Phase equilibria in the ZrCo–ZrNi–Zr$_2$Ni–Zr$_2$Co partial system

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This work presents an experimental study of the ternary Co–Ni–Zr system in the ZrCo–ZrNi–Zr$_2$Ni–Zr$_2$Co composition region by means of optical microscopy, X-ray diffraction and differential thermal analysis. The study shows that the ZrCo–ZrNi section is pseudobinary and has a peritectic character. Including the phase equilibria in the binary systems, the partial ternary system may be characterized by the following invariant equilibria,

- $P$: $L + ZrCo \leftrightarrow ZrNi$,
- $E$: $L \leftrightarrow ZrCo + Zr$_2$Co$,
- $U$: $ZrCo + L \leftrightarrow Zr$_2$Co$_{1-x}$Ni$_x$ + ZrNi,
- $H$: $L \leftrightarrow ZrNi + Zr$_2$Ni$.

The Zr$_{57}$Co$_{43}$–Zr$_{57}$Ni$_{43}$ section has been constructed.

Phase diagram / Crystal structure / Intermetallics

Introduction

The aim of this paper is to present part of our work carried out to experimentally determine the phase equilibria in the Co–Ni–Zr system. It has been shown [1] that the Zr$_2$Ni–Zr$_2$Co section is a pseudobinary one and that a continuous solid solution is formed between these compounds. The binary compounds ZrNi and ZrCo melt congruently; ZrNi exhibits an oS8-CrB type structure, whereas ZrCo adopts a cP2-CsCl type structure [2,3]. We expected the ZrNi–ZrCo section to be pseudobinary one, because of the close similarity of the atomic diameters and electrochemical properties of Ni and Co.

Investigations of the reciprocal solubility of ZrNi and ZrCo have enabled us to characterize the phase equilibria in the ZrCo–ZrNi–Zr$_2$Ni–Zr$_2$Co composition region.

Materials and experimental methods

Alloys were prepared from Co (99.9 %), Ni (99.9 %) and Zr (99.9 %) by arc melting under an atmosphere of purified argon. The ingots were typically 25-30 g. To purify the argon atmosphere, a Ti-Zr button was used as a getter and was melted before the ternary alloys. Each specimen was turned over and remelted 6 times for better homogenization. The composition was checked by X-ray fluorescent analysis, using a VRA-30 spectrometer.

Experimental methods such as powder X-ray diffraction, optical metallography and differential thermal analysis (DTA) were used. The X-ray diffraction patterns were obtained using CuK$\alpha$ radiation. The accuracy of the measurements for the differential thermal analysis in the interval 1000-2000 °C was ±7 °C, the heating and cooling rate was 1.3 °C/s. The samples investigated by optical microscopy were prepared using conventional metallography techniques.

Results and discussion

The X-ray investigations of the binary alloys ZrCo and ZrNi showed good agreement with the lattice parameters reported in the literature. The structure study showed that the ZrCo-based alloys containing up to 10 at.% Ni have cubic CsCl-type structure, whereas the alloys with more than 20 at.% Ni have orthorhombic CrB-type structure. The lattice parameters vs. the Ni content in the ZrCo–ZrNi alloys are presented in Fig. 1.

The DTA study confirmed that the ZrCo–ZrNi section is a pseudobinary system and is characterized by a peritectic transformation. The temperature of the peritectic reaction was found to be 1290 °C. The results obtained for the ZrCo–ZrNi isopleth section are given in Fig. 2.

Taking into account the existence of a continuous solid solution between Zr$_2$Co and Zr$_2$Ni, the eutectic equilibria $L \leftrightarrow ZrCo + Zr$_2$Co$ and $L \leftrightarrow ZrNi + Zr$_2$Ni$ in the binary systems, and the peritectic reaction $L + (ZrCo) \leftrightarrow (ZrNi)$ in ternary alloys, the transition from ZrCo to ZrNi should be realized by a U-type
reaction as $\text{ZrCo} + \text{L} \leftrightarrow \text{Zr}_2\text{Co}_{1-x}\text{Ni}_x + \text{ZrNi}$. To establish the parameters of this invariant reaction, the phase equilibria in the $\text{Zr}_{57}\text{Co}_{43}-\text{Zr}_{57}\text{Ni}_{43}$ section were examined.

According to the X-ray analysis, this section crosses three phase regions at room temperature. The first two-phase region consists of the $\text{cP2}$-type (ZrCo) phase and the $\text{tI12}$-type $\text{Zr}_2(\text{Co},\text{Ni})$ phase and extends up to 8 at.% Ni. The three-phase region $\text{Zr}_2(\text{Co},\text{Ni}) + \text{ZrCo} + \text{ZrNi}$ is located between 8 and 18 at.% Ni. The alloys with a Ni content higher than 18 at.% consist of the orthorhombic (ZrNi) and the tetragonal $\text{Zr}_2(\text{Co},\text{Ni})$ phases. The composition dependence of the lattice parameters of the ZrCo and ZrNi phases is shown in Fig. 3.

Combining the results of DTA, X-ray diffraction and metallographic analysis, the isopleth $\text{Zr}_{57}\text{Co}_{43}-\text{Zr}_{57}\text{Ni}_{43}$ was constructed and is presented in Fig. 4.
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Fig. 4 The Zr$_{57}$Co$_{43}$–Zr$_{57}$Ni$_{43}$ section.

References
