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The effect of pressure on the binary zinc–gallium phase diagram

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Abstract
The temperature dependence of the electrical resistance is measured for zinc–gallium alloys under various pressures. The appearance of a new intermediate phase is suggested from results of the measurements around 3 GPa. An isobaric phase diagram with the intermediate phase is proposed.

1. Introduction

The effects of pressure on the eutectic-type equilibrium phase diagram have been investigated in many binary systems. Notable pressure effects on the phase boundaries were often found in the equilibrium phase diagrams [1–3]. The zinc–gallium system also has a simple eutectic-type phase relation with the eutectic composition located on the extremely gallium-rich side. However, the phase relation under high pressure has not been sufficiently investigated for the binary system. On the other hand, a ternary phase diagram of the Al–Zn–Ga system at atmospheric pressure has been investigated, in relation to applying cathode protection via aluminium sacrificial anodes, widely used for protecting steel structures in marine environments [4, 5]. According to the isothermal sections of the ternary phase diagram, a phase field with fcc structure is stable near the binary phase diagram of the Zn–Ga system. The fcc structure is stable over a wide range of composition in the binary Al–Zn system and the phase field tends to be stable on applying pressure [2]. These facts suggest the appearance of an fcc phase in the binary phase diagram of the Zn–Ga system as a pressure effect.

In the present study, the effect of pressure on the phase boundaries and stability of the intermediate phase in the Zn–Ga phase diagram were investigated by means of electrical resistance measurement.

2. Experimental procedure

Five kinds of zinc–gallium alloy with gallium contents of 10, 20, 40, 70 and 90 mol% were prepared by quenching the melt in evacuated quartz ampoules into ice water. The Zn–70% Ga and Zn–90% Ga alloys were rolled to thin foil and cut to strips for measuring the electrical resistance. The other alloys were so brittle that they were crushed and a small piece was selected for the sample.

A cubic-type multi-anvil press (TRY250) was employed for the measurement of electrical resistance. Pressure was applied between 2 and 7 GPa. Pressures in the experiment were determined in terms of applied load from a previous calibration of the apparatus. Temperature at the sample was measured by means of a 13% Rh/Pt–Pt thermocouple without correction for the influence of pressure.

The sample assembly and the other experimental conditions are described in detail elsewhere [3, 6].

3. Results and discussion

3.1. Measurements of electrical resistance

Initially, the pressure dependence of the electrical resistance–temperature (R–T) curves of pure zinc and gallium was measured. High-pressure phases of Ga II and Ga III are known in pure gallium [7]. The kinks appearing in the R–T curves of each element corresponded to the temperatures of the phase transformation shown in the pressure–temperature (P–T) phase diagrams [7, 8].

Figure 1 shows R–T curves of the cooling cycle for the Zn–10, 40, 70, 90% Ga alloys at pressures of 3 and 6 GPa. The measurement was carried out down to room temperature. Usually the cooling rate was $10^\circ\ \mathrm{min}^{-1}$ below the liquidus temperature and it was higher around the liquidus temperature. In the R–T curves of the Zn–40% Ga, Zn–70% Ga and Zn–90% Ga alloys at 6 GPa (figure 1(b)), we can recognize three kinks showing the phase transformations. The kink indicated as A is interpreted as the phase transformation at liquidus. Two invariant horizontals can be observed at about 130° and 65°. The temperatures indicated as B and C seem to be a little higher than the transformation temperatures of pure gallium at liquid (L) $\Leftrightarrow$ Ga III and Ga III $\Leftrightarrow$ Ga II, respectively. This results suggest that the phase transformations at the invariant horizontals are caused by the reactions of the peritectic (L + Zn $\Leftrightarrow$ Ga III) at B and the peritectoid (Zn + Ga III $\Leftrightarrow$ Ga II) at C.

In the R–T curves at 3 GPa (figure 1(a)), we can detect the reactions corresponding to liquidus (A) and peritectic (B). The peritectoid reaction (C) shown in figure 1(b) was not observed in the R–T curves at 3 GPa. The transformation temperature of pure gallium at Ga II $\Leftrightarrow$ Ga III decreases with decreasing pressure [7]. Therefore, the peritectoid reaction at 3 GPa would occur below room temperature. An additional change in the electrical resistance designated by X is recognized in the R–T curve at the pressure. The reaction occurs over the melting temperature of pure gallium. This result means that the invariant reaction at X does not include the terminal phase of the gallium side.

The reaction corresponding to X was also detected in R–T curves at 2 and 4 GPa.

3.2. Intermediate phase in the binary Zn–Ga system

The phase transformation at X suggests the appearance of an intermediate phase in the binary Zn–Ga system. The kink corresponding to X was detected in the R–T curves of the alloys with gallium contents of 40, 70 and 90%. But it was not observed in those of the Zn–20% Ga and Zn–10% Ga alloys. This suggests that the X phase is stable around a gallium content of 30 mol% at the pressure. This composition is near the phase field of the fcc structure shown in the isothermal sections of the Al–Zn–Ga phase diagram at atmospheric pressure. Present

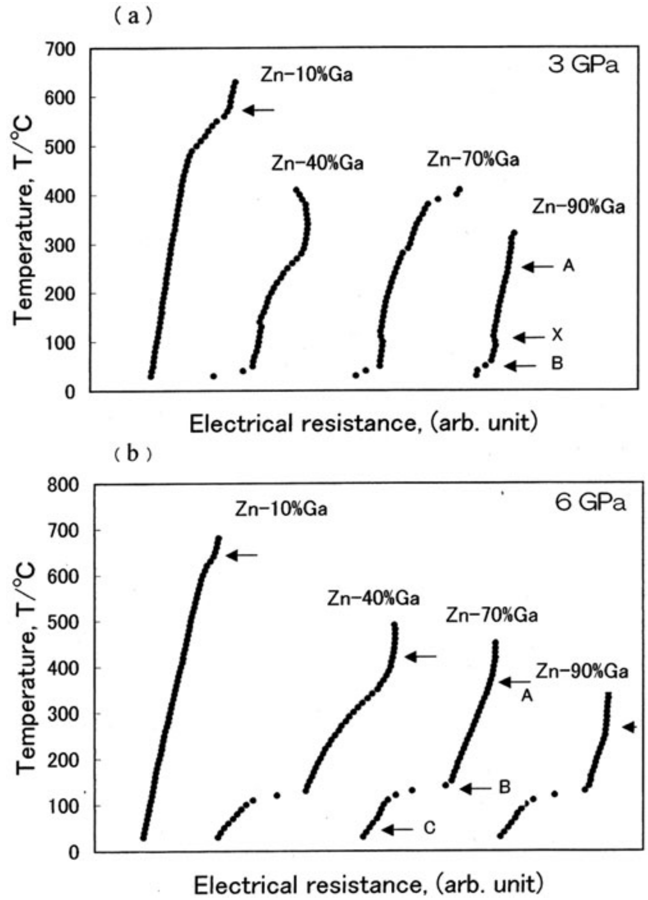

Figure 1. Temperature variation of the electrical resistance of the Zn–Ga alloys: (a) 3 GPa, (b) 6 GPa.

results support the expectation of the appearance of the fcc phase on the binary Zn–Ga phase diagram. In order to confirm the existence of the X-phase field, structure identification is required for the binary Al–Zn system.

The phase transformation corresponding to the X phase was not detected in the R–T curve at 6 GPa. This is considered to indicate that the more stable terminal phase (Ga III) appears at this pressure.

3.3. Isobaric phase diagram under high pressure

We obtained the pressure dependence of the liquidus and invariant horizontals on the binary Zn–Ga system. The change in the electrical resistance around the liquidus was unstable during the measurement below about 4 GPa, especially for the alloys with low gallium contents. Therefore, considerable error occurs for determining the liquidus temperature under these conditions. It is considered that the non-uniform shape of the sample is deformed inhomogeneously in the gasket under relatively low pressure.

In the Zn–Ga system, the peritectic composition locates on the extremely gallium-rich side within the present applied pressure range. The peritectic composition and the maximum

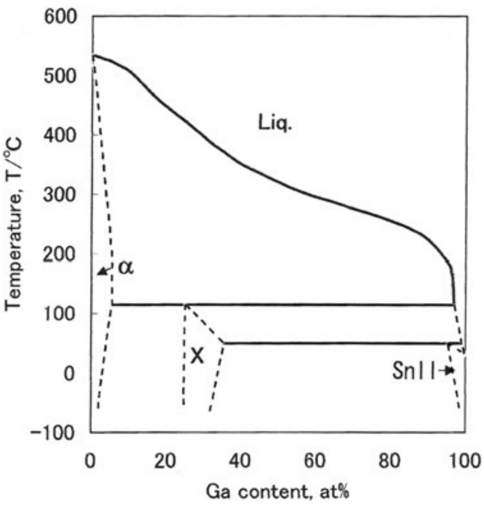

Figure 2. A proposed isobaric binary phase diagram of the Zn–Ga system at 3 GPa.

solubility of zinc in gallium seem to be at gallium contents between 90 and 100 mol% in the binary phase diagram. The solidus and solvus on the zinc-rich side were difficult to detect by means of measurements of the electrical resistance.

Figure 2 shows a proposed isobaric phase diagram of the Zn–Ga system at 3 GPa including the phase field of the X phase constructed from the basis of the present experimental results.

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