

AN INTERNAL FRICTION STUDY OF PHASE TRANSFORMATIONS IN MAGNESIUM-INDIUM ALLOYS

R.A. Berrisford and G.M. Leak

Department of Metallurgy, University of Manchester, Manchester, U.K.

Abstract. - Order-disorder reactions in magnesium-indium alloys have been studied by internal friction techniques. Damping measurements during continuous slow heating and cooling of alloys between 21 at% In and 62 at% In have shown that the FCC β' and FCT β'' superlattices form by solid-state reactions which are thermodynamically first-order. A characteristic feature is the occurrence of discontinuous changes in damping, at two distinct temperatures, the order and disorder temperatures, T_0 and T_d . Between these temperatures, the damping changes rapidly and is directly dependent on the relative volume fractions of the phases present.

The overall decrease in damping accompanying the development of the β' -phase, near the composition Mg_3In , is explained by an inherently low background damping in structures exhibiting long-range order. The overall increase in damping associated with the formation of the ordered β'' -phase, near the composition $MgIn$, results from an appreciable damping contribution from transformation twins in that phase.

A necessary condition for the occurrence of discontinuities in damping is that the microstructure should be essentially at equilibrium at the heating and cooling rates employed.

1. **Introduction.** - Preliminary work by Brozel and Leak (1976) on magnesium-indium alloys revealed discontinuities in damping, for some compositions, on both heating and cooling. These were tentatively associated with the superlattice reactions. The phenomenon has now been studied in more detail and an explanation developed which has helped to elucidate the magnesium-indium phase diagram. Specimen preparation from 5N indium and 4N magnesium has been described by Leak and Berrisford (1980). Specimens were tested in an inverted torsion pendulum (vacuum better than 10^{-5} torr) at heating or cooling rates of about $1^\circ C \text{ min}^{-1}$. The specific heat spectra of samples cut from certain specimens were later obtained by differential scanning calorimetry.

2. **Results.** - Every specimen exhibited discontinuous changes in damping at two distinct temperatures on heating or cooling. Between these temperatures the damping changed rapidly. The discontinuities always fell in the temperature range of the specific heat lambda-peaks associated with the superlattice reactions. For compositions up to about 30 wt% In, the dual discontinuities bounded an overall decrease in damping, while between 30 at% In and about 62 at% In they were associated with an overall increase (figures 1 and 2). Generally, hysteresis was associated with the discontinuities; they were shifted to slightly higher temperatures on heating. However, the discontinuity temperatures were independent of frequency within the available range (0-2 Hz). Between 30 at% In and 62 at% In, specimens underwent spontane-

ous rapid twisting in the temperature range between discontinuities. At 61.49 at% In, a much-distorted 'peak' on fast cooling transformed to a well-defined, dual discontinuity on slower cooling. In all cases the temperature interval between discontinuities was very narrow, typically 3-5^oC.

3. Discussion

(a) The Magnesium-Indium phase diagram is still not unequivocally established. At higher indium contents, atmospheric corrosion is rapid (Ohno et al 1979). This makes metallography difficult, and X-ray diffraction studies unreliable, unless extreme care is taken during specimen preparation and storage (Hiraga et al 1968). The thermodynamic order of the two superlattice reactions occurring between about 20 and 60 at% In is uncertain. It is with this second problem that the present work is concerned.

Below the solidus, between about 20 and 85 at% In there exists a homogeneous, single-phase, disordered FCC solid solution, β (Al) (Feschotte 1976, Pickwick et al 1969). On cooling, near the composition Mg₃In, β is replaced by an FCC Ll₂ superlattice, β' , while near the equiatomic composition an FCT Ll₀ superlattice develops, β'' . β' and β'' are homologues of the Cu₃AuI and CuAuI ordered structures respectively. However, in contrast to copper-gold alloys, the development of β' and β'' cannot be suppressed by quenching (Ino et al 1965).

(b) The thermodynamics of order-disorder reactions. - There has been considerable controversy concerning the thermodynamic order of order-disorder reactions. It was first thought that all such reactions were second order, as is the case in β -brass. However, it has become increasingly obvious that first-order superlattice formation also occurs and, indeed, second-order reactions now seem to be the exception (Kornilov 1974, Kikuchi and Sato 1974, Clapp 1970).

Figure 3 shows a partial phase diagram for a first order reaction. Relevant factors have been discussed briefly by Leak and Berrisford (1980). The reaction exhibits a two-phase region with the volume fraction of ordered phase rising from zero to unity between the disorder temperature T_d and the order temperature T_o , during cooling. There is little increase in the long range order parameter S during this process. (Marcinkowski and Zwell 1963, Sinclair and Thomas 1975). A typical example is Pt-Co.

A second order reaction exhibits a continuous increase in S during cooling with only one distinguishable phase present. (Tanner and Leamy 1974). Discontinuities are observed in heat capacity (d^2G/dT^2 by scanning calorimetry) compressibility and thermal expansion.

Such a reaction is best termed a "transition", since it occurs within a single phase.

Christian (1965) suggest an empirical guide that superlattice development is thermodynamically first-order when one or other of the structures in the reaction is close-packed, being second-order only when close-packed lattices are not involved. Magnesium-indium alloys should thus exhibit first-order reactions. Ino et al (1965) and Hirabayashi et al (1966) using specific heat measure-

ment found broad peaks with the $\beta' \rightarrow \beta$ order-disorder reaction, on heating. This was explained by the existence of a two-phase region, bounded by the ordus and disordus, indicating first-order thermodynamics. Pickwick et al (1969) however observed that development of both β' and β'' on cooling was accompanied by a marked drop in electrical resistivity at only one temperature, with no second abrupt change in slope at a lower temperature, as was observed by Newkirk et al (1951) on platinum-cobalt alloys. Pickwick et al therefore assumed a second-order reaction.

4. Dependence of internal friction on superlattice development. - Since no new phase develops, in a second order reaction damping changes result only from the variation of long-range order with temperature. Only one anomalous change in internal friction with temperature should occur at T_c on heating or cooling. Further the damping curve must remain continuous through T_c . These conclusions have been verified for β -brass (Berrisford 1980) which orders in this way. While the long-range order parameter, S , remains high, specimen damping remains low. The progressive decrease of S with temperature on heating towards T_c is paralleled by a progressive increase in damping. On cooling, the process is reversed, figure 4.

Consider now a first-order reaction. Assume that the microstructure is at equilibrium under the heating and cooling rates employed and so will contain a decreasing or increasing amount of ordered phase, whose long-range order parameter does not change appreciably as its volume fraction, V_{ord} , ranges between zero and unity (figure 2). A step change occurs in the measured value of S at T_d on cooling, after which it remains constant, independent of the volume fraction of the ordered phase. Consequently, in contrast to the case of a second-order transition, any anomalous variation in damping through a first-order superlattice reaction must be associated with the changing volume fractions of the phases present, not with the small change in S of the ordered phase between T_d and T_o . It is possible to assign a level of background damping to the ordered and disordered phases. These levels may, hypothetically, be extended into temperature ranges where their respective phases are thermodynamically unstable, or stable only in the two-phase microstructure between T_d and T_o . A subsidiary study (Berrisford 1980) suggests that the ordered background will rise only slowly with temperature and will, therefore, fall below the disordered background (figure 5). The specific damping capacity of the specimen at any temperature T may then be written as:

$$\left(\frac{\Delta W}{W} \right)_{T_{specimen}} = \frac{\Delta W_{T_{ord}}}{W} \cdot V_{T_{ord}} + \frac{\Delta W_{T_{dis}}}{W} \cdot V_{T_{dis}} \quad (1)$$

where $\Delta W_{T_{ord}}$ and $\Delta W_{T_{dis}}$ are the energies dissipated per cycle per unit volume of ordered and disordered phases, respectively, at temperature T . $V_{T_{ord}}$ and $V_{T_{dis}}$ are the volume fractions of ordered and disordered phases, respectively, in the microstructure at temperature T .

At temperatures greater than T_d the ordered structure is unstable $V_{T_{dis}} = 1$ and $V_{T_{ord}} = 0$. Below T_o the disordered phase is unstable,

$V_{T_{dis}} = 0$ and $V_{T_{ord}} = 1$. Hence, above T_d and below T_o , on heating or cooling, the damping should follow the background levels associated with the disordered and ordered phases respectively. However, in the narrow two-phase range between these temperatures, the measured damping must be the weighted average of contributions from both phases, as indicated in equation (1). Thus, ignoring hysteretic effects, the overall damping spectrum, on heating or cooling, would be as shown in figure 6, where discontinuous changes in damping occur at T_d and T_o .

5. The Present Study. - Clearly, the damping anomalies associated with the superlattice reactions in magnesium-indium alloys are compatible only with first-order thermodynamics. Accordingly, apart from hysteresis, the discontinuity temperatures yield the ordus and disordus values. The overall decrease in damping through the two-phase temperature range during the formation of the β' superlattice is understandable, since a high value of long-range order parameter seems to keep the background level low, while the isostructural development of this phase does not involve the appearance of transformation twins within it. By contrast, the neostructural development of a superlattice like β'' is accompanied by fine-scale twinning of the ordered phase (Tanner and Ashby 1969). This transformation twinning occurs to offset the misfit strains between phases. The unexpectedly high damping levels in the β'' are probably due, therefore, to a substantial contribution from these micro-twins. The high internal stresses present during the formation of β'' between T_d and T_o also explain the spontaneous twisting observed in the near-equiatomic alloys. A necessary condition for the appearance of discontinuities in the damping spectrum is that at any temperature within the two-phase range, on either heating or cooling, the equilibrium volume fraction of each phase should be present in the microstructure and that the ordered phase should exhibit its equilibrium value of long-range order parameter at that temperature. Pickwick and Alexander (1969) pointed out that the ratio of disordus temperature to solidus temperature, T_d/T_s for this system is about 0.85, at least up to 55 at% In. Other systems exhibit much lower values typically between 0.4 and 0.5. Consequently, in magnesium-indium alloys, atomic mobility is high between T_d and T_o so that the transformation can occur rapidly (indeed it cannot be suppressed by quenching). Thus at a heating or cooling rate of 1°C min^{-1} the microstructure must be near equilibrium. This view is confirmed by the observation of a distorted 'peak', at 61.49 at% In, which becomes the usual dual discontinuity on slower cooling. At this composition the value of T_d/T_{sol} is plunging, so that atomic mobility is reduced. Consequently, equilibrium was not maintained at the higher cooling rate, but was achieved on slower cooling. On this basis, a dual discontinuity was predicted and subsequently observed in a magnesium-50at%cadmium alloy (Berrisford 1980). This composition exhibits the highest value of T_d/T_{sol} in that system.

A composite magnesium-indium phase diagram, incorporating all the information obtained in the present study, is shown in figure 7.

5. Conclusions. - Discontinuous changes in damping at two different temperatures

on heating or cooling magnesium-indium alloys in the range 21at%In to 62at%In indicate that the order-disorder reactions occurring in this composition range are thermodynamically first-order. A necessary condition for the observation of such discontinuities is that microstructural equilibrium should be maintained at the heating and cooling rates employed.

6. References

- Berrisford, R.A. (1980). Ph.D. Thesis, University of Manchester.
- Brozel, M.R. and Leak, G.M. (1976). *Il Nuovo Cimento* 336, 270.
- Christian, J.W. "The Theory of Transformations in Metals and Alloys". Pergamon Press (1965).
- Clapp, P.C. "Ordered Alloys" 3rd Bolton Landing Conference. Claitors Publishing Div. Baton Rouge (1970).
- Feschotte, P. (1976). *Less Common Metals*, 46, 51.
- Hirabayashi, M., Koiwa, M. and Ino, N. (1966). *Sci.Rept.Res.Inst.Tohoku Univ.*, A18, Suppl. 337.
- Hiraga, K., Koiwa, M. and Hirabayashi, M. (1968). *J.Less Common Metals*, 15, 109.
- Ino, N., Hirabayashi, M. and Ogawa, S., *Trans.Jap.Inst.Met.*, 6, 172.
- Kikuchi, R. and Sato, H. (1974). *Acta Met.*, 22, 1099.
- Kornilov, I.I., *Proc.Int.Symp.Order-Disorder Transformations in Alloys*. Tubingen. Springer-Verlag (1974).
- Leak, G.M. and Berrisford, R.A.(1980). *Proc.Third European Conf.on Int.Friction and Ultrasonic Attenuation in Solids*. (ed. C.C. Smith). Pergamon Press, Oxford p.333.
- Marcinkowski, M.J. and Zwell, L. (1963). *Acta Met.* 11, 373.
- Newkirk, J.B., Smoluchowski, R., Geisler, A.H. and Martin, D.L. (1951). *J.Appl.Phys.*, 22, 290.
- Ohno, H., Ino, S. and Iwasaki, H. (1979). *Trans.Jap.Inst.Met.*, 20, 11.
- Pickwick, K.M. and Alexander, W.A. (1969). *J.Less Common Metals*, 19, 105.
- Pickwick, K.M., Alexander, W.A. and Gamble, R.H. (1969). *Canad.J.Chemistry* 47(3), 3417.
- Sinclair, R. and Thomas, G. (1975). *J.Appl.Cryst.* 8, 206.
- Swalin, R.A. "Thermodynamics of Solids". John Wiley and Sons (1972).
- Tanner, L.E. and Ashby, M.F. (1969). *Phys.Stat.Sol.* 33, 59.
- Tanner, L.E. and Leamy, H.J., *Proc.Int.Symp.Order-Disorder Transformations in Alloys*. Tubingen (1974).

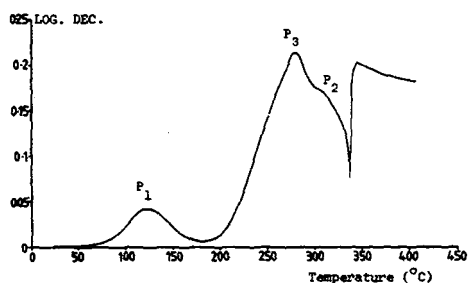


Figure 1

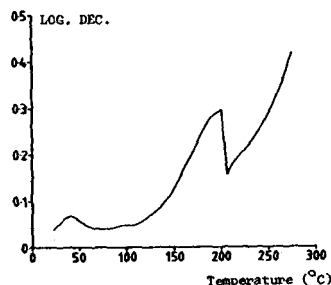
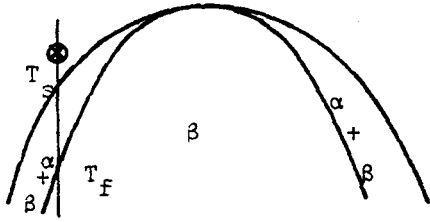


Figure 2

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α Structure stable.

Figure 3

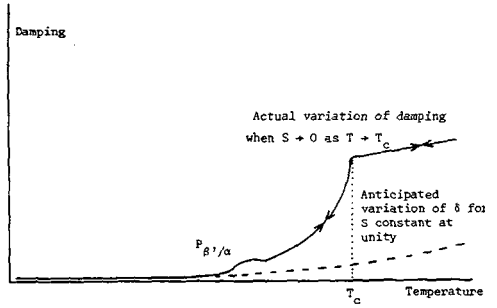


Figure 4

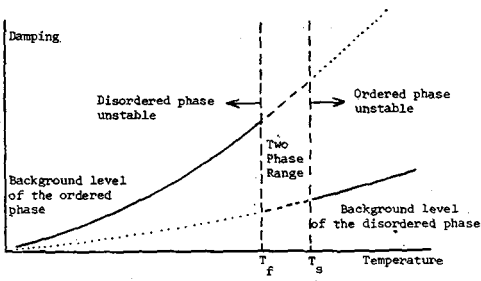


Figure 5

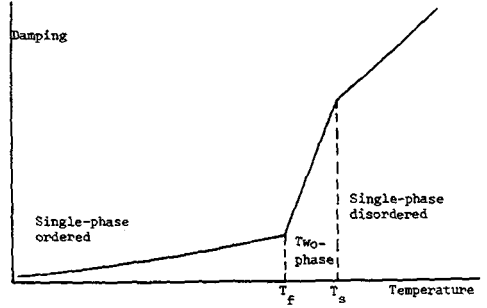


Figure 6

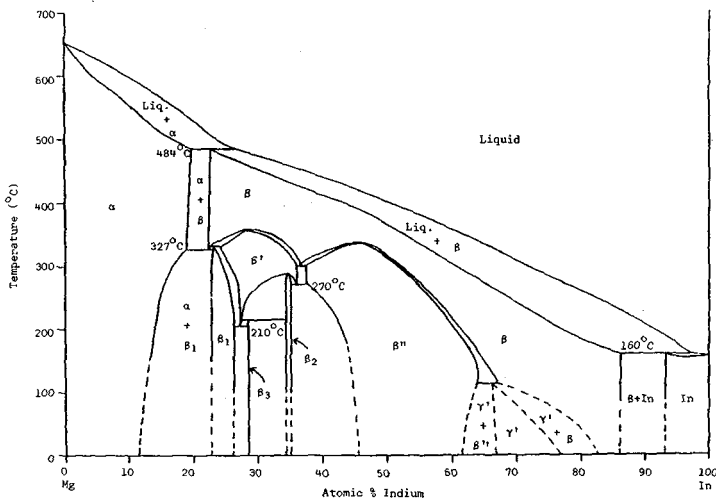


Figure 7