LETTERS TO THE EDITORS

X-ray Analysis of Strain and Crystallite Size in Tungsten Carbide Compressed at High Pressure

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The X-ray line profile of WC shows appreciable broadening by mechanical treatment such as grinding⁽¹⁾. The X-ray line broadening is due to structural factors, such as crystallite size and lattice strain, as well as to instrumental effects. Furthermore, it has been reported⁽²⁾ that the large increase in line width is found in MgO subjected to a high pressure of 60 kbar. Work is now in progress here on the investigation of the X-ray line broadening of WC subjected to high pressures of 5 to 40 kbar. Work is also made on WC annealed at temperatures of 800° to 1200°C after being subjected to 40 kbar.

The starting material of WC powder is as-carbonized tungsten powder at a high temperature and about 1.2 μ

Photo. 1 (a) Electron microphotographs of WC powder, (a) as received and (b) subjected to 40 kbar. ($\times 3000$)

in mean grain size as shown in Photo. 1 (a). The WC powder was compressed at pressures of 5, 10, 20, 30 and 40 kbar in the piston-cylinder type high pressure apparatus⁽³⁾. The pressure in the apparatus was calibrated in reference to electrical resistance transitions of cerium, bismuth, thallium and barium. The WC powder subjected to 40 kbar was annealed at temperatures of 800°, 1000° and 1200°C for an hour.

The X-ray results were obtained using a Geiger counter diffractometer. Ten diffraction lines in the θ (Bragg's angle) range of approximately 20° to 60° were examined for each specimen. The α_1 and α_2 doublet components of the filtered Cu $K\alpha$ radiation were separated by Rachinger's method⁽⁴⁾, and the integral breadth, B for each observed diffraction profile was then obtained.

The subdivision of a sample into crystallites smaller than 2000 Å results in the line broadening of β_d , which varies with the wave length of the X-ray radiation λ and Bragg's angle, according to the expression, $\beta_d = \lambda/\eta \cos \theta$, where η is the apparent crystallite size. The effective internal strain ϵ is related to the spectral line width β_s by the equation, $\beta_s = \epsilon \tan \theta$. A Gaussian profile shape was assumed, and though this gives a little bit higher value of strain than a closer approximation to the true line shape based on an average value between those of Cauchy and Gaussian, the present estimation may not introduce a great error since the line broadening in this case can be assumed to be mainly due to lattice strain. Therefore, the breadth for the pure diffraction profile B was expressed by the equations, $\beta^2 = B^2 - b^2 = \beta_d^2 + \beta_s^2$, where b is the breadth due to the instrument. The instrumental line broadening was assumed to be that of an annealed specimen which shows a minimum line broadening. To obtain this line broadening, the WC powder was annealed for four hours at 1400°C and then cooled in air down to room temperature.

Substituting the values of β_d and β_s and using Bragg's relation, the following equation is obtained :

$$(B^2 - b^2) \cos^2 \theta = \frac{\eta^2}{\lambda^2} + 16 \epsilon^2 \sin^2 \theta.$$

Accordingly, if a plot of $(B^2 - b^2) \cos^2 \theta$ against $\sin^2 \theta$ gives a straight line for a particular diffraction pattern, then a measurement of the intercept and the slope will lead directly to mean values of the crystallite size and apparent lattice strain for the specimen studied. A similar approach has been attempted by Willets⁽⁵⁾.

Values of $(B^2 - b^2) \cos^2 \theta$ are plotted against $\sin^2 \theta$ for a specimen as received, for specimens subjected to high pressures and also for a specimen ground in a ball mill for 72 hours for reference (Fig. 1). The lattice strain and the crystallite size of WC powder as received were 1.02×10^{-3} and 620 Å, respectively. As the mean grain size of WC is about 1.2 μ , it is considered that a WC grain in the starting material consists of about 8×10^3 of crystallites. The relationships between η , ϵ and pressure are given in Fig. 2. With increasing pressure the strain increases and the crystallite size decreases, but they gradually approach constant values. Photo. 1 (b) shows an electron microphotograph of the WC powder subjected to 40 kbar. The grain and crystallite sizes determined from the microphotograph and X-ray analysis are about 0.6 μ and 300 Å, respectively,

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(3) P. N. LaMori : *High Pressure Measurement*, Butterworth, Washington D. C., 1963, P. 321.

(4) W. A. Rachinger : J. Sci. Instrum., 25 (1948), 353.

(5) F. M. Willets : Brit. J. Appl. Phys., 16 (1965), 323.

the values being about one-half of those of the WC powder as received.

Although the WC powder ground in a ball mill for 72 hours shows a substantial increase in strain and also a considerable decrease in crystallite size in a way dif-

ferent from the WC powder subjected to a high pressure, so that the crystallite size becomes finer than that of the WC powder subjected to 40 kbar, but the introduced strain is relatively low. The grains are pulverized by impact at grinding in a ball mill, whereas the grains are not so finely pulverized under hydrostatic pressure that they show plastic deformation to have a relatively large lattice strain.

Fig. 1 Plot of $(B^2 - b^2) \cos^2 \theta$ vs. $\sin^2 \theta$ for WC powder as received, subjected to the indicated pressures and ball milled for 72 hr.

Fig. 2 Variation in strain and crystallite size of WC powder with pressure.

Fig. 3 Variation in strain and crystallite size of WC powder subjected to 40 kb, with annealing temperature.

The results of the X-ray analysis of the WC powder subjected to 40 kbar and subsequently annealed at temperatures of 800°, 1000° and 1200°C for an hour are shown in Fig. 3. Generally, with increasing annealing temperature, the strain decreases and the crystallite size increases. However, the grain growth is not so significant in the temperature range 800° to 1200°C. On the contrary, the lattice strain decreases rapidly above 1000°C. Therefore, it may be noted that the relatively low temperatures of 800° to 1200°C for the annealing of WC have a greater effect on the removal of strain than on the crystal growth. This result agrees with that of Montgomery et al.⁽²⁾ on MgO.

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By Katsuya Kudakaba*

* Mitsubishi Metal Mining Co., Central Research Lab., Obmiya, Japan.