JOURNAL OF MATERIALS SCIENCE 20 (1985) 2647–2652

Condensation and morphology of magnesium particles in vapour plumes

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A plume chamber study of condensation in magnesium vapour was performed in flowing argon at atmospheric pressure and source temperatures (T_0) up to 1213 K. The wall temperature (T_∞) was at 300 K. Sampled particles closely resembled those from zinc and cadmium aerosols and included spheres and prisms, indicative of vapour–liquid and vapour–solid nucleation. The spheres solidify from single rafts, and in addition to the hexagonal prisms that grow from dendrites, flatter and elongated forms occur as twins. The presence or absence of either spheres or prisms was found to depend on the setting of T_0, in agreement with theory, which predicts that T_0 will determine the position of the nucleation threshold temperature (T_n) relative to the melting point (T_f). The occurrence of particles condensed as solid as well as liquid nuclei when T_n was higher than T_f showed that supersaturated vapour states can persist as the vapour cools below T_n. The twinned particles observed with magnesium do not occur with zinc or cadmium at atmospheric pressure. It is suggested that the presence of hydrodynamic stresses causes twinning in magnesium whereas in zinc and cadmium it results in malformed hexagonal prisms.

1. Introduction

An investigation of aerosol particle condensation over magnesium heated in an upward flow of argon is described. In previous work on the h c p metals zinc and cadmium [1, 2] the uniaxial crystal symmetry was an advantage in interpreting the nucleation, growth and evaporation mechanisms involved in particle formation. The initial studies on the condensation mechanisms of zinc and cadmium were carried out in the stagnant atmosphere of the heat-pulse cloud chamber [1, 2], with which it is possible to observe the effect of varying the wall, or sink, temperature (T_∞) from the ambient level up to the melting point (T_f) or higher. A plume chamber method was introduced recently which allows the evaporation–condensation plume to develop naturally in laminar flow. This method also makes it easier to investigate the effects of different source temperatures (T_0) on the aerosols produced. The design of the plume chamber and its application in a study of the morphology of particles in zinc aerosols was reported in a previous paper [3].

There would be difficulties in attempting to use the cloud chamber to study magnesium in view of its reactivity towards the refractories in the walls and probes. In the plume chamber, the vapour from the source material, heated electrically in a stainless-steel boat, is entrained by a flow of cold, inert gas and does not accumulate at the walls. Using this form of apparatus, fumes of a reactive metal such as magnesium can be generated and samples collected while the source is maintained at a steady temperature.

2. Experimental techniques

The plume chamber was operated as described previously [3], the walls being at room temperature. The test material was magnesium of 99.99% purity in the form of wire of 1 mm diameter. The source temperature was varied by

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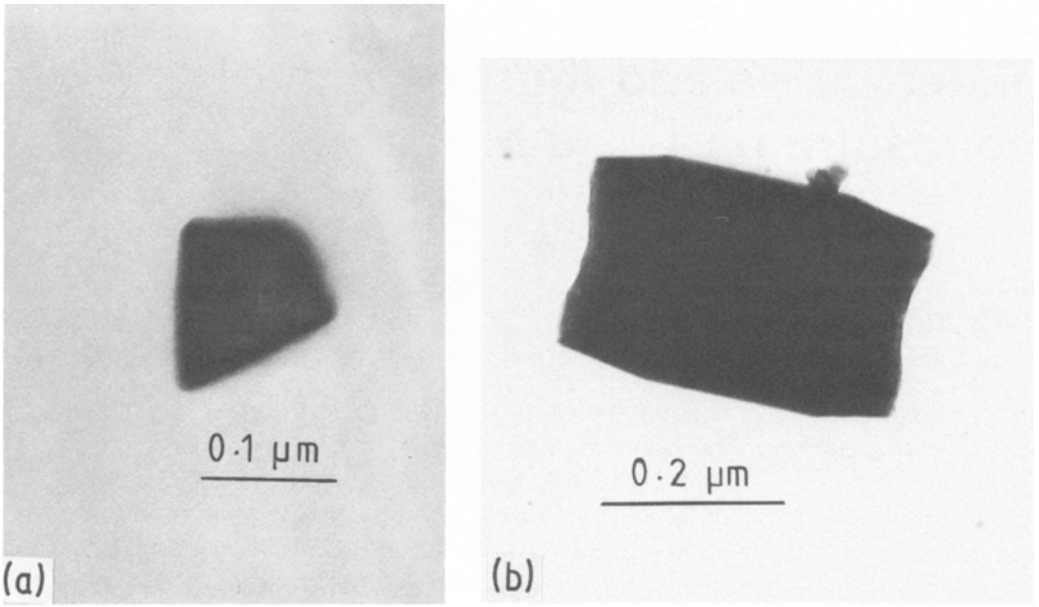

Figure 1 Typical examples of particles observed in the lower range of source temperatures: (a) coffin-shaped (cf. profile formed by ADGF projected on a plane normal to direction AB in Fig. 5); (b) waisted prism.

adjusting the boat voltage, and at each steady level of T_0 the metal vapour was allowed to mix naturally with a laminar upward stream of argon of 99.9999% purity flowing at a mean speed of 1 cm sec^{-1}. The source temperatures were 853, 873, 898, 968, 1028, 1033, 1138, 1145, 1165 and 1213 K. Particles were collected from the plume on carbon-coated specimen grids at 22.5 cm above the source. Following the application of a protective coat of carbon by evaporation, the specimens were examined in the Philips 301 transmission electron microscope.

3. Results

At low source temperatures (853, 873 and 898 K) the fume was barely visible, and relatively few particles were subsequently found on the specimen grids. Many of the particles resembled the zinc particles produced in plume chamber experiments at low source temperatures [3], and included small waisted prisms and smooth well-formed prisms. Examples of dendrites, from which these prisms originate in zinc and cadmium, were not seen in magnesium samples in spite of the low temperature of the source.

As with zinc, there were no spheres at low temperatures, but a considerable number of very small and thin prismatic particles of elongated outline occurred, the extent of the elongation being variable between particles. Similar shapes have been reported in particles from magnesium aerosols condensed from the vapour at reduced pressure [4]. Since the outlines resembled that of a coffin, these particles are referred to below as coffin-shaped. In this low temperature range particles were on the whole mostly below 0.2 μm across, although some were as much as 0.5 μm. Fig. 1 shows typical examples.

At intermediate temperatures (968, 1028 and 1033 K) the particles were more abundant, and as the temperature was increased the proportion of smooth prisms increased while that of waisted prisms decreased. In addition there were large numbers of coffin-shaped prisms and some particles of less regular, angular outlines, but still there were no spheres. Particles were larger (0.5 to 1.0 μm) than when generated at lower temperatures (Fig. 2).

At even higher temperatures (1138, 1145 and 1213 K) large numbers of spherical particles made their appearance, the numbers increasing with T_0, while at the same time the proportion of prisms, including the coffin-shaped variety, decreased. At 1213 K only a small number of smooth and coffin-shaped prisms were present besides spheres. The sizes of all types of particle again tended to be larger (0.5 to 2.0 μm).

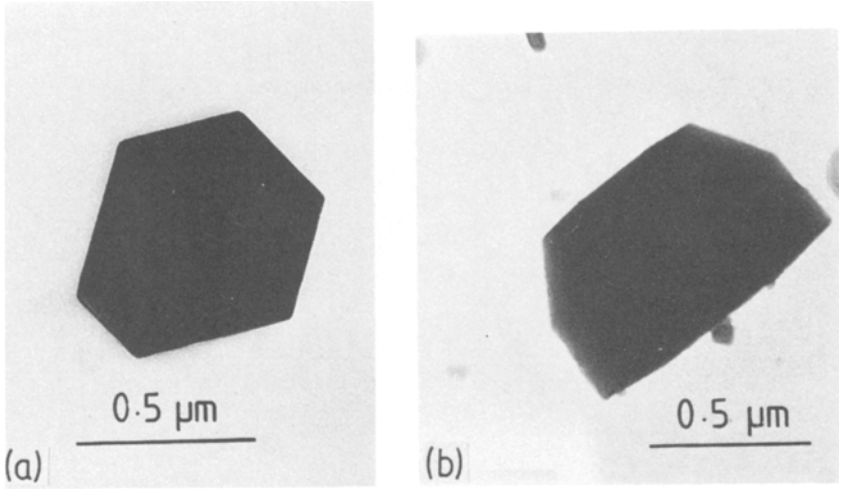

Figure 2 Particles at intermediate source temperatures: (a) coffin-shaped (cf. profile formed by ADGHEB projected on plane containing BCH in Fig. 5); (b) modified hexagonal prism.

The orientation of the spheres in the microscope specimens occasionally revealed the presence of a single flat (Figs. 3a and b), and by analogy with results for zinc and cadmium [1, 2] it may be concluded that this is evidence of the basal raft, and that the spherical magnesium particles condense in the liquid state. The residue of a spherical particle after evaporation in the beam of the electron microscope is shown in Fig. 3b, and reveals that the particle was lying on the basal flat. The ratio of raft:sphere radius may be put roughly at 0.55, and is similar to that observed for zinc.

Electron diffraction patterns of coffin-shaped particles were taken and the reflection indexed. These particles were found to be twinned in the (1 0.1) mode. Fig. 4a is a bright-field electron micrograph of a particle, and Figs. 4b and c are dark-field micrographs of the same particle taken with the $(1\,\bar{1}.1)_t$ and $(\bar{1}\,1.\bar{1})_m$ reflections, respectively. In order to make clearer the relationships of the twin orientations to the outlines of the particles in Figs. 1a and 2a, a schematic diagram is given in Fig. 5.

Other prisms had outlines which did not resemble those expected of (1 0.1) twins. The

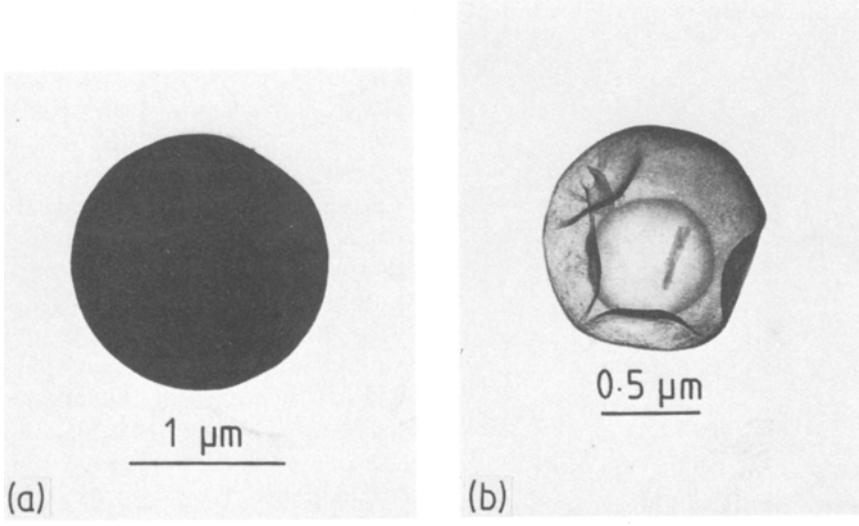

Figure 3 Spherical particles: (a) intact particle showing basal flat; (b) carbon residue of a sphere lying on the basal flat.

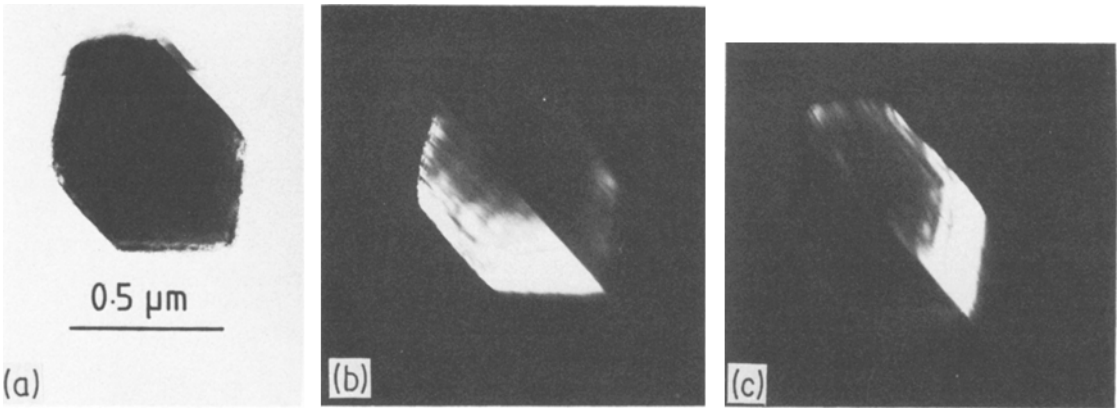

Figure 4 Electron micrographs of a twinned crystal: (a) bright-field; (b) dark-field, taken with $(1\,\bar{1}.1)_t$ reflection; (c) dark-field, taken with $(\bar{1}\,1.\bar{1})_m$ reflection.

particle in Fig. 2b, for instance, is shaped like the capped hexagonal prisms in zinc aerosols [2]. It was not possible to obtain and index diffraction patterns of these other particles, which were considerably thicker. They might have included examples of other twinning modes, since it is well-known that magnesium deforms by twinning on other pyramidal planes, such as (1 0.2) [5].

4. Discussion

4.1. Sequence of nucleation events

The results of the experiments on magnesium show the occurrence, once again, of two condensation mechanisms in metallic vapours [3]. Fig. 6 is a diagram of the theoretical profiles (curves A–H) of the supersaturation ratio (S) of magnesium vapour as it leaves the source at various T_0 settings and cools to a sink temperature T_∞ of 300 K. Each profile cuts, at a point marked n, the curve of the critical supersaturation ratio (S^*, curve Z), which has been derived from nucleation theory assuming a nucleation rate of $1\,m^{-3}sec^{-1}$. The position of the intersection establishes the temperature (T_n) at the point in the flow at which the threshold of nucleation is reached. The level of the temperature T_n in relation to that of the melting point (T_f = 923 K) will decide whether liquid droplets can be present among the fume particles nucleated in the flow. Only if T_n lies at or above T_f will the first nuclei grow into liquid particles.

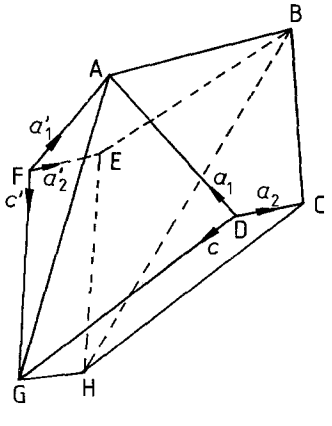

Figure 5 Schematic diagram of a magnesium particle twinned on the (1 0.1) system. Crystallographic axes in matrix and twin are parallel to a_1, a_2, c and a_1', a_2', c', respectively.

The absence of spheres in samples generated at source temperatures up to at least 1033 K is in agreement with theory, since it is seen that in such cases T_n lies below T_f. The experiments also showed, however, that even when T_0 was high enough for T_n to exceed T_f, the spherical droplets, now to be expected, were still accompanied by prisms. This observation indicates that even when T_n lies above T_f supersaturated states can persist in the flow at points where the temperature has fallen below T_f.

The form of the supersaturation profile beyond point n (dashed regions in curves A–H, Fig. 6) is hypothetical, no allowance having been made in theoretical calculations for the loss of metal vapour from the gas phase by condensation. The true profile must collapse from supersaturated levels at some position downstream of the threshold n, with the arrest of

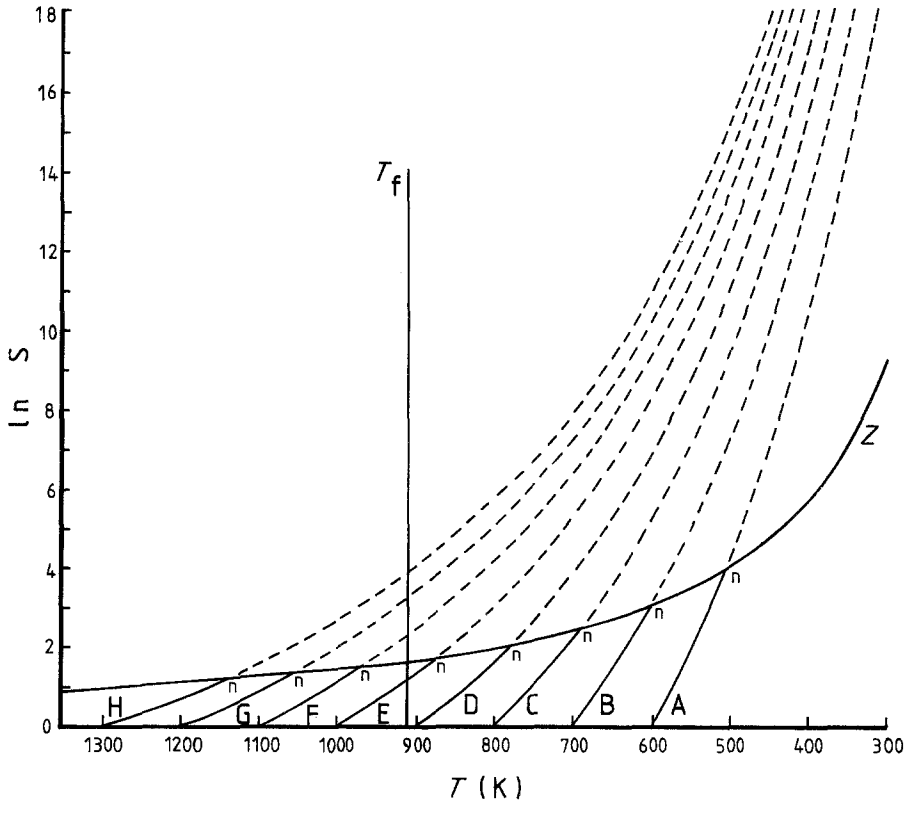

Figure 6 Nucleation threshold diagram for magnesium.

nucleation. Other things being equal, the higher the setting of T_0 the higher will be the temperature at the point of collapse. If this exceeds T_f, no condensation nuclei will be formed in the solid state. The point of collapse will also, presumably, depend on T_∞, and for low values such as 300 K collapse may be delayed until T_f is passed. The presence of prisms when $T_0 = 1213$ K suggests collapse at $T < T_f$. The large sizes to which some of the prisms grew indicates that they could not all have been formed during the brief run-up to the final temperature.

4.2. Twinned prisms

Twinned crystals, such as those now described in magnesium aerosols, have not been observed with zinc or cadmium at atmospheric pressure, although they have at low pressure [6]. The presence of elongated, twinned crystals in addition to the usual monocrystalline prisms suggests that an alternative mechanism of crystal growth may be operating in magnesium at atmospheric pressure. In interpreting results for zinc, three stages in the evolution of the hexagonal prism were distinguished, namely, the dendritic stage, the waisted prism stage and the final stage of the well-formed prism with smooth and flat faces [1, 2]. The dendrites are not always detected in zinc and cadmium, and it appears that they grow rapidly to waisted prisms. Apparrently this is also the case with magnesium, no dendrites having been observed in the samples taken from the plume chamber. The presence of the waisted prism, however, is indicative of an earlier dendritic stage.

The formation of zinc and cadmium dendrites and prisms in shapes severely deformed from the hexagonal has also been reported, and the suggestion made that the malformation originates in strains set up by hydrodynamic forces in the delicate structure of the dendrite [7]. In some instances malformed zinc and cadmium particles bear a crude resemblance to simple or multiple twins. However, separate growth regions can still be distinguished in the dendrite in such cases [7]. Even the smooth prisms show signs of imperfection, especially the large ones [8], and the formation under conditions of rapid expansion of thin, crystalline particles of zinc resembling

the twins found with magnesium [6] strengthens the case for a hydrodynamic explanation of these growth modifications also.

There remains the question why magnesium crystallizes in an elongated, twinned form at atmospheric pressure in addition to the more equiaxed form of the hexagonal prism. It is possible that growth of elongated twins by magnesium is the favoured alternative to the production of malformed prisms under high-stress conditions, and that the only difference with zinc and cadmium is that more extreme conditions are required before the growth of twins is induced. Further study would seem to be necessary to establish conclusively that deformed prisms are not produced with magnesium.

Twinning in the macroscopic monocrystal takes place by actual shear when certain slip planes and slip directions subtend suitable angles with the direction of the applied stress [9]. For the very early stage of growth now under consideration a description of twin formation in terms of plastic deformation would appear to be inappropriate, and even one in terms of the operation of a source of twinning dislocations during the growth of the nucleus may be of questionable value. Relatively few reports of (1 0.1) twinning in the hcp metals exist, and physical data that relate to the phenomenon in a micro-particle are not available. Estimates of the resolved shear stress for twinning, calculated by Orowan's method from the theoretical shear in the (1 0.1) mode [10], indicate that the stress required should be lower in magnesium than in zinc. This is in keeping with the morphological evidence obtained in the present investigation.

Acknowledgements

The authors wish to acknowledge the continuing support of the Science and Engineering Research Council for this work. The apparatus was constructed with the support of the Department of Trade and Industry, Warren Spring Laboratory.

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Received 6 September
and accepted 13 September 1984