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DETERMINATION OF THE OXIDE PARTICLE DENSITY IN ODS ALLOYS BY MEANS OF TRANSMISSION ELECTRON MICROSCOPY

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ABSTRACT

Stereological estimation of second phase particle density N_V by means of transmission electron microscopy (TEM) has been carried out. Modern transmission electron microscopes, with the possibility of convergent-beam electron diffraction (CBED), allow accurate measurement of specimen thickness and therefore for particle density estimation. The method of thickness measurement using CBED is described in detail.

Quantitative TEM metallography has been performed on an ODS alloy, where second phase particles (oxides) are randomly but homogeneously distributed in the matrix. For the measured specimen thickness t of 115 nm and the estimated value of mean oxide diameter of $\overline{D} = 2.14 \cdot 10^{-5}$ mm, the estimated particle density N_V was $120.00 \cdot 10^{10}$ mm^{-3}.

Keywords: CBED, ODS alloys, particle density, TEM, thickness measurements

INTRODUCTION

A quantitative description of the microstructure of various materials is of great importance in many research programmes. The determination of particle density, particle size distribution and

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interparticle spacing as well as their variation with time is essential for estimation of the service life of materials. In many cases where quantitative information about a material's microstructure is required, the measurements are performed using transmission electron microscopy (TEM). Microstructural investigations of materials using TEM frequently involve the determination of the second phase particle density. This requires a direct and precise measure of the specimen thickness. The most accurate method of crystalline specimen thickness determination is a technique using convergent-beam electron diffraction (CBED) patterns. In the present investigations, the oxide particle density in an oxide dispersion strengthened (ODS) alloy INCOLOY MA956 has been determined using TEM-CBED. This is a part of broader studies on the strengthening mechanisms and high temperature oxidation properties of INCOLOY MA956 (e.g. Dubiel et al, 1997; Czyrska-Filemonowicz et al, 1995). INCOLOY MA956 is an Fe-20Cr-5Al-0.5Y_2O_3 alloy produced by a mechanical alloying process which provides a fine dispersion of the incoherent oxide particles in the ferritic matrix. The alloy exhibits outstanding strength and oxidation resistance at temperatures around 1000°C. For the application of MA956 at high temperatures, the strengthening and failure mechanisms are of considerable interest and therefore the methods of accurate measurement of microstructural parameters affecting these mechanisms (e.g. oxide particle density) are very important.

ESTIMATION OF PARTICLE DENSITY N_V USING TEM

In the ODS alloys, the oxide phase appears in the microstructure as discrete particles which are distributed in the material's space. To a first approximation, the particle shape can be regarded as a sphere and particles do not overlap in the projected image. Therefore, quantitative TEM metallography of the ODS alloys is based on thin section stereology of a dilute system of spheres, which are distributed randomly but homogeneously in space. An important parameter of the system is the particle density N_V, which gives the average number of particles per unit volume. Let D be the diameter of a sphere. Then $\overline{D}$, a mean diameter of the spheres is an additional parameter of the system. The system of particles is intersected by two parallel planes separated by a distance t. Only the projection of the parts of spheres lying between the top and bottom surfaces of a thin foil is observed. For low values of t and for dilute system of spheres, the overlapping of the projection circles can be neglected. In this case N_A is the projection circle density in the projected plane. If d is

the circle diameter, then $\overline{d}$ is the mean diameter of circles in the projected plane. The following stereological equation is well known (Cahn and Nutting, 1959; Ryś, 1995):

$$N_V = \frac{N_A}{t + \overline{D}} \quad . \tag{1}$$

The N_V estimation by TEM metallography which is based on Eq. (1) requires the measurement of the three values: N_A, $\overline{D}$ and t. If the projection circles do not overlap an unbiased N_A estimation can be performed by counting measurements in the observed image plane. Because of the particle section effect, there is a difference between the $\overline{d}$ value measured in the projected plane and the particle parameter $\overline{D}$. Let A_A and L_A be the projection area and perimeter density, respectively. When the particle diameters are smaller than t, then $\overline{D}$ for a dilute dispersion can be estimated approximately by the formula (Wiencek and Czyrska-Filemonowicz, 1997):

$$\overline{D} = \frac{\overline{d} \cdot t}{t - \overline{d} + \frac{\pi A_A}{L_A}} \quad . \tag{2}$$

It is important to notice that the parameters A_A and L_A in equation (2) can be easily calculated for a given set of empirical diameters d.

For the estimation of N_V, an accurate value of the specimen thickness t is significant.

SPECIMEN THICKNESS *t* DETERMINATION

Although thickness measurements, precisely done in the area of the analyses are very important, they are rarely done because of time, difficulties (e.g. for magnetic materials) and poor accuracy. There are several methods for thickness determination, such as trace analysis of projected defects, thickness fringes, the contamination spot technique (Lorimer et al.,1975), latex balls of known diameter (Heimendahl, 1973), EDS spectrum peak heights, intensity of EELS peaks and CBED. Reviews of those methods are given by Lorimer and Cliff (1984), Williams (1984) and Scott and Love (1987).

The most accurate method for thickness determination of crystalline specimens is from a CBED pattern technique. The procedure to determine the foil thickness from the fringes in

CBED patterns was firstly described by Kelly èt al. (1975) and developed in detail by Allen (1981). The detailed procedure is described by Scott and Love (1987) as well as by Williams and Carter (1996). It is also mentioned by Ryś and Garbarz (1990) in a paper describing CBED technique.

Fig. 1a shows a typical convergent beam electron diffraction (CBED) pattern taken under two-beam diffracting conditions.

From an experimental point of view, for accurate thickness measurement it is necessary to establish:

- a CBED pattern in which the discs do not overlap; the so-called Kossel-Möllenstedt CBED pattern (Kossel and Möllenstedt, 1939),
- good two-beam diffraction conditions,
- as the measurement is made in the direction of the incident beam, it is important that the angle of inclination of thin foil is known or, preferably, the specimen is not tilted.

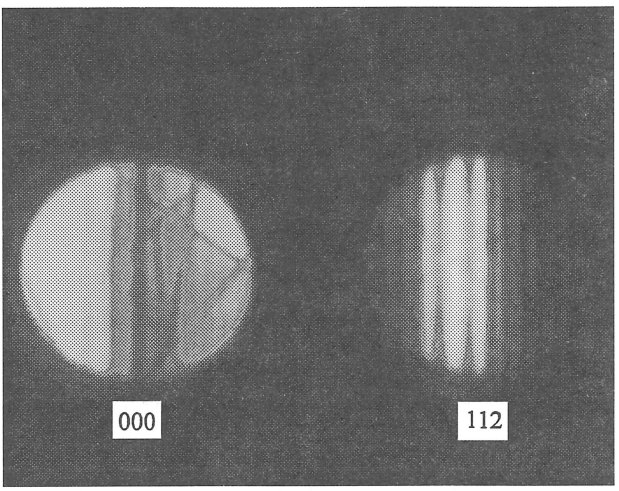

Fig.1a. Convergent-beam electron diffraction (CBED) pattern.

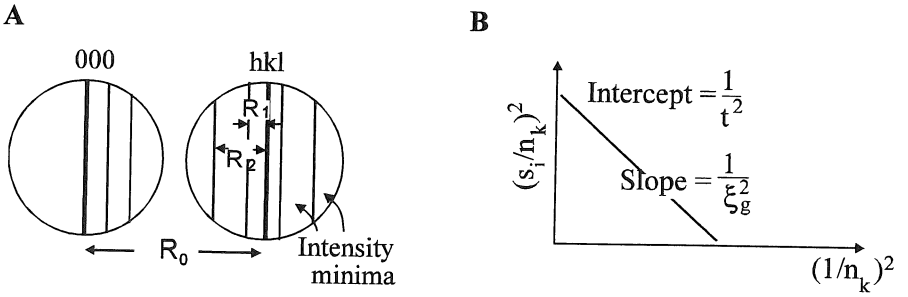

Fig.1b. Schematic diagram for measurements necessary to determine a foil thickness from CBED fringes (A) and plot $(s_i/n_k)^2$ against $(1/n_k)^2$ (B).

CBED patterns display the variation of diffracted intensity as a function of the angle between the incident electron beam and the diffracted beam. According to the two-beam dynamical theory of electron diffraction (e.g. Hirsch et al., 1965), the diffracted intensity is a function of the thickness of the sample, t, of the deviation parameter from the exact Bragg condition, s and of the extinction distance, ξ_g. As CBED discs reveal the intensity as a function of the parameter s, the two-beam dynamical condition generates parallel fringes („pendellösung" fringes; Reimer, 1989), where the deviation parameter s, continuously changes across the diffracted discs (the rocking curve). The maximum diffracted intensity will be observed for the incident beam which is exactly in the Bragg position ($s = 0$). As a result a bright line will appear in the middle of the diffracted disc. The visibility of fringes depends on the size of the diffracted disc (larger discs contain more fringes) as well as the electron probe size. The number of fringes, n, increases by one every time the thickness increases by one extinction distance, ξ_g. If the specimen is less than one extinction distance thick, the variation of intensity within the CBED discs disappears completely and the discs are uniformly bright (no fringes). Thus, for extremely thin specimens (e.g. for high resolution electron microscopy, HREM) the method is not useful. Fig. 1b shows the schematic diagram for measurements necessary to determine the foil thickness from a CBED pattern. The central bright fringe in the diffracted disc is at the exact Bragg condition when a deviation parameter $s = 0$. The fringe spacings are the successive position of the intensity minima relative to the Bragg position.

According to the two-beam dynamical theory of electron diffraction (Hirsch et al., 1965), the intensity minima occur in the diffracted disc when:

$$\frac{s_i^2}{n_k^2} + \frac{1}{\xi_g^2 n_k^2} = \frac{1}{t^2} \quad , \tag{3}$$

where:

- t - specimen thickness to be measured
- s_i - deviation for the ith fringe (i = 1, 2, 3, ..., n) from the exact Bragg position
- n_k - an integer that numbers the dark fringes (counting outwards from the bright middle line); k is given by $k = i + j$, where j is the largest integer $< (t/\xi_g)$
- ξ_g - extinction distance of an excited reflection g for hkl diffracted beam.

The s_i is defined as follows:

$$s_i = \frac{\lambda}{d_{hkl}^2} \cdot \frac{Ri}{R_0} \quad , \tag{4}$$

where:

- λ - electron wavelength
- d_{hkl} - hkl interplanar spacing
- R_0 - the distance from transmitted disc to hkl diffracted disc
- R_i - the distance from the centre of the diffracted disc to the ith dark fringe

If the extinction distance ξ_g for the reflection is known, the foil thickness t can be determined from equation (3). If the extinction distance ξ_g is not known, the graphical method by plotting the measurements for several fringes is used. The diagram shown in Fig. 1b is made by plotting $(s_i/n_k)^2$ against $(1/n_k)^2$. If n_k was chosen correctly, the plot would yield a straight line. If n_k is incorrect (at larger thickness, fringes 1, 2, 3 gradually disappear so the dark fringes n_k becomes 2, 3, 4 etc.) the n_k should be then increased until a straight line plot is obtained.

The intercept of the straight line corresponds to $(1/t^2)$, thus giving the foil thickness, while its slope is equivalent to $(-1/\xi^2_g)$ giving the extinction distances ξ_g.

The thickness measurements performed using CBED patterns are of high accuracy. If the pattern is magnified (or a 10x magnifier is used) it is easy to measure the distances between the bright excess line and each of dark fringes with an accuracy of about ± 0,1mm. The error of this method can be as little as 1-2% in the foil thickness. This procedure lends itself to computerization. It is possible to digitize the fringes on line by scanning the pattern across the STEM detector or use a CCD camera. The thickness measurement method by means of CBED - TEM is precise, repeatable and easy, however it is limited to crystalline specimens.

EXPERIMENTAL PROCEDURE

INCOLOY alloy MA956 was supplied by INCO Alloys International as hot extruded and recrystallized (1330°C/1 h) bars of 20 and 30 mm diameter. The composition of the alloy investigated was as follows (in wt %): 0.02 C, 0.09 Si, 19.8 Cr, 0.13 Ni, 0.03 Co, 0.31 Ti, 4.6 Al, 0.03 N, 0.52 Y_2O_3, bal. Fe.

Structural analyses were performed using optical metallography and TEM. Most of the TEM investigations of particles in the metallic matrix were performed using thin foils prepared from the material under examination. The methods for thin foil preparation are described elsewhere (e.g. Thompson-Russel and Eddington, 1977; Williams and Carter, 1996). Thin foils from INCOLOY MA956 were prepared by dimpling followed by electropolishing in a 10% solution of perchloric acid in glacial acetic acid at about 10°C and 50 V. The preparation of thin foils for quantitative TEM analyses has been performed very carefully to obtain flat and undistorted thin foils. The TEM investigations were carried out using a JEM 2010ARP microscope equipped with an energy dispersive X-ray spectrometer from Oxford Instruments.

A quantitative analysis of the microstructure of the material tested was performed on micrographs in test fields of a total area A = 144165 mm^2 at a magnification of 200 000. A diameter d was measured for each particle in the test area using an Opton's semi-automatic particle size analyser TGZ-3.

RESULTS AND DISCUSSION

The microstructure of the as-received INCOLOY MA956 (Fig. 2) consisted of mixed Y-Al oxide particles (dispersoids) and some larger precipitates of pure alumina and titanium carbonitrides in a ferritic matrix. The dominant finest particles, which influence the creep resistance, were mostly tetragonal $Y_3Al_5O_{12}$ (YAT). The oxide chemical composition was determined using an energy dispersive X-ray spectrometry (EDS) method. The quantitative analyses of the fine oxide parameters have been performed by means of TEM of thin foils prepared from different parts of the bar tested. The oxide particle density N_V was determined using equations (1) and (2). The parameters of the set of projected particles measured are as follows: the mean diameter $\bar{d} = 2.11 \cdot 10^{-5}$ mm, the particle density $N_A = 16.37 \cdot 10^7$ mm^{-2}, the area density $A_A = 0.074$ and perimeter density $L_A = 10.99 \cdot 10^3$ mm^{-1}.

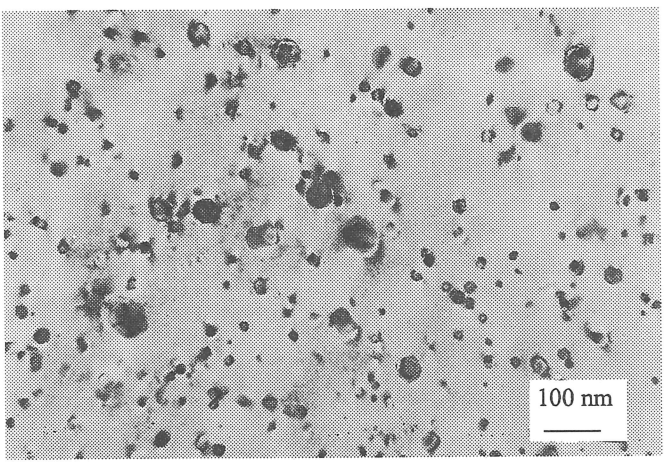

Fig.2. The microstructure of as received INCOLOY MA956.

Thin foil thickness t was determined using CBED patterns according to the method described previously. Fig. 3 a shows an example of a CBED pattern obtained from the area measured. In this pattern (photographically enlarged) the distance corresponding to R_0 is 66.1 $\pm$ 0.1 mm. In a diffracted disk nine dark fringes can be measured. The values used for thin foil thickness

determination are given in Table I. For the evaluation, the following values were taken: $\lambda = 0.00265$ nm (for the 200 kV accelerating voltage of the microscope), $d_{112} = 0.117$ nm.

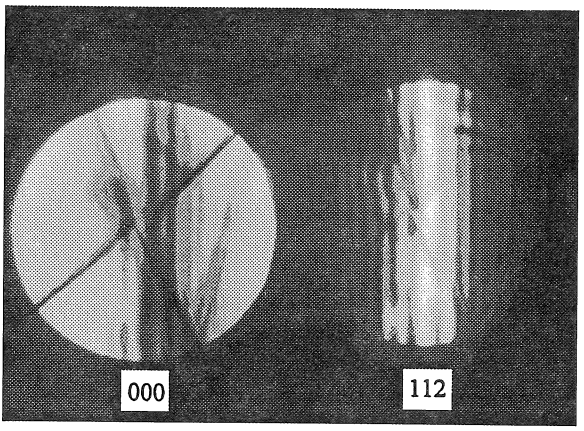

Fig. 3a. CBED pattern obtained from the area measured.

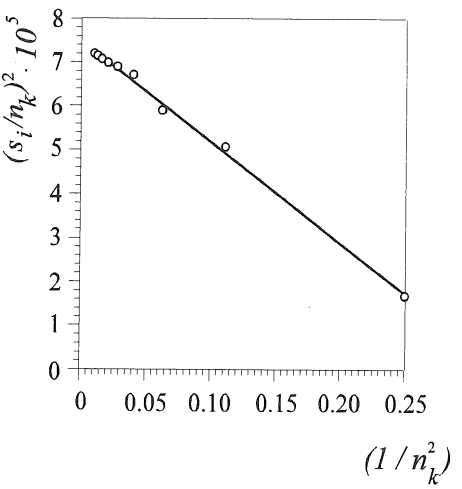

Fig. 3b. Plot of $(s_i / n_k)^2$ against $(1 / n_k)^2$ for n_k indices starting with 2.

Table I. Measured values for a worked example.

n_k	2	3	4	5	6	7	8	9	10
R_i [mm]	2.8	7.3	10.5	14.0	17.0	20.1	23.2	26.1	29.0
s_i [nm^{-1}]	0.008	0.021	0.031	0.041	0.050	0.059	0.068	0.076	0.085

The graphical method by plotting the measurements for several fringes was used. The diagram showed in Fig. 3 b is made by plotting $(s_i/n_k)^2$ against $(1/n_k)^2$. The n_k numbers were increased until a straight line plot was obtained. The plot yields the straight line if the first fringe is number 2 . An intercept of the y axis ($= 1/t^2$) = $7.5 \cdot 10^{-5}$ nm^{-2}, therefore the specimen thickness is 115 nm. The slope of the line is -0.00023 resulting in an extinction distance of 65.8 nm.

The mean oxide diameter, estimated using equation (2), is $\overline{D} = 2.14 \cdot 10^{-5}$ mm and is approximately equal to the $\overline{d}$ value. This means the diameters of circle sections lying in parallel planes could be neglected. Here, the ratio $t / \overline{D} \approx 5$.

Finally, equation (1) gives the estimated particle density $N_V = 120.00 \cdot 10^{10}$ mm^{-3}.

In order to obtain some information about the precision of the N_V estimation used, a simulation for the simplest case with the known specimen thickness t (i.e. given exactly) was made. For this reason the oxide dispersion was modelled by a dilute Boolean spheres model (Stoyan et al. 1995). The model parameters were chosen to be similar to that of the oxide particles. A model realisation in a thin slice simulates the dispersion in a thin foil. For 15 simulations, the mean N_V and the standard deviation σ are as follows: $\overline{N_V} = 1.10 \cdot 10^{12}$ and $\sigma = 0.04 \cdot 10^{12}$ (because s denotes the deviation parameter given above, here σ is the empirical standard deviation). The value $2\sigma / N_V$ (in %) is less than 10% and gives an impression about the precision of the N_V estimation.

CONCLUSIONS

The oxide particle density N_V is a fundamental quantitative parameter of the microstructure of ODS alloys. Because the dispersed particles, which are nanometer sized objects, the N_V estimation is only possible by quantitative TEM-metallography. If the approximation of the dispersion by a model in the form of a dilute spheres system is possible, the stereology is relatively simply. Consequently,

direct measurements can be reduced to the measurement of the projected particle diameters in the TEM image. For a given set of empirical diameters one can calculate all the projected parameters, which appear in the stereological equations (1) and (2). The final N_V estimation required an additional measurement of the TEM specimen thickness t. In the present study the t was determined using a modern CBED method which guarantees a high accuracy. The precision of the N_V estimation is dependent on the accuracy of the metallographic data and on the measured t value. Provided that t is given exactly, the statistical precision of the N_V estimation can be determined by a model simulation. From simulation results, based on ca 600 measured projection diameters, the relative error of the oxide dispersion N_V is less than 10%.

The quantitative TEM metallography presented is a relatively easy procedure and can be of practical importance in cases where a dilute spheres approximation is acceptable and when the specimen thickness measurement by CBED is possible.

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