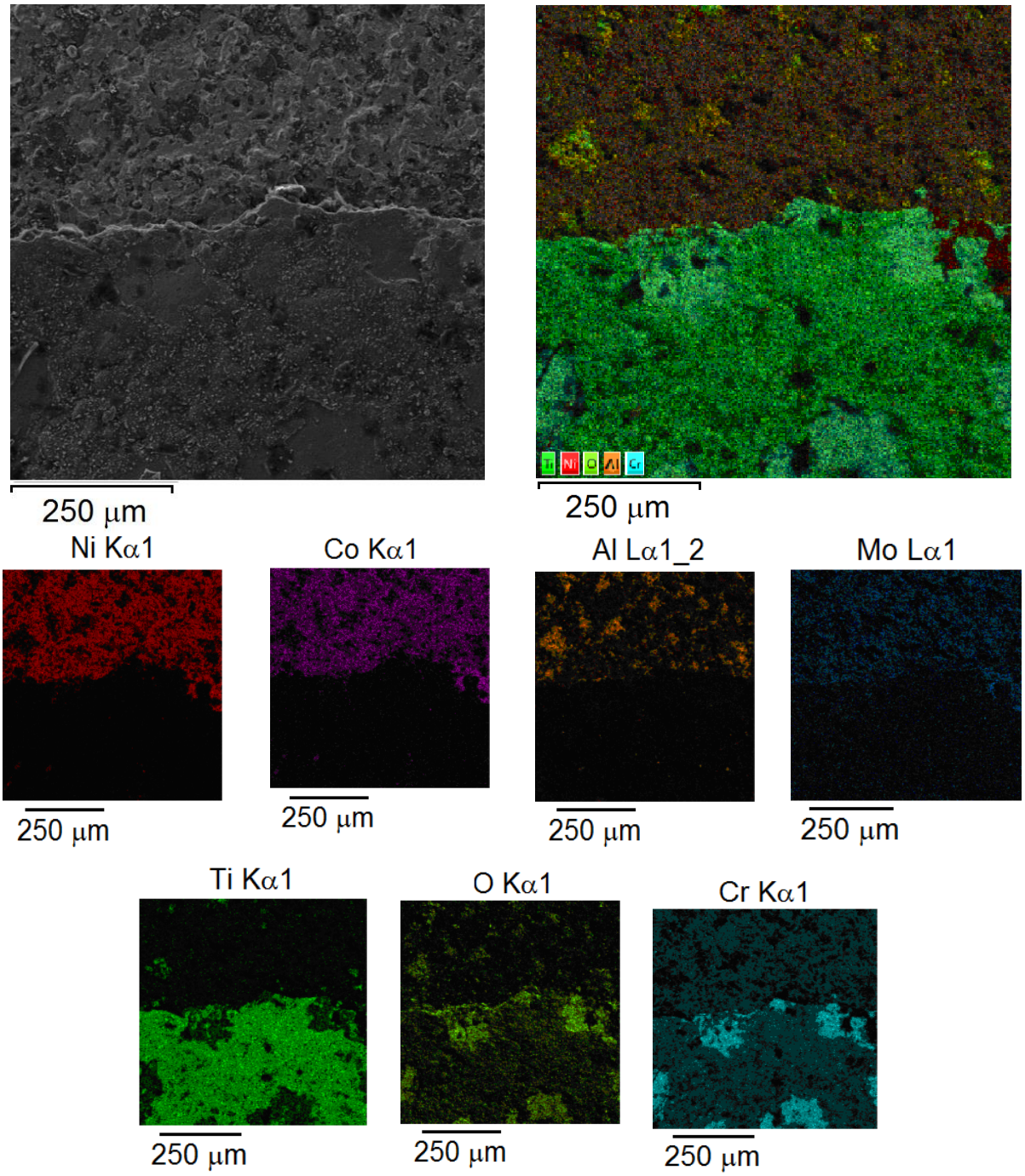


Fig. 6. SEM micrograph of sample (iii) and passivation oxide layer with summary X-ray maps of elements.
(full colour version available online)

Bright-field TEM image of the characteristic microstructure of the investigated sample (i) is shown in Fig. 7 with γ matrix and γ´ precipitates.

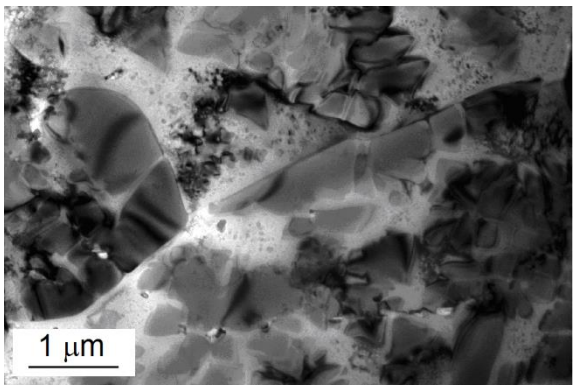


Fig. 7. Bright-field TEM image showing distribution of the γ matrix and γ' strengthening precipitates microstructure of the (i) unexposed sample.
(full colour version available online)

In this case, γ´ phase was dissolved in the sample (ii) (see Fig. 8). It was caused by high temperature annealing over γ´ solvus ($T_{\gamma'}$ = 1154 °C).

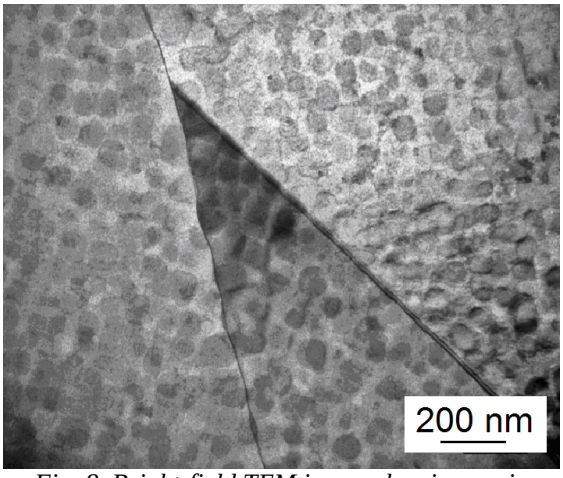


Fig. 8. Bright-field TEM image showing grain boundaries of sample (ii) after annealing treatment at 1 200 °C.
(full colour version available online)

When the precipitates arise close to the solvus temperature they grow larger which subsequently restrict the grain growth pinning grain boundaries. Bright-field TEM images of a γ´ precipitate in the superalloy (see Fig. 9) showing the dissolution of small precipitates after exposition during the creep test at 1100 °C. Total γ′ volume fraction (V_f): 75 %, primary γ ′ (~ 22 %) with an equivalent diameter ($d_{\gamma'}$) of 1 μm – 5 μm, secondary γ′ (~ 49 %) with an equivalent diameter ($d_{\gamma'}$) of 300 nm – 1 μm, tertiary γ′ (~ 4 %) with $d_{\gamma'}$ = *30 - 50 nm*.

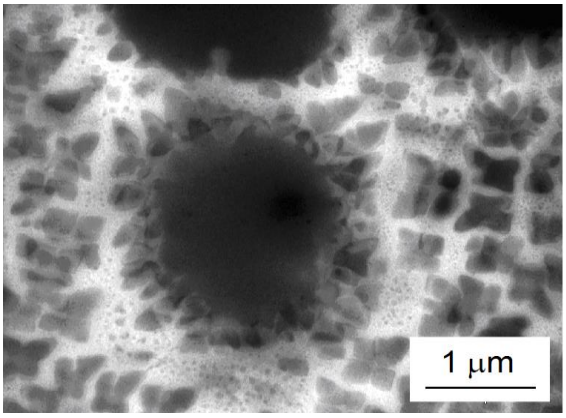


Fig. 9. Bright-field TEM image showing the microstructure of the sample (iii) after creep test with formed primary, secondary and tertiary γ´phase.
(full colour version available online)

The phases in the sample (iii) after the creep test at 1100 °C were the object of thorough observation. Results obtained from this sample using the TEM/STEM are illustrated in Fig. 10. Based on EDX analysis and the conventional TEM image analysis combining with the crystallographic analysis we can assume that it is precipitate Ni_3 (Ti, Al). The chemical composition of the sample (iii) observed by EDX is given in Table 5.

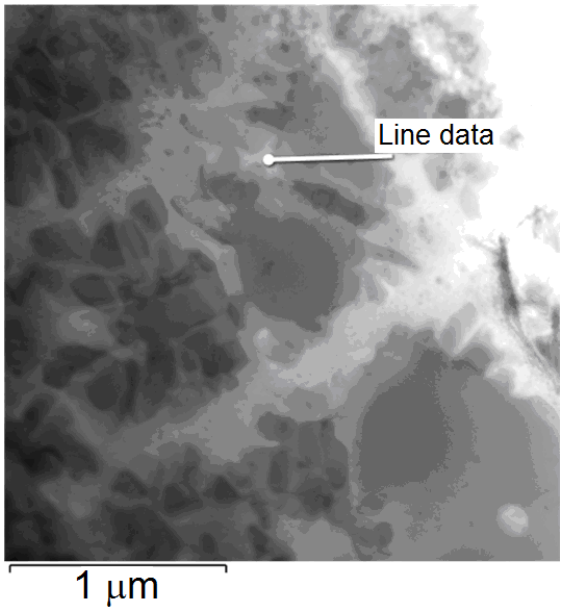
Table 5
Chemical composition of selected STEM EDX line (wt. %) in Fig. 10.

Element	Chemical composition
Ni	66.2
Co	12.1
Ti	6.9
Cr	6.7
Al	5.0
Mo	3.1

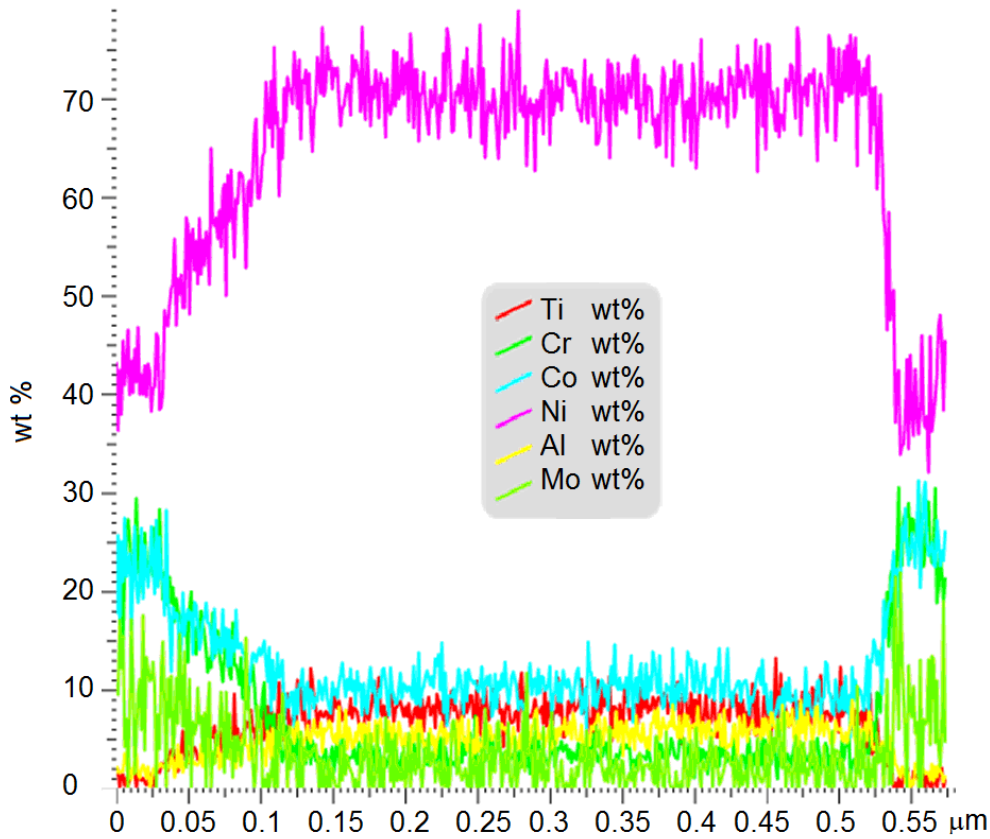
3.4 Measurement of hardness

A Vickers hardness test was performed on the three studied samples. The value

of hardness decreased from unexposed 432 HV5 to the value of approximately 362 HV5 after the creep test. The results of hardness measurements are presented in Table 6. It is evident that the value of hardness of the samples after the thermal treatment (annealing) and after the creep test has notably decreased. This coincides with the formation of new γ' phase, which leads to a lower hardness of the investigated material.



a)



b)

Fig.10. 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 results across the study phase revealed enrichment of Ni, Ti and Al.
(full colour version available online)

Table 6

Measurement of hardness.

Sample	HV5
The unexposed sample (i)	432
The annealed sample (ii)	418
The sample after creep test (iii)	362

4. Conclusions

Conclusions can be summarized in the following points:

- As with all properties that are governed by plastic deformation processes, creep properties are sensitive to microstructure. Because superalloys are exposed to high temperature under stress for prolonged periods, a high resistance to time-dependent creep deformation is essential.
- Depending on the chemical composition, we can conclude that there is significant influence of temperature above 1100 °C on the microstructure stability of the studied superalloy samples.
- The studied Ni base superalloy has identical chemical composition as indicated by the producer.
- We can conclude that a hardness of sample (iii) after the creep test decreased by more than 70 HV5 to approx. 362 HV5.
- According to [10] the temperature of the gamma phase solvus (phase transformation) is 1154 °C. Due to this fact at temperatures 1100 - 1150 °C this material has very low creep strength and it is not suitable material for creep tests at temperatures over 1000 °C.
- The EDX area scan and the EDX mapping of the oxides show that the corrosion surface is completely filled with oxides (oxygen map). There is a Cr and Ti rich oxide on the affected area.
- The degradation (chemical oxidation) of the investigated material is possibly due to chemical interaction between the grips and the atmosphere of the furnace (air humidity). The mechanism of the interaction was not fully analyzed.
- We propose a more detailed study of Ni-15Cr-18Co-4Al-3.5Ti-5Mo superalloy, perform creep tests and investigate the microstructure dependence on i) different annealing temperatures, ii) the environment in the furnace (air humidity) during creep tests.
- As a solution, it is recommended to find a new suitable material of the grips for creep machine for temperatures above 1000 °C as well as procedure for dehydration of furnace environment prior to the creep test.

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