The Zr-Ni-Cr System at 1000 °C in the ZrCr₂-ZrNi-Ni-Cr Region

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The isothermal section of the Zr-Ni-Cr ternary system was determined at 1000 °C in the ZrCr₂-ZrNi-Ni-Cr region. The nature and composition of the phases involved in the different equilibria were determined by metallographic analysis, electron probe microanalysis (EPMA), and x-ray powder diffraction (XRD) analysis. Substitution of Cr by Ni in the Laves phase ZrCr₂ is possible in large quantities resulting in the formation of ternary Laves phases. However formation of the ZrNi₂ compound was not observed. This substitution reduces the content of Zr and induces transformations from C15 to C14 and to the C15 structure through two two-phase regions.

Introduction

Some metals or intermetallic compounds (Pd, LaNi₅, TiFe, ZrCr₂) are known to absorb reversibly large amounts of hydrogen at room temperature. The hydrides can be used for hydrogen or its isotope storage, heat pumps, or hydrogen purification. The most promising application is found in nickel-hydride batteries for replacement of nickel-cadmium ones with increased capacity and reduced toxicity. Some Laves phases (ZrX₂: X = V, Cr, Mn) can be hydrogenated up to ZrX₂H₄, but their corresponding hydride equilibrium pressure is too low for reversible applications like the electrochemical one. Substitution of X by another transition metal allows modification of the thermodynamic properties of the hydrides. This work aimed to measure the solubility of Ni in ZrCr₂, to study the change of structure of the Laves phases, and to determine the nature of the equilibria in which they are involved. For this purpose, the phase diagram of the Zr-Ni-Cr ternary system was determined at 1000 °C in the region surrounding the Laves phases existence domain. In a subsequent work, this study will be applied to measure the effect of the substitution of Ni and of precipitation of secondary phases on the hydriding properties of the Laves phases. A brief description of the relevant binary diagrams is given here, and the limited data on the ternary system are reviewed. Then, the experimental results are described and discussed.

The Zr-Cr System

Arias and Abriata [86Ari] evaluated the complete diagram. Three nonstoichiometric compounds of the Laves phase structures exist in this system. Their polymorphism in temperature ranges were studied by Petkov et al. [73Pet]. At temperatures below 1592 °C, the stable structure is the cubic C15, MgCu₂-type structure. It transforms above 1592 °C into the hexagonal C36, MgNi₂-type structure. The high-temperature phase appears at 1622 °C, belongs to the hexagonal C14, MgZn₂-type structure, and melts congruently.

The Cr-Ni System

The Cr-Ni system, which forms no intermetallic compounds, was assessed by Nash (cited in [86Mas]). At 1000 °C, the solubility of Ni in (Cr) is 5 at.% whereas that of Cr in (Ni) is 45 at.%.

The Zr-Ni System

The Zr-Ni diagram was assessed by Nash and Jayanth [84Nas]. Eight intermetallic compounds are reported, seven of which are stable at 1000 °C, with the following structural types: A1₂Cu for Zr₂Ni [72Hav], BCr for ZrNi [62Kir1], Zr₅Pt₁₁ for Zr₅Ni₁₁ [73Pan], Zr₇Ni₁₀ for Zr₇Ni₁₀ (Aba₂ or Pbca space groups as a function of stoichiometry) [62Kir2], Hf₅Ni₁₂ for Zr₅Ni₁₂ [79Bse], Zr₂Ni₇ for Zr₂Ni₇ [72Esh], AuBe₅ for ZrNi₅ [57Smi]. Petkov et al. [72Pet] reported the existence of the Laves phase ZrNi₂ with the C15, MgCu₂-type structure. This compound was not obtained by Bsenko [79Bse] and seems to be an oxygen stabilized phase.

Table 1 summarizes the literature data concerning the unary and binary phases.

The Zr-Ni-Cr System

Substitution of Cr by Ni in ZrCr₂ was studied by Svechnikov et al. [72Sve] at 900 °C. According to [72Sve] and Petkov et al. [72Pet], total replacement of Cr by Ni might be possible. They reported two isothermal changes of the structure of the compound Zr(Cr₁₋ₓNiₓ)₂ passing through two, two-phase areas. At 900 °C, it has the C15 structure for 0 ≤ x ≤ 0.1, the C14 struc-
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Table 1  Zr-Ni-Cr Unary and Binary Phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature, °C</th>
<th>Reaction type</th>
<th>Pearson symbol</th>
<th>Space group</th>
<th>Prototype</th>
<th>Lattice parameters, nm</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>863</td>
<td>Allotropic</td>
<td>hP2</td>
<td>P6/mmc</td>
<td>Mg</td>
<td>0.3233 ... 0.5148 ...</td>
<td>...</td>
<td>[91Vil]</td>
</tr>
<tr>
<td>Zr</td>
<td>863 to 1855</td>
<td>Allotropic to</td>
<td>cP2</td>
<td>Im3m</td>
<td>W</td>
<td>0.3699 ...</td>
<td>...</td>
<td>[81Kin]</td>
</tr>
<tr>
<td>Ni</td>
<td>1455</td>
<td>Melting</td>
<td>cF4</td>
<td>Fm3m</td>
<td>Cu</td>
<td>0.3523 ...</td>
<td></td>
<td>[91Vil]</td>
</tr>
<tr>
<td>Cr</td>
<td>1863</td>
<td>Melting</td>
<td>cF4</td>
<td>Fm3m</td>
<td>MgCu2</td>
<td>0.7215 ...</td>
<td></td>
<td>[73Pet]</td>
</tr>
<tr>
<td>Zr2Cr (C15)</td>
<td>1592</td>
<td>Allotropic</td>
<td>hP24</td>
<td>P6/mmc</td>
<td>MgNi2</td>
<td>0.5100 ... 1.661 ...</td>
<td></td>
<td>[73Pet]</td>
</tr>
<tr>
<td>Zr2Cr (C14)</td>
<td>1592 to 1622</td>
<td>Allotropic to</td>
<td>hP24</td>
<td>P6/mmc</td>
<td>MgZr2</td>
<td>0.5102 ... 0.8273 ...</td>
<td></td>
<td>[84Sup]</td>
</tr>
<tr>
<td>Zr2Ni</td>
<td>1120</td>
<td>Melting</td>
<td>t12</td>
<td>I4/mcm</td>
<td>Al6Cu</td>
<td>0.6483 ... 0.5267 ...</td>
<td></td>
<td>[72Hav]</td>
</tr>
<tr>
<td>ZrNi</td>
<td>1260</td>
<td>Melting</td>
<td>eC8</td>
<td>Cmcm</td>
<td>BCr</td>
<td>0.3268 ... 0.9397 ... 0.4101 ...</td>
<td></td>
<td>[62Kir1]</td>
</tr>
<tr>
<td>Zn2Ni11</td>
<td>978 to 1170</td>
<td>Eutectoid to</td>
<td>t40</td>
<td>I4/m</td>
<td>Zr2Pt11</td>
<td>0.990 ... 0.662 ...</td>
<td></td>
<td>[73Pan]</td>
</tr>
<tr>
<td>Zr7Ni10</td>
<td>1160</td>
<td>Peritectic</td>
<td>oC68</td>
<td>A2/a</td>
<td>Zr7Ni10</td>
<td>0.9211 ... 0.9156 ... 1.2386 ... Zr poor</td>
<td>62Kir2</td>
<td></td>
</tr>
<tr>
<td>Zr2Ni21</td>
<td>1180</td>
<td>Peritectic</td>
<td>aP29</td>
<td>F1</td>
<td>HfNi21</td>
<td>0.6472 ... 0.8065 ... 0.8588 ... (\alpha = 75.19^\circ, \beta = 68.04^\circ, \gamma = 75.26^\circ)</td>
<td>79Bsc</td>
<td></td>
</tr>
<tr>
<td>Zr5Ni3</td>
<td>920</td>
<td>Peritectoid</td>
<td>hP8</td>
<td>P6/mmc</td>
<td>SnNi3</td>
<td>0.5309 ... 0.4303 ...</td>
<td></td>
<td>[79Bec]</td>
</tr>
<tr>
<td>Zr5Ni7</td>
<td>1440</td>
<td>Melting</td>
<td>mC36</td>
<td>C2/m</td>
<td>Zr5Ni7</td>
<td>0.4698 ... 0.8235 ... 1.2193 ... (\beta = 95.83^\circ)</td>
<td>72Esh</td>
<td></td>
</tr>
<tr>
<td>Zr5Ni8</td>
<td>1300</td>
<td>Peritectic</td>
<td>cP24</td>
<td>F4/m</td>
<td>AuBe5</td>
<td>0.671 ...</td>
<td></td>
<td>[57Smi]</td>
</tr>
</tbody>
</table>

From [84Nas] and [86Ari].

Experimental Procedure

The alloys (5 to 13 g) were obtained by induction melting of the pure components (99.9% Zr, 99.9% Ni, 99.99% Cr) in a water-cooled copper crucible. The starting materials were outgassed under secondary vacuum at 1000 °C for 3 h and then melted under pure argon atmosphere to prevent weight loss due to evaporation. Each alloy was remelted 5 times and inverted between each melting to ensure good homogeneity. It was then wrapped in a tantalum foil and annealed in a secondary evacuated silica tube at 1000 °C for 30 days to ensure equilibrium. The silica tube was then quenched into water. The weight loss during synthesis and heat treatment was typically less than 0.5%.

Samples were characterized by optical metallography, scanning electron microscopy (SEM) (JEOL JSM840, JEOL Ltd., Tokyo, Japan), electron probe microanalysis (EPMA), and x-ray diffraction (XRD). The X-ray powder diffraction was measured to obtain the mass density by a Philips PW1752 diffractometer (Philips Analytical X-ray, Almelo, The Netherlands). Those obtained for the alloys containing Zr2Ni7 showed a very large, strain-induced line broadening due to its mechanical properties, and only the parameters of additional phases could be measured. The other diagrams were analyzed, after identification of the phases, with the full pattern fitting program, FULLPROF [90Rod] with the Rietveld refinement method. Starting from the literature data concerning the crystal structures of the binary compounds, the lattice parameters and the atomic positions could be refined. The program gave very good accuracy even when convolution of diffraction peaks belonging to different phases existed.

For the construction of the phase diagram, the nature of the phases involved in the different equilibria were from XRD results, and the reported compositions were determined by EPMA.

Results

Figure 1 shows the Zr-Ni-Cr diagram at 1000 °C. It was constructed considering the results obtained with 27 different samples. Table 2 gives the phase characteristics for each composition.

The solubility of Cr in (Ni) was found in sample No. 23 where a three-phase equilibrium was observed (Fig. 2a) to be 43 at.% whereas that of Ni in (Cr) was 6 at.%. In each case, the solubility of Zr is less than 1 at.% and does not affect the binary two-phase equilibrium.

Contrary to the results of Kramer [59Kra] from a metallographic study at 1000 °C, which indicates an homogeneity range of 15.5 to 17 at.% Zr for ZrNi5, our analysis of this phase in sample No. 27 (Zr_{16.6}Ni_{83.2}Cr_{0.3}) shows that no reduction of Zr stoichiometry seems possible. This result agrees with the Kirkpatrick and Larsen [61Kir] XRD measurements, which indicate a maximum homogeneity range of 0.2 at.%. The existence domain was, therefore, shown as a line in Fig. 1.

The solubility of Cr in the Zr-Ni binary compounds is generally weak (<2.5 at.%) except for Zr2Ni7, where Cr is dissolved to an amount of 7.8 at.% (sample No. 20). Zr2Ni7 has a great...