METALLURGY

Reversion of Nodules Formed by the Grain Boundary Reaction in Aluminium-Zinc Alloys

THE grain boundary reaction is a phenomenon by which nodules with large lamellar precipitates grow from grain boundaries during artificial ageing of super-saturated solid solution alloys. It is called discontinuous or cellular precipitation by some workers. There have been many studies on the grain boundary reaction in aluminium-zinc alloys (Fig. 1). We have recently shown that the crystallographic orientation of nodules formed by the reaction is identical with that of the adjoining crystal grain, from which the nodules grow.[1] However, the reversion process, which dissolves the lamellar precipitates in the nodules into matrix and reduces the nodules to the homogeneous solid solution, has not yet been reported.

Optical microscopic observations were made on the reversion process of the nodules in aged aluminium-zinc alloys containing 30 and 40 per cent zinc. Specimens with nodules were solution heat-treated for a short time in a salt-bath regulated at a uniform solid solution temperature. As the heating went on, the lamellar precipitates gradually dissolved into matrix. The surface of the nodules became wavy by electrolytic polishing (Fig. 2) on account of the varying zinc concentration, but it became flat by chemical polishing. By further heating all precipitates were dissolved into matrix, though the advancing boundaries of the nodules scarcely changed their positions. A polygonization-like structure was
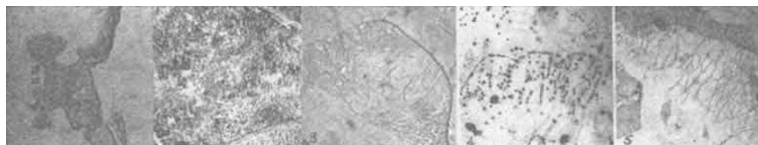

Fig. 1. 22 per cent zinc, aged for 16 hr. at 100°C. (×40). Fig. 2. 30 per cent zinc, aged for 40 hr. at 100°C. and heat-treated for 40 sec. at 300°C. (×400). Fig. 3. 30 per cent zinc, aged for 40 hr. at 100°C. and heat-treated for 160 sec. at 300°C. (×400). Fig. 4. 40 per cent zinc, aged for 10 hr. at 100°C. and heat-treated for 20 sec. at 400°C. (×80). Fig. 5. 40 per cent zinc, aged for 15 hr. at 100°C. and heat-treated for 20 sec. at 400°C., then re-aged for 12 hr. at 100°C. (×80).

observed in them (Fig. 3). When the specimens were chemically polished and etched with a solution of 2 parts nitric acid, 2 parts hydrochloric acid, 1 part of hydrofluoric acid, and 30 parts of ethanol, etch pits were formed within the nodules (Fig. 4). The density of these etch pits is greater than that of matrix grains, and moreover they lie on lines nearly perpendicular to the advancing boundaries. The same specimens were re-aged and etched with Wassermann's reagent, when a network structure was clearly observed, caused by preferential precipitation (Fig. 5). The nodules in Fig. 5 are those which were newly formed by re-ageing.

It is presumed that this phenomenon may be a kind of polygonization, that is, a formation of sub-boundaries composed of an array of dislocations. These dislocations may be due to the misfitting boundaries formed by a union of the minute nodules grown at the same grain boundary, as was shown in dendritic growth[2], or the incomplete annealing of localized plastic deformation produced from the rapid

volume changes of nodules owing to the rapid dissolution of precipitates.

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[1] Watanabe, R., and Koda, S., Nature, 183, 1667 (1959).
[2] Forty, A. J., and Gibson, J. G., Act. Met., 6, 137 (1958).

CHEMISTRY

A Paper-Chromatographic Method for the Determination of Suitable Buffer Systems for Countercurrent Distribution

BETINA recently described[1] a method for the determination of suitable pH values for the extraction of antibiotics. He used air-dried buffered paper, which is absorbent and tends to lead to the formation of 'comets', and he did not take into account the ratio of the volumes of the moving and stationary phases, r, which also influences the R_F value. Thus the accuracy of his method is rather limited. Using a relatively moist paper and taking into account some quantitative relationships involved, it is possible to make this method more precise.

The distribution of a solute between an organic solvent and a buffer solution is given by:

$$K = \frac{k}{1 + K_B/[OH^-]} \text{ (bases)} \atop = \frac{k}{1 + K_A/[H^+]} \text{ (acids)} \Biggr\} \quad (1)$$

where K = partition ratio (ratio of overall concentrations of solute in organic and water phase); k = partition coefficient (ratio of concentrations of unionized solute in organic and water phase); K_B, K_A = ionization constant of base or acid.

Assuming that paper chromatography is a continuous extraction process, the R_F is expressed[3] by:

$$R_F = \frac{Kr}{Kr + 1} = \frac{kr}{kr + 1 + K_B/[OH^-]} \text{ (bases)} \atop = \frac{kr}{kr + 1 + K_A/[H^+]} \text{ (acids)} \Biggr\} \quad (2)$$

where r is the ratio of the volumes of the moving and stationary phases: $r = V_{org}/V_{aq}$.

Plotting of R_f against pH gives S-shaped curve whose shape and position depends on:

(a) The partition number kr. The higher kr the higher and further to the left is the curve. At kr values higher than 50 the shape of $R_F = f(pH)$ curves is independent of kr and only their position depends on kr. Thus an x-fold increase of kr shifts the curve to the left by $\log x$ pH units.

(b) The ionization constant K_B (K_A). The smaller the constant the further to the left is the curve. An x-fold decrease in K_B (K_A) shifts the curve by $\log x$ pH units to the left (higher pH values for acids and lower pH values for bases).