

Fig. 4

There are dark and light areas which are not evident in the photomicrographs. We believe these to be high concentrations of cadmium and tin, respectively. This indicates that the alloy was not thoroughly mixed.

We thank the reactor staff at the University of Missouri at Rolla, and Nelson Beck of Argonne National Laboratory, for their help. We thank the Indium Company of America and the American Smelting and Refining Company for materials.

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## **Diffusion Creep in Polycrystalline Magnesium**

LIGHTLY stressed polycrystalline metals may deform by the vacancy diffusion mechanism proposed by Nabarro<sup>1</sup> and Herring<sup>2</sup>. At high temperatures,  $\sim 0.8$  of the absolute melting temperature Tm, lattice self-diffusion is rapid and an appreciable diffusion creep may take place at a rate (¿) given by2:

$$\dot{\varepsilon} = \frac{B_1}{d^2} \frac{\Omega \sigma}{kT} D_l \tag{1}$$

where  $B_1$  is a constant, ~10 for equiaxed polycrystals;  $\Omega$  the atomic volume of the material;  $\sigma$  the small applied stress;  $D_l$  the lattice self-diffusion coefficient; d the mean grain diameter; and kT has the usual meaning.

An equation for the contribution to diffusion creep by grain boundary self-diffusion (coefficient  $D_{gb}$ ) has been suggested by Coble<sup>3</sup>:

$$\dot{\varepsilon} = \frac{B_2}{d^3} \frac{\Omega \sigma}{kT} \omega D_{gb}$$
(2)

where  $B_2$  is a constant, ~ 150; and  $\omega$  is the grain boundary width.

As equation (2) has a stronger grain size dependence than equation (1) and the activation energy for grain boundary diffusion is smaller than that for lattice diffusion<sup>4</sup>, vacancy creep controlled by the grain boundary mechanism will be favoured by fine grain sizes and lower temperatures of deformation (~0.6 Tm).

This communication describes experiments which confirm that diffusion creep may be controlled by either the lattice or grain boundary mechanisms according to the test temperature. Magnesium was selected for these experiments since convincing metallographic evidence for diffusion creep has been obtained previously during deformation of a magnesium alloy containing internal markers5,6

In the first experiment, polycrystalline magnesium of 99.95 per cent purity and grain size  $\sim 8 \times 10^{-3}$  cm was stressed in argon at 425° C ( $\sim 0.75$  Tm). At stresses above  $\sim 1.4 \times 10^7$  dynes/cm<sup>2</sup>, slip lines were observed on

the specimen surface and the marked stress dependence of the steady creep rate  $(\dot{\epsilon}\alpha\sigma^5)$  was typical of a dislocation climb process<sup>7</sup> in agreement with previous work<sup>8</sup>. Below this stress, however, and down to  $\sim 1.7~\times~10^6~\rm dynes/cm^2$ no slip lines were observed, and the creep rate was a linear function of the stress. These creep rates agreed within a factor of two with those predicted from equation (1) using known values for  $\Omega = 2.32 \times 10^{-23}$  cm<sup>3</sup> and the lattice self-diffusion parameters<sup>9</sup> ( $D_{0l} = 1.0 \text{ cm}^2/\text{sec}$ ,  $Q_l = 32.0 \text{ kcal/mol}$ ). This must be considered good agreement in view of the approximations in the theoretical derivation of the value of  $\hat{B}_1$ . In addition, at a stress of  $9.6 \times 10^6$  dynes/cm<sup>2</sup>,  $\dot{\epsilon} \propto 1/\dot{d}^2$  for grains between 8 and  $40 \times 10^{-3}$  cm in diameter and direct determinations of the activation energy for creep by the temperature cycling technique<sup>10</sup> yielded values  $30.8 \pm 5.6$  kcal/mol at a stress of  $3.5 \times 10^6$  dynes/cm<sup>2</sup> and a temperature of 412.5° C. These results indicate that diffusion creep rates in magnesium at 0.75 Tm follow equation (1) and are controlled by lattice self-diffusion.

In the second experiment, carried out at 270° C (0.59 Tm) on specimens of  $\sim 5 \times 10^{-3}$  cm grain size,  $\dot{\epsilon} \propto \sigma^5$  for stresses in excess of  $2.8 \times 10^7$  dynes/cm<sup>2</sup> while at lower stresses  $\dot{\epsilon} \propto \sigma^{1.0}$ . Under these conditions of linear stress dependence the experimental rates were more than thirty times faster than those predicted from equation (1), suggesting the dominating importance of equation (2). In order to compare the experimental rates with equation (2), values for  $D_{gb}$  and  $\omega$  were required. Following work on zinc<sup>11</sup> and cadmium<sup>12</sup> we take for magnesium  $D_{0gb} \sim$ 1.0 cm<sup>2</sup>/sec with  $\omega \sim 5 \times 10^{-8}$  cm while the activation energy for grain boundary diffusion is  $Q_{gb} \sim 0.6 Q_{l}$ , giving  $Q_{gb} \sim 19.2$  kcal/mol. From equation (2)  $\dot{\epsilon}/\sigma = 3.5 \times 10^{-16}$  $cm^2/dyne$  sec at 270° C in good agreement with the experimental value of  $\dot{\epsilon}/\sigma \sim 8 \times 10^{-16} \text{ cm}^2/dyne$  sec. Some support is given to this calculation by direct determinations of  $Q_{gb}$  by the temperature cycling technique. Initial results are  $Q_{gb} = 20.0 \pm 1.9 \text{ kcal/mol at } 6.9 \times 10^6 \text{ dynes/}$ cm<sup>2</sup> and 285° C, indicating control by the grain boundary mechanism.

The practical importance of vacancy creep in metals and alloys operating at high fractions of the melting temperature has been pointed out previously<sup>6</sup>. The foregoing results demonstrate, for the first time, that vacancy creep by a mechanism involving grain boundary diffusion can be of dominating importance in fine-grained metals stressed at lower temperatures (~ 0.6 Tm).

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## CRYSTALLOGRAPHY

## Growth of Single Crystals of $Ba(B_{0.33}Ta_{0.67})O_3$ Perovskite-type Compounds

A REVIEW of the literature revealed that a considerable effort has been expended in the past few years on investigations of a large number of new compounds with the general formula,  $A(B'_xB''_y)O_3$ , where B' and B'' are two different elements in the octahedrally co-ordinated cation