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Analysis of Ir-base alloys

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We found that Ir-base alloys with fcc + $L1_2$ two-phase structure similar to Ni-base superalloys are promising as high temperature structural materials [1]. To improve mechanical properties at high temperature, multicomponent alloys are necessary. However, there are only a few investigations for phase diagrams of multicomponent Ir systems, and it is difficult to develop new alloys. To investigate a phase diagram, analysis of alloy and phase composition is very important. However, there are some difficulties in analyzing Ir alloys, such as Ir-Nb-Zr alloys. For example, it is necessary to fuse samples in a solution for chemical analysis, but it is difficult for Ir or Ir alloys to dissolve in even strong acid. It is reported that fusion of bulk Ir by sodium peroxide is the most promising method [2]. In the previous study, we succeeded fusing Ir-2.6 wt%Al and Ir-15.3Nb-1.9Ni-0.3Al (wt%) alloys in sodium peroxide [3]. Then, in this study, the fusion method in sodium peroxide was attended for Ir-Nb-Zr alloys. For physical analysis, such as electron probe X-ray micro analyzer (EPMA), Zr-Lα and Ir-Mβ X-ray lines are overlapped and then accurate intensity of Zr cannot be obtained. In this study, we tried two kinds of analysis methods in EPMA for Ir-Nb-Zr alloys and found suitable analysis condition. For references, the Ir-Nb and Ir-Zr binary alloys were also analyzed.

Button ingots with 5 g of nominal compositions, Ir-25 at%Nb, Ir-25 at%Zr, and Ir-12.5Nb-12.5Zr (at%) were prepared by arc melting method. These samples are single $L1_2$ phase. Then, a sample with 3 × 3 × 1 mm in size was cut from the ingot and heat treated at 1500 K for 72 h to homogenize the sample in a vacuum furnace. They were embedded to a resin and polished to analyze in EPMA. For chemical analysis, the heated samples were crushed to a fine powder below 75 μm in size.

The powder sample of 0.2 g was put in a Ni crucible and 5 g sodium peroxide covered up the powder samples. Then, the sample in the Ni crucible was heated at 573 K for 10 min in the furnace. Furthermore, temperature was increased every 100 K, and kept for 10 min at each temperature until 1073 K. At 1073 K, the sample was heated for 30 min. Thus, the sample was completely fused in sodium peroxide. Then, the sample was cooled to room temperature by air cooling. The fused sample in the Ni crucible was washed out by 120 ml of aqua regalis and put in a fluoroplastic beaker. Furthermore, the Ni crucible was again washed by 50 ml of hydrochloric acid and the rinse was also put in the fluoroplastic beaker with the fused sample. Then, the solution in the fluoroplastic beaker was heated to 473 K on a sand bath. To protect hydrolysis of Nb, 10 g of citric acid and 20 ml of hydrofluoric acid were added in the solution. The content of the solution was investigated by inductively coupled plasma-optical emission spectrometory (ICP-OES, Shimadzu, ICPS-2000). To protect corrosion of the plasma torch in ICP-OES by hydroflouric acid, 10 g of boric acid was also added in the solution. The fusion scheme is shown in Fig. 1. To calibrate the contents of elements in the solution, solutions with different concentrations were prepared using standard solutions of Ir, Nb, and Zr. The emission intensities of the solution for calibration were investigated in ICP-OES and plotted as a function of the concentration. Then, the intensities of samples were plotted on the calibration curve and the contents of each element were estimated. The wavelengths used to analyze Ir, Nb, and Zr were 212.681, 319.498, and 343.823 nm in ICP-OES.

The calibration curves of Ir, Nb, and Zr are shown in Fig. 2. The monochromator and polychromator were used for Ir and other elements, respectively. The experimental error was within 0.5 μg/ml for Ir and 0.1 μg/ml for Nb and Zr. The correlation function was 0.9998, 0.9998 and 1.0 for Ir, Nb, and Zr, respectively. The concentration and emission intensity of each element demonstrated a good linear relationship in the standard solution. The concentration of each element was estimated from Fig. 2 and is summarized in Table I. These results indicate that the fusion in sodium peroxide was successful for Ir-Nb, Ir-Zr, and Ir-Nb-Zr alloys as well as Ir-Al and Ir-Al-Nb-Ni alloys.

Two kinds of analysis methods in EPMA were tried using Jeol JXA-8900R and Jeol 733 at 20 kV accelerating voltage, with a stabilized beam current of 5×10^{-8} A. Ir was analyzed for a Ir-Lα X-ray line using LIF as the diffracting crystal. Nb and Zr were analyzed for their Lα X-ray lines using PET crystal. Sixteen points were measured in each alloy. The raw intensity ratios were obtained using standard samples. The true composition of alloys was estimated by employing ZAF corrections due to the atomic number, absorption and fluorescence effects.

First, the Ir-Nb-Zr alloy was analyzed qualitatively. Although the Ir-Lα and Nb-Lα lines can be identified independently, the Ir-Mβ line (2.053 keV) overlapped at the Zr-Lα line (2.042 keV) (Fig. 3). Then, we investigated the intensity of Ir-Mβ at the same energy as a Zr-Lα line (2.042 keV) and Ir-Lα at 9.174 keV in pure Ir. They were 8231 and 557102 cps, respectively. The intensity ratio of Ir-Mβ ($I_{\mathrm{Ir(ZrL\alpha)}}$) and Ir-L$\alpha$ ($I_{\mathrm{IrL\alpha}}$), after the background intensity (I_{b}) was subtracted,

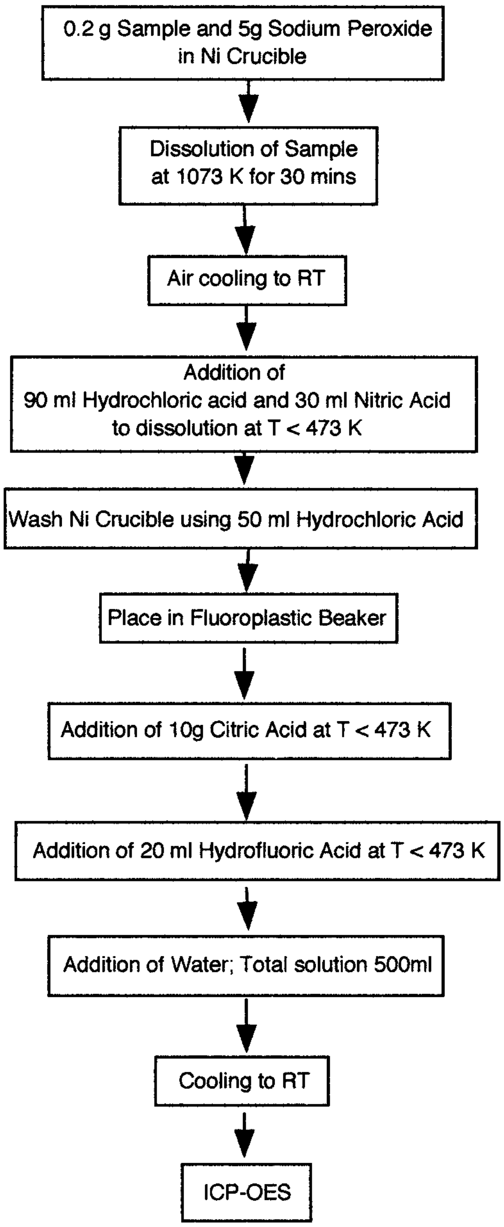

Figure 1 Flow chart of the fusion methods of Ir alloys.

was

$$\frac{I_{\mathrm{IrL}\alpha}}{I_{\mathrm{Ir(ZrL}\alpha)}} = \frac{557102}{8231} = 67.68 \tag{1}$$

This value was used for the Ir-Nb-Zr alloys because the ratio does not depend on the Ir concentration. The intensity of Zr-Lα ($I_{\mathrm{ZrL}\alpha}$) was estimated the following way. From Equation 1,

$$I_{\mathrm{Ir(ZrL}\alpha)} = \frac{I_{\mathrm{IrL}\alpha}}{67.68} \tag{2}$$

$$I_{\mathrm{ZrL}\alpha} = (I_{\mathrm{ZrL}\alpha})_0 - I_{\mathrm{Ir(ZrL}\alpha)} \tag{3}$$

where $(\mathrm{I}_{\mathrm{ZrL}\alpha})_0$ is the measured intensity of the Zr-Lα line. The obtained intensity was compared with the intensity of the pure element and the estimated alloy composition.

In the Jeol 733, the qualitative analysis cannot be used and it is difficult to detect peak overlap. In this case, comparison with standard samples is used as the following equation.

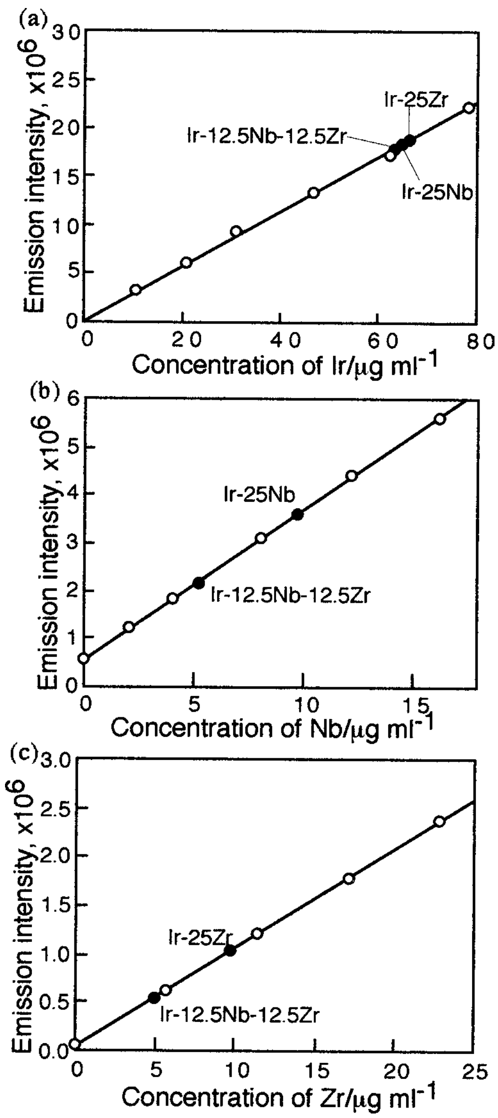

Figure 2 Calibration curves of (a) Ir, (b) Nb, and (c) Zr with ICP-OES. Open symbols represent standard solutions. Closed symbols represent the alloy solution prepared using the fusion method with sodium peroxide.

$$\frac{I_{\mathrm{A}}}{(I_{\mathrm{A}})_0} = \frac{C_{\mathrm{A}}}{(C_{\mathrm{A}})_0} \tag{4}$$

where I_{A} and C_{A} are the intensity and the concentration of element A in the sample. $(I_{\mathrm{A}})_0$ and $(C_{\mathrm{A}})_0$ indicate

TABLE I Chemically analyzed results

Alloy (at%)	Ir	Nb	Zr
Ir-25Nb			
Nominal (wt%)	86.1	13.9	–
Chemical analysis (μg/ml)	65.0	9.7	–
Calculated value (wt%)	87.0	13.0	–
Ir-25Zr			
Nominal (wt%)	86.3	–	13.7
Chemical analysis (μg/ml)	65.8	–	9.9
Calculated value (wt%)	86.9	–	13.1
Ir-12.5Nb-12.5Zr			
Nominal (wt%)	86.2	7.0	6.8
Chemical analysis (μg/ml)	62.0	5.2	5.0
Calculated value (wt%)	85.9	7.2	6.9

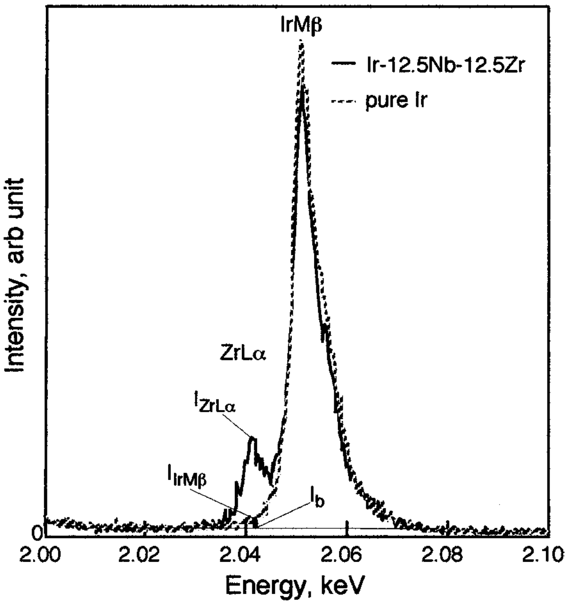

Figure 3 Peaks of IrMβ and ZrLα lines of pure Ir and Ir-Nb-Zr alloy obtained in EPMA.

the intensity and the concentration of element A in the standard sample. As standard samples, pure elements and the Ir-12.5Nb-12.5Zr alloy itself were used. When the Ir-Nb-Zr alloy was used as a standard sample, the chemically composition was used $(C_A)_0$.

The experimental error was about 0.5 wt% in method 1. The obtained concentrations are summarized in Table II. In the binary alloys, the Nb and Zr concentrations obtained in EPMA were 0.6 wt% and 1.6 wt% higher than the chemically analyzed concentration. In the ternary alloy, the Nb and Zr concentrations were 0.6 wt% and 0.2 wt% higher than the concentration analyzed chemically. This indicates that we can obtain the concentration close to the chemically analyzed composition by method 1. If a sample is a single phase, the alloy composition can be obtained using method 1 without the chemical analysis. This is beneficial because the chemical analysis of Ir alloys is difficult.

Method 2 was tried for only the Ir-Nb-Zr ternary alloy. The analysis data were variable and the experimental error was about 1 wt%, higher than that in method 1. When pure elements were used as standard samples, the total composition was over 100 wt% and the concentration of Zr was lower than the nominal one as shown in method 2a in Table II. Based on a 100% for the total composition, the calibrated compositions are shown in brackets. The concentration of Zr was 2 wt% smaller than the nominal value. This indicates that pure elements are not suitable as standard samples. Then, we chose the Ir-12.5Nb-12.5Zr alloy as a standard sample because if we consider the standard sample to have a similar composition as the unknown samples, the effect of peak overlapping becomes smaller. When the Ir-12.5Nb-12.5Zr alloy was used as a standard sample, the total composition became around 100% and the obtained concentration of each element was close to the chemically analyzed value as shown in method 2b in Table II. This suggests that if we have a standard sample whose composition is known by chemical analysis, method 2 is also useful even if it is difficult to detect the peak overlapping. Thus, we conclude that both analysis methods in EPMA can be useful to analyze Ir-Nb-Zr alloys.

TABLE II Results analyzed in EPMA

Alloy (at%)	Ir	Nb	Zr
Ir-25Nb			
Method-1	86.6	13.4	–
Ir-25Zr			
Method-1	85.6	–	14.4
Ir-12.5Nb-12.5Zr			
−1	86.7	7.6	7.0
−2a	95.51 (87.9)	7.8 (7.2)	5.3 (4.9)
−2b	86.0	7.2	6.8

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