

CHARACTERIZATION OF THE EARLY STAGES OF PHASE SEPARATION BY ATOM PROBE TOMOGRAPHY

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ABSTRACT

An atom probe tomography characterization of the early stages of phase separation in the Fe-Cu-Ni system has been performed. The development of the copper-enriched regions into copper precipitates has been investigated during isothermal ageing at 573 K and 673 K for times up to 10,000 h. The formation and growth of the secondary precipitates in the nickel based superalloy, Alloy 718, have been determined during isothermal ageing at 873 K. These secondary precipitates were found to be a mixture of the $L1_2$ -ordered γ' phase and the DO_{22} -ordered γ'' phase.

INTRODUCTION

Atom probe tomography provides a unique real space experimental tool that may be used to characterize the earliest stages of phase separation in metal systems. In this instrument, the three-dimensional coordinates and the identity of the atoms in a small volume may be determined with near atomic precision [1]. The size, shape and composition of ultrafine features such as embryos and precipitates may be determined from the spatial distribution of the atoms. Due to the high spatial resolution of this technique, features at the subnanometer scale may be characterized. Therefore, the earliest stages of phase separation become accessible to experimental study. At the earliest stages of phase separation, it is difficult to classify whether a given aggregation of solute is in the form of a cluster, embryo or precipitate. This uncertainty arises because the experimental data are an instantaneous view of the solute distribution and it is not possible to ascertain whether a particular feature is metastable or unstable. Therefore in this paper, all aggregations of solute will be referred to as precipitates.

In this paper, the early stages of decomposition have been characterized in a Fe- 1.1% Cu- 1.4% Ni model alloy [2] and niobium-containing nickel based superalloy, Alloy 718. The Fe-Cu-Ni alloy is a model system for the technologically important steels used in the pressure vessel of a nuclear reactor. In these systems, the initial copper precipitates that form during low temperature ageing or neutron irradiation appear to be a metastable body centered cubic phase rather than the equilibrium face centered cubic γ -phase. Alloy 718 is a niobium-containing nickel base superalloy that obtains its high temperature strength from a dispersion of lenticular DO_{22} -ordered γ'' precipitates and roughly spherical secondary precipitates [3-8]. The secondary precipitates were determined to be a mixture of $L1_2$ -ordered γ' and DO_{22} -ordered γ'' phases.

EXPERIMENTAL

Two materials were characterized in this investigation. The first material was an Fe- 1.1 at. % Cu- 1.4% Ni model alloy that was annealed for 5 h at 1123 K and water quenched. Previous atom probe analysis revealed that the copper level in solution after this treatment was 0.91 ± 0.04 at. % Cu with a hardness of 79.2 ± 3.1 VPN [2]. The difference between the nominal composition and this measured value is due to some copper precipitation on grain boundaries and dislocations. This material was then isothermally aged at 573 K and 673 K for times up to 10,000 h. The composition of the Alloy 718 used in this investigation was Ni- 21.8 at. % Cr, 20.3% Fe, 3.2% Nb, 1.81% Mo, 1.15% Ti, 0.96% Al, 0.26% Co and 0.26% C. This material was given a standard heat treatment of 1 h at 1311 K. The alloy was investigated after subsequent isothermal ageing treatments at 873 K for times from 10 to 2,012 h. The specimens were water quenched to room temperature between each stage.

The materials were characterized in the ORNL energy-compensated optical position-sensitive atom probe (ECOPoSAP) [1]. Solute clustering and precipitation may be visualized by examining the distribution of the solute within the analyzed volume with the use of an atom map, as shown in Fig. 1a. Locally high solute concentrations indicate the presence of clusters or precipitates. In order to compare the data, a consistent method must be applied to establish whether an individual solute atom belongs to a precipitate or the matrix. The method adopted in this paper was to assign all solute atoms that are within a specific distance of one another to a precipitate and the remaining solute atoms are considered to be in solid solution in the matrix. The elimination of the isolated solute atoms in the matrix also improves the clarity of the atom map, as shown in Fig. 1b. The selection of the maximum separation distance requires care. If too large a value is chosen, some solute may be erroneously assigned to precipitates and some additional precipitates may be detected. If too small a value is chosen, the true extent of a precipitate may be underestimated and some precipitates may appear to be divided into two or more precipitates. Therefore, the value of the maximum separation distance was determined from three different sets of data. The first set was from data in which there were coarse precipitates. The second set was data obtained from the alloy aged for 5 h at 1123 K in which the distribution of solute should conform to a random solid solution. The third set was from simulated data of a random solid solution with the same mean copper concentration and detection efficiency as the experimental data. The relative numbers of precipitates containing different number of atoms for a series of maximum separations are presented in Table 1 for the second and third sets. The results from these two sets of data are in reasonable agreement indicating that the experimental data conformed to a random solid solution. From these three data sets, a value of 0.5 nm was selected for the maximum separation distance because it provided the optimum compromise between assigning all the copper atoms to a precipitate and minimized the creation of artificial precipitates.

Table 1. The relative numbers (in percent) of precipitates containing different numbers of atoms for a series of maximum separations for the Fe-Cu-Ni alloy aged 5 h at 1123 K and for a computer simulation of a random solute distribution with the same solute content (0.91 at. % Cu) and detection efficiency (65%) as the experimental data. Both data sets contain $\sim 10^6$ atoms.

Atoms	Fe-Cu-Ni alloy aged 5 h at 1123 K (850°C)					Computer simulation				
	0.3 nm	0.4 nm	0.5 nm	0.6 nm	0.7 nm	0.3 nm	0.4 nm	0.5 nm	0.6 nm	0.7 nm
1	97.4	94.2	89.8	84.8	77.5	96.2	96.2	85.1	83.9	74.8
2	2.4	5.2	8.2	11.6	14.9	3.6	3.6	12.2	12.8	16.2
3	0.2	0.60	1.6	0.75	4.6	0.27	0.27	2.0	2.4	5.4
4		0.01	0.30	0.33	1.5			0.50	0.66	2.3
5		0.03	0.08	0.10	0.69			0.12	0.14	0.64
6			0.03	0.02	0.40			0.02	0.08	0.33
7			0.03	0.02	0.19			-	0.02	0.17
8			0.02	0.02	0.06			-	-	0.07
9				0.03	0.06			0.02	0.02	0.02
10					0.10					0.02

The size of these precipitates was also determined from the distribution of the solute atoms in the precipitates. The radius of gyration, l_g , is given by

$$l_g = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2 + (y_i - \bar{y})^2 + (z_i - \bar{z})^2}{n}},$$

where x_i , y_i and z_i are the spatial coordinates of all atoms in that precipitate, n is the number of atoms associated with the precipitate. The center of mass (\bar{x} , \bar{y} , \bar{z}) of a feature, where all atoms are the same (i.e., the same mass) may be determined from [9]

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}, \quad \bar{y} = \frac{\sum_{i=1}^n y_i}{n}, \quad \text{and} \quad \bar{z} = \frac{\sum_{i=1}^n z_i}{n}.$$

The radius of gyration provides a parameter that is smaller than the actual size of the feature. The Guinier radius, r_G , which represents the actual size of the precipitate, is given by $r_G = \sqrt{5/3} l_g$.

RESULTS AND DISCUSSION

Fe-Cu-Ni Model Alloy

The relative numbers of precipitates containing different numbers of atoms for the low temperature aged Fe-Cu-Ni alloy are summarized in Table 2. In contrast to the random solid solution in the material aged for 5 h at 1123 K, all the ageing conditions examined exhibited several precipitates with more than 10 copper atoms. As phase separation proceeds, the number of larger copper precipitates increases at the expense of the individual and pairs of copper atoms in solid solution in the matrix. The largest precipitate observed in the material aged for 10,000 h at 573 K contained 95 copper atoms, exhibited a maximum copper concentration of 38% Cu, and had a radius of gyration of 0.77 nm and a Guinier radius of 1 nm. The nickel was found to be depleted in the core of the precipitate and enriched at the precipitate-matrix interface indicating rejection of nickel from the precipitate. In the material aged for 100 h at 673 K, approximately 30% of the copper was determined to be in precipitates containing between 10 and ~100 copper atoms. In this material, the largest copper precipitate encountered contained 96 copper atoms, exhibited a maximum copper concentration of 67% Cu, had a radius of gyration of 0.61 nm and Guinier radius of 0.79 nm. A comparison of this precipitate with the largest precipitate observed in the material aged for 10,000 h at 573 K reveals that although the precipitate in the material aged at 673 K contained a similar number of copper atoms, the maximum copper concentration was significantly higher but the size was smaller. This behavior is probably a result of kinetic limitations on the early stage of phase separation.

The various sizes of precipitates will have slightly different influences on the interactions with dislocations and hence the mechanical properties of the alloy. Therefore, the information on number and distribution of copper atoms associated with each precipitate should provide a more complete description of the microstructure and may be used to model the mechanical properties.

Table 2. The relative numbers (in percent) of precipitates containing different number of atoms for the low temperature aged Fe-Cu-Ni model alloy. Maximum separation = 0.5 nm.

Atoms within 0.5 nm	4,000 h 573 K	10,000 h 573 K	50 h 673 K	100 h 673 K
1	87.7	85.5	80.0	80.1
2	9.7	11.2	16.7	11.4
3	1.9	2.0	1.6	3.1
4	0.21	0.79	0.81	1.1
5	0.10	0.18	0.61	0.57
6	0.16	0.08		0.34
7	0.10	0.08		0.11
8	0.03			0.40
9		0.04		0.45
10	0.05	0.06	0.20	2.4
Hardness, VPN	91.9±5.6	96.0±5.0	94.9±5.0	129.4±8.0
Matrix Cu, at. %	0.80±0.05	0.63±0.01	0.71±0.03	0.54±0.08

Alloy 718

Previous atom probe and transmission electron microscope characterization of this alloy have revealed that no intragranular precipitation occurs during the 1 h at 1311 K heat treatment.

Lenticular primary DO₂₂-ordered γ precipitates are formed during a standard second stage heat treatment of 8 h at 1143 K [3-6]. No primary γ precipitates are formed when the standard second stage heat treatment is omitted as in the material investigated in this study. Roughly spherical secondary precipitates are formed in the γ matrix during subsequent isothermal annealing treatments at lower temperatures.

The evolution of the secondary precipitates during isothermal annealing at 873 K is shown in the isoconcentration surfaces shown Fig. 5. After 10 h and 2012 h of annealing at 873 K, the average diameters of the precipitates were determined to be ~1.8 and 11 nm, respectively. The coarsening of these secondary precipitates was found to follow a classical $t^{0.34}$ power law. Atom maps of sections through some secondary precipitates for the material isothermally aged for 10 and 2012 h at 873 K are shown in Fig. 6a and 6b, respectively. At the initial stage of precipitation, the solute distribution indicates that the precipitate was niobium-enriched indicating that the initial nucleus was the γ phase. After annealing for 2012 h, the secondary precipitates were not found to be uniform throughout their volume but to be divided into two distinct types of regions enriched in either niobium or in aluminum and titanium that are characteristic of the δ and ϵ phases, respectively.

CONCLUSIONS

The early stages of precipitation in a model Fe-Cu-Ni model alloy and the initial stages of secondary precipitate formation in Alloy 718 have been characterized by atom probe tomography. This microanalytical technique enables the size and composition of the initial precipitates to be determined.

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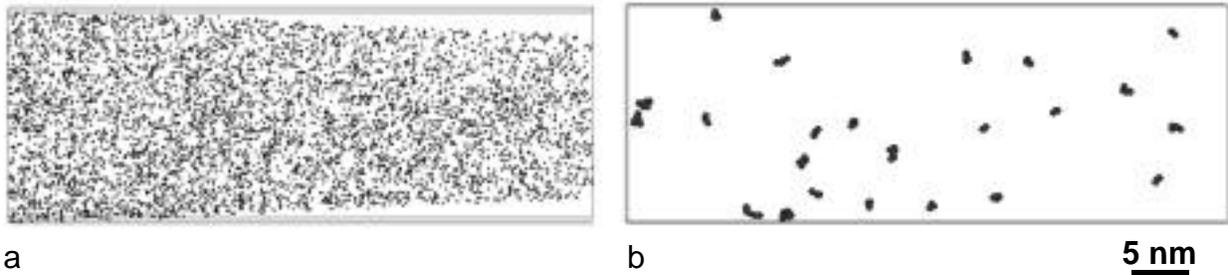


Fig. 1. Atom maps of the Fe-1.1% Cu-1.4% Ni aged for 5 h at 1123 K: a) all copper atoms; b) copper atoms that are within 0.5 nm of another copper atom.



Fig. 2. Atom map of the Fe-1.1% Cu-1.4% Ni alloy aged for 5 h at 1123 K and 4,000 h at 573 K. Only precipitates containing 4 or more copper atoms are shown.

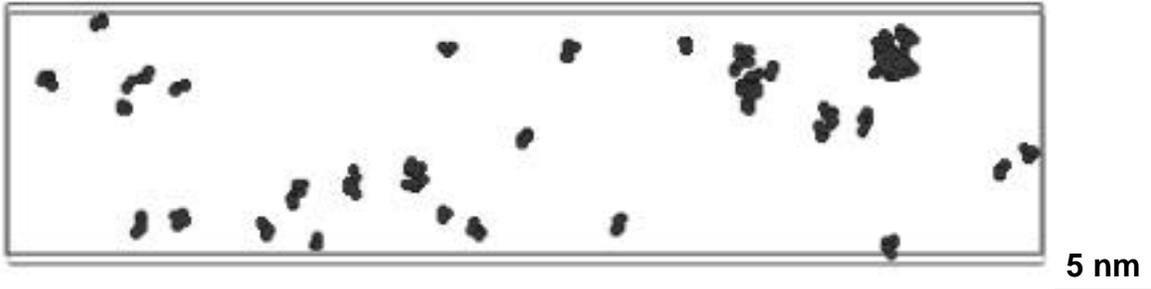


Fig. 3. Atom map of the Fe-1.1% Cu-1.4% Ni alloy aged for 5 h at 1123 K and 10,000 h at 573 K. Only precipitates containing 4 or more copper atoms are shown.



Fig. 4. Atom map of the Fe-1.1% Cu-1.4% Ni alloy aged for 5 h at 1123 K and 100 h at 673 K. Only precipitates containing 4 or more copper atoms are shown.

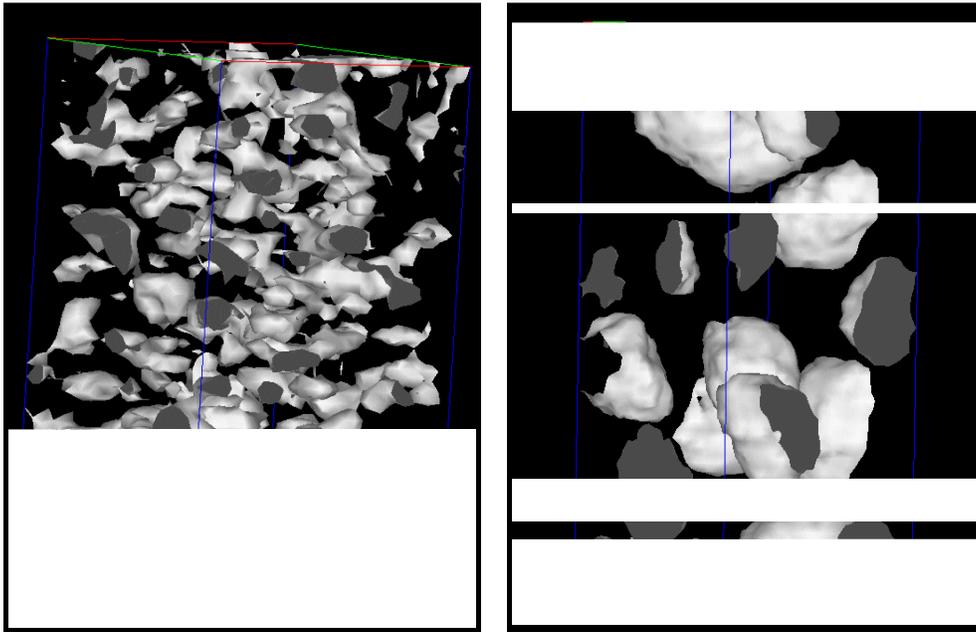


Fig. 5. Isoconcentration surfaces (Fe+Cr) outlining the secondary precipitates in Alloy 718 aged for 1 h at 1311K and a) 10 h and b) 2012 h at 873 K.

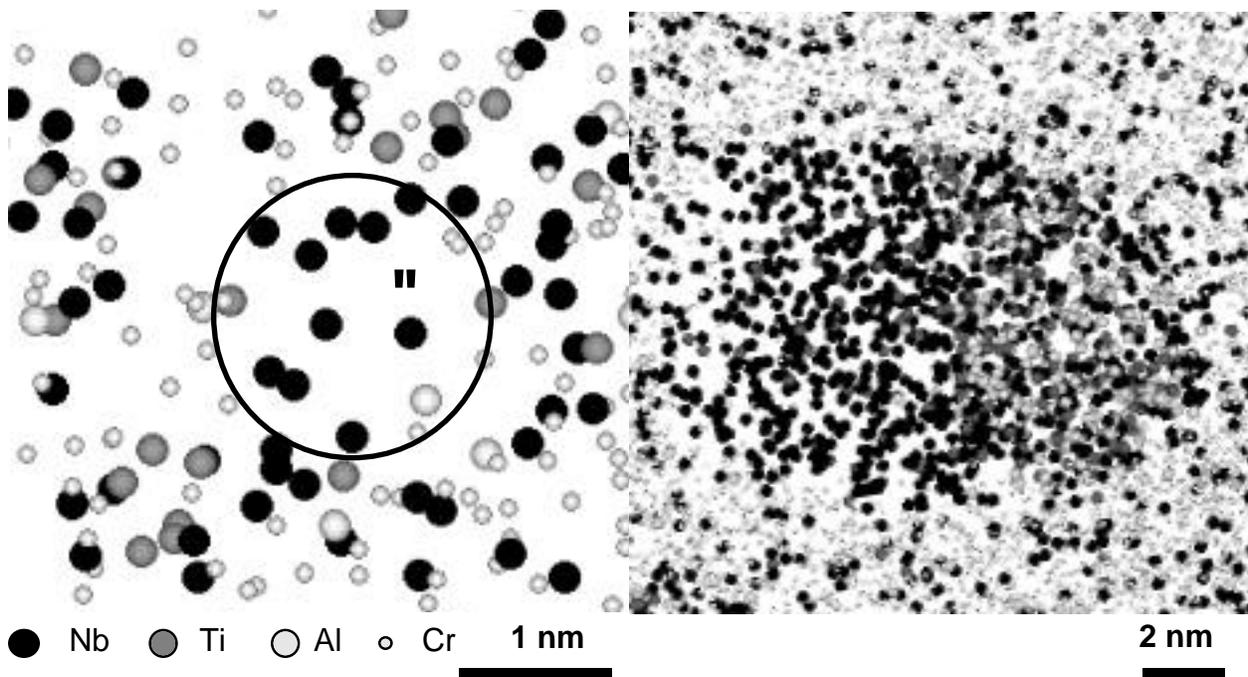


Fig. 6. Atom maps of the central region of secondary precipitates. a) A ~2-nm-diameter precipitate in Alloy 718 aged for 1 h at 1311K and 10 h at 873 K. The circle is a two-dimensional section through the Fe+Cr isoconcentration surface that denotes the approximate position of the precipitate. b) A precipitate in Alloy 718 aged for 1 h at 1311K and 2012 h at 873 K. Only Nb, Ti, Al and Cr atoms are displayed.