NEGATIVE CREEP OF WASPALOY

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Abstract

Some structural materials for aircraft turbine applications show a volume contraction of up to 0.1% in service. This shrinkage is mainly revealed during turbine maintenance and often referred to as “Negative Creep”. Since the mechanism of this phenomenon is not well understood the objective is to find out whether microstructural changes occur and which ones cause this volume contraction. Waspaloy is a common Ni-base superalloy used for manufacturing of turbine disks. Samples of this alloy are isothermally annealed without external load. Annealing is carried out for times up to 10,000 hours at various temperatures. The dimensional changes are measured using high resolution length measurement before and after annealing. The lattice parameters of the different annealing states are determined with X-ray diffraction and are found to decrease. Phase stability and morphology and their influence on lattice parameter are considered as well as effects of oxidation. Scanning electron microscopy is used to characterize the microstructural changes.

Estimations are carried out in order to quantify the effect of phase transformations and compositional effects. The calculation of phase diagram method (CALPHAD) is used to calculate equilibrium conditions for phase fractions and also for calculating the composition of matrix and γ' . The results are compared to experimental data. This preliminary presentation of an ongoing research also makes first conclusions referring those changes to the phenomenon of negative creep.

Introduction

Before 1981 the existence of the phenomenon “Negative Creep” for temperatures above 600°C for Ni-base alloys was mainly unknown and was seen as a measurement error. The effect of volume contraction was limited to temperatures below 550°C and explained by the formation of Ni₂Cr superlattice. The constraints were low to medium temperatures and the volume only could be explained for long times > 10,000 hours [1]. From 1983 the first systematic investigations were carried out concerning higher temperatures and several Ni and Co-based alloys at relevant times with and without external load [2,3]. The following studies revealed contradictory explanations for negative creep. Changes in volume fraction of γ' were found to be responsible for the phenomenon [4]. The same explanation is excluded in other studies which suggest the carbide reaction to give reason for the contraction [5].

The carbide reaction is often described in literature [5] to be

with MC – metal carbide, γ – matrix, γ^* – matrix with different composition

This means that metal carbide (MC) dissolves and forms carbide $M_{23}C_6$ and γ' [5]. Additionally γ^* is formed. Formation of σ phase expected from this formula can only be verified for long annealing times > 10.000 hours. The lattice parameters are found to change due to the compositional change caused by the reaction (1) [5].

The knowledge about influence of composition on lattice parameter traces back to Vegard's work from 1921 [6]. He investigates the influence of alloying elements on the unit cell of solid solution [6]. Further investigation was done to measure alloying influence in particular for the most important alloying elements for Ni-solid solution and for γ' phase [7]. Their influence is dependent on the element, the concentration and the phase. The lattice parameter a can be calculated taking the lattice parameter of the pure phase as a basis and add the sum of all element concentrations C_i multiplied with the particular Vegard's coefficient V_i [8] So for calculating the lattice parameter of the matrix and gamma prime the following formulas can be used:

$$a_\gamma = a_0^{Ni} + \sum V_i^{Ni} \cdot C_i^\gamma \quad (2)$$

$$a_{\gamma'} = a_0^{Ni_3Al} + \sum V_i^{Ni_3Al} \cdot C_i^{\gamma'} \quad (3)$$

For the approximation the lattice parameters and Vegard's coefficients for the particular elements in pure Ni and Ni_3Al are used. An approach used to approximate the element concentrations is the CALPHAD method.

Experimental

Samples were taken from Waspaloy turbine disc material provided from MTU Aero Engines AG. The overall composition is shown in Tab. I. The material was subjected to a standard heat treatment (1040°C/4h/oil; 845°C/4h/air; 760°C/16h/air, as described in Ref. [9]) in order to achieve the microstructure consisting of γ -matrix and γ' precipitates. This condition is used as initial state for the subsequent research. Cylindrical specimen with a length of 100 mm and a diameter of 10 mm were manufactured by MTU Aero Engines AG. Their length was precisely measured using a laser-measurement system (Mahr ULM Rubin 1500, MTU Aero Engines AG) with an accuracy of 0.2 μm ($\Delta l/l = \pm 2 \cdot 10^{-6}$) before and after temperature exposure in an air conditioned room to avoid thermal dilatation. The samples were exposed without external load at temperatures of 550°C, 650°C and 750°C for times of 300, 1000 and 3000 h, respectively and subsequently air cooled to room temperature.

Lattice parameters of γ and γ' were measured using X-ray diffraction (Bruker D8, Cu, $K\alpha 1$) with a Bragg-Brentano geometry and evaluation of (200) peaks using the curve fitting of software Topas (Bruker).

The phase diagram for Waspaloy was calculated with CALPHAD method with the software Thermo-Calc [10] and TTNi7 [11] database. The volume fractions as well as phase compositions were calculated. Vegard's Law was used to estimate the influence of the calculated

compositional changes of matrix and γ' phases on their lattice parameter using the formulas (4) and (5) taken from Ref. [7,8]. The Vegard's coefficients were derived from measurements of several binary alloys containing the pure phase and additions of the particular element [7]. So the composition is not similar to Waspaloy.

$$a_{\gamma} (\text{\AA}) = 3.524 + 0.478 C_{Mo}^{\gamma} + 0.422 C_{Ti}^{\gamma} + 0.179 C_{Al}^{\gamma} + 0.115 C_{Fe}^{\gamma} + 0.110 C_{Cr}^{\gamma} + 0.0196 C_{Co}^{\gamma} \quad (4)$$

$$a_{\gamma'} (\text{\AA}) = 3.57 + 0.208 C_{Mo}^{\gamma'} + 0.258 C_{Ti}^{\gamma'} - 0.004 C_{Fe}^{\gamma'} - 0.004 C_{Cr}^{\gamma'} - 0.014 C_{Co}^{\gamma'} \quad (5)$$

The microstructure was investigated using scanning electron microscope (SEM, Zeiss 1540 EsB) equipped with energy dispersive X-ray spectroscopy (EDS). The samples were grinded, polished and etched for revealing the fine γ' microstructure. Phase fractions of γ' and carbides were determined by stereological image analysis (Olympus soft imaging solutions GmbH, Stream View 1.4).

Table I. Composition of Waspaloy

	Ni	Cr	Ti	Al	Co	Mo	C	Fe
wt.%	57.5 (bal.)	19.6	3.1	1.4	13.4	4.2	0.04	0.9
at.%	55.8	21.3	3.6	2.8	12.9	2.5	0.2	0.9

Results

Dimensional Changes

The samples were found to contract and the phenomenon of negative creep could therefore be confirmed for Waspaloy without external load in the investigated temperature range. The qualitative development of the length changes compared to the initial state (dashed line) is shown in Fig. 1. Each point refers to one sample.

It is obvious that the biggest contraction can be observed for the lowest temperature, 550°C. The contraction curve for 650°C shows a similar behavior slightly shifted to higher values. All investigated samples for both temperatures shorten during exposure for all annealing times. The contraction within the first 300 hours shows the biggest drop, longer annealing times do not affect the contraction. In order to prove this finding exposures for 10,000 hours are going on.

Conditions are somewhat different for temperature exposure at 750°C. After 300 hours the sample did also shorten but the effect is way smaller compared to the lower temperatures. Contrary to both other curves it is ascending with increasing annealing time and after little more than 1000 hours a contraction to dilatation transition is found.

For both 550°C and 650°C oxidation can be neglected. At 750°C an oxide layer is growing up to a thickness of about 4 μm .

Figure 1. Measured length change during temperature exposure (dashed line refers to initial state)

Lattice parameter

In order to refer these macroscopic sample length changes to a microscopic scale XRD measurements are evaluated regarding the lattice parameters. The peaks of the diffraction pattern (not shown here) show broadening on their rising edge which corresponds to γ' phase with higher lattice parameter than the matrix. The lattice parameters are determined for both phases separately from annealed samples cooled to room temperature and are found to decrease with decreasing annealing temperature. In order to obtain the total lattice parameter change with time and temperature the assumption of a two phase ($\gamma+\gamma'$) microstructure is made. The lattice parameters a_γ and $a_{\gamma'}$ are multiplied with their volume fraction V_γ and $V_{\gamma'}$:

$$a_{\gamma+\gamma'} = a_\gamma V_\gamma + a_{\gamma'} V_{\gamma'} \quad (6)$$

The volume fractions are taken from the calculated phase diagram. The approach will be described in the subsequent chapter. The qualitative development of the lattice parameters in Fig. 2 shows pretty good accordance with the length changes (Fig. 1). Again the contraction during exposure at 550°C exceeds the values for 650°C and all values for both temperatures decrease compared to the initial state. A deviation can be found for exposure temperature 750°C. The measured contraction of lattice parameters for 300 hours and 1000 hours exceeds the lower temperatures which is not observed for total sample length change. The negative to positive transition between 1000 hours and 3000 hours correlates in both curves (Fig. 1 and 2).

Figure 2. Total lattice parameter: combination of γ and γ' lattice parameters regarding the calculated volume fractions

Calculation of phase diagram and phase fractions

The calculated phase diagram (Fig. 3) shows thermodynamically stable mole percentage of phases over temperature. As the lattice parameter of the matrix and γ' precipitations differ little from each other, mole percentage and volume percentage are taken to be the same. The phase diagram shows a decrease of gamma prime volume fraction with increasing temperature. Equilibrium fraction at 550°C is 26.5%. Elevation of temperature to 650°C and 750°C leads to γ' volume fractions of 25.4% and 23.4%, respectively. A stereological determination of the volume fraction reveals values of about $24 \pm 2\%$ for all samples. The calculated volume fractions using Thermo-Calc are used for calculations (Fig. 2).

Figure 3. Calculated phase diagram for Waspaloy based on calculations using Thermo-Calc Software and TTNi7 database

Figure 4. γ/γ' microstructure a) in initial state and after annealing for 3000 hours at b) 550°C, c) 650°C and d) 750°C

Additional to γ/γ' microstructure (Fig. 4) two different kinds of carbides with low phase fractions can be found in the calculated phase diagram as well as in the investigated samples. TiC is calculated to be stable at temperatures between the melting point and 970°C. In the samples two different kinds of TiC can be found: one of them contains a core of Ti(C,N) and shows blocky shape, the other does not. Both of them show a content of Mo substituting for Ti. At temperatures below 970°C Cr_{23}C_6 is the stable carbide phase, which also contains Mo substituting for Cr. Therefore temperatures below 970°C are expected to reveal ongoing carbide reaction (1) which is observed in the samples exposed at 750°C very clearly by the formation of Cr_{23}C_6 around TiC particles (Fig. 4). σ and μ phases are not observed in the investigated samples and therefore neglected for calculation.

Figure 5. a) initial state: TiC, b) 750°C, 3000 h: formation of Cr_{23}C_6 edge around TiC

Reasons for the lattice parameter change

In order to find the reasons for the lattice parameter change established earlier two attempts will be made.

Compositional changes and effect on lattice parameter

Using CALPHAD method it is also possible to estimate the equilibrium composition of each phase calculated depending on the temperature. The calculated compositions of the matrix and γ' are shown in Tab. II and III. Variations of the chemical composition can be found for both phases and for all elements. For γ matrix the biggest changes occur for Ti followed by Cr, Ni and Al; γ' shows a difference mainly in Ni and Co content, but also for Ti and Cr.

Table II. Calculated equilibrium composition of γ matrix in at.%

	Ni	Cr	Ti	Al	Co	Mo	C	Fe
750°C	51.95	26.98	4.39	0.92	15.39	3.13	0.002	1.19
650°C	51.21	27.69	1.60	0.58	15.93	3.21	0.0003	1.23
550°C	50.65	28.10	0.05	0.32	16.39	3.25	-	1.25

Table III. Calculated equilibrium composition of γ' precipitations in at.%

	Ni	Cr	Ti	Al	Co	Mo	C	Fe
750°C	69.77	1.69	13.97	9.15	5.19	0.11	-	0.11
650°C	70.60	1.52	13.73	9.50	4.44	0.12	-	0.08
550°C	71.42	1.39	13.49	9.84	3.66	0.13	-	0.06

Carbide reaction

Fig. 4 demonstrates the most obvious evidence for carbide reaction. The quantification of this finding is done by stereological analysis of SEM images and shown in Fig. 6. The values for Cr_{23}C_6 refer only to intragranular precipitations, twin boundaries and around TiC particles. The amount of Cr_{23}C_6 at grain boundaries is not analysed by this stereological method.

Figure 6. Development of volume fraction of TiC and Cr_{23}C_6

As expected concerning the calculated phase diagram (Fig. 3) and the formula (1), the amount of TiC is decreasing with time and the decrease is faster for the exposure at a temperature of 750 °C than it is for both lower temperatures except one outlier. While TiC is dissolved the formation of Cr_{23}C_6 can be observed by an increasing amount. Again the highest temperature shows the fastest and biggest increase.

Discussion

Dimensional Changes

The monitoring of sample lengths before and after annealing shows dimensional changes of temperature exposed Waspaloy samples. These dimensional changes show a length contraction which is dependent of exposure temperature and time. The lower temperatures produced greater magnitudes of length contraction the investigated temperature range of 550 °C to 750 °C. The measured values for sample contraction at 550 °C and 650 °C show the same tendency, the course of the curve is mainly the same while all values for 550 °C are shifted to lower values compared to exposure temperature of 650 °C. The samples exposed to 750 °C show a different performance with a contraction-to-dilatation transition. The samples annealed at 750 °C are the only ones to show a significant growth of an oxide layer, but the dilatation of the sample cannot be explained by the growth of an oxide layer.

This behavior with contraction maximum at medium exposure temperatures was found for other Ni-base alloys and also Co-base alloys. All show a temperature with maximum contraction while higher temperatures lower the effect or cause a dilatation [5].

Lattice parameter

In order to relate the changes in lattice parameter to the length change of the whole sample not only the lattice parameter change itself but also the volume fraction of the respective phases has to be considered. Because the amount of carbides is very small compared to the phase fractions of γ matrix and γ' precipitates it is neglected in this case. The γ / γ' phase fraction is taken as 100% (assumption of a two phase alloy) and therefore calculated. As the calculated phase diagram gives very precise values for the phase fractions these are used instead of the stereological investigated values as the inaccuracy measurement is bigger than the change in the phase fraction. For a calculation of the total lattice parameter change this method is suitable.

The qualitative course of the lattice parameter changes illustrated in Fig. 2 corresponds well to the length change in Fig. 1. The graphs for 550°C and 650°C show the same proceeding and so does the curve for 750°C. The main difference is the bigger contraction for 750°C after 300 hours and 1000 hours. The accordance of both, measured length and lattice parameter changes shows that there is a strong relationship between microstructural effects and macroscopic length contraction of the samples.

As it was also observed for the volume contraction the biggest length drop can be recognized for shorter annealing times and it little exceeds with exposure time. Also the samples and lattice parameters annealed at 750°C show a contraction for shorter times up to 1000 hours. It is most likely that the contraction effect for all samples is the same, but stronger for lower temperatures while for higher temperature a dilating effect takes place with longer incubation times and high temperature to emerge. The relative change of the lattice parameter with regard to the initial state is larger than the one measured for sample length change which means the volume contraction can be related to this lattice parameter decrease.

Reasons for the lattice parameter change

Compositional changes and effect on lattice parameter

The lattice parameter change due to compositional variations is a well-known phenomenon. The calculated phase diagram not only shows a slight change in volume fractions of γ' phase for the exposure temperatures investigated but also involved variations in the composition of γ and γ' . As the fraction of γ' increases at lower temperatures (Fig. 3) the depletion of the matrix concerning Ti and Al is the most significant compositional change but also the other elements show slight compositional variations due to carbide reaction and different equilibria conditions.

According to the formulas (4) and (5) the elements Mo and Ti show the biggest influence on the lattice parameter of both phases, followed by Cr and Al which mainly influences the γ matrix. Using these compositions with formulas (4) and (5) it is possible to get a rough estimation of the lattice parameter change due to compositional variations. The positive lattice misfit of Waspaloy can be confirmed by these calculations. The effect on the lattice parameters for both γ matrix and γ' phase compared with measured values are shown in Fig. 6.

Figure 7. Calculated equilibrium lattice parameters (grey circles) and measured values after 3000 h exposure (black boxes) for a) gamma phase and b) gamma prime phase

Calculated lattice parameters as well as the measured ones show the tendency of decreasing with decreasing temperatures for both phases. This tendency is much more distinctive for the measured values. After temperature exposure the lattice parameters for the matrix phase are below the measured value of the initial state. The calculated equilibrium lattice parameters are shifted to lower values compared to the measured ones. The measured lattice parameters of γ' phase are considerably below the calculated values but only the value for 550°C is smaller than the initial state while for higher temperatures a dilatation can be observed.

Reference [5] shows that no change in γ' volume fraction can be found by phase isolation or stereological methods for IN738LC and therefore negative creep can definitely not be caused by changes in γ' morphology. For phase isolation isothermally exposed samples with higher γ' weight fractions than the initial state are observed. Increasing temperature shows decreasing γ' phase fraction which corresponds to the calculations in this work. The stereological measured volume fraction in Ref. [5] does not show temperature dependence but all values up to 10,000 hours are below initial state. These results are contrary to each other and the measurement errors are quite high. In this case it would not be possible to recognize changes in the range of the calculated phase fractions that, in the investigated range in this work are 2.1%. Stereological measurements for Waspaloy show γ' volume fractions of $24 \pm 2\%$, so it is also not possible to find the calculated variations in very high accuracy with this method. Looking for an effect causing a sample length change as small as maximum 2×10^{-4} , this change should not be neglected.

The calculated compositions show a chemical difference of matrix and γ' for the different exposure temperatures (Tab. 2 and 3). The application of Vegard's Law shows a decrease in the lattice parameter of both phases for decreasing temperature. This estimation of the lattice parameters lies for the γ matrix clearly below the measured ones while for γ' it is significantly higher. This could be attributed to many reasons. First of all the calculation using Thermo-Calc Software and TTNi7 database is not necessarily absolutely exact and therefore the calculated composition maybe does not exactly correspond to the real one because it shows the composition for thermodynamic equilibrium which is not reached in the experimental investigation. There might also be slight compositional variations within the samples. Above this the use of Vegard's Law can only be seen as a rough estimation which contains a lot of potential for errors containing the exact Vegard's coefficients determined for binary Ni alloys [12]. A lattice parameter for initial state cannot be calculated as it requires thermodynamic stability and standard heat treatment ageing steps are much shorter than exposure times in this work, so the relative calculated lattice parameter change is not accessible. But it is possible to compare the relative length difference between the calculated lattice parameters for 550°C and 750°C with the relative length differences of the samples exposed to these temperatures for 3000 hours. They show the same order of magnitude. This result may not be neglected as they are part of the explanation for the lattice parameter changes.

Effect of carbide reaction

An effect on the matrix and γ' precipitate lattice parameter is induced by the carbide reaction. For all investigated samples TiC was found although it is calculated to be unstable within the investigated temperature range. The stable volume fraction for Cr_{23}C_6 is slightly increasing with decreasing temperature, nevertheless higher volume fractions were measured for increasing temperature with stereological analysis. This shows that carbide reaction proceeds very slowly. TiC volume fraction is the smallest for high temperature because the kinetic is faster for higher temperature and also precipitation of Cr_{23}C_6 is faster therefore the measured volume fraction is

higher with increasing temperature. For both, decrease of TiC and increase of Cr_{23}C_6 no saturation can be seen after 3000 hours as the equilibrium state from the phase diagram is not reached. The carbide reaction has two effects on the sample length change:

The dissolution or precipitation of a phase is known to influence the surrounding matrix composition and therefore the lattice parameter. The consumption of elements such as Cr and Mo for the formation of Cr_{23}C_6 lowers the concentration of these elements in the matrix and therefore reduces the lattice parameter. Dissolution of TiC containing low percentage of Mo also changes the lattice parameter of the surrounding matrix, as two of the most dilating elements are released. According to (1) most of these atoms are used for γ' formation and Mo is also consumed by formation Cr_{23}C_6 [13]. So the lattice parameter contraction predominates [5]. Local range of variation is likely to occur.

The density of the carbides is below the density of Waspaloy. Waspaloy has a density of 8.2 g/cm^3 , TiC 4.9 g/cm^3 and Cr_{23}C_6 6.9 g/cm^3 [14]. Therefore a decrease of carbide fraction leads to a contraction of the whole sample while carbide formation results in a sample dilatation. This effect can impact the whole sample length.

Conclusion

Regarding the complex characteristic of the very small volume contraction leading to negative creep it is not possible to reduce this phenomenon to one single mechanism, as it can be seen from the current state of the ongoing research. It is clearly found that lattice parameter changes show the right tendency to explain the macroscopic measured length change.

To explain these changes in lattice parameter the change of volume fraction of γ and γ' is connected with the slight compositional variation of both phases. This results in a decrease of lattice parameter with decreasing temperature. The fraction of γ' phase with bigger lattice parameter decreases with increasing temperature. Also the carbide transformation has an effect on the surrounding lattice parameter. The macroscopic sample length is also influenced by dissolution and formation of carbide phases with lower density.

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