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## Massive and Martensite Transformations in Sn-Cd Alloys

By J. Koike,\* Y. Koyama\*\* and O. Nittono\*\*\*

The morphological change of substructures and the shape memory effect associated with the simple hexagonal $\leftrightarrow\beta$ -Sn structural transformation in Sn-(4.2-5.3) at% Cd alloys have been investigated. The alloys were quenched from a temperature at which the simple hexagonal structure was stable to various temperatures. Their substructures were observed by means of an optical microscope and their crystal structures were identified by means of an X-ray diffractometer. The massive transformation as well as the martensite one takes place as a diffusionless transformation. The massive transformation temperature ( $M_a$ ) is independent of the solute content, while the martensite transformation temperature ( $M_s$ ) decreases with increasing solute content. A shape memory effect was observed in Sn-Cd alloys and was remarkable for the specimen quenched below 160 K. The shape-recovery amount of the specimen, which is quenched below the  $M_s$  temperature and reveals a massive substructure, is considerably small. These features can be explained well by considering that the massive transformation is diffusionless and is controlled by a thermally activated process. Atoms are considered to move individually in the process of the massive transformation.

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**Keywords:** martensite transformation, massive transformation, tin-cadmium alloy, simple hexagonal structure,  $\beta$ -tin structure, shape memory effect

### I. Introduction

As is well known, Sn has the  $\beta$ -Sn structure ( $\beta$ -phase) at room temperature. It has also reported that Sn-based alloys containing In<sup>(1)</sup>, Cd<sup>(2)</sup> and Hg<sup>(3)</sup> in the range of electron-atomic ratios from 3.6 to 3.95 have the simple hexagonal (s.h.) structure ( $\gamma$ -phase). Raynor and Lee<sup>(4)</sup> have reported that these two structures are closely related: One can be transformed into the other by a simple atomic displacement of the interatomic distance. Figure 1 shows the crystallographic relationship between s.h. and  $\beta$ -Sn structures, which is schematically drawn on the basis of their model. In Fig. 1(a), the

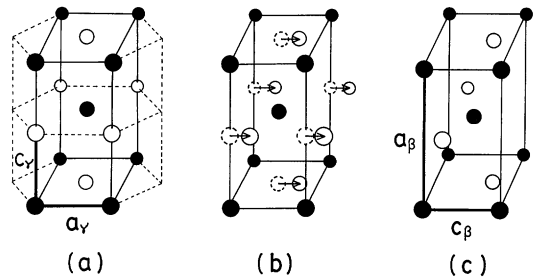


Fig. 1 The crystallographic relationship between simple hexagonal and  $\beta$ -Sn structures. (a) The two simple hexagonal structures (dotted line) expressed in terms of b.c.o. lattice. (b) The translation of b.c.o. lattice. (c)  $\beta$ -Sn structure formed by deforming b.c.o. lattice to b.c.t. lattice.

s.h. structure is indicated by the dotted line, and two unit s.h. cells are expressed in terms of the body centered orthorhombic (b.c.o.) lattice indicated by the solid line. When each atom indicated by the open circle moves by  $a_\gamma/4$  against the atoms indicated by the solid circles (Fig. 1 (b)) and b.c.o. lattice is deformed to b.c.t. lattice,  $\beta$ -Sn structure can be produced (Fig. 1 (c)). In this case, a volume change caused by the lattice deformation is 0.5%<sup>(4)</sup>.

So far, the authors have investigated a

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transformation behavior between these two phases in Sn-In alloys from the crystallographical point of view. Consequently, we have found out that the transformation from  $\gamma$  to  $\beta$  is martensitic<sup>(5)</sup> and the shape memory effect occurs on heating to the parent phase.<sup>(6)</sup>

In Sn-Cd alloys, the  $\gamma$  phase exists in a hatched region of the equilibrium phase diagram shown in Fig. 2. The  $\gamma$  phase is decomposed into  $\beta$  phase and a solid solution Cd by the diffusion of atoms in the process of slow cooling. However, if the specimen is quenched rapidly, the  $\gamma$  phase is expected to be transformed into  $\beta$  phase in a diffusionless manner similar to Sn-In alloys<sup>(5)</sup>. It is also expected that the shape memory effect can be associated with the reverse transformation.

In the present work, we have mainly performed a morphological study of quenched Sn-Cd alloys, using an optical microscope. The crystal structure of the product phase and the magnitude of the shape memory effect were investigated. On the basis of the obtained results, the kinetics of the  $\gamma \rightarrow \beta$  transformation was discussed qualitatively from the viewpoint of the cooperative and the individual movement of atoms.

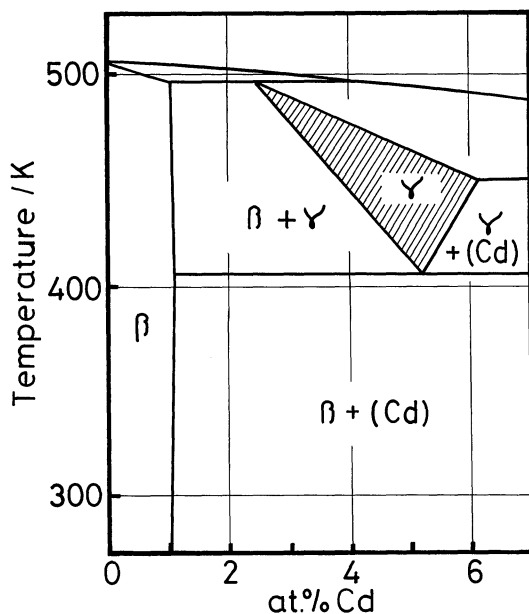


Fig. 2 Sn-rich portion of the equilibrium phase diagram in the Sn-Cd alloy system.

## II. Procedure

The alloys were made from pure Sn (99.999%) and Cd (99.99%). The compositions of the alloys were Sn-(4.2-5.5) at% Cd. The preparation of the specimens was as follows: Each alloy element was melted together several times in an evacuated Pyrex tube just above the liquidus temperature, in order to prevent the evaporation of Cd whose vapor pressure is considerably high. The resultant ingot was annealed at 470 K for 3 days, in order to homogenize its concentration. Alloy sheets (800  $\mu\text{m}$  and 200  $\mu\text{m}$  in thickness) were obtained by rolling at room temperature and annealed again under the same condition described above in order to eliminate the strain. Polycrystalline cut out from the recrystallized sheet were used in the following experiments.

They were held at 450 K for 900 s and then quenched to various temperatures in air. Each quenched specimen 800  $\mu\text{m}$  in thickness was chemically polished, and its substructure was observed at room temperature by means of an optical microscope. An X-ray diffractometer using Cu  $K\alpha$  radiation was used for the identification of the crystal structure of the quenched specimen 200  $\mu\text{m}$  in thickness. The shape memory effect was further examined for the 200  $\mu\text{m}$  thick specimen. The experimental method was similar to the previously reported one<sup>(7)</sup> and will be represented in detail later. The magnitude of the shape recovery was interpreted in relation to the substructure.

A surface relief was not observed, because a smooth  $\gamma$  phase specimen was difficult to prepare by polishing. Furthermore, in the present study, electron microscopic observations of martensite and massive substructures were not made, because the precipitation rate of Cd solid solution from a metastable  $\beta$  phase was too fast even at room temperature.

## III. Results and Discussion

### 1. General features of the substructures

X-ray reflection profiles of Sn-5.1 at% Cd alloys quenched to 340, 270 and 158 K

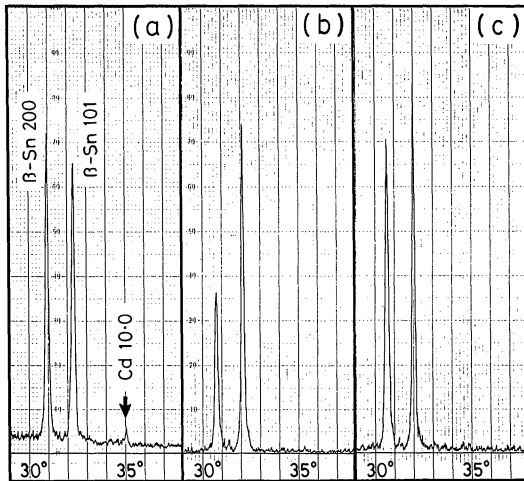


Fig. 3 X-ray reflection curves (Cu  $K\alpha$ ) of an Sn-5.1 at% Cd alloy, quenched to (a) 340 K, (b) 270 K and (c) 158 K, respectively. X-ray examinations were made at room temperature within a few minutes just after quenching to the temperatures above.

(hereafter, referred to as quenched temperature) are shown, respectively, in Fig. 3 (a), (b) and (c). Figure 3 (a) shows that the specimen quenched to 340 K is decomposed into  $\beta$  phase and Cd solid solution. From the phase diagram (Fig. 2), it is clear that these phases were formed by a eutectoidal decomposition that is a diffusional transformation. On the other hand, the specimen quenched to 270 K has only a  $\beta$  phase, as shown in Fig. 3 (b). Figure 3 (c) also reveals only reflection peaks of  $\beta$  phase. Any appreciable peak of Cd was not observed in (b) and (c). Therefore, we conclude that a macroscopic change in the solute content which leads to the decomposition of a parent phase does not occur during quenching and that  $\gamma$  phase is transformed into  $\beta$  phase diffusionlessly when it is quenched below 270 K.

Figure 4 (a), (b) and (c) show optical micrographs of Sn-5.1 at% Cd alloys which were quenched to 338, 270 and 158 K respectively, and followed by chemical polishing. In Fig. 4 (a), large grains are observed. Figure 4 (b) shows several small grains which have irregular boundaries. This complex substructure is similar to those of Cu-based alloys<sup>(8)</sup> and Ag-based alloys<sup>(9)</sup> which are caused by the massive transformation. The substructure indicated by

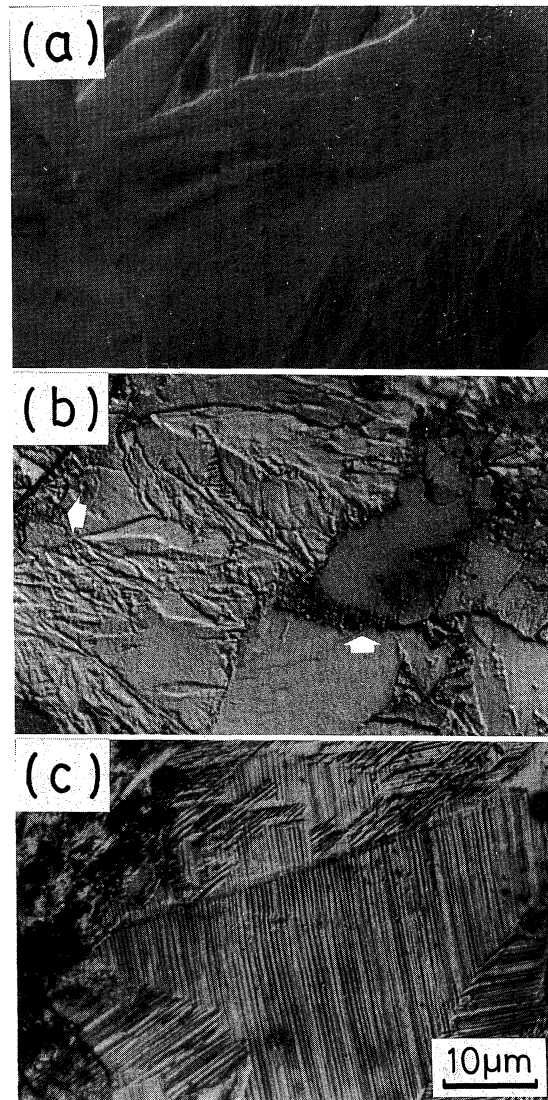


Fig. 4 Optical micrographs showing the substructures of Sn-5.1 at% Cd alloys quenched to (a) 338 K, (b) 270 K (c) 158 K, respectively.

the arrows is considered to be formed by very small grains. Figure 4 (c) shows a banded substructure as well as very small grains on the left side in the figure. A similar banded relief and substructures have been observed in case of the martensite transformation in Sn-In alloys.<sup>(5)</sup>

Consequently, the comparison between the X-ray reflection profiles and the optical micrographs suggests that the substructure in

Fig. 4 (a) was formed by the diffusional transformation. On the other hand, the complex substructure in (b) and the banded one in (c) are considered to be formed by the diffusionless transformations, which are the massive and the martensite transformation, respectively.

## 2. Phase diagram in a metastable state

We examined other specimens of Sn-(4.2–5.5) at% Cd in the same experimental manner. Figure 5 shows the summarized results schematically. In the figure, cross marks, open circles and solid circles denote that the substructures obtained by quenching are classified into the types of (a), (b) and (c) in Fig. 4, respectively. From the results, the martensite transformation temperature ( $M_s$ ) and the massive transformation temperature ( $M_a$ ) are determined, as shown in Fig. 5. The  $M_s$  decreases linearly with increasing solute content, while the  $M_a$  is independent of the composition and is nearly constant, being 305 K within the error of  $\pm 10$  K. As for the

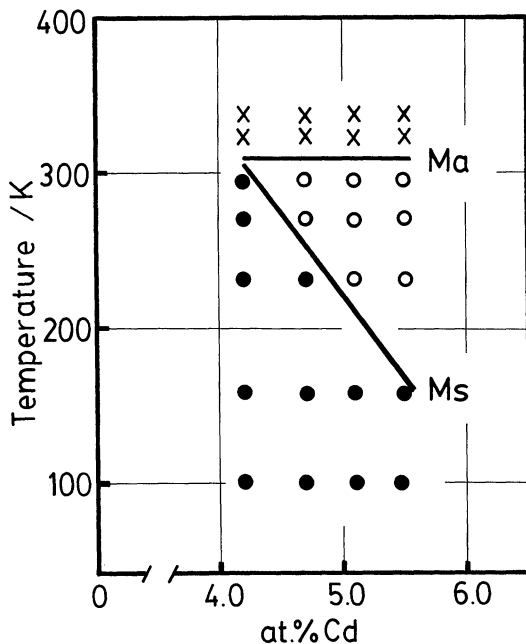


Fig. 5 The schematic diagram of the substructure in terms of the quenched temperature and Cd content. See text for the particulars.  $M_a$ : massive transformation temperature  $M_s$ : martensite transformation temperature.

relation between massive and martensite transformations, Kittle and Rodriguez<sup>(10)</sup> have studied both transformations in Cu-Ga alloys and concluded that at the cooling rates higher than  $2 \times 10^4$  K/s, the massive transformation was suppressed and the martensite transformation fully took place.

These features of the massive transformation suggest that its nucleation and growth process is a thermally activated one which never leads to the phase decomposition but leads to only a structural change. The activation energy for the massive transformation in various alloys has been reported to be much smaller than that of diffusional one<sup>(11)</sup>. Furthermore, the fact that the massive transformation takes place at such a low temperature as 160 K suggests a diffusionless character of the massive transformation. Finally, together with the results of X-ray examination, we can conclude that the massive transformation is diffusionless and is controlled by a thermally activated process.

## 3. Shape memory effect

As shown in Fig. 6, a shape memory effect took place in Sn-Cd alloys. This property is confirmed according to the following experimental procedure: After a ring-shaped specimen was held at 455 K for 1.8 ks (Fig. 6 (a)), it was quenched into an ethanol bath cooled to 80 K and subsequently deformed into a linear shape at 158 K (Fig. 6 (b)). When it was up-quenched to 370 K ( $> A_s$ ), the linear specimen recovered its original shape, with increasing temperature, although its recovery was imperfect (Fig. 6 (c)). The imperfect shape recovery is explained by considering that the deformation strain is too big to be accommodated only by the displacement of martensite variants and also that the lattice relationship between  $\beta$  and  $\gamma$  is not perfectly reversible.<sup>(12)</sup>

In this experiment, we evaluated the magnitude of the shape recovery in terms of the curvature ratio of the up-quenched specimen shown in Fig. 6 (c) to that of its original ring shown in (a). Figure 7 shows the curvature ratio against the quenched temperature in Sn-5.3 at% Cd alloys. As

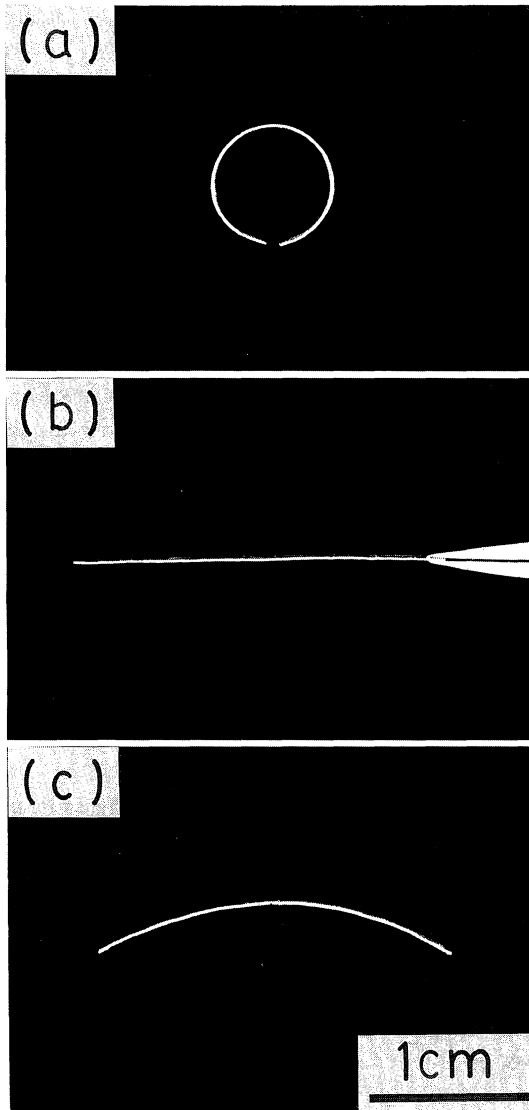


Fig. 6 A series of photographs showing the shape change in an Sn-5.1 at% Cd alloy. The specimen was held at (a) 445 K and then deformed at (b) 158 K after having been quenched to 80 K, and subsequently up-quenched to (c) 370 K.

shown in the figure, the curvature ratio is almost constant, when the specimen is quenched to a temperature lower than 160 K. However, when the specimen is quenched above 160 K, the curvature ratio decreases rapidly with increasing quenched temperature. The temperature at which the decrease occurs is almost the same as  $M_s$  temperature estimated from Fig. 5 within an experimental

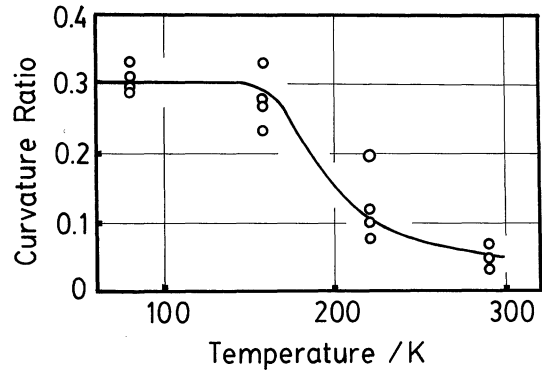


Fig. 7 Variation of the curvature ratio of an Sn-5.3 at% Cd alloy with quenched temperature.

error. This result is apparently consistent with the fact that the shape memory effect is remarkable when the quenched temperature is below  $M_s$  temperature.

Other results from the alloys with various Cd contents are also shown in Fig. 8. The  $M_s$  temperature of each alloy is also indicated in the figure. The temperature at which the rapid decrease of the curvature ratio occurs is independent of the  $M_s$  temperature and is almost the same (160 K) for each alloy. This result is interpreted as follows: In this alloy system, the optical micrograph of the specimen quenched below the  $M_s$  temperature does show not only the martensite substructure but also the massive one, as already shown in Fig. 4. The appearance of the massive substructure is considered to lead to the reduction in the shape recovery. Consequently it is concluded that the atomic movement in the process of the massive transformation is rather individual than cooperative. However, as shown in Fig. 8, even the specimen quenched above the  $M_s$  temperature, which shows only the massive substructure, reveals a slight shape recovery. This also suggests that the atomic movement forming the massive substructure is not completely individual. The details of the atomic movement will be discussed in relation to the martensite transformation in the next paper<sup>(12)</sup>.

It is further shown in Fig. 8 that alloys with the higher  $M_s$  temperatures reveal the smaller curvature ratios. Strictly speaking on this experimental procedure, the cooling rate changes simultaneously with change in the quenched

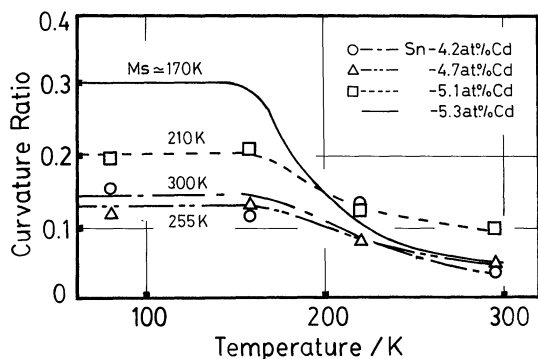


Fig. 8 Variations of the curvature ratio with Cd content and quenched temperature.

temperature: The lower the quenched temperature is, the faster the cooling rate is. Therefore, both the quenched temperature and the cooling rate are considered to affect the nucleation and growth rate of the massive transformation, and accordingly, the shape recovery.

#### IV. Summary

The substructure and the shape memory effect were investigated in Sn-Cd alloys quenched from a temperature of the  $\gamma$  phase region to various temperatures. The main results are as follows:

(1) When  $\gamma$  phase is transformed into  $\beta$  phase by quenching below 305 K, two kinds of diffusionless transformations, which are martensite and massive ones, take place.

(2) The temperature at which the massive transformation starts is independent of the alloy composition.

(3) The shape memory effect accompanying the martensite transformation is observed.

(4) The massive transformation in Sn-Cd alloys is accompanied with a slight amount of a shape memory effect.

(5) Consequently, the massive transformation is a diffusionless one which is controlled by a thermally activated process. The atomic movement of the massive transformation is partly individual.

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