"IN SITU" SMALL ANGLE NEUTRON SCATTERING STUDY OF

γ' PRECIPITATES IN AM1 SUPERALLOY SINGLE CRYSTALS

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Abstract

"In situ" experiments have been performed using Small Angle Neutron Scattering to study the coalescence and the precipitation of the γ' phase on AM1 superalloy. From the analysis of the position and of the shape of the correlation peaks the coarsening and ordering of the precipitates during heat treatments are determined. The influence of the cooling rate on the precipitation of the γ' phase is demonstrated. Comparison with measurement obtained by wide angle diffraction experiments is suggested.

Introduction

In superalloys prepared for single crystal applications and containing a high volume fraction of γ' phase, it has been shown that the mechanical properties strongly depend on the morphology of the precipitates and on their changes when they are submitted to thermo-mechanical treatments. For instance improved mechanical properties have been observed for the superalloy CMSX2 with cuboidal γ' precipitates of 0.45 μm edge-size (1). In these complex materials, the shape, the size and the arrangement of the precipitates are controlled by numerous external and internal parameters. The coalescence is controlled by the chemical composition, by the type of heat treatments and is also sensitive to applied stresses. Moreover, microscopic quantities are also of importance such as the value and the sign of the lattice parameter mismatch (2) and possible chemical inhomogeneities associated with the dendritic structure (3), but their respective role is not completely clear. For instance tetragonal distortions of the lattice of the γ and/or γ' phases have been observed in crept samples by X-ray (4) and neutron diffraction (5), but it is difficult to decide if they are associated to relaxations of internal stresses in the rafted precipitates or if they are at the origin of the rafting as suggested in (6). Thus one can expect that the microscopic mechanisms could be better understood by high temperature studies of the morphology and the structure of γ' precipitates and of their kinetics of evolution.

Among the techniques used to investigate the morphology of the precipitates, electron microscopy is the most usual but it needs destructive thinning of the specimen in the case of TEM and is limited to surface studies in the case of SEM. Furthermore, in both cases, only a small part of the sample can be observed and "in situ" thermo-mechanical treatments are difficult to perform. We have used small angle neutron scattering (SANS) which yields bulk averaged information in a non destructive way, through relatively thick samples.

In a previous paper (7) results obtained at room temperature on specimens submitted to different thermo-mechanical treatments have shown the capability of this technique which takes advantage of the single crystal nature of the material. Indeed it permits an analysis of the anisotropy of the SANS patterns and also gives further information when the orientation of the sample with respect to the incident neutron beam is changed. The small q -range provides information on the centre-to-centre correlations between γ' precipitates, while asymptotic behaviours in the intermediate q -range are determined by the shapes of the interfaces between γ and γ' phases. Among the results reported so far, we recall:

- the characteristic change of the SANS patterns from fourfold to twofold symmetry when the precipitates evolve from cuboids to platelets,
- the evolution of the position of the correlation peaks due to the coalescence of the precipitates during annealing,
- the appearance of unexpected diffuse streaks which are probably associated with truncatures of the corners of the cuboids (after 128 hours of annealing at 1050°C).

In this paper, we first report complementary room temperature measurements of samples annealed at 1100°C for different times. Then we report "in situ" observations of (i) the first stage of the coalescence of the γ' precipitates at 1150°C and (ii) the precipitation of the γ' phase as a function of the cooling rate from 1300°C.

Sample description and experimental procedure

We have investigated AM1 superalloy (8). Its melting point is 1350°C and the γ' phase dissolves at about 1290°C (9). After quenching, the volume fraction of the γ' phase is about 70 % at room temperature, and it remains almost constant upon heating to 1000°C. For this superalloy, the usual heat treatments which produce cuboidal precipitates with a mean edge-

size of 0.45 μm and an optimum spatial arrangement is 1100°C / 5 h and then 870°C / 16 h.

All our samples were cut from the same single crystal with a cylindrical shape (diameter 13 mm) grown at the SNECMA foundry by directional solidification. The growth axis was parallel to the $\langle 001 \rangle$ crystallographic direction. A homogenizing heat treatment (4 h at 1300°C) and quenching in air were performed in order to obtain small size γ' precipitates. The crystal was cut by spark erosion in the form of disks of thickness 1 mm perpendicular to the $\langle 001 \rangle$ axis. One disk was kept on hand for "in situ" experiments, while the others were annealed at different temperatures, for different durations.

The SANS experiments were performed on the D11 instrument at the Institut Laue Langevin (10,11) using the following configuration :

Sample-detector distance 35 meters
Collimation length 40 meters.

With the selected wavelength $\lambda = 10 \text{ \AA}$, (FWHM 9 %) the accessible scattering vector range

is $6 \cdot 10^{-4} \text{ \AA}^{-1} < q < 6 \cdot 10^{-3} \text{ \AA}^{-1}$, with $q = \frac{4\pi \sin \theta}{\lambda}$ and 2θ the scattering angle.

From the chemical composition of each phase (12), the following average scattering lengths were calculated :

$$b_{\gamma} = 0.75 \cdot 10^{-12} \text{ cm}$$

$$b_{\gamma'} = 0.83 \cdot 10^{-12} \text{ cm}$$

Due to this noticeable difference, the superalloys produce intense neutron scattering at small angles. Thus, with the high neutron flux of the ILL, measurements could be performed in a few minutes. This time, which is short enough compared to the coalescence rate of the γ' precipitates in the temperature range studied, thus permits "in situ" measurements. These have the further advantage of using the same sample without modification of orientation with respect to the neutron beam. For the purpose of "in situ" measurements, a furnace was built and adapted to the small angle facility. Its principle is similar to standard ILL furnaces (10) but special care was taken to prevent spurious diffuse scattering by the sample environment. Only a sapphire window is added in the neutron path and a boron nitride sample holder is used which serves also as a diaphragm, thus making the parasitic scattering from the furnace negligible (see Fig.3). The operating temperature ranges from room temperature to 1300°C. Temperatures were measured with a W-Rh thermocouple and the dissolution of the γ' phase, which is easily observed, was used for calibration.

Experimental results

Coalescence of the γ' precipitates

The coalescence of the γ' phase precipitates was studied at two annealing temperatures. At 1100°C, the kinetics of coalescence is rather slow, so the measurements were not performed "in situ". Four selected SANS patterns are shown in Figure 1. They illustrate the main features of the evolution which were observed from the initial state (a) up to 100 hours of annealing (d). Although the background scattering is small compared to the scattered intensity, it was subtracted, taking into account the slight difference in thickness between samples.

Similar measurements for the "in situ" experiment at 1150°C are shown in Figure 2. A difference is observed between the two initial states of the Figures 1 and 2. This is attributed to a beginning of the coarsening during the heating of the sample which took about 30 minutes from 900°C to 1150°C, due to the inertia of the furnace.

Figure 1- SANS iso-intensity contours obtained from AM1 samples annealed at 1100°C for a) 0 mn b) 1 h 30 mn, c) 9 h 30 mn, d) 100 h.

Figure 2- SANS iso-intensity contours obtained "in situ" from AM1 samples annealed at 1150°C for a) 0 mn, b) 15 mn, c) 1 h 30 mn, d) 5 h.

Except for this small difference in the initial conditions, similar qualitative evolutions of the scattering patterns are observed in the two experiments.

Their main features are :

- the strong anisotropy of the iso-intensity contours with a marked fourfold symmetry and a build up of elongated streaks along the $\langle 100 \rangle$ cubic directions.
- the observation of correlation peaks along the $\langle 100 \rangle$ directions (and in some cases along the $\langle 110 \rangle$ directions).
- the evolution of the shape and of the position of these correlation peaks.

Precipitation of the γ' phase

Afterwards, the same sample was used to study the precipitation of the γ' phase after dissolving at high temperature. "In situ" measurements were performed during cooling from 1300°C to 1150°C with rates of 60 K/mn and 2.5 K/mn .

It is shown in Figure 3 a that the scattered intensity at 1300°C is very weak, confirming the low value of the background. The strong influence of the cooling rate on the precipitate morphology is clearly shown by the two iso-intensity contours at 1150°C . For slow cooling, the fourfold symmetry has practically disappeared and the correlation peaks are not observed. From the results obtained by electron microscopy (13), this is interpreted by a large size of the precipitates; thus the correlation peaks cannot be resolved because they are too close to the direct beam. Comparable results have been obtained in a second series of measurements during cooling from 1300°C to 950°C with rates from 190 K/mn to 12.5 K/mn .

Figure 3- Shape of a) SANS iso-intensity contours from AM1 sample and b) wide angle neutron diffraction patterns from CMSX2 sample after precipitation at slow and fast cooling rate.

Discussion

Coalescence of the γ' precipitates

As discussed previously in ref.(7), the fourfold symmetry of the iso-intensity contours of Figures 1 and 2, indicates that both the shape and the arrangement of the precipitates evolve with a strong anisotropy along the crystallographic directions of the specimen. The observation of correlation peaks along the $\langle 100 \rangle$ directions (and in some cases along the $\langle 110 \rangle$ directions) shows that the precipitates are rather regularly arranged on the nodes of a simple cubic "superlattice" of parameter L , parallel to the crystallographic fcc lattice. The value of L , which corresponds to the average centre-to-centre distance of the precipitates, is deduced from the position q^* of the correlation peaks (Figure 4) using the relation $L \approx 2\pi / q^*$. Table I shows the evolution of L as a function of the annealing time for the two temperatures. According to LSW theory the following behaviour is expected (14):

$$L^3(t) - L^3(0) = K_0 \cdot t \cdot \exp\left(-\frac{Q_a}{R \cdot T}\right)$$

where

t is the annealing time

T is the annealing temperature (in Kelvin)

Q_a is an activation energy

K_0 is a prefactor supposed to be almost temperature independent

annealing time at 1150°C	L (μm)	q^* ($10^{-3} \text{ \AA}^{-1}$)	annealing time at 1100°C	L (μm)	q^* ($10^{-3} \text{ \AA}^{-1}$)
0 mn	0.35	1.81			
15 mn	0.35	1.81	1 h 30 mn	0.33	1.90
30 mn	0.39	1.61	5 h 30 mn	0.40	1.57
1 h	0.43	1.47	9 h 30 mn	0.44	1.43
2 h 30 mn	0.55	1.14	15 h 30 mn	0.53	1.19
5 h	0.67	0.94	24 h	0.59	1.06

Table I- Centre-to-centre spacing L between precipitates and position of the correlation peaks q^* for different annealing times at 1150°C and at 1100°C.

Figure 4- Intensity profiles along the $\langle 010 \rangle$ axis obtained from the iso-intensity contours for different time of "in situ" annealing at 1150°C.

Figure 5 shows that this relation is satisfied during the first stages of the coalescence and that the values of the slope for both temperatures are in agreement with other determinations (15). From these results and complementary measurements performed between 1000°C and 1200°C a value of the activation energy has been estimated: $Q_a=340$ kJ/mole ($Q_a=3.5$ eV) in agreement with previous determinations (15,16).

Figure 5- Evolution of the average volume of the γ' precipitates versus annealing time (■) at $T=1100^\circ\text{C}$ and (○) at $T=1150^\circ\text{C}$.

Figure 6- a) Schematic representation of the longitudinal broadening $\Delta q_{//}$ and of the transverse broadening $\Delta q_{\perp}$ chosen to measure respectively the distribution of interdistances of precipitates and the distribution of orientation of the centre-to-centre vectors
b) Evolution of $\Delta q_{//}$ and of $\Delta q_{\perp}$ versus annealing time at 1150°C , the dotted line represents the order of magnitude of the instrumental broadening.

The shape of the correlation peaks was also analysed by means of their full width at half maximum (FWHM). For a complete analysis, both the widths perpendicular and parallel to the scattering vector have to be measured. Indeed $\Delta q_{//}$ corresponds to a distribution of interdistances of the precipitates while $\Delta q_{\perp}$ is associated to the distribution of orientation of the centre-to-centre vectors. In order to minimize the instrumental broadening due to the divergence and the size of the neutron beam, $\Delta q_{//}$ was estimated from the (010) peak and $\Delta q_{\perp}$ from the (100) peak (see Fig.6 a). The results as a function of time for the "in situ" annealing are reported in Figure 6 b where the instrumental resolution is also indicated. For both full-widths a rather fast decrease is observed during the first hour of annealing indicating an ordering of the precipitates along the crystallographic axes. At longer times the value of $\Delta q_{\perp}$ becomes close to the instrumental resolution and one can estimate that the distribution of orientation of the centre-to-centre vectors is smaller than 5 degrees; while the distribution of interdistances of the precipitates $\Delta L/L$ remains noticeable in consistency with the weakness of second order reflections. Comparable results have been obtained for the annealing at 1100°C but the ordering is reached after about 5 hours which corresponds to the heat treatment recommended by SNECMA for the AM1 superalloy.

Precipitation of the γ' phase

For the slow cooling rate the size of the precipitates is much larger than 0.7 μm and could not be measured with the present experimental set-up. Thus in the observed q range ($q \gg q^*$) the almost isotropic shape of the iso-intensity contours shows that the shape of the precipitates is far from that of a cube. In the case of fast cooling rate the existence of weak correlation peaks and the fourfold symmetry of the intensity contours indicates the presence of small precipitates (0.4 μm) with a rather regular arrangement and a shape not far from that of a cube. In this case the precipitation is controlled by nucleation instead of coalescence. More systematic studies are needed to observe the transition between the two mechanisms. It is worth noting here that the influence of the cooling rate has also been observed by neutron diffraction at wide angle (17). Figure 3 b shows the results obtained on CMSX2 superalloy. The shape of the diffraction peaks, and therefore the lattice parameter mismatch between the two phases, depends on the cooling rate and it would be interesting to combine wide and small angle scattering from the same sample.

Conclusion

These results show the interest of the SANS technique which has the advantage of being non destructive and of averaging the measurements over a large number of precipitates ($\approx 10^{12}$). Moreover the possibility of performing "in situ" experiments permits one to work on the same sample with the same orientation and to study the kinetics of the coalescence without the necessity of quenching the structure at different stages of the evolution. As samples of a few millimeters of thickness can be studied by the SANS technique, measurements on the thin parts of turbine blades are possible. Thus characterization and control of the precipitation and of the coalescence of the γ' phase are feasible and in a next step, one can envisage a control of the "rafting" of the precipitates in turbine blades after operating cycles.

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