Phase equilibria in the Ir-rich portion of the Ir–Al–X (X: Ti, Zr and Hf) ternary systems

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Abstract

Isotherms of the Ir-rich portion of the Ir–Al–X (X: Ti, Zr, Hf) systems are presented. In all of the isotherms three-phase equilibrium is found and no ternary compound is observed. Solid solubility of each phase is confirmed by chemical analysis by wavelength dispersive X-ray spectroscopy (WDS). The direction of the solubility lobe of $L1_2$–Ir_3X with Al addition is explained in terms of the nearest neighbor interactions. Liquidus surfaces are also established by taking into account the microstructure of as-cast alloys, differential thermal analysis (DTA) data, Ir–X binary phase diagrams reported previously and the phase equilibria of the Ir–Al binary system investigated in the present study.
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1. Introduction

Ir-based alloys have been studied and developed as high temperature materials for special uses such as a container for a radioactive fuel in radioisotope thermoelectric generator heat sources [1,2]. Recently, as a candidate for new heat resisting materials, Yamabe-Mitarai et al. [3–6] have proposed alloys based on high melting-point metals with a face centered cubic (f.c.c.) structure, such as Ir and Rh, with an $L1_2$ intermetallic compound as dispersoids, having a similar microstructure as commercial Ni-based superalloys. Ir- and Rh-based $L1_2$ compounds also show an excellent high temperature strength [7,8]. Therefore, these alloys are expected for much higher temperature application than Ni-based alloys.

In order to obtain a prospect of developing materials, however, not only mechanical and physical properties but also related behavior such as microstructure evolution and oxidation at high temperatures should be understood. Present authors have carried out extensive studies on the physical properties of $L1_2$–Rh_3X and Ir_3X, and B2–IrAl compounds [9–12] and on the mechanical properties of $L1_2$–Rh_3X compounds [8]. These alloys have a common problem: the quite low sublimation points of Ir and Rh oxides. However, it was reported that both Ir and Rh show a lower penetration rate of oxygen than Al_2O_3 and SiO_2 [13–16]. So far Hosoda et al. demonstrated quite a unique result that the B2 intermetallic compound IrAl and its alloys show good oxidation resistance, originating from the self-organization of both Al_2O_3 outer-layer and the Ir inner-layer at the alloy surface during oxidation [15–22]. This oxidation-resistant structure repairs by itself through the consumption of IrAl compound, and IrAl coating is expected

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to be applicable as an oxidation-resistant "smart" coating. A similar finding was also reported on B2–$Ir_xRu_{1-x}Al$ [23]. Besides, B2–IrAl was also reported to exhibit an excellent high temperature strength [24,25].

For the development of these B2–IrAl- or RhAl-based coatings on the proposed Ir- or Rh-based materials, information of the phase equilibria is crucial to avoid the brittle intermediate phases such as the sigma phase in the composition range of concern. Also required is the information on the occurrence of the evolution of microstructures composed of f.c.c. and $L1_2$ phases in Ir- and Rh-based alloys caused by Al migration from the coating by diffusion processes. However, only a very limited information on the phase diagram and microstructure evolution is available for the Ir-rich portion of Ir–Al–X and the Rh-rich portion of Rh–Al–X ternary systems with various elements X which form $L1_2$ intermetallic compounds with Ir or Rh [26,27]. In order to correlate the phase diagrams with mechanical and physical properties of Ir- and Rh-based alloys, the isothermal sections and liquidus surfaces of the Ir-rich portion of Ir–Al–X (X: Ti, Zr, Hf) ternary systems were investigated in the present study. The direction of the solubility lobe of $L1_2$–Ir_3X with Al addition was also determined experimentally and explained in terms of the nearest neighbor interactions.

2. Experimental procedures

In the present study, all the compositions of alloys will be presented in atomic percent. Fig. 1 shows the Ir-rich portion of the (a) Ir–Ti, (b) Ir–Zr and (c) Ir–Hf binary systems [28]. In the Ir–Ti binary system, a peritectic reaction Liquid (L) + $(Ir)_{ss}$ → Ir_3Ti is found at 2388 K. The single-phase region of the $L1_2$–Ir_3Ti phase ranges from 23 to 27% Ti and the solid solubility limit of Ti in $(Ir)_{ss}$ is 10% at 1923 K. In the Ir–Zr binary system, there is a eutectic reaction L → $(Ir)_{ss}$ + Ir_3Zr at 2393 K. The single-phase region of the $L1_2$–Ir_3Zr phase ranges from 19 to 30% Zr, and the solid solubility limit of Zr in $(Ir)_{ss}$ is 2% at 1923 K. In the Ir–Hf binary

Table 1
Nominal composition (at.%) and the result of DTA for the binary and ternary alloys investigated

	Ir	Al	X	DTA
Binary alloys	65	35	–	No peaks
	75	25	–	–
X: Ti	70	20	10	–
	70	24	6	No peaks
	76	12	12	–
X: Zr	70	20	10	–
	70	24	6	No peaks
X: Hf	70	20	10	No peaks

system, there is also a eutectic reaction L → $(Ir)_{ss}$ + Ir_3Hf at 2523 K. The single-phase region of the $L1_2$–Ir_3Hf phase ranges from 22 to 27% Hf, and the solid solubility limit of Hf in $(Ir)_{ss}$ is 5% at 1923 K.

The nominal composition for each ternary alloy was chosen by taking the phase relationship in the binary phase diagrams into account, and is listed in Table 1 with the compositions of the binary alloys. Ir–25Al and Ir–35Al alloys were also prepared to examine the Ir-rich side of the Ir–Al binary phase diagram. All specimens with about 10 g were prepared from 99.9% Ir, 99.5% Ti, 99.6% Zr, 95% Hf and 99.99% Al by arc-melting several times in an Ar atmosphere on a water-cooled copper hearth. The samples were cut by a wheel cutter and prepared for the observation of the as-cast microstructures. Remaining portions were wrapped in tantalum foil and subjected to a heat treatment for homogenization at 1923 K for 24 h in an Ar-flow atmosphere. Microstructural observation by scanning electron microscopy (SEM) and chemical analysis by wavelength dispersive X-ray spectroscopy (WDS) with pure Ir, Ti, Zr, Hf and Al as references were carried out on mounted and polished specimens. As the scatter of the composition in each phase measured by SEM–WDS was small (<0.1 at.%), it is concluded that the heat treatment condition is enough to attain equilibrium. $(Ir)_{ss}$ and Ir_3Hf are hard to distinguish by WDS because the atomic number of Hf is close to that of Ir. Therefore, area analysis was con-
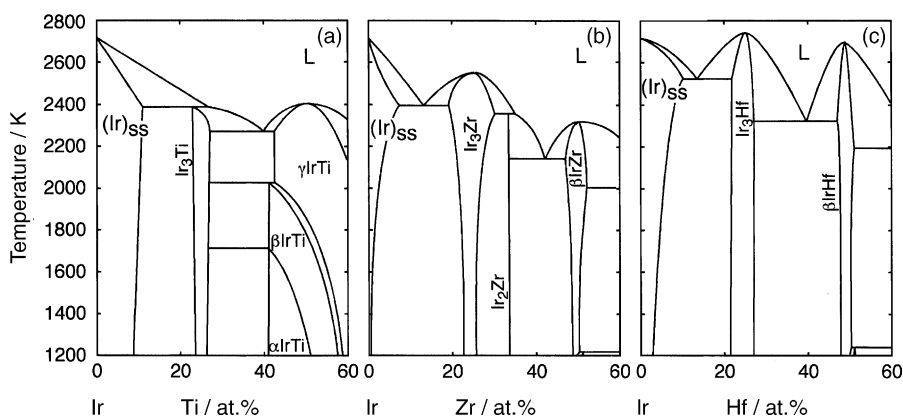

Fig. 1. Ir-rich portion of: (a) Ir–Ti, (b) Ir–Zr and (c) Ir–Hf binary systems redrawn from [28]. L means liquid phase.