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The two-phase region at Cd_3Mg

F. W. NOBLE, W. FAIRHURST
Department of Metallurgy and Materials Science, University of Liverpool, Liverpool, UK

The two-phase mixture of ordered and disordered phases associated with the order-disorder transformation in alloys based on Cd_3Mg has been identified metallographically in single crystal specimens. The morphology of the two-phase structure is such that the disordered phase forms lamellae in an ordered matrix. The habit plane on which the lamellae form has been established by two-surface analysis and the orientation relationship determined using back-reflection Laue technique. The results are shown to be consistent with the notion that the habit plane of the lamellae is determined by minimum atomic mismatch in the interface between lamellae and matrix. Previously obtained hardness data are explained in terms of the conditions required to produce the two-phase structures.

1. Introduction

The equilibrium diagram associated with the order-disorder transformation in the vicinity of Cd_3Mg has been established by Kamath, Craig, and Wallace [1] and subsequently confirmed by Frantz and Gantois [2]. The diagram obtained by the former workers using X-ray techniques is reproduced in Fig. 1. It is characterized by a fairly extensive two-phase region, within which the ordered and disorered phases co-exist, and there is no maximum associated with the stoichiometric composition Cd_3Mg. The ordered α-phase, based on Cd_3Mg, has the hexagonal DO_{19} structure with $c/a = 0.807$ (or 1.614 if a is taken as the nearest-neighbour distance in the basal plane). The c/a ratio of the disordered β-phase, which is cph, is always greater than the latter figure, being 1.78 for the 17 at. % Mg alloy (at room temperature) and 1.73 for the stoichiometric composition (at 87°C). All these data are taken from Ref. 1.

At room-temperature, therefore, the phase-diagram indicates that alloys with compositions between 17 at. % Mg and 25 at. % Mg should exist as a two-phase mixture of α and β phases with c/a ratios of 1.614 and 1.78 respectively. Independent confirmation of the existence of the two-phase region between these composition limits at room temperature has been provided by the internal friction data of Lulay and Wert [3] but, as in the previous studies, apparently no attempt was made to detect the existence of the two phases metallographically.

In the course of a current investigation [4, 5] into the mechanical properties of single crystals of alloys based on Cd_3Mg, it became clear that the co-existing phases were metallographically detectable in alloys within this composition range, and this paper reports the results of a study of the geometrical relationships between the phases, using metallographic and X-ray techniques. As the two-phase structure could best be developed in an alloy containing 22 at. % Mg, the work is mainly confined to this composition.

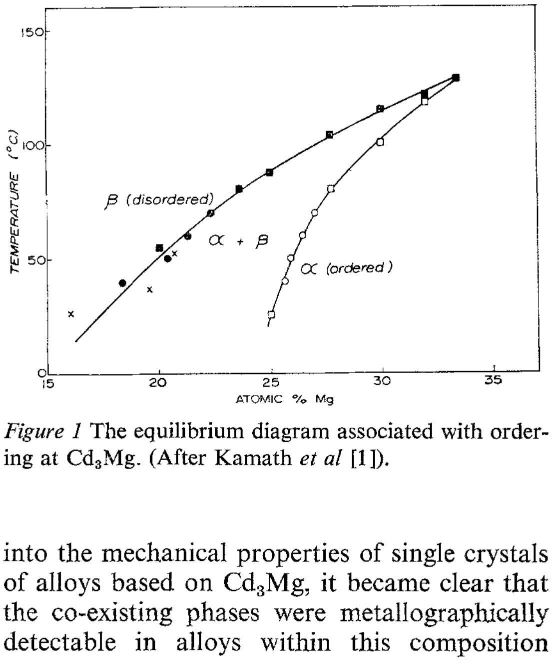

Figure 1 The equilibrium diagram associated with ordering at Cd_3Mg. (After Kamath *et al* [1]).

2. Experimental procedure

The preparation of Cd-Mg alloys of the type used in this work has been described elsewhere [5]. The single crystal growth method employed was the Bridgman technique, the alloy being contained in a graphite mould under an atmosphere of argon and lowered through the hot zone of a furnace at a rate of about 1 cm per hour. Electropolishing of the resulting crystals was carried out using an 8% nital solution. Back-reflection Laue patterns were obtained from the crystals using a tungsten target and diffractometry on polycrystalline samples, when carried out, was performed with CuK_α radiation.

3. Experimental results

The appearance of an electropolished surface of an "as-grown" single crystal is shown in Fig. 2.

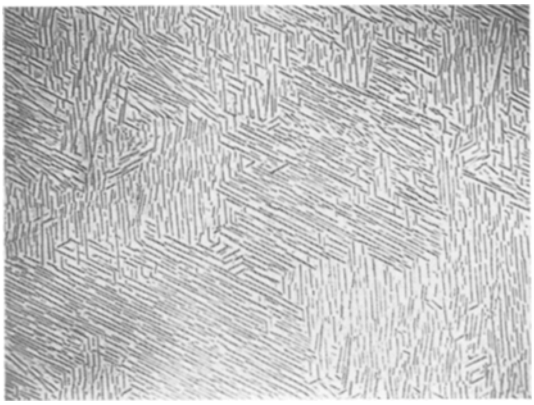

Figure 2 The two-phase structure in a 22 at. % Mg alloy single crystal (× 500).

The surface has been etched during electropolishing and the lamellar structure which is revealed has six specific directions associated with it which were identical at all points on the surface. Identification of the lamellar structure with the two-phase region was achieved by heating the crystal above the two-phase region and quenching. This treatment eliminated the lamellar structure and a single-orientation Laue pattern, shown in Fig. 3, was obtained from the quenched crystal. The crystal was oriented such that the Laue spot just to the left of centre is the basal pole, and the associated six-fold symmetry can be seen. The corresponding Laue taken before re-heating and quenching is shown in Fig. 4. The orientation of the crystal with respect to the Laue film was slightly different but the intense basal spot near the centre of the film is easily distinguishable. The most significant difference between Figs. 3 and 4 is the presence of "extra" spots, particularly the array of six immediately surrounding the basal pole, which result from the presence of the lamellar structure in the crystal from which Fig. 4 was taken. The

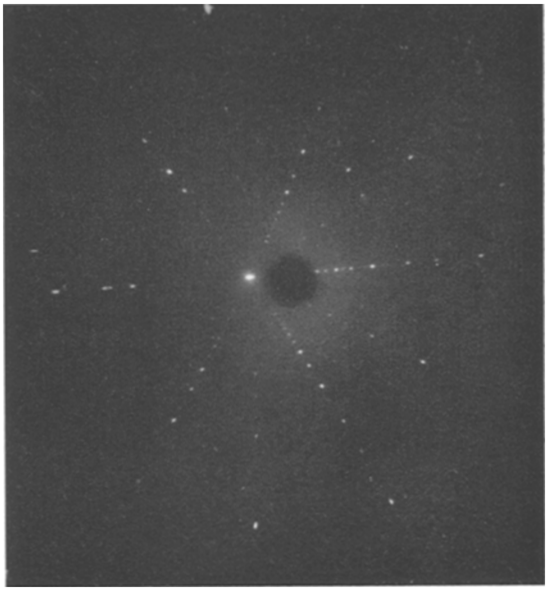

Figure 3 The Laue pattern of a single crystal containing 22 at. % Mg after quenching from above the two-phase region.

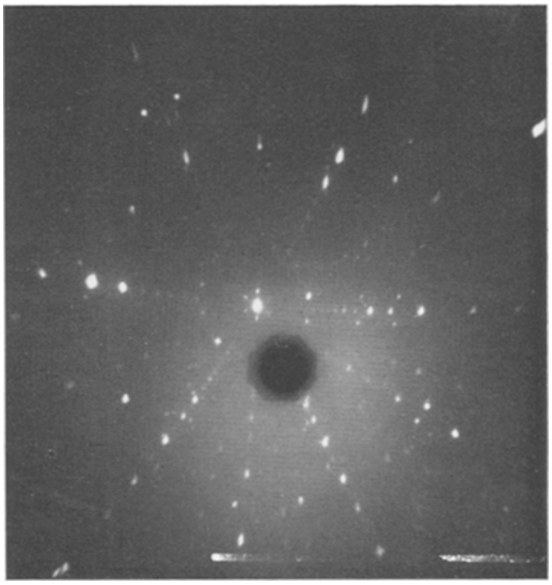

Figure 4 The Laue pattern of the same crystal as in Fig. 3 prior to re-heating and quenching i.e. in the "as-grown" condition and with the microstructure shown in Fig. 2.

"extra" spots exhibit sixfold symmetry with respect to the central basal pole and the Laue can be interpreted as the superimposition of six additional patterns on the seventh, the basic matrix pattern. The significance of the sixfold symmetry, then, is that the six patterns represent six variants of a single orientation relationship, each corresponding to a different lamellar orientation.

The above interpretation was verified by obtaining a region of crystal in which a single lamellar orientation predominated over a very large area. A micrograph of the area is shown in Fig. 5, and Fig. 6 shows the Laue pattern obtained from this area. In Fig. 6 the crystal is oriented to have basically the same orientation as in Figs. 3 and 4, and again the basal spot is close to the centre of the film. As expected, only a single "extra" spot is visible in the immediate vicinity of the matrix basal pole and this is associated with a hyperbola a′ – b′ which runs parallel to, but displaced 2° from, the hyperbola a – b of a $\langle 11\bar{2}0\rangle$ zone of the matrix pattern.

The orientation relationship between the matrix and the lamellar orientation responsible for the extra pattern in Fig. 6 was obtained by rotating the crystal until the basal pole appeared near the bottom of the film and additional hyperbolae of the superimposed pattern were revealed. The result is shown in Fig. 7, the zones of the two patterns have been indexed, with the set of indices associated with the matrix pattern being underlined for distinguishing purposes. Two significant pieces of information can be derived from this figure:

(*a*) The inter-spot spacing on each pattern can be measured with sufficient accuracy to distinguish which pattern is due to the ordered phase and which is due to the disordered phase, on the basis of the very different c/a ratios of the phases (1.61 for the ordered phase; 1.78 for the disordered). The results unambiguously show that the basic matrix pattern (underlined indices) is due to the ordered α-phase and the superimposed pattern results from the disordered, lamellar, β-phase. (The indices of the zones from the ordered phase are referred to the cph unit cell with $c/a = 1.614$ rather than to the DO_{19} unit cell.)

(*b*) The coincidence of the [0001] and $[1\bar{1}00]$ zones indicates that the phases are oriented such that $(0001)_\beta$ is parallel to $(1\bar{1}00)_\alpha$. The orientation relationship is unambiguously defined by the further observation that the $[11\bar{2}0]$ directions common to both these planes are 2° out of parallel, as shown by the non-coincidence of the zones a – b and a′ – b′ in Fig. 6 (which appear at the bottom of Fig. 7).

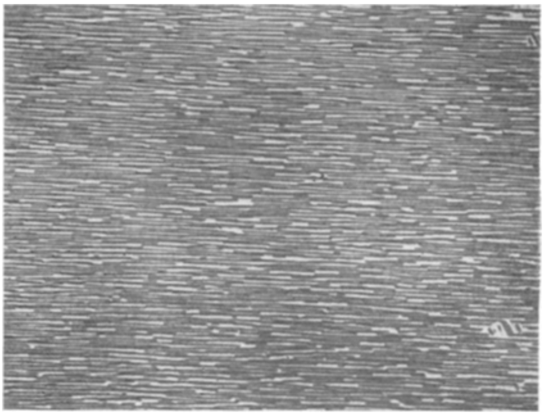

Figure 5 A region of single crystal exhibiting a predominantly single lamellar orientation (× 500).

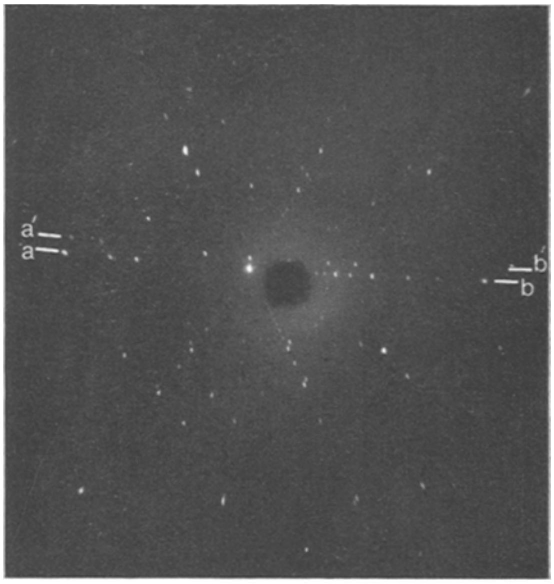

Figure 6 The Laue pattern corresponding to the structure shown in Fig. 5.

The significance of this orientation relationship becomes clear when the habit plane on which the lamellae form is taken into consideration. This was determined by two-surface analysis, each of the six lamellae directions visible on one face being followed onto the orthogonal face. The results showed that all six sets of traces corresponded to $\{11\bar{2}4\}$ planes referred to the matrix orientation (i.e. the

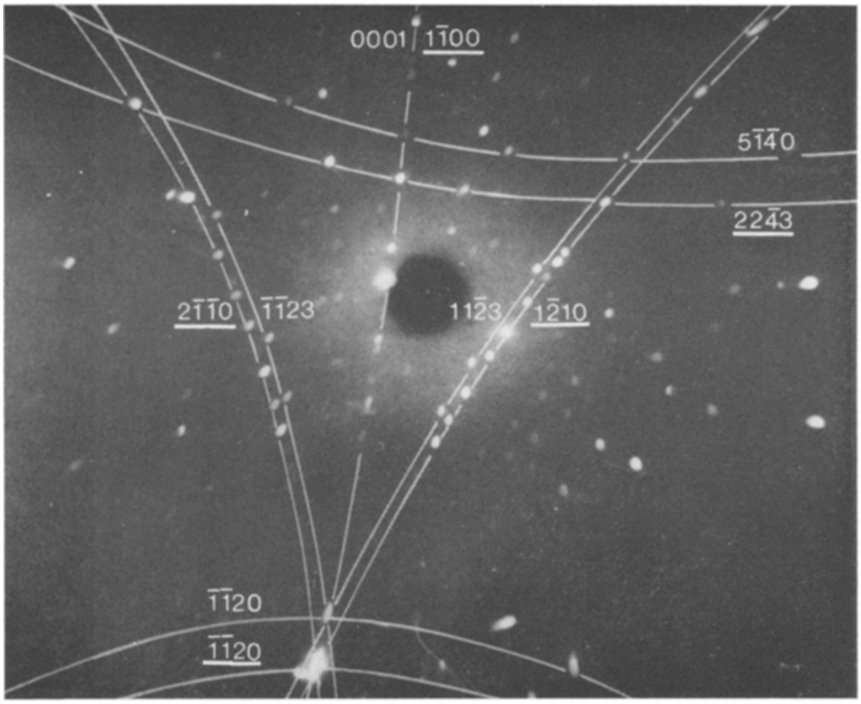

Figure 7 A rotated version of the Laue pattern shown in Fig. 6. The matrix basal pole is the intense spot at the bottom of the film; the underlined zonal indices refer to the ordered matrix, the others to the disordered lamellae.

ordered structure) or $\{3\bar{1}\bar{2}0\}$ planes in the disordered lamellae. In other words, the interface between lamellae and matrix is formed by $\{11\bar{2}4\}_\alpha$ planes and $\{3\bar{1}\bar{2}0\}_\beta$ planes. Fig. 8 illustrates the crystallography involved in the orientation relationship between the two phases and, for simplicity, no distinction between cadmium and magnesium atoms has been made in this diagram. The plane of the paper is $(0001)_\alpha$ or $(1\bar{1}00)_\beta$ giving the parallelism required by the orientation relationship. The common $[11\bar{2}0]$ directions have been drawn parallel, however, rather than the required 2° apart. The habit plane trace is denoted by x − y in the β-phase, x′ − y′ in the α-phase, and the angles made by these traces with $[11\bar{2}0]$ are shown (the habit planes are normal to the plane of the paper). The angle for the $(11\bar{2}4)_\alpha$ trace has been calculated from $c/a = 1.614$ [1]; the angle associated with the $(3\bar{1}\bar{2}0)_\beta$ trace is, of course, independent of c or a. In order to bring the two habit plane traces into coincidence a rotation of exactly 2° is required and consequently when the phases are joined across this interface $[11\bar{2}0]_\alpha$ will make an angle of 2° with $[11\bar{2}0]_\beta$ as required by Figs. 6 and 7.

4. Discussion

The matching interatomic spacings in the interface between the β and α phases are respectively x − y and x′ − y′ in the plane of Fig. 8. The corresponding spacings in the orthogonal direction are given by the c parameter of the β unit cell and by $\sqrt{3}/2$ times the a parameter of the α unit cell. The data of Kamath *et al* give x − y equal to 7.99Å while x′ − y′ is found to be 8.02Å. Similarly c_β is approximately 5.39Å while $(\sqrt{3}/2)a$ is about 5.40Å. There is, therefore less than $\frac{1}{2}\%$ mismatch between the corresponding atom spacings in the two phases and it appears that this factor has predominated in the choice of habit plane.

Although the compositions (as indicated by the measured c/a ratios) of the α and β phases agree well with the equilibrium diagram at room temperature, it is not suggested that the morphology and orientation relationships found under the conditions employed in the present work are

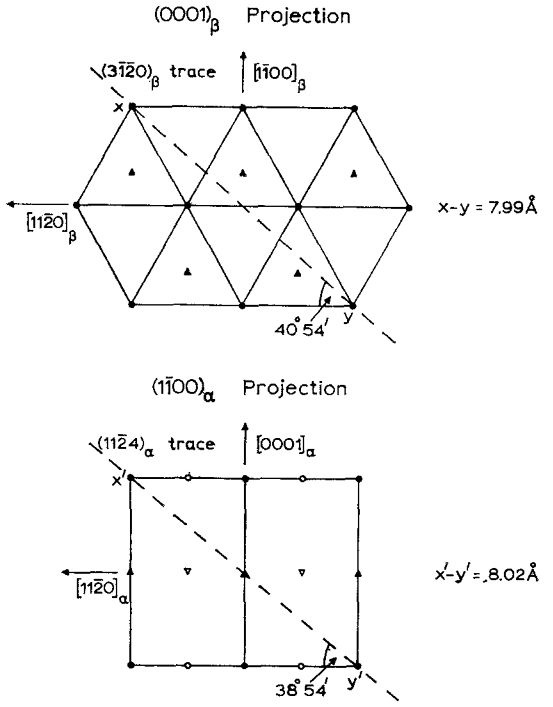

Figure 8 The orientation relationship deduced from Fig. 7. The projection of the ordered phase (lower diagram) is drawn without distinguishing between Mg and Cd atoms and is indexed with respect to the cph structure rather than the DO_{19}.

characteristic of the two-phase region as a whole. In fact there is considerable evidence that the β-lamellae are formed under conditions which are very far from equilibrium. Under equilibrium conditions, cooling through the two-phase region would be expected to result in the formation of regions of α-phase, precipitated within the original disordered β-matrix. In fact the opposite situation has been found here, the β-lamellae existing within the single orientation α-matrix, suggesting that uniform ordering of the alloy has occurred prior to its decomposition into α and β phases. Similarly, on heating the two-phase alloy, the equilibrium diagram would indicate the growth of the disordered β phase at the expense of the α phase, until the entire crystal was disordered. However, the crystal orientation after heating above the two-phase region and quenching (Fig. 3) is the same as the orientation of the ordered matrix in the previous two-phase structure (Fig. 4), indicating that the β-lamellae must have re-dissolved prior to complete disordering and then the matrix has uniformly disordered, the disordered crystal retaining the same orientation.

The Laue photograph shown in Fig. 3 corresponds (from c/a measurements) to the ordered phase even though the crystal has been quenched from the disordered region. This behaviour is consistent with that exhibited by stoichiometric alloys which have been shown [1] to order under the fastest quench. Under such conditions equilibrium phase separation during the quench is clearly out of the question and in the case of non-stoichiometric alloys any eventual decomposition into the equilibrium two-phase mixture after quenching must occur within an ordered matrix. This sequence would account for the present results if it is assumed that even under the conditions of crystal growth the cooling rate is sufficient to suppress equilibrium phase separation allowing rapid ordering prior to eventual decomposition into the two-phase structure observed.

It was possible to verify that isothermal decomposition of a quenched-in ordered matrix would occur at room-temperature, by means of X-ray diffractometry on a polycrystalline, 22 at. % alloy. The $(2\,0\,1)_\alpha$ line of the quenched ordered matrix was continuously scanned and the intensity peak began to show a distortion which was pronounced after $\frac{3}{4}$ h. After 5 h the distortion resolved itself into a second intensity peak which was identified as $(1\,0\,1)_\beta$. Metallographic examination of the specimen showed that the development of the $(1\,0\,1)_\beta$ line was accompanied, as expected, by the appearance of a lamellar structure in the specimen.

Finally, the present results may be taken, in conjunction with those of Kamath *et al*, to explain the hardness data of Savitski [6] reproduced in Fig. 9. These data show that at 25 at. % Mg the hardness of quenched and slow-cooled material are identical, but while the quenched alloys show a continuous decrease in hardness with decreasing magnesium content, the slow-cooled alloys show a hardness peak, at approximately 20.5 at. % Mg. The identical hardness values of the quenched and slow-cooled stoichiometric (Cd_3Mg) alloys are readily accounted for by the work of Kamath *et al* since the states of the alloys are identical after both treatments. The presence of the lamellar structure in the slow-cooled non-stoichiometric alloys, observed in the present work, however, suggests that the hardness peak on the Cd-rich side of stoichiometry is attributable to the two-

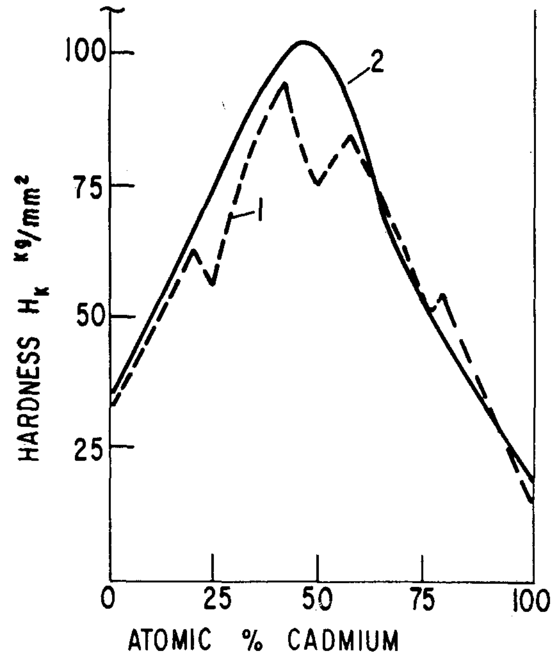

Figure 9. The room-temperature hardness of Cd-Mg alloys as a function of composition (after Savitski [6]). Curve 1 is for slow cooled alloys, curve 2 for quenched alloys

phase nature of the materials rather than to deviation from stoichiometry *per se* in single-phase long-range ordered material. The implication of the spontaneous development of order on quenching in the non-stoichiometric alloy studied here is that the quenched alloys in the vicinity of the peak are, in fact, long-range ordered, though, if this is the case, the continuous hardness decrease with increasing Cd content in the Cd-rich alloys is rather surprising.

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References

1. G. S. KAMATH, R. S. CRAIG, and W. E. WALLACE, *Trans. Met. Soc. AIME* **227** (1963) 26.
2. C. FRANTZ and M. GANTOIS, *Mem. Sci. Rev. Mét.* 1 (1970) 49.
3. J. LULAY and C. WERT, *Acta Metallurgica* **4** (1956) 627.
4. W. FAIRHURST and F. W. NOBLE, *J. Mater. Sci.* 7 (1972) 334.
5. W. FAIRHURST, Ph.D. Thesis, University of Liverpool (1972).
6. E. M. SAVITSKI, "Mech. Properties of Intermetallic Compounds", Ed. Westbrook (John Wiley, New York, 1960).

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