involving PbF_2 and aluminous muffles. It is possible that the "vapour-flux" process could be utilized to grow large crystals by controlling the rate of vapour transport into the flux.

Acknowledgements

The authors are grateful to Dr S. H. Smith for helpful discussions and technical assistance; to Mr F. R. Wondre for the X-ray powder patterns; to Mr W. Davison of the School of Physics, Newcastle University, for EPMA; and especially to Dr Z. Hauptman of the School of Physics, Newcastle University, for the initial suggestion of the "vapour-flux" transport mechanism.

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Received 14 March and accepted 22 March 1974

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Pre-precipitation phenomena in Zn—Cd alloys

It has been known for many years that pre-precipitation phenomena are present in some binary alloys: the aluminium-based alloys, especially Al–Cu, Al–Ag and Al–Zn, are the most well studied examples of them [1-3]. In all these alloys, before true precipitation there is a formation of small clusters of solute atoms whose size is normally in the order of 20 to 30 Å, and which are characterized by the coherence with the host lattice. These are called Guinier-Preston zones. Until now this kind of phenomena has not been observed in hexagonal close-packed metals and in particular in zinc-based alloys. Therefore, it is of interest that we have observed phenomena in Zn–Cd alloy which may be interpreted in this way.

The solubility of Cd in Zn is very poor at room temperature (in the order of 0.01 at. % or less) and maximum solubility is attained at about 350° C (1.5 at. %) [4]. Of course a certain amount of Cd may be maintained in solution at room temperature, at least for some time, by rapid quenching from high temperature. The alloys studied were obtained from high purity Zn and Cd (99.999 and 99.9% respectively) and contained 0.6 at. % (1 wt %) Cd and 0.2 at. % (0.36 wt %) Cd.

First precise lattice parameter measurements were obtained by the Debye-Scherrer powder method, taking three photographs (Cu$K\alpha$ radiation, 114.6 mm diameter camera and 3.5 h exposure) of each sample: the first (A) before thermal treatments, the second (B) immediately after annealing at 350° C in inert Helium atmosphere and quenching in water at 0° C (beginning the exposure 20 min after quenching) and the third (C) a few days after quenching. Typical results found for two of the alloys examined are shown in Table I.

It is important to note that before thermal treatment and some time after quenching the alloys exhibit equal lattice constants which are coincident with those of pure Zn, clearly indicating that the solute Cd is totally precipitated. The observation made shortly after quenching, shows a marked increase especially in the c value, related to the complete dissolution

TABLE I

	0.2 at. % Cd			0.6 at. % Cd		
	a (± 0.0004 Å)	c (± 0.0008 Å)	c/a (± 0.0006)	a (± 0.0004 Å)	c (± 0.0008 Å)	c/a (± 0.0006)
A	2.6648	4.9468	1.8563	2.6650	4.9465	1.8561
B	2.6649	4.9488	1.8570	2.6649	4.9522	1.8583
C	2.6650	4.9470	1.8563	2.6649	4.9467	1.8562

of the larger solute Cd atoms in the Zn matrix.

To follow the stages of the precipitation phenomenon we have extended the observations to small-angle scattering. Measurements of small-angle X-ray scattering have been carried out using a Kratky high resolution camera equipped with counter detection and fixed-time point-by-point recording of intensity data [5], employing a sample-to-detector distance of 286.5 mm. The samples, thin plates about 50 μm thick, were thermally treated as previously

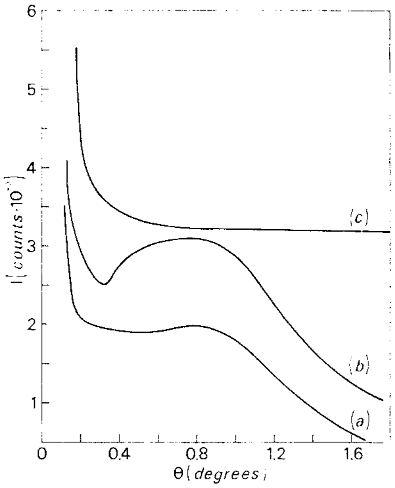

Figure 1 Small-angle X-ray diffraction spectrum (Cu$K\alpha$ radiation) for: (a) Zn sample containing 0.6 at.% Cd, observed 1 h after quenching; (b) Zn sample containing 0.2 at.% Cd, observed 1h after quenching; (c) Zn sample containing 0.2 at.% Cd, observed 10 h after quenching: interference effects disappeared.

reported for powders. The experimental results obtained about one hour after quenching are shown in Fig. 1, traces a and b are for the 0.6 and 0.2% alloy respectively. We ascribe the observed diffraction effects to a segregation phenomenon from the solid solution which results in coherent clusters (Guinier-Preston zones): the presence of a resolved maximum clearly indicates interference phenomena between zones [6]. These phenomena occur at room temperature and the small-angle scattering effects become undetectable, as expected [7], when the precipitates with their own characteristic lattices are formed. In our case, this happens about 10 h after quenching, as shown in Fig. 1, trace c.

The minimum gyration radius of the particles has been deduced by means of the classical Guinier plot [7] from the experimental curves and its value is about 15 Å; the mean distance between the clusters is about 60 Å. Otherwise, when the interference phenomena disappeared, we calculated a minimum gyration radius of about 100 Å. We would like to point out that the Guinier approximation gives precise results for the actual dimensions *only* for globular or nearly spherical clusters and for very diluted systems.

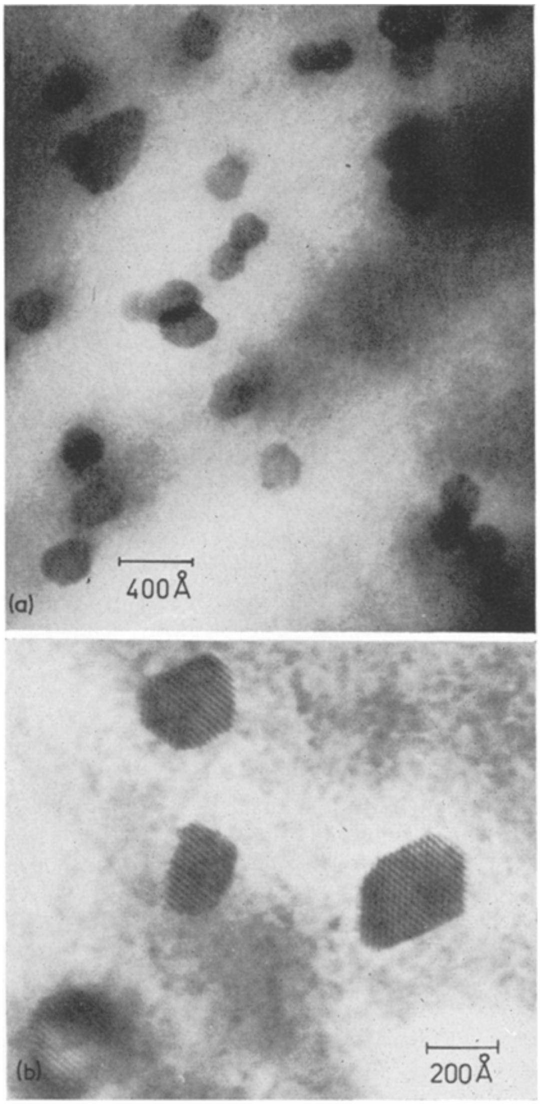

Figure 2 (a) Electron micrography of a Zn sample containing 0.6 at.% Cd, taken 10 h after quenching; (b) Enlarged view of the precipitates themselves, showing morphology of the Moiré pattern.

The electron microscope observations carried out on ion-beam thinned samples about 10 h after quenching, confirmed the main conclusions drawn from the X-ray small-angle analysis. In Fig. 2a, a uniform distribution of precipitates with Moiré patterns are present, as shown in greater detail in Fig. 2b. The appearance of the Moiré patterns and the invariance, by tilting the samples, of the contrast round the precipitates (i.e. there is not the typical elastic deformation of the coherent precipitate), lead us to interpret the precipitates as incoherent ones [8-10]. Moreover, micrographs and electron diffraction patterns show the two-dimensional nature of the precipitates. We emphasize that the thin platelets observed are equilibrium precipitates. In fact there is no evolution in their shape and distribution. At this stage the initial coherent structure has been transformed to another which is no longer coherent but which has a precise crystallographic orientation, thus producing the observed Moiré pattern.

On the basis of the electron microscopy observations, we have performed some preliminary theoretical calculations of small-angle X-ray scattering curves assuming the zones are disc shaped. By comparison with the experimental results we found that the mean "effective" radius of the Cd-rich platelets was about 20 Å. The interference maxima observed in the first ageing stages may be interpreted as interparticle effects due to a regular two-dimensional array ("superlattice") of the platelets themselves.

In conclusion we deduce that Guinier-Preston zones are present in Zn–Cd alloys. However, in order to have a complete characterization of the segregation phenomenon, we intend to correlate the lattice parameter measurements and the low-angle scattering with changes in mechanical and physical properties and in the electron micrographs and electron diffraction patterns of the specimen during the whole ageing sequence. These data are now being collected and will be reported in a following paper.

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Received 18 March and accepted 22 March 1974

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Hydrodynamically-induced crystallization from an homogeneous solution of two polymers

Crystal nucleation is readily induced by mechanical agitation in melts or solutions of both low molecular weight and high polymeric substances. Under such conditions crystallization generally occurs at lower supercoolings than are otherwise necessary. Hydrodynamically-induced crystallization from polymer solutions was first extensively reported by Pennings [1] for high density polyethylene. Many studies have followed that report, the majority of the research carried out on polyethylene [2-8] although work has also been published on polypropylene [8], polyoxymethylene [9], isotactic polystyrene [10] and polyethylene oxide [11]. The general conclusion drawn is that the fibrillar crystals so produced have a "shish-kebab" morphology consisting of folded-chain lamellae over-growing an extended-chain fibrillar or "row" nucleus.

It is known [12] from studies of crystallization from solution of low molecular weight materials, that the addition of a second solute