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HYDROGEN SORPTION BY SOME EARLY-LATE TRANSITION METAL GLASSES

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Abstract.- The hydrogen sorption behaviour of amorphous Cu_{62}Zr_{58}, Ni_{50}Ti_{50}, Ni_{61.4}Ti_{38.6}, Ni_{41.7}Zr_{29.3}, Ni_{61.4}Ti_{38.6}Zr_{9.2}, Ni_{63.7}Zr_{36.3} and Ni_{60}Nb_{40} obtained by melt spinning is described. The first three alloys have a relatively low crystallization temperature and these alloys either could not be made completely amorphous or crystallized during hydrogen sorption. The highest absorption occurs in Ni_{61.4}Zr_{29.3}: about 0.6 hydrogen atom per metal atom at a temperature of 333 K and a hydrogen pressure of 80 bar. Pressure-composition isotherms of Ni_{61.4}Zr_{29.3} show no pressure plateau in the range of temperatures and pressures investigated. The isotherms of crystalline Ni_{61.4}Zr_{29.3} and the intermetallic compound Ni_{60}Nb_{40} do show such a plateau. During 100 cycles of hydration and dehydration of amorphous Ni_{61.4}Zr_{29.3} splinters of 0.1 mm spalled off from the pieces of ribbon, but disintegration into still smaller particles was not observed. The X-ray diffraction and DSC-scan after 100 cycles are similar to those of as-quenched material. Magnetization and Rutherford-back-scattering results indicate surface segregation of Ni in a 100 times cycled sample.

INTRODUCTION

In recent years much attention is paid to metal hydrides, especially because of their possible application in hydrogen-storage systems.

In this paper we report about the hydrogen sorption characteristics of amorphous Cu_{62}Zr_{58}, Ni_{50}Zr_{50}, Ni_{61.4}Ti_{38.6}, Ni_{41.7}Zr_{29.3}, Ni_{63.7}Zr_{36.3}, Ni_{60}Nb_{40} and Ni_{60}Nb_{40}. Amorphous alloys are of interest, because these may offer advantages over crystalline materials. The well-known hydride-forming compound LaNi_{5} for example disintegrates into a very fine powder, which is technologically undesirable. Splat-quenched unhydrided alloys have a high yield stress and are ductile, contrary to intermetallic compounds and therefore will be less susceptible to disintegration.

EXPERIMENTAL DETAILS

Nominal compositions of the alloys investigated are Cu_{62}Zr_{58}, Ni_{50}Zr_{50}, Ni_{61.4}Ti_{38.6}, Ni_{41.7}Zr_{29.3}, Ni_{63.7}Zr_{36.3}, Ni_{60}Nb_{40} and Ni_{60}Nb_{40}. The preparation of the amorphous alloys and the method to measure the pressure-composition isotherms have been described in an earlier paper (1). Calorimetric measurements are performed with a differential scanning calorimeter. The hydrogen content of the purge gas used in the DSC (purified Ar) is monitored. In this way the hydrogen evolution and the heat effect are observed simultaneously. The magnetization measurements are performed with a vibrating sample magnetometer. Measurements of the surface composition are done by Rutherford-back-scattering of 2 MeV He ions.

RESULTS AND DISCUSSION

The crystallization temperatures and heats of crystallization measured by means of DSC are summarized in Table 1. X-ray diffractograms of Ni_{50}Zr_{50} and of Ni_{63.7}Zr_{36.3} indicated the presence of...
some crystalline material. Activation of most alloys was possible at about 530 K by cycling the hydrogen pressure between vacuum (10⁻² Torr) and 30-60 bar. Activation of Ni₆₄Zr₃₆ already occurred at 310 K. Unfortunately crystallization took place simultaneously: the DSC-scan after hydration showed no amorphous to crystalline transition and the X-ray diffraction pattern was very similar to that of crystalline Ni₅ZrH₃ (2; fig. 1). Also Cu₅₀Zr₅₀ crystallized during hydrogen sorption and the diffractogram showed lines corresponding to crystalline Cu and ZrH₂; the Ni₆₀- and Ni₇₀-alloys did remain amorphous (see Table 1). By heating hydrided Ni₄₆Zr₃₄, Ni₅₁Ti₃₉, Ni₆₀Nb₄₀, and Ni₆₀Nb₄₀ in the DSC under Ar purge gas hydrogen desorbed from 300 K, 500 K and 700 K respectively.

Ni₄₂Ti₃₉Zr₉ absorbed about 0.2 hydrogen atom per metal atom and Ni₄₄Zr₃₄ about twice that amount at nearly the same temperature.

Research was concentrated on Ni₄₄Zr₃₄ and related crystalline compounds. The isotherms of amorphous Ni₅₄Zr₃₆ did not show a pressure plateau (fig. 2). The 533 K P-C isotherms of amorphous and crystalline Ni₅₄Zr₃₆ are shown in figure 3.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>DSC-DATA</th>
<th>X-RAY DIFFRACTION DATA</th>
<th>MAXIMUM AMOUNT OF ABSORBED HYDROGEN</th>
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<tr>
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<td>CRYSTALLIZATION</td>
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<td>H/M MAX measured at 30 bar and a</td>
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<td></td>
<td>TEMPERATURE &amp; HEAT</td>
<td>A=Amorphous, C=Crystalline</td>
<td>temperature of: K</td>
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<tr>
<td></td>
<td>K kJ/mol</td>
<td>AS-QUENCHED</td>
<td>HYDRIDED</td>
</tr>
<tr>
<td>Cu₅₀Zr₅₀</td>
<td>720 4.6</td>
<td>A</td>
<td>C</td>
</tr>
<tr>
<td>Ni₅₄Zr₃₆</td>
<td>730 4.0</td>
<td>TC</td>
<td>C</td>
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<td>TC</td>
</tr>
<tr>
<td>Ni₆₂Ti₃₉Zr₉</td>
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<td>A</td>
<td>A</td>
</tr>
<tr>
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<td>A</td>
<td>A</td>
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<tr>
<td>Ni₆₀Nb₄₀</td>
<td>930 3</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Ni₆₀Nb₄₀</td>
<td>940 4</td>
<td>A</td>
<td>A</td>
</tr>
</tbody>
</table>
Ni_{64}Zr_{36} were almost similar, but the 433 K and 333 K isotherms showed a clear difference (fig. 3). Because crystalline Ni_{64}Zr_{36} is an eutectic alloy composed of the intermetallic compounds Ni_{10}Zr_{7} and Ni_{5}Zr_{2} also the 433 K and 333 K isotherms of these compounds were measured (fig. 4).

The isotherms of crystalline Ni_{64}Zr_{36} closely approximate a weighted average of the isotherms of Ni_{5}Zr_{2} and Ni_{10}Zr_{7}. From the absence of a pressure plateau in the P-C curves of amorphous Ni_{64}Zr_{36} it can be concluded that no hydride with a discrete composition is formed at temperatures between 333 K and 533 K. However, the presence of hysteresis at the lowest temperature points to hydride formation instead of an extended H-solution. Also the isotherms do not obey Sieverts' law.

From the P-C isotherms we calculated the enthalpy of formation of the ternary hydrides of Ni_{64}Zr_{36} and the related crystalline alloys. In Table 2 these values are compared with the results obtained from the alloy model developed by Miedema and co-workers (3-5). Only the values for Ni_{5}Zr_{2} differ widely, probably due to the low amount of hydrogen absorbed by this compound. These results will be discussed in detail elsewhere.

The enthalpies of formation of Zr-, Ti- and Nb-hydride are -163, -125 and -25 kJ/mol H_{2} respectively. Not understood is why the sequence of the temperatures at which hydrogen starts to desorb by heating in the DSC (300 K, 500 K and 700 K respectively) is just opposed to the sequence of the stability of the binary Zr-, Ti- and Nb-hydrides.

The amorphous Ni_{64}Zr_{36} samples did remain amorphous even after 100 hydrogen absorption-desorption cycles (fig. 5). In the hydrided state the samples were brittle (pieces of about 0.1 mm spalled off from the ribbon (10 mm x 1 mm x 0.04 mm)), but after dehydration the ductility was recovered, also of the small splinters. Besides the size of the splinters was still large compared to the particle size of the LaNi_{5}-hydride powder (< 0.005 mm).

![Fig 5. DSC and hydrogen desorption-scan of hydrided Ni_{64}Zr_{36}.](image-url)
As-quenched samples of Ni₆₄Zr₃₆ were paramagnetic, while samples which had undergone 100 sorption cycles were super-paramagnetic. The saturation value of the magnetization corresponded to the segregation of 1.7% of the Ni-atoms in the form of metallic Ni-clusters.

Fig. 6 shows the Rutherford-backscattering results for an as-quenched and a 100 times cycled sample of amorphous Ni₆₄Zr₃₆. We interpret the differences between both profiles as a Ni-enrichment near the surface of the hydrided sample. From the electronic stopping power, which is about 500 eV/nm, it is calculated that the thickness of the Ni-enriched surface layer is about 0.05 μm. Comparison with the magnetization measurements indicates that the segregation of metallic Ni also takes place in the bulk. For crystalline TiFe and LaNi₄ Schlaphbach et al. [6] and Siegmann et al. [7] found only a surface segregation of the second component (Fe, Ni respectively). For a 1500 times cycled sample of FeTi for example they found an Fe-enriched layer with a thickness of about 0.05 μm just below the surface.

CONCLUSIONS

- Of the alloys with a relatively low crystallization temperature (750 K or less), Cu₆₂Zr₃₈, Ni₆₂Zr₃₀ and Ni₆₂Ti₃₉, the first two crystallize during hydrogen sorption. The amount of crystalline material present in Ni₆₂Ti₃₉ does not increase.
- The alloys with a relatively high crystallization temperature (835 K or higher), Ni₄₁Ti₉Zr₉, Ni₄₄Zr₃₆, Ni₄₀Nb₄₀ and Ni₆₀Nb₅₀, do not crystallize during hydrogen sorption.
- Under Ar amorphous Ni₄₄Zr₃₆ desorbs hydrogen at lower temperatures than amorphous NiTi- and NiNb-alloys of comparable composition.
- The isotherms of amorphous Ni₄₄Zr₃₆ do not show a pressure plateau.
- The disintegration of amorphous samples during hydrogen sorption is less severe than that of crystalline intermetallic compounds.
- In a 100 times cycled sample of Ni₄₄Zr₃₆ segregation of Ni was found.

LITERATURE


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