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Domain Size Distribution in Deformed Ruthenium

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An X-ray study of deformed ruthenium was performed. Fourier and integral-breadth analysis of line profiles indicated absence of lattice distortion and also stacking faults. The average domain sizes found by using the two methods were 652 and 926 Å respectively. The absence of distortion and faulting has been used to determine the domain size distribution function.

Introduction

A detailed study of X-ray line broadening in filings of magnesium, titanium, zirconium and hafnium (Lele & Anantharaman, 1967*a*,*b*) was recently made by us under a program of study of hexagonal close-packed (h.c.p.) metals. We present here the results of an X-ray study of deformed ruthenium.

As is well known, it is not only possible to determine the average domain size but also to evaluate the size distribution function from a knowledge of the Fourier coefficients of the pure diffraction line profile (Bertaut, 1949*a*,*b*; Kobe, 1960; Bienenstock, 1963; Smith & Simpson, 1965). In practice, however, domain size broadening is generally accompanied by distortion and fault broadening. The effects of distortion and faulting cannot be removed in a rigorous manner unless the strain-distribution function and the fault probabilities are known. Consequently, it is usually not possible to determine the domain-size distribution. In the present study of deformed ruthenium, the state of the cold-worked powder was such that no stacking faults could be detected and strains were also negligible. Hence an actual determination of the domain size could be attempted.

Experimental procedure

Ruthenium powder of high purity (>99·9%) supplied by M/S Heraus (Germany) was used in the investigation. Deformation of the powder was accomplished by grinding in a powder-driven pestle and mortar (made of corundum) for one hour. The powder was then pressed into a briquette in a steel die at a pressure of about 16 kg.mm^{-2} by means of an Amsler hydraulic press. X-ray line profiles were continuously recorded before and after annealing the briquette *in vacuo* ($\sim 10^{-4}$ mm Hg) under identical conditions in a Philips diffractometer with filtered Cu $K\alpha$ radiation at a temperature of about 30 °C. All the patterns were obtained with a scanning rate of $\frac{1}{8}°$ in 2θ per minute using a time constant of 8 sec.

Three reflexions, *viz.* 0002, $10\bar{1}1$ and $10\bar{1}2$, along with their second orders were recorded. The $K\alpha_1$ peaks of the diffraction profiles of the cold-worked and annealed samples were located by an analytical method (Anantharaman & Christian, 1953) and the integral breadths B and b determined for both the cold-worked and annealed profiles. The pure diffraction breadth β was found by using each of the following three relations due to Scherrer (1920), Warren & Biscoe (1938) and Anantharaman & Christian (1956), respectively:

$$\beta^{S} = B - b;$$
$$\beta^{WB} = (B^2 - b^2)^{1/2};$$
$$\beta^{AC} = B - b^2/B.$$

The first and second relations hold when all the profiles follow the Cauchy and Gaussian functions respectively, while the last relation gives results correct to within ten per cent when the pure diffraction profile is Cauchy, the instrumental profile Gaussian and the observed profile intermediate (Halder & Wagner, 1966).

For Fourier analysis, the profiles were divided into 200 equal intervals with the $K\alpha_1$ peak as the origin. The amplitudes measured at these intervals were used for evaluating the Fourier coefficients $A_n + iB_n$ of the pure diffraction line profile on a digital computer (Elliot 803) by the method due to Stokes (1948). The sine coefficients B_n were small enough to be neglected. For the determination of the average domain size, the cosine coefficients A_n were expressed as a function of a length t perpendicular to the diffracting planes in the crystal, t being related to the harmonic number n through $t = n|\mathbf{a}|$, where $|\mathbf{a}|$ is the $\sin\theta$ interval over which the profile is expressed as a Fourier series.

Analysis of line profiles

The analyses (Fourier as well as integral breadth) have been performed by assuming an absence of lattice strain as well as stacking faults. These assumptions, which will be justified later, simplify the calculations considerably. The average domain size values D and D_B were found by using the following equations:

$$-\left(\frac{dA_t}{dt}\right)_{t=0} = \frac{1}{D}, \qquad (1)$$

$$\beta = \frac{\lambda}{D_B \cos\theta}. \qquad (2)$$

The domain size distribution function $P(n)$ may be found from (Bertaut, 1949*a*,*b*; Bienenstock, 1963; Smith & Simpson, 1965)

$$P_n = \frac{A_{n+1} - 2A_n + A_{n-1}}{A_0 - A_1} = -\frac{(d^2A_n/dn^2)}{(dA_n/dn)_{n=0}} . \quad (3)$$

However, owing to random fluctuations in the measured intensity and also possible errors in the choice of the background (Young, Gerdes & Wilson, 1967), there are fluctuations in the Fourier coefficients as well, which may give rise to meaningless results if the coefficients are directly substituted in equation (3). This necessitates a 'smoothing', *i.e.* a removal of fluctuations in the Fourier coefficients. A reasonable way to do this is to fit a polynomial in n to the Fourier coefficients by the least-square technique. The degree of the polynomial is arbitrary to a great extent. From elementary considerations, it can be shown that the polynomial must be at least a fourth degree one. The highest degree possible is naturally equal to the number of the Fourier coefficients. We have limited ourselves below to a fourth degree polynomial, which represents the maximum permissible smoothing:

$$A_n = a_0 + a_1 n + a_2 n^2 + a_3 n^3 + a_4 n^4 . \quad (4)$$

By differentiation, we get

$$-(dA_n/dn)_{n=0} = -a_1 , \quad (5)$$

$$(d^2A_n/dn^2) = 2a_2 + 6a_3 n + 12a_4 n^2 , \quad (6)$$

which on substitution in equation (3) yield

$$P(n) = \frac{2a_2 + 6a_3 n + 12a_4 n^2}{-a_1} . \quad (7)$$

The parameters a_i, $i=0$ to 4 in equation (4) can be found by the usual least-square theory, the solution in matrix form being

$$\begin{bmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} = \begin{bmatrix} S_0 & S_1 & S_2 & S_3 & S_4 \\ S_1 & S_2 & S_3 & S_4 & S_5 \\ S_2 & S_3 & S_4 & S_5 & S_6 \\ S_3 & S_4 & S_5 & S_6 & S_7 \\ S_4 & S_5 & S_6 & S_7 & S_8 \end{bmatrix}^{-1} \begin{bmatrix} T_0 \\ T_1 \\ T_2 \\ T_3 \\ T_4 \end{bmatrix} \quad (8)$$

where $S_0 = 15$, $S_i = \sum_{n=0}^{14} n^i$ and $T_i = \sum_{n=0}^{14} n^i A_n$. We have found the domain size distribution by the above method for the direction perpendicular to the $(10\bar{1}1)$ planes.

Results and discussion

Average domain size and distribution function

The domain size values as calculated from each of the available reflexions are given in Table 1. A comparison of the domain size values for three directions, namely [0001], $[10\bar{1}1]$, $[10\bar{1}2]$, found by averaging the values for the two orders shows that the domain size is nearly isotropic and hence that there is no observable contribution to the broadening due to faulting. Similarly, a comparison of the average value of the domain sizes for the first order reflexions, namely 0002, $10\bar{1}1$ and $10\bar{1}2$, and the average value for the second order reflexions, namely 0004, $20\bar{2}2$ and $20\bar{2}4$, shows that the domain sizes are independent of the order of the reflexion. The effect of strain is dependent on the order of the reflexion (Warren, 1959). Thus, had there been strains present in the lattice, we would have obtained low values of the domain size from the second order reflexions. This not being the case within experimental error limits, we consider it justifiable to conclude that there is no observable contribution to the broadening due to strains in the lattice.

The values of the percentage mean deviation from the mean are nearly equal. However, this is lower for the domain size values found from the Scherrer (1920) and Anantharaman & Christian (1956) equations than for the Warren & Biscoe (1938) equation. This supports the view that domain size profiles are closer to the Cauchy function in nature than to the Gaussian function (Warren, 1959).

The domain size distribution for the $10\bar{1}1$ direction is given analytically by

$$P(n) = 0{\cdot}0907 - 0{\cdot}00299(n - 5{\cdot}34)^2 . \quad (9)$$

The above equation represents a parabolic distribution function. The maximum permissible value of n according to equation (9) is 10·85. This represents a limitation in the domain size values which is unlikely to be true. It appears, therefore, that $P(n)$ may not be represented accurately by equation (9) for values of n near to and greater than 10·85. Normally the area under the $P(n)$ *versus* n curve must be unity; however, by integration of equation (9), it may be shown that

$$\int P(n)dn = 0{\cdot}66 .$$

Table 1. *Domain size values in deformed ruthenium*

hkil	θ (°)	B ($\times 10^3$ rad)	b ($\times 10^3$ rad)	β^S ($\times 10^3$ rad)	$D_B{}^S$ (Å)	β^{AC} ($\times 10^3$ rad)	$D_B{}^{AC}$ (Å)	β^{WB} ($\times 10^3$ rad)	$D_B{}^{WB}$ (Å)	D (Å)
0002	21·1	2·79	1·71	1·08	1536	1·74	951	2·20	751	735
$10\bar{1}1$	22·0	3·01	1·83	1·18	1409	1·90	876	2·39	696	697
$10\bar{1}2$	29·2	2·93	1·75	1·18	1492	1·89	934	2·35	750	640
0004	46·0	4·11	2·92	1·19	1876	2·03	1095	2·88	769	593
$20\bar{2}2$	48·5	5·65	4·09	1·56	1491	2·69	865	3·90	597	622
$20\bar{2}4$	77·1	15·11	10·18	4·93	1398	8·24	836	11·16	618	622
Mean value					1534		926		697	652
Percentage mean deviation from mean					7·5		7·2		8·6	6·0

It is probable that the remaining fraction of columns has a greater number of cells than 10·85.

A useful check on the distribution function may be obtained as follows: From equation (9), we can get values of the mean number, $\langle n \rangle$ and the mean square number, $\langle n^2 \rangle$ of cells per column, since

$$\langle n \rangle = \int nP(n)dn \Big/ \int P(n)dn , \tag{10}$$

$$\langle n^2 \rangle = \int n^2 P(n)dn \Big/ \int P(n)dn . \tag{11}$$

These give us the ratio

$$\chi = \frac{\langle n^2 \rangle}{\langle n \rangle^2} = \left[\frac{\int n^2 P(n)dn}{\int P(n)dn} \right] \Big/ \left[\frac{\int nP(n)dn}{\int P(n)dn} \right]^2 , \tag{12}$$

which is an absolute property of the shape of the distribution function and does not depend on particular numerical values of $\langle n \rangle$ and $\langle n^2 \rangle$. Evaluating the integrals in equations (10) and (11) by using equation (9) and substituting in equation (12), we get

$$\chi = 1{\cdot}34 .$$

This value of χ may be checked against another value found from (Bertaut, 1949*a*,*b*)

$$\chi = \frac{\langle n^2 \rangle}{\langle n \rangle^2} = \frac{D_B^{AC}}{D} . \tag{13}$$

Substituting $D_B^{AC} = 926$ Å and $D = 652$ Å, we get

$$\chi = 1{\cdot}42.$$

The close agreement between the two values of χ obtained by using equations (12) and (13) suggests that the assumption of a parabolic distribution function, which is implicit in the method used, is justified.

As pointed out earlier, the distribution function is not represented accurately by equation (9) for values of n near to and greater than 10·85. It is probable that the distribution function does not abruptly fall to zero at $n = 10{\cdot}85$, but tails off gradually to zero as n increases. This would have the consequence that the values of the mean number, $\langle n \rangle$, and the mean squared number, $\langle n^2 \rangle$, of cells in a column found from equations (10) and (11) would be lower than the actual values, which can be found from

$$\langle n \rangle = -1/a_1 , \tag{14}$$

and

$$\langle n^2 \rangle = 1{\cdot}42 \langle n \rangle^2 = 1{\cdot}42/a_1^2 . \tag{15}$$

The actual values confirm this expectation. Thus equations (10) and (11) give the following values:

$$\langle n \rangle = 5{\cdot}35 \text{ and } \langle n^2 \rangle = 38{\cdot}10 ,$$

while from equations (14) and (15), we get

$$\langle n \rangle = 9{\cdot}24 \text{ and } \langle n^2 \rangle = 121{\cdot}24 .$$

Stacking fault energy (S.F.E.)

According to Seeger (1955), the difference in energy between the h.c.p. and the f.c.c. structures and the S.F.E. for transitional metals are determined by the bonding between next nearest neighbour atoms provided by the *d* electrons. Following this argument, he predicts that ruthenium should have a low S.F.E. Tyson (1967) has recently put forward a hypothesis according to which h.c.p. materials with a low value of S.F.E. should favour basal slip as opposed to prismatic slip. It therefore appears that ruthenium should deform by basal slip which, however, is not consistent with the actual observation of prismatic slip in this metal (Rhys, 1959). The non-observance of stacking faults in this work seems to support the view that ruthenium has a high S.F.E. There is, however, the possibility that stacking faults may not be produced by the process of grinding with a mortar and pestle as in the present work, since the latter does not lead to the same amount of cold work as the filing operation generally employed in such studies.

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