Small-Angle Neutron Scattering Investigation of Precipitation in Single-Crystal Nickel-Based Superalloy ZS26

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Abstract

The influence of different heat treatments on the microstructure of ordered cuboidal γ' precipitates in the ZS26 superalloy (wt%: Ni 64, W 11, Co 9, Al 6, Cr 5, Nb 1.5, Ti 1, Mo 1, V 1) was studied by small-angle neutron scattering. The average shape and size of the precipitates were determined by modelling the scattering curves and by fitting them to the measured 2D data. The volume fraction of the precipitates was deduced from the fitted parameters under the assumption of a homogeneous distribution of particles inside the sample.

1. Introduction

A two-phase microstructure consisting of γ' precipitates growing in a γ-phase matrix is the basic feature that determines high creep resistance of Ni-based superalloys. The morphology of the precipitates and thus the mechanical properties of the material depend on the applied heat treatment. The morphology is conventionally studied by transmission electron microscopy (TEM); however, this and other standard methods in materials science do not usually characterize the microstructure completely.

Small-angle neutron scattering (SANS), which provides bulk-averaged information, has been found to be a powerful tool for the investigation of microstructural inhomogeneities in single-crystal alloys (Kostorz, 1991, 1993; Fratzl, Langmayr & Paris, 1993). A number of studies (e.g. Bellet, Bastie, Royer, Lajzerowicz, Legrand & Bonnet, 1992; Paris, Fährmann & Fratzl, 1993; Calderon, Voorhees, Murray & Kostorz, 1994; Sequeira, Calderon, Kostorz & Pedersen, 1995; Fährmann, Fratzl, Paris, Fährmann & Johnson, 1995) have demonstrated the applicability of SANS to the investigation of precipitation in single-crystal Ni-based alloys.

The aim of the presented SANS experiment was to study the influence of different heat treatments on the final microstructure of ordered cuboidal γ' precipitates in the ZS26 superalloy (Zrník, Hazlinger, Žiňianský & Wang, 1994). Earlier work (Strunz, Zrník, Wiedenmann & Lukáš, 1995) has proved that a particular shape of the precipitates can be determined from 2D anisotropic SANS data recorded at larger angles, where the scattering curve exhibits asymptotic character. In the present paper, we determine the average shape as well as the size of the precipitates and their volume fraction from the SANS data.

2. Experimental

The experiment was performed on the V4 pin-hole SANS facility of BENSAC at the Hahn-Meitner-Institut (HMI), Berlin, which is equipped with a 2D position-sensitive detector (PSD). Each sample was measured at two sample-to-detector distances (SDD) of 4 and 16 m, with corresponding collimation lengths. These geometries together with the selected wavelength λ = 10.0 Å provided a relatively wide range of scattering vectors Q, with magnitude Q between 0.002 and 0.04 Å−1 (Q = |Q| = |k − k0|, where k0 and k are wave vectors of the incident and scattered neutrons, respectively, and |k| = k0 = 2π/λ). The horizontal and vertical widths of the 2D resolution functions, ΔQx and ΔQy, were 0.0031 and 0.0047 Å−1, respectively, for the 4 m collimation, and 0.00084 and 0.00119 Å−1, respectively, for the 16 m collimation.

The cuboidal precipitates in the ZS26 superalloy grow with edges parallel to the (100) crystallographic directions of the single crystal. As the evaluation of 2D anisotropic scattering curves is considerably easier if one of these directions is parallel to the incident neutron beam, each sample was oriented by X-ray Laue method before the measurement so that the crystallographic direction [001] of the single crystal was parallel to the incident-beam axis.

Examples of the measured 2D anisotropic scattering data are presented in Fig. 1, together with the fitted curves, which are discussed later in the text.

3. Microstructural model

Generally, in order to interpret the results of SANS measurements in detail, an appropriate model representing the morphology of the particles has to be chosen. A previous modelling of the scattering curve of perfect
cubic γ' precipitates and its comparison with the measured data has shown that this model does not fully correspond to the results of the SANS experiment; thus an improved model had to be applied. TEM performed on a similar set of ZS26 samples (Zrník, Hazlinger, Ztiňanský & Wang, 1994) indicated a possible method for the creation of the appropriate model. We focused on a shape variation from the exact cubic form and partly on an angular misorientation of the precipitates. These two effects can influence the SANS pattern to a great extent.

For data evaluation, a model of cuboids arranged on a square grid was used. The model of one particle was based on a spatial intersection of three identical and mutually perpendicular objects, where the object is something between a cylinder and a column having a square base. The resulting model was a cube having rounded surfaces and edges. The ratios \( r_1/a \) and \( r_2/a \), where \( r_1 \) and \( r_2 \) are the radii of curvature of the surfaces and edges, respectively, of the cuboid, and \( a \) is the original edge size of the cube, are two parameters that fully describe the shape of this object. Fig. 2 shows the meaning of the variables \( r_1/a \) and \( r_2/a \). Therefore, it is useful to introduce a dimensionless parameter \( q \), which describes how closely the precipitate shape approaches the perfect cube.

Another reason for introducing this parameter is the fact that rounding of the surfaces and rounding of the edges are mutually interchangeable for shapes that deviate greatly from the cubic form. This means that nearly the same particle shape can be obtained using different pairs of \( r_1/a \) and \( r_2/a \). We suggest the parameter

\[
q = \left[ \frac{o_1}{(o_1 + o_2)} \left( 2^{1/2}a/2r_1 \right) + \frac{o_2}{(o_1 + o_2)} \right] (2r_2/a),
\]

which depends only on the ratios \( r_2/a \) and \( r_1/a \) (\( o_1 \) and \( o_2 \))

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**Fig. 1.** Measured (dashed lines) and fitted (solid lines) curves for samples 2 and 5 (see Table 1): (a) sample 2, SDD = 4 m, (b) sample 2, SDD = 16 m, (c) sample 5, SDD = 4 m, (d) sample 5, SDD = 16 m (the crystallographic direction \([100]\) was parallel to the horizontal edge of the PSD in cases (c) and (d) and tilted by 45° in cases (a) and (b)). The \( Q \) ranges on both the horizontal and vertical axes are in \( \text{Å}^{-1} \). Displayed contour lines correspond to the equidistant levels of the macroscopic differential cross section \( d\Sigma/d\Omega \) (cm\(^{-1}\) sr\(^{-1}\)) in the logarithmic scale.
are also dependent only on these ratios). It provides simple, but to a great extent satisfactory, information about the precipitate shape. The parameter \( q \) ranges from 0 (for the perfect cube) to 1 (for the shape most distinct from the cube: \( r_1/a = 2^{1/2}/2 \) or \( r_2/a = 1/2 \)). The latter case can be reached by a complete rounding of surfaces or, equivalently, edges. The precipitates in measured ZS26 superalloys create rather dense systems (total volume fraction \( C_p \approx 60\% \) or greater) and, moreover, they are ordered into a cubic grid. Therefore, it is necessary to take into account interparticle interference between the precipitates, at least at low \( Q \) values. This phenomenon was treated automatically in the evaluation by putting a set of the model particles into the 3D real-space array in which computations were performed. The center-to-center distance, \( l \), between the particles then became another parameter of the model.

The planes coinciding with interfacial surfaces of the cuboids in the real sample are not mutually ideally parallel or ideally perpendicular [see, e.g., the TEM micrographs in the paper by Zrník, Hazlinger, Žitnianský & Wang (1994)]. We simulated this effect by an orientation distribution of precipitates around the axis parallel or ideally perpendicular to the incident neutron beam. It should be noted that this is only an approximation of the real spatial misorientation. The employed orientation distribution was described by a Gaussian function with a full width at half-maximum (FWHM) of \( \Delta \psi \).

Heat treatment of Ni-based superalloys in several steps frequently gives rise to a second population of precipitates having relatively small size [see, e.g., Sequeira, Calderon, Kostorz & Pedersen, 1995]. However, the model used for the evaluation of our data considers only the influence of large particles on the SANS pattern. The reasons are twofold:

(i) There is no indication of the influence of small particles on the scattering curve in the measured \( Q \) range.

(ii) Computer simulations proved that the volume fraction of the small precipitates (up to 3\%) does not influence the scattering curve of the large particles (a higher volume fraction is not expected in samples containing a large number of large precipitates surrounded by depleted zones).

### 4. Evaluation

Complete data evaluation was performed using the procedure described by Strunz & Wiedenmann (1997). The scattering curve corresponding to the model described above, smeared by wavelength distribution, by instrumental curve and by multiple-scattering effects, was computed numerically and then fitted to the experimental data by using the least-squares method.

Because of the expected size of the precipitates (>3000 Å), it was supposed that the measurements performed at the 4 m SDD covered the asymptotic part of the \( Q \) range in which the shape of the 2D scattering curves was not influenced by the size and distance of the particles. In this way, we were able to determine an average shape of the \( \gamma' \) precipitates, represented by the parameter \( q \), for each sample. However, the scattering curve is also influenced by the misorientation of the precipitates, which has, to some extent, a similar effect to surface rounding.

On the other hand, some influence of the precipitate size and arrangement on the scattering at the 16 m SDD can be expected. The modelled scattering curves exhibit a higher sensitivity to the thickness of the \( \gamma' \)-phase layer between the precipitates \( s \) than to the size of the precipitates. This is because the predicted thickness \( s \) is significantly smaller than \( a \).

The parameters \( l \), \( s \) and \( a \) are mutually connected by the relation \( l = s + a \) (for simplicity, we do not consider any size distribution in this explanation). Because of this relation, a change of \( l \) has an effect on the parameters \( s \) and/or \( a \) and it can thus also influence the scattering curve. Among the three parameters, \( s \) can be directly evaluated from our measurements. The possibility of refining the size (which is equal to the difference \( l - s \)) is conditional on the knowledge of \( l \).

As the distance between precipitates can be determined by using double-bent-crystal (DBC) SANS measurements (Strunz, Lukáš, Mikula, Šaroun, Keilová & Kočík, 1994), we performed a complementary experiment using the DBC SANS diffractometer V12 of BENSC, at HMI, Berlin, on the same set of samples (Strunz, Šaroun, Mikula, Lukáš & Eichhorn, 1997). Then we used the values of \( l \) determined from that experiment for the consequent evaluation of the pin-hole SANS data.

The measurements with the 16 m SDD are also influenced by the misorientation \( \Delta \psi \), as well as by the surface and edge rounding. However, the rounding does not play an important role in this case. Therefore, the measurements were evaluated in the following sequence:

![Fig. 2. The geometrical description of the cut through the center of the precipitate model. The square represents the projection of the original cube, \( o_1 \) and \( o_2 \) are the lengths of the arcs which correspond to the surface and the edge part of the cuboid, respectively; \( r_1 \) and \( r_2 \) are the radii of curvature of the surfaces and edges, respectively.](image-url)
Table 1. The applied heat treatments and parameters of the ZS26 samples

N₂ means cooling in liquid nitrogen. q is the shape parameter, Δψ is the FWHM of the orientation distribution, l is the center-to-center distance of precipitates (found by means of DBC SANS), aₒ is the mean size of the precipitates, Δs/sₒ is the relative FWHM of the distribution of the y-phase layer thickness, c is the geometrical volume fraction and Δρ is the scattering contrast calculated using c.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat treatment</th>
<th>q</th>
<th>Δψ (°)</th>
<th>l (Å)</th>
<th>aₒ (Å)</th>
<th>Δs/sₒ (%)</th>
<th>c</th>
<th>Δρ (10⁸ cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>1493 K/4 h/N₂</td>
<td>0.32</td>
<td>26</td>
<td>7200</td>
<td>6000</td>
<td>110</td>
<td>0.41</td>
<td>4.2</td>
</tr>
<tr>
<td>10</td>
<td>1553 K/4 h/N₂</td>
<td>0.28</td>
<td>30</td>
<td>6300</td>
<td>5480</td>
<td>110</td>
<td>0.50</td>
<td>3.7</td>
</tr>
<tr>
<td>2</td>
<td>1553 K/12 h/N₂ + 1323 K/16 h/N₂ + 1033 K/16 h/furnace</td>
<td>0.43</td>
<td>35</td>
<td>10100</td>
<td>9920</td>
<td>64</td>
<td>0.71</td>
<td>3.7</td>
</tr>
<tr>
<td>1</td>
<td>1553 K/8 h/N₂ + 1433 K/6 h/N₂ + 1033 K/12 h/furnace</td>
<td>0.33</td>
<td>31</td>
<td>10800</td>
<td>10310</td>
<td>56</td>
<td>0.70</td>
<td>3.9</td>
</tr>
<tr>
<td>5C</td>
<td>1553 K/12 h/N₂ + 1433 K/6 h/N₂ + 1033 K/12 h/furnace</td>
<td>0.24</td>
<td>15</td>
<td>13300</td>
<td>13040</td>
<td>45</td>
<td>0.79</td>
<td>4.3</td>
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<tr>
<td>4</td>
<td>1553 K/8 h/N₂ + 1433 K/6 h/N₂ + 1153 K/12 h/furnace</td>
<td>0.15</td>
<td>14</td>
<td>10600</td>
<td>9980</td>
<td>69</td>
<td>0.75</td>
<td>4.3</td>
</tr>
<tr>
<td>5</td>
<td>1553 K/12 h/N₂ + 1433 K/6 h/N₂ + 1113 K/16 h/furnace</td>
<td>0.12</td>
<td>17</td>
<td>10600</td>
<td>9970</td>
<td>41</td>
<td>0.76</td>
<td>4.4</td>
</tr>
</tbody>
</table>

(i) 4 m SDD measurements with fixed parameters aₒ and Δψ and with free r₁/a and r₂/a.
(ii) 16 m SDD measurement with fixed parameters l, r₁/a and r₂/a and with free Δψ, s₀ and Δs (s₀ is the mean thickness of the y-phase layer and Δs is the FWHM of a size distribution of the thickness s; this distribution was approximated by a Gaussian function in the evaluation procedure).

This sequence was repeated several times in order to allow the parameters to converge to the final values.

5. Results and discussion

The results of the refinement for the individual samples are presented in Table 1. The size of the precipitates is derived from the parameter l and the corresponding fitted value of s₀. Although the fitting of s₀ was performed relatively precisely, the overall e.s.d. of aₒ is ±4% due to the uncertainty of the l value. Fig. 3 displays projections of the real-space models corresponding to the fitted curves (see Fig. 1) for two of the measured samples.

Fig. 4 shows the TEM micrographs of the ZS26 microstructure for two different heat treatments. The parameters found by SANS (size, distance and shape of the precipitates) correspond well with those observed in these pictures (cf. Table 1, Fig. 3). The sizes of the precipitates found by means of SANS were also compared with the sizes derived from TEM experiments performed on the similar set of samples (Znik, Hazlinger, Žitňanský & Wang, 1994). While we found the size of precipitates to be about 1 μm in the samples heat treated in three steps, the TEM experiment suggested sizes of 0.7–0.85 μm. The discrepancy can be explained either by a slightly different heat treatment (our samples were cooled in liquid nitrogen whereas the older ones were water quenched) or by the different character of the results. The TEM experiments yield information from one planar section of the sample and the observed size distribution is number-weighted. On the other hand, SANS provides bulk-averaged information and the size distribution is volume-weighted (this causes a shift of the center of the size distribution towards the larger particles). In these circumstances, SANS results are in good agreement with those of TEM studies.

The combination of pin-hole SANS and DBC SANS measurements enables computation of the geometrical volume fraction c of precipitates using only the geometrical parameters of the microstructure determined from the two complementary experiments. This means that knowledge of the scattering contrast Δρ (which can be strongly affected by different heat treatments) is not necessary in this case. If the y' precipitates are spread homogeneously over the whole irradiated sample volume, the total volume fraction is equal to the geometrical volume fraction (cₚ = c). On the other hand, if there exist some parts in the sample without y' precipitates, c would be greater than cₚ and it is necessary to know Δρ for a proper calculation of the value of cₚ. However, the distribution of precipitates in ZS26 heat treated in three steps can be assumed to be homogeneous.

Table 1 contains the computed values of c. The e.s.d. of the parameter c is about ±10%. Under the assumption cₚ = c, this SANS measurement provides the volume

![Fig. 3. Projection of the real-space model of the microstructure of (a) sample 2 and (b) sample 5 to the PSD plane.](image_url)
fraction of precipitates. It can be determined also by TEM but with a rather large error, particularly for particles which are not cubic or spherical and which are not distributed randomly (Fährmann, Fratzl, Paris, Fährmann & Johnson, 1995). When \( c_p \) is known, the scattering contrast \( \Delta \rho \) can be derived, too (see Table 1).

### 6. Conclusions

Although SANS experiments performed on single-crystal samples can be in some cases evaluated by means of standard methods for isotropic scattering (Sequeira, Calderon, Kostorz & Pedersen, 1995), the strong anisotropy of the 2D data does not allow this simplification in the present case. Moreover, the anisotropic SANS pattern carries more information (Kostorz, 1991) than the isotropic one (e.g. shape and arrangement of the precipitates). The present evaluation procedure can be employed, with some modifications, for treatment of data from other SANS experiments that yield anisotropic data. However, the procedure could be improved. For example, in some cases the spatial misorientation of particles instead of the misorientation around the beam axis could enhance the correspondence of the model and real microstructures.

Finally, we summarize the relations between the applied heat treatment and the resulting microstructure:

(i) The precipitates in the samples heat treated by the three-step procedure (see Table 1) exhibit either nearly cubic form (samples 4, 5 and 5C) or more spherical shape (samples 1 and 2). It is obvious that the main influence on the shape can be related to the second step of the heat treatment. This confirms TEM observations for the ZS26 superalloy (Zrnik, Hazlinger, Žišnansky & Wang, 1994). The samples with the nearly cubic shape of the precipitates (i.e. the shape yielding the best mechanical properties of the superalloy) also exhibit the smallest misorientation of the \( \gamma' \) cuboids.

(ii) TEM micrographs suggested the butterfly morphology as the most appropriate model for precipitates in the samples heat treated in one step only (samples 10 and 12). The applicability of this model has been confirmed by the SANS experiment.

(iii) The three-step heat-treatment procedure leads to large precipitates (size about 1 \( \mu \)m) and to large volume fractions (above 70%), while the one-step procedure results in precipitates with sizes of approximately 0.55 \( \mu \)m and occupying approximately 45% of the volume.

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