JOURNAL OF MATERIALS SCIENCE 4 (1969) 681–684

The Effect of Temperature on Microstrains and Crystallite Growth in Alumina

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Received 2 February 1969

The effects of temperature on the microstrains and crystallite growth in milled alumina have been examined, using a modern method of X-ray diffraction profile analysis. The microstrains may be relieved by annealing at temperatures between 600 and 1000° C, and this relief is accompanied by crystallite size growth. Isotropy was observed with regard to the residual stresses and cleavage properties, in the milled crystals.

1. Introduction

There has recently been a considerable effort devoted to the measurement of microstrains in materials normally considered brittle. These microstrains have been shown to exert considerable influence on the physical and chemical properties of such materials. For example, it has been demonstrated that the induced microstrain energy produced by the grinding of alumina is significant, compared with the surface free energy of the particles [1], and this has also been shown for yttrium iron garnet [2]. The effects of cold-working on the characteristics of tungsten carbide powder has been reported with reference to the importance of microstrains in the sintering of tungsten carbide in the manufacture of tool tips [3].

It therefore seemed worthwhile to examine the influence of temperature on the microstrains and crystallite sizes produced in alumina by grinding, and to extend the work on this material initiated by Lindley [4].

2. Experimental Details

High purity alumina powder was deformed using a Glen Creston M 280 vibratory mill, the grinding cylinder and ball also being made of alumina. Several batches of powder were deformed, each to a different amount, by varying the times of grinding. From each batch of milled powder, samples were annealed at different temperatures for a period of 1 h. The range of annealing temperatures extended from room temperature to 1500° C.

Prolonged annealing of a sample of milled powder from batch 1 was carried out at a temperature of 750° C. This temperature was selected as being one near the centre of the region of microstrain relief and also near the onset of caking [7].

The microstrains, and corresponding crystallite sizes, were measured, both for the cold-worked and the annealed samples, using X-ray line broadening methods. Chart recorded profiles were obtained using a Philips powder diffractometer with Ni-filtered CuKα radiation. The slowest scanning speed of $\frac{1}{8}$°/min in deviation angle, 2θ, was chosen.

It has recently been shown that most of the modern methods of X-ray profile analysis give comparable results with regard to microstrains and crystallite sizes [5]. The integral breadth method of Wagner [6] was selected for this work as being the easiest to apply to alumina, with its many overlapping reflections. In this method, the broadening, β_S^*, due to the presence of microstrains and due to the reduction in size of the coherently diffracting domains, is obtained by subtracting the instrumental broadening, β_I^*, from the total broadening, β_T^*, by means of the equation

$$\beta_S^* = \beta_T^* - \frac{(\beta_I^*)^2}{\beta_T^*}, \qquad (1)$$

where

$$\beta^* = \frac{\beta \cos\theta_0}{\lambda};$$

β = integral line breadth; θ_0 = Bragg angle corresponding to the peak of the reflection; λ = wavelength of X-rays. Values for the microstrains, ϵ_{hkl}, and crystallite sizes, D^{PF}, are obtained using the equation

$$(\beta_s^*)^2 = \frac{1}{(D^{\mathrm{PF}})^2} + \frac{16\epsilon_{hkl}^2 \sin^2\theta_0}{\lambda^2}. \quad (2)$$

Plots of $(\beta_s^*)^2$ against $(d_{hkl}^*)^2$ $[= (2\sin\theta_0/\lambda)^2]$ are made, and multiple orders must be used, so that the microstrains and crystallite sizes in particular directions are obtained individually. The slopes of such plots give $4\epsilon_{hkl}^2$, and the intercepts on the $(\beta_s^*)^2$ – axis give $(1/D^{\mathrm{PF}})^2$. Only three reflections were found to offer two usable orders of reflection, i.e. $(01\bar{1}2)$, $(11\bar{2}0)$ and $(11\bar{2}3)$ (hexagonal indices), because of the overlapping of reflections and intensity considerations.

3. Results

Fig. 1 shows the variation of microstrain and crystallite size with temperature, and includes curves for the three sets of reflections. Below 500° C, only a small amount of microstrain was relieved, with little increase in crystallite size. The rate of microstrain relief increased above this temperature, and in the range 600 to 1000° C, a maximum was reached. The whole process is similar to that observed during the annealing of metals. Crystallite sizes increased from the initial values of about 200 to 300 Å in the cold-worked state, to about four times those values, at temperatures in excess of 1250° C.

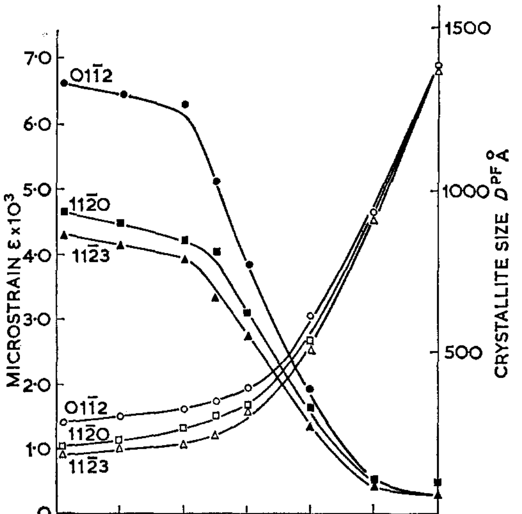

Figure 1 Effect of annealing on microstrains (ϵ) and crystallite sizes (D^{PF}). Annealing time was 1 h. Filled symbols, microstrains, open symbols, crystallite sizes.

An examination of the three sets of curves reveals the existence of anisotropy both in the microstrains and crystallite sizes, produced by the ball-milling of the powder. The greatest microstrains and crystallite sizes were obtained for directions normal to the $(01\bar{1}2)$ planes, and the least for directions normal to the $(11\bar{2}3)$ planes. As the annealing temperatures were increased, the differences between the microstrains and the crystallite sizes for these two sets of planes were reduced. This indicates that high temperature annealing produced a powder of isotropically and weakly strained crystallites, which were approximately equiaxed.

Similarly shaped curves were obtained for the other two batches of powder, having different initially induced microstrains. Table I shows the ratios of the microstrains for the three sets of reflecting planes in respect of each cold-worked condition of the powder. The corresponding ratios are also shown for the crystallite sizes. In each case, the ratios are nearly a constant.

Ball-milling times for the three batches of powder were 30, 13, and 6 h respectively, but prolonged grinding up to 120 h produced no further increase in microstrains or reduction in crystallite size, indicating a strain saturation for these particular conditions of milling.

Fig. 2 shows the variation of microstrains and crystallite sizes as a function of time for prolonged annealing at 750° C. An exponential relationship appears to hold.

4. Discussion

Because of its low impact strength, alumina is generally considered to be a brittle material, with

TABLE I Ratios of microstrains and crystallite sizes in different crystal directions

	$\epsilon_{01\bar{1}2}/\epsilon_{11\bar{2}3}$	$\epsilon_{11\bar{2}0}/\epsilon_{11\bar{2}3}$	$D_{01\bar{1}2}/D_{11\bar{2}3}$	$D_{11\bar{2}0}/D_{11\bar{2}3}$
Batch 1	1.5	1.1	1.6	1.1
Batch 2	1.4	1.1	1.5	1.2
Batch 3	1.4	1.1	1.3	1.1

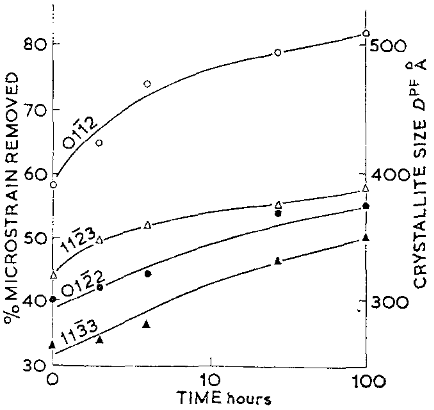

Figure 2 Effect of prolonged annealing at 750° C. Filled symbols, microstrains, open symbols, crystallite sizes.

brittle-ductile transitions occurring in the regions of 900 to 1000° C for single crystals [8] and 1300 to 1400° C for polycrystalline specimens [9]. However, low temperature plastic flow has been reported for massive specimens. For example, deformation twinning has been observed at temperatures as low as −196° C [10] and under conditions of hydrostatic compressive stresses [11], whilst slip bands have been seen to result from room temperature wear experiments [12]. X-ray microbeam studies on polycrystalline alumina have shown that fracture is accompanied by plastic flow [13]. It was found that the highly distorted regions extended to a depth of some 10 μm, and the less distorted regions to about 60 μm.

In all such cases, however, the plastic flow appears to have been localised within narrow regions some 5 to 50 μm across. From these considerations, it can be assumed that the X-ray line broadening can be attributed, at least in part, to plastic flow in the milled alumina particles, whose dimensions are orders of magnitude smaller than those of the strained regions observed in the deformation phenomena mentioned above. It is not to be assumed, however, that the strain distribution will be uniform throughout the crystallites; it may well vary in a manner similar to that of other milled powders [14].

It has been suggested by Stokes and Wilson [15], that, if the assumption of an isotropic stress distribution is made, the average strain measured from an (*hkl*) reflection can be related to the Young's modulus, E_{hkl}, appropriate to crystal directions normal to the *hkl* planes. They suggested the equation $\epsilon_{hkl} \times E_{hkl} =$ a constant, σ_{hkl}, where σ_{hkl} is called the stress function. Assuming no stacking faults, the stress function was calculated for the directions normal to the $\{01\bar{1}2\}$, $\{11\bar{2}0\}$ and $\{11\bar{2}3\}$ planes. The values of E_{hkl} were calculated from the standard expression involving the compliances, s_{ij}, whose values were obtained from Huntington [16]. Table II shows the values of the stress function for the fully strained condition of all three batches, and for two annealed conditions of batch 1. The table shows that, for each condition of the powder the stress function is approximately constant.

Fig. 3 shows, for the three batches of milled powder, the curves obtained by plotting $\log(1/\epsilon_{hkl})$ against $\log d_{hkl}$, where d_{hkl} is the interplanar spacing of the *hkl* planes. These curves have very nearly the same slope. Table III shows the ratio, *N*, of the crystallite size, D^{PF}, to the interplanar spacing, *d*. *N* is seen to be approximately constant for the three batches, indicating that, although the crystallite size exhibits anisotropy, the number of reflecting planes does not.

Thus we see that, in any of the crystallites produced by the milling, residual stresses and the number of interplanar spacings are isotropic. The fact that the stresses are isotropic may follow from the fact that the conditions in a ball-mill may be regarded, in some circumstances, as giving a hydrostatic type stress [17]. The fact that the number of interplanar spacings is isotropic seems to imply that the cleavage properties of the planes are also isotropic in these very small and highly deformed crystals.

Hey and Livey [18] have noted that the kinetics

TABLE II Values of the stress function for cold-worked samples, and for two annealed samples

hkl	$E_{hkl} \times 10^{11}$ Nm^{-2}	Stress function, $\sigma = E_{hkl} \times \epsilon_{hkl} \times 10^{7}$ Nm^{-2}				
		Batch 1	Batch 2	Batch 3	Batch 1	
					750° C	1000° C
$01\bar{1}2$	2.66	175	112	53	107	51
$11\bar{2}0$	3.45	160	110	59	107	57
$11\bar{2}3$	3.69	159	110	55	100	49

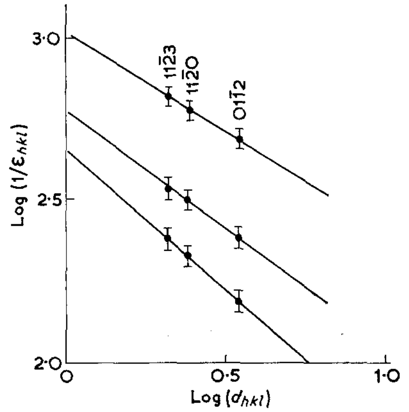

Figure 3 The relationship between microstrain and interplanar spacing.

of crystal growth over the temperature range 600 to 900° C obey a relationship $D^n - D^n{}_0 = \mathrm{K}t$, where D is the crystallite size at various times, t, and n has a value of seven to ten, one factor being the purity of the material. The overall results obtained in this work do not agree well with such power laws, the rate of growth during the early stages being relatively much greater than the later rates. These differences indicate a more complicated relationship, and may be explained by the presence of considerable microstrains in the crystallites in the early stages of growth. The later stages of crystallite growth would be more influenced by surface area effects and it is these later stages which are in better agreement with the law of Hey and Livey. The crystals investigated by Hey and Livey were strain-free.

It has been shown, by Anderson and Morgan [19], that water vapour at low pressures will have large effects on crystal growth rates in MgO at temperatures around 1050° C. These effects were not investigated in the present work. The water vapour conditions were the same in all experiments.

TABLE III The number of Bragg planes, *N*, for the cold-worked samples, in different directions

hkl	$N = D_{hkl}/d_{hkl}$		
	Batch 1	Batch 2	Batch 3
$01\bar{1}2$	81	123	145
$11\bar{2}0$	84	142	175
$11\bar{2}3$	86	135	187

5. Conclusions

Alumina can be induced to give considerable X-ray line broadening by grinding. Integral breadth profile analysis indicates that microstrains form the main contribution to this line broadening, and that ground alumina exhibits considerable anisotropy in its behaviour as regards the presence of microstrains, and the reduction of crystallite size. The microstrains may be relieved by annealing between 600 and 1000° C, and this relief is accompanied by crystallite size growth. Isotropy was noticed with regard to the residual stresses and cleavage properties in the milled crystals.

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