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Effect of Order-Disorder Transition on Young's Modulus of Magnesium-Cadmium Alloys

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Order-dependent change in the Young's modulus of the alloy Mg_3Cd and MgCd has been measured. On the alloy Mg_3Cd, both the heating curves and the isothermal annealing curves have been examined. The results show that the Young's modulus increases with ordering. From the isothermal ordering curves, obtained during annealing quenched (disordered) alloy at various temperatures below the critical temperature, the activation energy of the ordering process has been estimated to be 19.5 Kcal./mol.

In the alloy MgCd, the difference of the Young's modulus between as-quenched and annealed states at room temperature is much smaller than that observed in Mg_3Cd alloy. The measurements have been also carried out on pure magnesium and cadmium metals.

§1. Introduction

At high temperatures numerous alloy systems have disordered solid solution in which the different kinds of atoms are arranged more or less at random on the common lattice. In some cases the alloys transform themselves to ordered structure at sufficiently low temperatures when they are properly heat-treated. The ordered structure is characterized by a regular arrangement of the atom species on the lattice sites.

Variation of the physical properties accompanied by the order-disorder transition is very intresting subject to make clear the mechanism of it.(1)(2)

In the magnesium-cadmium alloy system which forms the continuous series of solid solution over whole composition range, the alloy consists of a hexagonal close-packed structure with a random distribution of the two kinds of atom at high temperatures above about 250°C. But on annealing at a low temperature, it is well known that the three ordered structures are produced at the compositions corresponding to Mg_3Cd, MgCd and $MgCd_3$, as shown in the equilibrium diagram (Fig. 1).(3)

The close-packed hexagonal lattice can be divided into four sublattices as in the case of face-centered cubic lattice. Fig. 2 shows atomic configuration on (0001) basal plane of it, where four kinds of atomic configuration corresponding to the four sublattices are distinguished by open, solid, hatched and double circles, respectively. When the crystal is completely disordered, the distribution of magnesium and cadmium atoms on the lattice points is random. In the ordered structure of Mg_3Cd, three of these four sublattices are occupied by magnesium atoms and remaining one is occupied by cadmium atom, and similar configuration is taken in the $MgCd_3$ ordered structure, but the situation of magnesium and cadmium atoms is interchanged. In the ordered structure of MgCd, two of them are occupied by magnesium atoms and the other two by **cadmium** atoms.

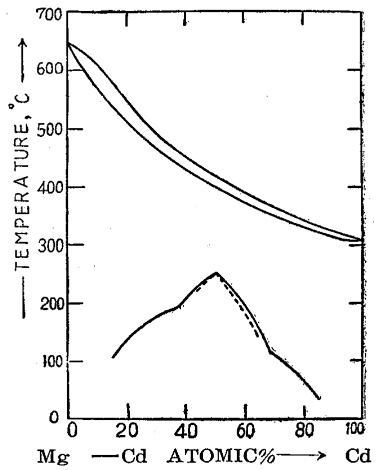

Fig. 1. Phase Diagram of Magnesium-Cadmium System (*after* Hirabayashi)(3)

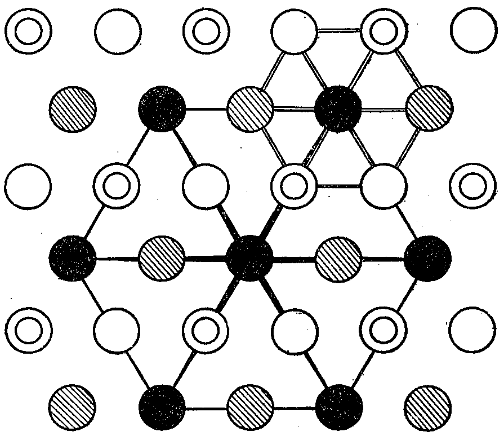

Fig. 2. Atomic Configuration on (0001) Basal Plane of the Close-Packed Hexagonal Lattice, devided into four Sublattices.

On the change of the various properties of magnesium-cadmium alloys accompanied by the order-disorder transition, such as crystal structure,(4)–(9) electrical resistance,(10) specific heat(11)–(15) and so on,(16)–(28) many studies have been carried out.

It seems that the Young's modulus is suitable as a measure for the study of the order-disorder transition in alloys, because of its sensitivity to change in the atomic configuration. Many interesting results are reported on the Young's modulus of some superlattice alloys.(29)–(33) For example; it has been shown that the Young's modulus *versus* temperature curves correspond exactly with the degree of order *versus* temperature curves and further that at the transition point, the Young's modulus changes discontinuously in Cu_3Au alloy but continuously in CuZn alloy, corresponding to similar behavior of the degree of order in each of the alloys.

The objects of this work were to measure temperature variation of the Young's modulus of the magnesium-cadmium system, to examine its relation to the temperature dependence of the degree of order, and further to measure the isothermal change of the Young's modulus, which occurs accompanied with the ordering, when the specimen of disordered state, obtained by quenching, is annealed at various temperatures below the transition point.

§2. Experimental Procedure

The alloys were made from 99.9% cadmium and commercially pure magnesium. The metals were melted in a graphite crucible under KCl–LiCl (1 : 1) flux, and cast into a chill mold. The ingot was homogenized at 300°C for more than 24 hours. The rod specimens of Mg_3Cd and MgCd were scraped by lathe to dimension, when they are in perfect ordered state at 25°C, 1.12 cm in diameter and 13.25 cm in length, and 1.00 cm in diameter and 12.00 cm in length, respectively. Chemical analysis showes that the compositions of cadmium are 60.95 weight% and 80.00 weight%, respectively, which correspond nearly to the atomic ratios 3 : 1 and 1 : 1, respectively.

Full details of the dynamical method employed for the measurement of the Young's modulus have been described in our previous paper.(38) The Young's modulus can be determined based on observed resonance frequency, f, of the longitudinal forced vibration of the rod sample which is given by electrical oscillator. The Young's modulus is not proportional to square of the resonance frequency exactly, because the length and density of the sample change slightly during the ordering process. But the change of them found to be negligible compared with net change of the Young's modulus due to the transition. Even on the measurements of temperature variation of the Young's modulus, the thermal expansion does not affect the general feature of the curve appreciably. Therefore we have taken the value f^2 as a measure of the Young's modulus. The internal friction was determined from half value width of the resonance curve.

The specimens for the isothermal measurements were quenched into water from 200°C in the case of the alloy Mg_3Cd and from 300°C in the case of the alloy MgCd, after heat treatment at respective temperatures for an hour which is necessary for perfect disordering. Then they were annealed at various temperatures below the critical temperature in an oil-bath at the earlier stage and in an electrical furnace at the later stage of annealing. Measurements were made at room temperature, about 23°∼27°C, after quenching from various annealing temperatures into water. Time required for a measurement was 3∼5 minutes, during which almost no further variation of the Young's modulus occured.

Heating rate for the measurements of heating curves was about 1°C per minute. Temperature was measured using Copper-Constantan thermocouple which was set closely near the specimen.

§3. Experimental Results and Discussion

(1) Mg_3Cd Alloy

a) *Variation of Young's Modulus with Temperature*

Fig. 3 shows the heating curve of the Young's modulus of the alloy Mg_3Cd measured during reheating the specimen which was slowly-cooled at a rate of 10°C per hour from 200°C to room temperature prior to the initiation of the experiment. From room temperature to 160°C, as shown by solid curve marked by **AB,** the value decreases continuously. The slope of the curve increases remarkably at temperatures just below the temperature of **B.** At point **B,** which corresponds to 160°C, the curve shows a sharp change in its slope, and above 160°C, the value decreases linearly as shown by **BC.** Point **B** is in agreement with the critical temperature for the order-disorder transition of this alloy which has been hitherto reported by other workers.(7),(11)(12)(15) As-quenched value of the same specimen is indicated by point **D,** which falls exactly on extrapolation of the line **CB.** When the sample was quenched from 450°C, the same as-quenched value was obtained as in the case of 200°C quenching. Therefore the line **DBC** may show the temperature dependence of the Young's modulus of the alloy, if it is in the perfect disorder state at all temperatures.

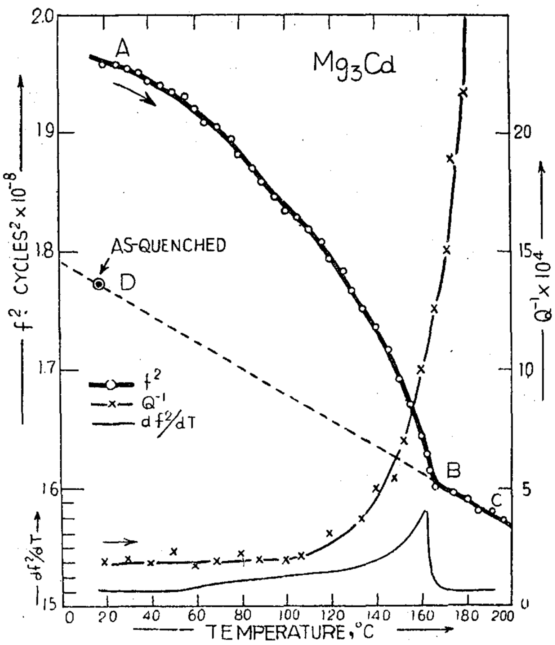

Fig. 3. Young's Modulus *versus* Temperature Curve and Internal Friction *versus* Temperature Curve of the Mg_3Cd Alloy.

The behaviour of the curve, **ABC,** is found to be quite similar to the electrical resistance and the thermal expansion *versus* temperature curves, obtained by other workers.(6)(11) To distinguish more clearly the behaviour of the Young's modulus *versus* temperature curve, the derivative curve of it is calculated and shown in the same figure. It will be noted that the shape of the derivative curve of the Young's modulus is very similar to the specific heat and expansion coefficient *versus* temperature curves obtained by Hirabayashi *et al.*(11),(12),(15) Moreover, since a discontinuous change can not be observed at the critical temperature, it seems that the order-disorder transition in the alloy Mg_3Cd is the second-order transition in conformance with other measurements.(11),(12),(15) Temperature dependence of the internal friction was measured at the same time and the result is also shown in Fig. 3. At about 130°C, a marked increase of the internal friction was observed. Similar steep increase has been also observed with the polycrystalline specimens of pure magnesium, pure cadmium, and some other metals and alloys, as described later. Besides, no inflection point has been detected at the transition temperature in the internal friction *versus* temperature curve. This phenomenon seems, therefore, to be independent of the order-disorder transition.

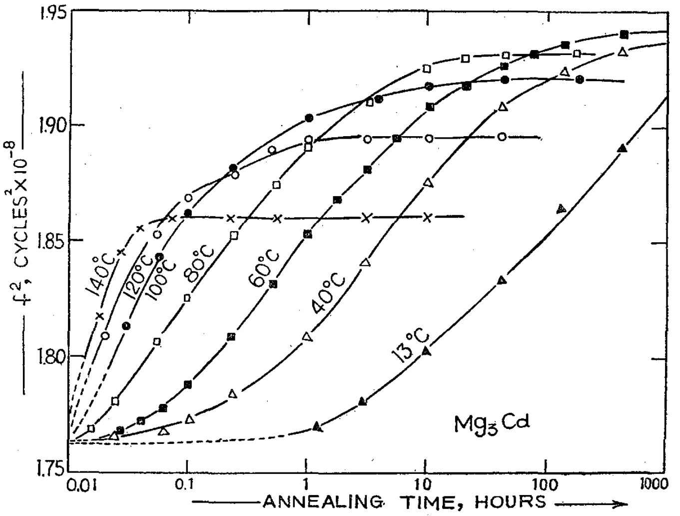

Fig. 4. Isothermal Variation of Young's Modulus of the Alloy Mg_3Cd with Time of Annealing at various Temperatures after Quenching.

b) Isothermal Variation of Young's Modulus with Time

The isothermal time variation of the Young's modulus accompanied by the ordering process during annealing the disordered specimens, which were obtained by quenching rapidly from 200°C to room temperature, at various temperatures, is shown in Fig. 4. After some incubation period, although it can not be detected clearly in the case of higher annealing temperature, the Young's modulus begins to increase monotonously to approach to the value of the equilibrium state fixed by the annealing temperature.

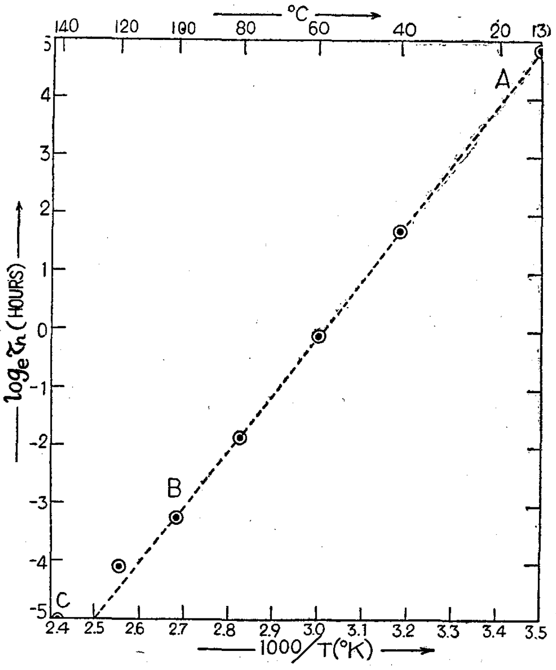

Fig. 5. Relation between $\log_e \tau_h$ and $1000/T$ of the Mg_3Cd Alloy.

τ_h, which is the time to reach the half value of the equilibrium state, is used as a measure of the rate of ordering. Table 1 and Fig. 5 show the observed relation between $\log_e \tau_h$ and $1/T$ (T is the absolute annealing temperature). It may be noted that in Fig. 5 each point falls on a straight line at the temperature range 13°C and 100°C as denoted by AB, but the points deviate upward slightly at the temperature range between

120° and 140°C as shown by **BC**. This may be interpreted as follows; In the higher annealing temperature, such as at 120° and 140°C, τ_h could not be measured with adequate accuracy, since the time required to reach the annealing temperature after the water-quenching was some one minute even in the case of oil-bath annealing, while τ_h seems to be shorter than one minute. Therefore τ_h must be overestimated beyond the net annealing time. The activation energy for the ordering process determined from the relation between $\log_e \tau_h$ and $1/T$ at the range of **AB** in Fig. 5 was 19.5 Kcal./mol.

Table 1.

T°(K)	$1000/T$	τ_h(hour)	$\log_e \tau_h$
286	3.50	13.0	4.9
313	3.20	5.6	1.7
333	3.00	0.92	−0.08
353	2.83	0.16	−1.9
373	2.68	0.038	−3.3
393	2.55	0.017	−4.1
413	2.42	0.006	−5.1

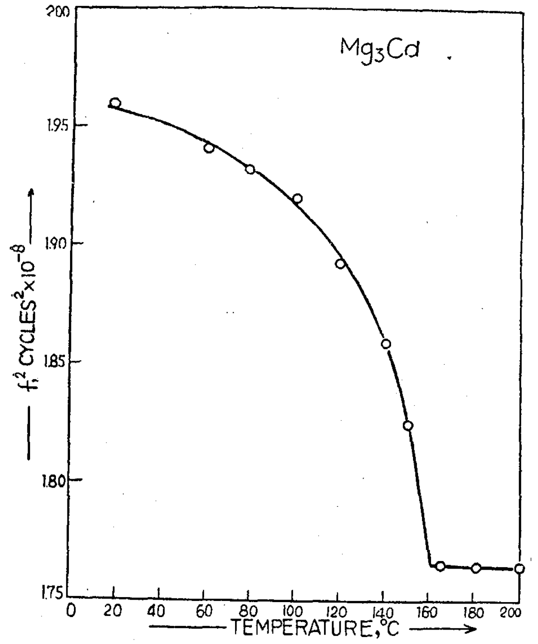

Fig. 6. Equilibrium Values of Young's Modulus of the Mg_3Cd Alloy.

By our experimental arrangements, it can not be permitted to observe the change in the Young's modulus within one minute after the initiation of the annealing as stated above, the study could not been carried out perfectly on the initial stage of the ordering process. The direct measurements of Young's modulus or electrical resistance at the annealing temperature without quenching for the measurements may give more useful informations on this point.

The equilibrium value of the Young's modulus at each temperature was obtained from Fig. 4 and represented as a function of annealing temperature in Fig. 6.

(2) MgCd Alloy

On the alloy MgCd, we attempted similar experiment. But we failed in the heating measurements, because the internal friction increases with temperature, as shown in Fig. 7, even at temperatures lower than the critical temperature of this alloy, 250°C, and the measurement of the Young's modulus near the critical temperature could not be made with accuracy. When the internal friction increases considerably as in this case, the resonance curve becomes so diffuse that it is difficult to determine the resonance frequency. The result of the isothermal measurement at room temperature is shown in Fig. 8. It was confirmed that the difference in the Young's modulus between as-quenched and annealed specimens is much smaller than that observed in Mg_3Cd alloy, although a tendency of increasing was clearly observed. Another trouble in the experiment on MgCd specimen was caused by its susceptibility to corrosion in air.

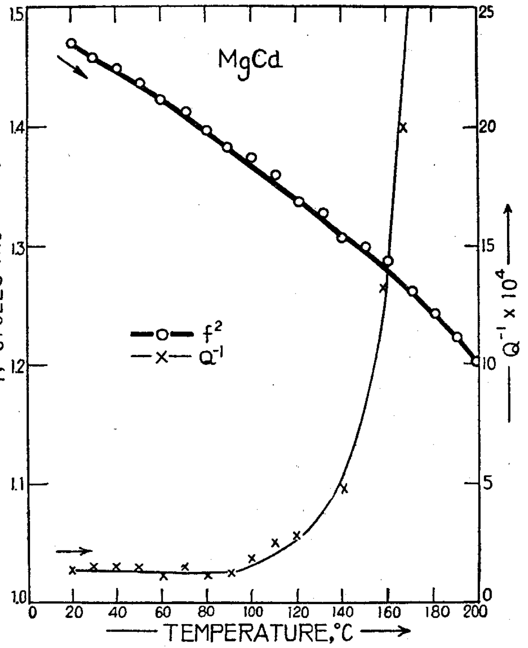

Fig. 7. Young's Modulus *versus* Temperature Curve and Internal Friction *versus* Temperature Curve of the MgCd Alloy.

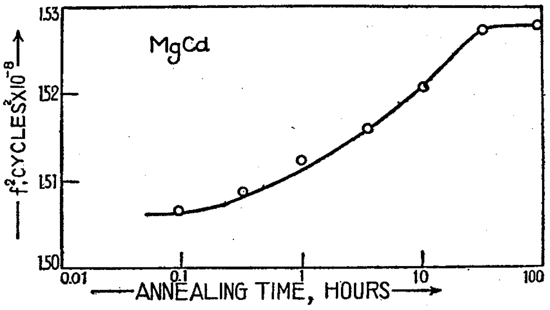

Fig. 8. Isothermal Variation of Young's Modulus of the Alloy MgCd with Time of Annealing at Room Temperature after Quenching.

(3) Pure Magnesium and Cadmium Metals

The Young's modulus and the internal friction *versus* temperature curves of pure magnesium and cadmium metals have been measured and shown in Figs. 9 and 10 respectively. It has been observed that the Young's modulus of magnesium decreases with rising temperature linearly.(40) The Young's modulus *versus* temperature curve of cadmium has not been measured with sufficient accuracy, because the internal friction increases with temperature starting from even room temperature.

Increasing of the internal friction at higher temperature was also observed in other metals and alloys,(38)(41) and it was found that the higher the melting point of metals or alloys, the higher is the temperature of the steep increasing of the internal friction. It seems that further studies are required to see whether this relation really holds or not.

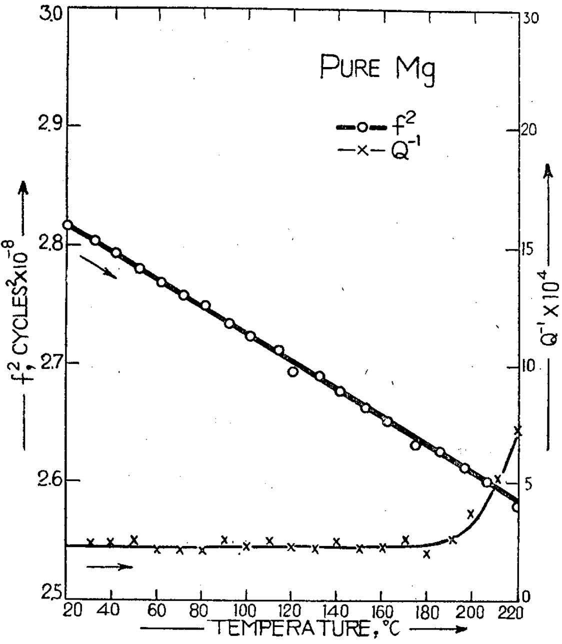

Fig. 9. Young's Modulus *versus* Temperature Curve and Internal Friction *versus* Temperature Curve of Pure Magnesium.

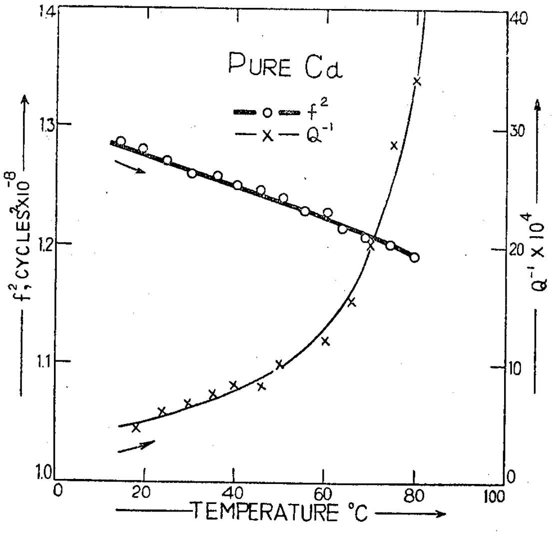

Fig. 10. Young's Modulus *versus* Temperature Curve and Internal Friction *versus* Temperature Curve of Pure Cadmium.

Acknowledgements

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