INVESTIGATION OF GAMMA PRIME MORPHOLOGY DEVELOPMENT IN CREEP EXPOSED NICKEL BASE SUPERALLOY

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Abstract

The creep degraded nickel base single crystal superalloy CMSX-4 of two axial orientations [001] and [111] was investigated with aim to assess the structure degradation. Constant load creep tests were conducted in the stress/temperature ranges of 250 – 780 MPa / 750 – 950°C resulting in rupture time variation from 50 to 4000 hours. A combination of scanning electron microscopy (SEM) and non-destructive small-angle neutron scattering method (SANS) was used to investigate the directional coarsening (rafting) of the gamma prime (γ’) precipitates in relation to the stress and temperature applied as well as to the initial crystallographic orientation of the specimens. The SANS results are discussed in terms of the correlation with the raft development, the axial orientation of specimen, the creep parameters and the mechanical properties.

Key words: Ni base superalloy, single crystal, creep, structure, small angle neutron scattering.

1. INTRODUCTION

Nickel base superalloys are widely used for heavy duty gas turbine buckets, where stability of microstructure is an important factor determining mechanical properties under service conditions. The basic microstructure of single crystal (SX) nickel base superalloys contains two phases – the γ matrix which is hardened by precipitates of γ’ phase. The drawback of SX superalloys is their metallurgical instability at high temperatures. The changes in their morphological characteristics are most sensitively reflected in their deformation behaviour and result usually in an acceleration of structure degradation process [1, 2]. In these alloys, the morphological evolution of the γ’ precipitates at high temperatures may be considerably altered by the application of a (uniaxial) external stress [3]. Under high temperature creep conditions, the γ/γ’ microstructure first becomes rafted, then slowly coarsens and becomes irregular [4, 5]. This phenomenon, known as directional coarsening or “rafting”, corresponds to a breaking of the overall cubic symmetry of the precipitate shape and results in the formation of large plates, or long rods or platelets, perpendicular to the stress direction. The extent of degradation in the microstructure reduces then the mechanical properties of SC superalloys.

To check the response of the structural parameters especially to the applied load at elevated temperatures, both destructive and non-destructive testing can be used. Small-angle neutron scattering (SANS) [6, 7] proved to be an effective non-destructive tool for the assessment of the microstructure of alloys. To assess the morphological changes responsible for or connected with the orientation dependence of mechanical parameters, SANS can be used together with the local information obtained by SEM.

The aim of this study was to assess the morphological changes of gamma prime precipitates matching to the observed dependence of mechanical properties on mutual crystallographic and load direction orientation in crept single crystal superalloy CMSX-4. The investigation was conducted employing SEM and SANS techniques.
2. EXPERIMENTAL

2.1 Microstructure

The CMSX-4 SX was experimental material, which has outstanding combination of the high temperature strength and corrosion resistance. The composition of the alloy in mass % is as follows: 9.7Co, 6.5Cr, 0.6Mo, 6.4W, 5.7Al, 1Ti, 0.1Hf, 6.5Ta, 3Re, the balance is being nickel. The alloy was provided in the form of cylindrical bars with growth direction of [001] and [111]. All bars, for both growth directions, had the abovementioned crystallographic direction oriented within 10° around the longitudinal axis. The standard, three step heat treatment was applied to optimize structural parameters of γ’ including the size, morphology and volume fraction.

The microstructure of the heat treated SX specimens and creep exposed specimens was then examined by the scanning electron microscopy (SEM). Samples for observation were metallographically prepared and etched. SEM observations of the creep exposed specimens were performed on section cut parallel to the crystallographic direction (specimen axis) of [001] or [111]. The representative microstructure of cuboidal γ’ phase deposited in gama matrix is presented in fig. 1.

![SEM micrograph of γ’ in CMSX4 alloy structure after standard heat treatment.](image)

**Table 1** Experimental creep conditions and results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Load axis</th>
<th>Temp (°C)</th>
<th>Nominal stress (MPa)</th>
<th>Time to rupture (h)</th>
<th>Creep strain to rupture</th>
<th>Morphology by SANS and SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>C397h</td>
<td>[001]</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C397</td>
<td>[001]</td>
<td>750</td>
<td>780</td>
<td>1000</td>
<td>15</td>
<td>no rafting</td>
</tr>
<tr>
<td>D431</td>
<td>[001]</td>
<td>900</td>
<td>500</td>
<td>100</td>
<td>21</td>
<td>partial rafting</td>
</tr>
<tr>
<td>E430</td>
<td>[001]</td>
<td>900</td>
<td>300</td>
<td>2000</td>
<td>27</td>
<td>rafted</td>
</tr>
<tr>
<td>E415</td>
<td>[001]</td>
<td>950</td>
<td>250</td>
<td>500</td>
<td>30</td>
<td>rafted</td>
</tr>
<tr>
<td>B398h</td>
<td>[111]</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>B398</td>
<td>[111]</td>
<td>750</td>
<td>780</td>
<td>500</td>
<td>22</td>
<td>no rafting</td>
</tr>
<tr>
<td>C404</td>
<td>[111]</td>
<td>900</td>
<td>500</td>
<td>50</td>
<td>22</td>
<td>partial rafting</td>
</tr>
<tr>
<td>E451</td>
<td>[111]</td>
<td>900</td>
<td>300</td>
<td>4000</td>
<td>20</td>
<td>rafted</td>
</tr>
<tr>
<td>A396</td>
<td>[111]</td>
<td>950</td>
<td>250</td>
<td>2000</td>
<td>20</td>
<td>rafted</td>
</tr>
</tbody>
</table>

2.2 Creep testing condition. The specimens for the creep rupture tests (gauge length of 60 mm, diameter of 6 mm) for both orientations were machined from the heat treated SC bars. The constant load creep tests were performed until rupture. The creep test conditions are stated in Table 1. One sample for each particular creep condition was tested.

2.3. SANS measurement. CMSX-4 was investigated by SANS after various loadings (temperature, stress) and at two orientations of the load axis mentioned above. An Euler cradle (for adjustment of ω, χ and ψ angles) was used to set the samples to several special orientations. The measurements of neutron scattering were carried out on the V4 instrument of BENS at Berlin (HMI) [8].

The scattering data were collected at several geometries. However, the one used for anisotropic data evaluation was: sample – to 16 m and the neutron the neutron wavelength λ=7.5 Å (in order to avoid a multiple Bragg scattering at certain sample orientations). The covered range of the scattering vector magnitude $Q = |\mathbf{Q}|$ was approximately $3 \times 10^{-3} \text{Å}^{-1}$ to $0.02 \text{Å}^{-1}$, where the magnitude $Q = |\mathbf{Q}|/|\mathbf{k}_0|/|\mathbf{k}_0|$ and $\mathbf{k}$ being the wave vectors of the incident and scattered neutrons, respectively, and $|\mathbf{k}| = |\mathbf{k}_0| = 2\pi/\lambda_{\text{inc}}$. The measured raw data were corrected for background scattering and calibrated to absolute scale by the measurement of the attenuated primary beam [9].
3. RESULTS

3.1 Mechanical test. The specimens of the single-crystal superalloy CMSX-4 were subjected to various tensile creep stresses at different temperatures and they showed a different deformation behaviour with regard to the strain to rupture and the lifetime for two load-axis orientations of [001] and [111]. The creep data for different strain and testing temperature are presented in Table 1. As shown in Fig. 2, the time to rupture is significantly larger for [100] load axis for the low temperatures and high stresses. On the other hand, the time to rupture is much larger for the [111] exposure when the sample undergoes deformation at a relatively high temperature and low stress.

3.2 Creep microstructure characteristics. The microstructure of SC superalloy after standard heat treatment, which is composed of γ matrix and γ' phase, is documented in Fig. 1. The cuboidal precipitates are arranged uniformly through the γ matrix. The average edge length of the cuboidal γ' precipitate is about 0.5 μm. The volume fraction of γ' is over 65%.

The SEM micrographs of the crept specimens for the various creep conditions (stated in Table 1) are presented in Fig. 3a for the [001] axis orientation and Fig. 3b for the [111] axis orientation.

Generally, for both load-axis orientations, the crept specimens exposed at the lower temperature of 750°C and at higher stress showed no rafting. The specimens exposed at the higher temperature of 900°C and medium stress of 500 MPa showed partial rafting. The other specimens exposed at 900°C/300 MPa as well as at 950°C/250 MPa are fully rafted. A quantitative comparison of [111] and [001] creep exposed specimens, considering the start of raft formation, shows no striking differences, although variations in γ' morphology were observed, as shown in Fig. 3.
3.3 SANS results. The measured and fitted 2D data are displayed in Figs. 4 and 5 for the selected specimens and orientations. Each specimen was then measured in 9 orientations, including those with low-index crystallographic directions parallel to the incoming beam as well as those without this special relation. The 2D anisotropic data were fitted at once in order to take into account the strong anisotropy of a 3D cross section in the reciprocal space, corresponding to the cuboidal and/or rafted shape of the precipitates. The precise orientation of the crystal lattice with respect to the sample axis and edges ($\omega_0$, $\chi_0$ and $\psi_0$ angles) was also determined by the fit. Two selected (out of nine) orientations are plotted in Figs. 4 and 5 for the selected samples.

4. EVALUATION

4.1 Modeling. The measurements were evaluated by the NOC program for anisotropic SANS data treatment [10]. The analysis procedure is based on the numerical simulation of a scattering profile generated from a three-dimensional (3D) microstructural model of a particle system. The calculated profile is matched with the experimental curve by a weighted least square method in order to find the microstructural parameters which can be in principle extracted from the measured data. In agreement with the direct-imaging technique (SEM) and with the symmetry of the SANS data at various sample orientations, ordered cuboidal or rafted particles were used as a model for the non-exposed and all the variously exposed samples. The shape of one individual particle can be varied in simple way using only one shape parameter $\beta$ [10], which is 0 for a cubical particle. In the case when $\beta = 1$, the particle has a spherical or elipsoidal shape. These particles compose an array resembling $\gamma'$ precipitates in a superalloy using the mean distance and its variance as well as the mean size and its variance.

Fig. 4 The selected 2D SANS patterns and the optimum model for the load axis [111]. Exposure (a) none, (b) T=900°C, $\sigma=500$ MPa, (c) T=900°C, $\sigma=300$ MPa.
Additionally, an orientational distribution of the 3D modelled cross section is included, which in fact represents an orientational distribution of normals to the $\gamma - \gamma'$ interface. This distribution is characterized by its full width in half maximum (FWHM).

### 4.2 Fitting.

In the present case, where the precipitates in CMSX-4 after standard heat treatment are large, the measured scattering curves do not contain information on the size and distance. Therefore, the mean distance was fixed at a reasonable value. The precipitate sizes in [100] and in [001] directions could be fitted in a similar way. However, as they indirectly determine the amount of interface perpendicular to [100] and the amount of interface perpendicular to [001] (see the models in Fig. 4) and thus also the degree of the rafting, it was left free. A certain variation of the size and distance of the modelled particles, which can be observed in Figs. 4 and 5, was allowed using non-zero variances of the size and distance distributions in the preliminary fit. The size and distance variation was performed basically only in order to correspond better with variations visible in the SEM micrographs. Because the measurement was performed at nine various orientations, the representation of the 3D cross section is sufficient to refine the orientation angles $\omega_0$, $\chi_0$ and $\psi_0$ together with fitting of the microstructural parameters. The parameters, which can be determined, are: morphology (cuboids or rafted precipitates; their particular shape defined by $\beta$), interface orientation distribution FWHM and specific interface between $\gamma$ and $\gamma'$. The sections through 3D real-space models representing the precipitates, which match best the measured data for the selected samples, are depicted in Figs. 4 and 5. It should be pointed out that three equivalent subsets of rafts, perpendicular to the crystallographic directions [100], [010] and [001] are in fact modeled in the case of the [111] deformed samples (Fig. 5).
DISCUSSION

Microstructure evaluation with creep exposure. Among the samples with the load axis [001], the sample exposed at 750°C with 780MPa (time to rupture 1000h) showed practically no rafting indication (as the scattering pattern has nearly fourfold symmetry when both [100] and [001] are perpendicular to the beam), except the small elongation mentioned above. The sample exposed at 900°C with 500MPa (100h) clearly showed partial rafting. It can be deduced that the diffusion effects do not last long enough to form rafts for the samples exposed at lower temperatures and higher stresses. The other two samples exposed at 900°C with 300MPa (2000h) and at 950°C (250MPa, 500h) exhibited a full rafting (practically no dependence of the SANS pattern on the rotation around the load axis). The rafting thus occurs only above a temperature threshold which is between 750 and 900°C.

The estimation of the morphology of the precipitates for samples with load axis [111] is more difficult as the raft microstructure is more complex. It can be deduced that there is no raft formation with interfaces perpendicular to the stress axis (i.e. to [111]). The coarsening occurs uniformly in all three planes (100), (010) and (001). Due to this equivalence (unlike the samples stressed along [001]), there is no change in the general character of the SANS pattern: streaks do not disappear fully in certain crystallographic directions during the rafting process, they are only more smeared for the more exposed samples. By combining SANS and SEM, similar morphology to the [001] exposed samples can be deduced (except that the morphology to [001] exposed samples can be deduced (except that the morphology is equivalent for all three directions [100], [010] and [001] in the case of [111] deformation whereas it was uniaxial in the case of the samples exposed along [001]).

Specific surface. This parameter can be obtained by fit of the specific area of the interface between γ and γ'. In order to obtain its evolution in an absolute scale, a qualified estimation of the scattering contrast has to be carried out. It can be obtained by using an estimation of the average precipitate size in a non-exposed condition (0.5μm) and γ' volume-fraction estimation (65%) from SEM. Using this scattering contrast estimation, the evolution of the specific interfacial area in absolute magnitude is plotted as showed in Fig 6.

![Fig. 6 The dependence of the interfacial area btw γ and γ' on exposure.](image)

It can be seen when comparing the non-exposed sample with the one loaded at 750°C/780 MPa that even without rafting occurrence there is a change of the interfacial area. As no rafting occurred here, the specific interface decrease is here caused by disappearance of small precipitates from the distribution. Further decrease of the specific surface (temperatures 900 and 950°C) is caused by coarsening of the precipitates due to rafting, which removes some interfaces and thus lowers the specific area. The growth of the precipitates is the second cause of the strong decrease of the interfacial area.

CONCLUSIONS

There is no significant observable morphological difference at low temperatures and high stresses between samples loaded along [001] and [111] axes (initial and 750°C/780MPa as well as 900°C/500MPa loaded samples). There is either no or only partial rafting in these samples. Nevertheless, among these samples, the [001] exposed ones exhibit higher time to rupture than [111] ones. It is likely that the dislocations pass through the samples loaded along [111] more easily. This is understandable as three equivalent slip plane...
systems are favorably oriented in this case. SANS showed that there is no or only a very small impact of this fact on the γ' morphology.
On the other hand, as soon as full rafting occurs (900°C/300MPa and 950°C/250MPa loaded samples), the more favorable (from the point of view of the time to rupture) are, in turn, the [111] samples. Here, the microstructural difference between [001] and [111] samples are evident:
a) The rafts are formed equivalently perpendicular to crystallographic directions [100], [010] and [001] in the case of [111] deformed samples (a "zigzag" form) whereas the rafts are exclusively perpendicular to [001] in the case of [001] deformed samples;
b) Orientation distribution of the interfaces between γ and γ' is much larger for [111] samples.
Most probably, both effects help to hinder the movement of dislocations and/or crack propagation and are thus responsible for the more stable microstructure of the [111] loaded samples in the cases where rafting occurs. However, it is difficult to assess which of these two features is dominant.

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REFERENCES