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Authors

Dutkiewicz, J.
Sinclair, R.

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OBSERVATIONS OF B19 ORDERING IN Mg_3Cd THIN FOILS

J. Dutkiewicz* and R. Sinclair

Department of Materials Science and Engineering
University of California, Berkeley, CA 94720 USA*On leave from Institute of Metallurgy, Polish Academy of Sciences
30-059 Krakow, ul. Reymonta 25, PolandIntroduction

During examination of Mg_3Cd by high resolution transmission electron microscopy (TEM) an unusual phase transformation was found to occur in the thinnest foil areas. The purpose of this note is to describe this reaction and to account for the conditions under which it is likely to proceed.

Experimental Procedure

An ingot of Mg_3Cd was produced from pure elements in an arc furnace under an argon atmosphere. Chemical analysis showed the composition to be 24.97 at %Cd. The alloy was homogenized at 400°C for 10 hrs and then hot and cold rolled down to 0.08mm sheet. After a disordering anneal at 400°C, the material was water-quenched and aged in the temperature range 20-120°C. Thin foils were prepared by jet-electropolishing 3mm discs in an electrolyte consisting of 30% HNO_3 and 70% methanol at -50°C, and were examined in a Philips EM301 electron microscope.

Crystallography of Phases in Mg-Cd System

The accepted equilibrium phase diagram is that of Moore and Raynor (1) which shows (fig. 1) that near 25%Cd the DO_{19} ordered structure (Strukturbericht notation) is stable below about 160°C. This structure is a simple Mg-Cd first nearest neighbor ordering in an hcp structure (fig. 2a). At higher Cd content the orthorhombic structure, B19, occurs, centered on the composition Mg_3Cd . The orthorhombic B19 unit cell is outlined in fig. 2b against the modified DO_{19} unit cell. It may be produced from the DO_{19} lattice by the replacement of Mg atoms by Cd along one particular [2110] direction, together with the appropriate lattice distortions. Both phases are stable over a fairly wide range of composition.

As drawn, the phase diagram shows that the two phase order plus disorder field disappears at B, indicating a second or higher order phase transition above this Cd content (~30%Cd). Such a transition is forbidden by the Landau-Lifshitz symmetry rules (2) for the $\text{hcp} \rightarrow \text{DO}_{19}$ reaction, with a first-order transition being predicted. The latter mechanism has been the one generally observed for the composition Mg_3Cd (3-5). This, together with the unusual hump in the order-disorder boundary near 26%Cd (at A) and the fact that B is a critical point, unusual in metallurgical systems (6), would indicate that a more detailed phase diagram study, preferably with recent experimental techniques, is desirable.

Results

It was established by conventional X-ray diffractometry that the bulk sheet material exhibits the normal behaviour of Mg_3Cd by undergoing the $\text{hcp} \rightarrow \text{DO}_{19}$ ordering reaction at room temperature. Figure 3 shows the corresponding increase of Bragg-Williams long-range order parameter.

To observe and record high resolution TEM images, it is necessary to use a high intensity electron beam. Under these conditions it was found that a transformation occurred very rapidly near and at the edge of thin foils of both disordered and fully ordered Mg_3Cd specimens. Within a few seconds at the edges (i.e. in the thinnest areas) a domain structure developed

which consisted of highly crystallographic, trapezoidal domains. This contrasts with the smoothly-curved antiphase domain boundary structure of DO_{19} and Mg_3Cd (3-5). In slightly thicker regions long thin domains were produced whilst regions away from the foil edge remained unaffected. This transition of microstructures is illustrated by fig. 4.

The basal plane electron diffraction pattern of trapezoidal areas is identical to that of fully ordered DO_{19} , with weaker superlattice reflections at half the reciprocal lattice vector of fundamental reflections. However, three different domain variants are present, as found by taking dark field micrographs with each of the $\{01\bar{1}0\}$ DO_{19} superlattice reflections in turn. Conversely, in the thicker foil regions the characteristic domain contrast of DO_{19} is, as expected, identical in each case. These observations are consistent with the nucleation of three orientations of the B19 phase in thin areas with their b direction parallel to the three, 120° related principal axes of hcp or DO_{19} . Thick areas remain in the DO_{19} structure. Direct lattice imaging and corresponding optical diffraction results, which are reported elsewhere (7), confirm this interpretation.

Discussion

For formation of the B19 phase in Mg_3Cd , either the composition of the alloy must change locally to that of B19 or the phase is produced at a composition outside the normal equilibrium phase limits. The authors regard the latter to be more likely.

Net loss of Mg is required to alter the composition to that of equilibrium B19. This might occur by:

- i) oxidation;
- ii) vapourisation;
- iii) diffusion,

but all these possibilities can be ruled out.

The first is the likeliest. Oxidation was not observed in the present experiments to any large extent, neither by the appearance of oxide reflections in the selected area diffraction patterns nor by commensurate deterioration of image quality. Cadmium has the higher vapour pressure at any temperature and so this species, not Mg, would vapourise preferentially. In addition, (i) and (ii) are surface phenomena and would occur over the whole foil rather than being confined to only the thinnest areas. Finally, diffusion from one region to another would not be possible in the time involved in the reaction and a driving force for such a large-scale segregation is difficult to suggest.

The presence of B19 is proposed to be its greater inherent stability, in the absence of constraint effects. Lattice constant differences between B19 and hcp structures at 25% Cd, estimated from data in Pearson (8) and Moore and Raynor (1), are quite substantial: ~4% expansion in the b direction of B19, ~3% and ~2% contractions in the c and a directions respectively upon ordering. This may be compared with the almost exact registry in the basal plane between hcp and DO_{19} , with only ~0.4% contraction along c . Formation of B19 in the bulk crystal of either disordered hcp or ordered DO_{19} Mg_3Cd would result in high strain energy. In situations where this strain can be relieved by change of specimen shape, B19 may be possible if it has lower free energy than that of DO_{19} . We suggest that this is the case for extremely thin crystals of Mg_3Cd . However, in bulk material, or in thicker TEM foils, the strain energy required to accommodate a B19 nucleus raises the total free energy above that for DO_{19} . The latter is then formed preferentially. The strain energy, estimated from the approximate elastic modulus of Mg_3Cd and the above strains, is 930 J/mole. This is substantial when compared to the ordering energy of the hcp- Mg_3Cd reaction (~590 J/mole (9)) and would certainly be sufficient to suppress this reaction.

B19 has not been found in previous studies of Mg_3Cd . This is attributed to the considerably higher electron flux used in our attempts at lattice imaging as well as the high quality thin foils necessary for such studies. Nucleation of B19 may also be aided by foil distortion under high beam heating conditions and thus the foil movement observed accompanying the initial stages may promote its formation as well as being a consequence of the change of specimen shape. The kinetics of the reaction were affected by the intensity of the electron beam but are probably not enhanced by radiation damage as the electron energy (100keV) is below that for displacement of both species. The absence of the B19 reaction from a recent hot-stage high voltage electron microscope study (5) may arise from the thick foils commonly used at higher voltages and a cross-over of thermodynamic stability of B19 with DO_{19} at higher temperatures.

Finally the departure from MgCd stoichiometry is large in the present case. The diffraction patterns indicate that the excess Mg atoms are distributed randomly on the Cd sites.

Conclusions

In very thin foils of Mg_3Cd ($\leq 500\text{\AA}$), the off-stoichiometric B19 structure (normally based on MgCd) is produced rapidly under high electron flux conditions in a transmission electron microscope. This phase is thought to be the most inherently stable at this composition but is prevented from nucleating in bulk or thick specimens by the high strain energy involved in the transformation.

Acknowledgements

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Fig. 1

DO₁₉ (Mg₃Cd)

B19 (MgCd)

○ Mg ● Cd

Fig. 2

XBL 753-5916

XBL 747-6835

Fig. 3

Fig. 4

XBB 753-2304

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