TDPAC Study of Cadmium-Indium Alloys

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TDPAC (Time Differential Perturbed Angular Correlation) is a powerful tool to study problems in material science. In this report, a phase diagram of binary alloy, namely Cd-In alloy, is investigate by mean of TDPAC. Here TDPAC spectra of Cd-In alloys are measured for various solute (In) concentrations and temperatures and compared with the phase diagram of the alloy determined by conventional macroscopic method. This may give us microscopic informations about the state of the solute atom in alloys which remain only as speculations in the alloys studies where conventional method of the resistivity measurement or thermal analysis are employed.

Cd-In alloys are prepared by melting 5-nine Cd with various amount of In in a vacuum or in an Ar atomosphere. Subsequently they are rolled to 0.5 mm thickness and annealed at 200°C followed by a quench into water. All specimens are fine grained polycrystals. The concentration of In studied in the present is between 0.04 and 5 at%. The alloy specimens are irradiated by a proton beam to produce ^{111}In probe atoms by ^{112}Cd(p,2n)^{111}In reaction near 77 K. Subsequently, specimens are warmed up to the room temperature (RT) and TDPAC spectra are measured.(As Irradiated State) After the measurement of the as-irradiated state, specimens are annealed at higher temperatures for several 10 hrs below 400 K and several minutes near the melting point. This annealing is to obtain the solute equilibrium at the temperature. To preserve the equilibrium, specimens are quenched into water after the annealing. Since the concentration of ^{111}In probe atoms (several 10 at ppm at most) is much less than that of the alloying element of In atoms (400 at ppm for the most dilute alloy in the present experiment) and also the chemical behavior of ^{111}In atoms are completely the same with that of the alloyed In atoms, the TDPAC spectra of ^{111}In atoms sensitively reflect the metallurgical state of the alloyed In atoms. The principle is the same with the isotope dilution method employed in the chemical separation of the radioactive elements. Although 6 alloys are studied in the present, results for Cd-In(0.04), Cd-In(4.8 at%) alloys are shown through Fig. 1 to Fig. 3.

For the case of the Cd-In(0.04) alloy, the TDPAC spectra are the same with that of the polycrystalline pure Cd with the precession signal of 55 nsec period where only ^{111}In atoms are present and hence is a dilute limit of Cd-In alloys. Since it has been proved that ^{111}In in pure Cd is at the substitutional site without trapping any lattice defects or impurity, the In atoms in Cd-In(0.04) alloy are also at the same site. Namely, the Cd-In(0.04) alloy forms an α-solid solution at RT and remains so between RT and 466 K. No

evidence of pairing or clustering of In atoms is observed in this alloy.

For the case of Cd-In(0.26 at%) alloy, however, the spectra show different behavior from that of Cd-In(0.04) alloy. First, the spectrum in the as-irradiated state (R.T. annealed) has no well defined 55 nsec period signal of the ^{111}In in the substitutional site. Namely, in this alloy In atoms are not in the state of α-solid solution after annealing at RT. This result will be discussed later. Upon annealing the specimen between 369 K and 445 K, the 55 nsec signal takes place to show that In atoms transform into α-solid solution in this temperature range. With annealing above 500 K, however, the amplitude of the 55 nsec signal becomes smaller and a new signal of very long period takes place. The period of the new signal is more than the time range which can be studied in the present (370 nsec) and hence observed as the convex curve toward the upward. According to the phase diagram of the Cd-In alloys[1] as shown in Fig. 4, In atoms are in two different phases above 500 K for this concentration of alloy. Namely, a part is in α solid-solution and another part is in liquid state with a high In concentration. The In atoms to give the long period signal, therefore, should correspond to the ones in the liquid state at the annealing temperatures. Since specimens are quenched to RT for measurement, it is possible that the liquid phase is separated into α+Cd_3In phase or into α+α-In phase according to the phase diagram. Since the measured TDPAC spectrum of ^{111}In in In metal[2] (face centered tetragonal structure) is different from the present one in Fig. 2 although the period is in the same magnitude, the second possibility of α+α-In phase is unlikely. The left possibility is the compound phase of Cd_3In, although further experimental works are necessary for the alloy of the exact Cd_3In composition before a definite conclusions is obtained.

Figure 3 shows the result of the highest In concentration Cd-In(4.8 at%) alloy, where the spectra are almost flat with only a long period component. The sites of In atoms in this alloy to give the long period component should be the same ones that give the long period term in In(0.26)-alloys in Fig. 2 above 500 K. The phase diagram in Fig. 4 shows that the part of In atoms in α-solid solution is quite low and hence it is reasonable no 55 nsec α-phase signal is observed in this alloy. Summarizing the results in Fig. 2 and Fig. 3, almost flat long term takes place when In atoms are in the sites where high In atoms concentration expected. With this experimental conclusion in mind, the spectrum of Cd-In(0.26) alloy in the as-irradiated state will be discussed next.

Since the production of ^{111}In probe nuclei is a random process, most of ^{111}In atoms should be present as an isolated atom without any alloyed In atoms nearby when they are produced by irradiation. Therefore, if the ^{111}In atoms are immobile up to the RT, the 55 nsec signal for the α-solid solution should take place in all alloys in the measurements at RT. On the contrary, all alloys except the Cd-In(0.04) alloy, the flat spectrum is obtained after warming up to RT from 77 K. This shows a high In concentration phase is

formed between 77 K and RT. Although the structure of the high concentration phase is not known yet, we call it as an In cluster. Since the equilibrium concentration of the thermal vacancy is negligible below RT for Cd, the migration of In atoms to form cluster due to the thermal vacancy is unlikely. One possibility to explain it is a mechanism of the radiation enhanced diffusion. (R.E.D.) Due to the high energy proton irradiation to form ^{111}In nuclei, lattice vacancies are also produced which have been known to migrate at around 140°K.[3] Therefore if the binding energy of In atoms with vacancies are high not to dissociate during the migration and annihilation of vacancies around 140 K, In atoms are carried to sinks to be accumulated to form In atoms clusters. This mechanism may explain the formation of In cluster below RT. For the case of Cd-In(0.04) alloy, the cluster may not be stable at RT since the α solubility limit of In may exceed the In concentration. Further TDPAC measurements of Cd-In alloys between 77 K and RT are now in progress to examine the R.E.D. possibility.

Acknowledgements

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References

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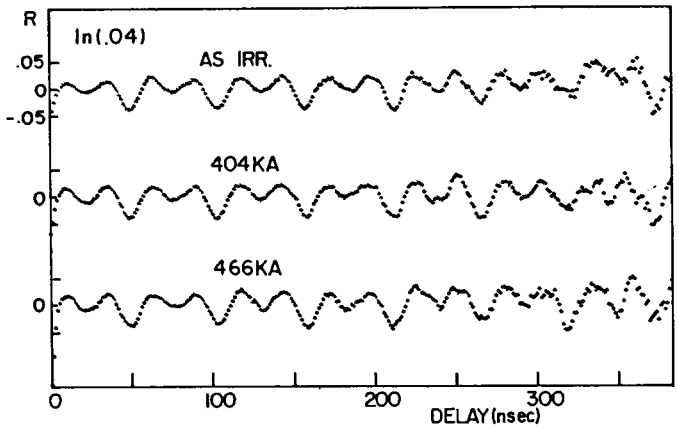

Fig. 1. TDPAC spectra for Cd-In(0.04 at%) alloy. R.T. measurement. $R = (N(\pi)-N(\pi/2))/(N(\pi)+N(\pi/2))$ is shown for Fig. 1 - Fig. 3. $N(\pi)$: Counts for the detector at 180° relative to $\vec{k}_1$. $N(\pi/2)$: Counts for the detector at 90° relative to $\vec{k}_1$.

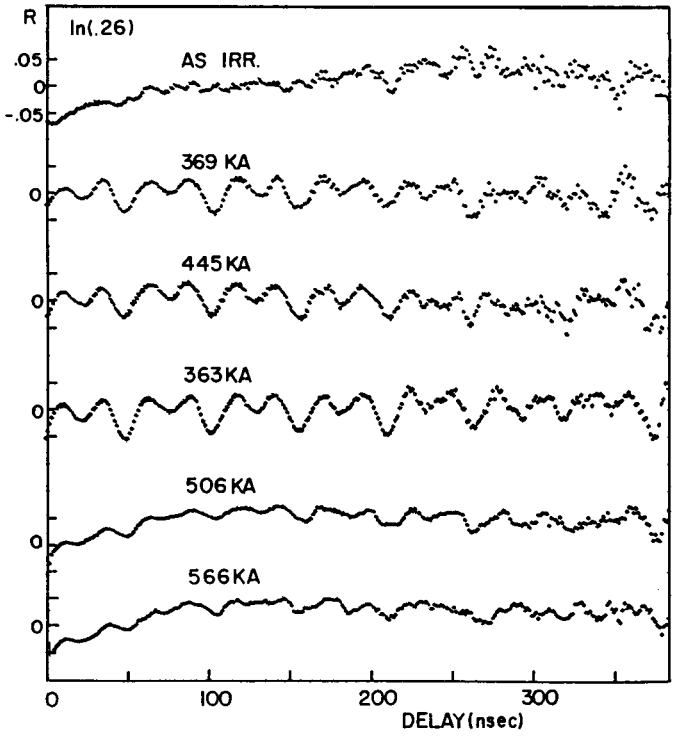

Fig. 2. TDPAC spectra for Cd-In(0.26 at%) alloy.

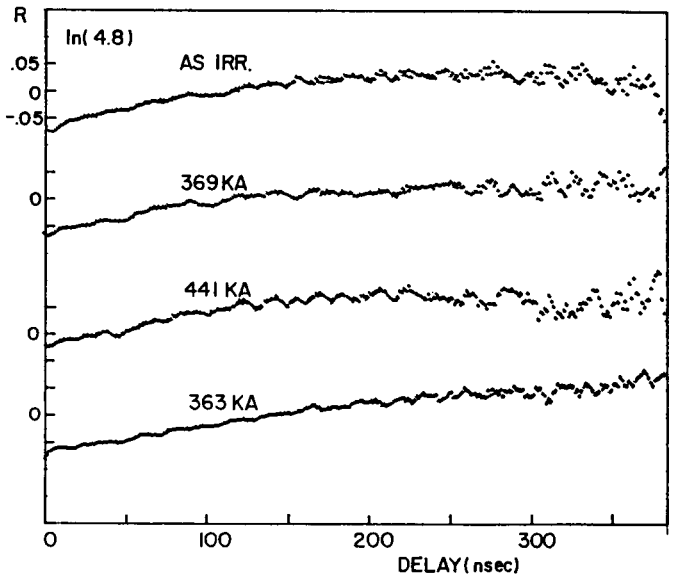

Fig. 3. TDPAC spectra for Cd-In(4.8 at%) alloy.

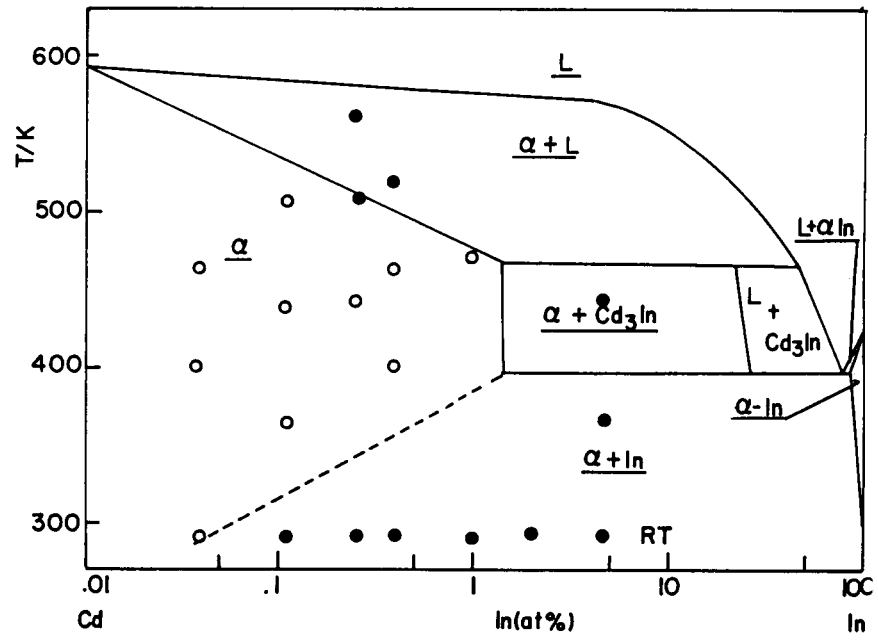

Fig. 4. A phase diagram of Cd-In alloy due to Elliot (Ref. 1). To show the part of low In concentration more clearly, the horizontal scale is plotted in logarithmic scale. Open circle: α-phase signal observed. Closed circle: no α-phase signal observed.