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HAL Id: jpa-00220327
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Submitted on 4 Feb 2008

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HYDROGEN SORPTION BY SOME EARLY-LATE TRANSITION METAL GLASSES

F.H.M. Spit, J.W. Drijver, W.C. Turkenburg and S. Radelaar

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Abstract.—The hydrogen sorption behaviour of amorphous $\text{Cu}_{56.2}\text{Zr}_{50}$, $\text{Ni}_{50}\text{Ti}_{40}$, $\text{Ni}_{50}\text{Ti}_{20}$, $\text{Ni}_{50}\text{Ti}_{20}$, $\text{Ni}_{50}\text{Ti}_{20}$, $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$, $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$, and $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$ 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 $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$: about 0.6 hydrogen atom per metal atom at a temperature of 333 K and a hydrogen pressure of 30 bar. Pressure-composition isotherms of $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$ show no pressure plateau in the range of temperatures and pressures investigated. The isotherms of crystalline $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$ and the intermetallic compound $\text{Ni}_{61.4}\text{Ti}_{38.6}$ do show such a plateau. During 100 cycles of hydration and dehydron of amorphous $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$ 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 $\text{Cu}_{56.2}\text{Zr}_{50}$, $\text{Ni}_{50}\text{Zr}_{50}$, $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$, $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$, $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$, and $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$. Amorphous alloys are of interest because these may offer advantages over crystalline materials. The well-known hydride-forming compound $\text{LaNi}_5$ 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 $\text{Cu}_{56.2}\text{Zr}_{50}$, $\text{Ni}_{50}\text{Zr}_{50}$, $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$, $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$, $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$, $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$.

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-backscattering 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 $\text{Ni}_{50}\text{Zr}_{50}$ and of $\text{Ni}_{41.7}\text{Ti}_{29.1}\text{Zr}_{19.2}$ 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 Ni$_{64}$Zr$_{36}$ 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 NiZrH$_3$ (2; fig. 1). Also Cu$_{50}$Zr$_{50}$ crystallized during hydrogen sorption and the diffractogram showed lines corresponding to crystalline Cu and ZrH$_2$; the NiNb- and NiTi-alloys did remain amorphous (see Table I). By heating hydried Ni$_{44}$Zr$_{56}$, Ni$_{44}$T$_{12}$, Ni$_{60}$Nb$_{40}$ and Ni$_{60}$Nb$_{60}$ in the DSC under Ar purge gas hydrogen desorbed from 300 K, 500 K and 700 K respectively. Ni$_{60}$T$_{12}$Zr$_{9}$ absorbed about 0.2 hydrogen atom per metal atom and Ni$_{64}$Zr$_{56}$ about twice that amount at nearly the same temperature.

Research was concentrated on Ni$_{64}$Zr$_{56}$ and related crystalline compounds. The isotherms of amorphous Ni$_{64}$Zr$_{56}$ did not show a pressure plateau (fig. 2). The 533 K P-C isotherms of amorphous and crystal-

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>DSC-DATA</th>
<th>X-RAY DIFFRACTION DATA</th>
<th>MAXIMUM AMOUNT OF ABSORBED HYDROGEN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CRYSTALLIZATION TEMPERATURE &amp; HEAT</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>kJ/mol</td>
<td>AS-QUENCHED</td>
</tr>
<tr>
<td>Cu$<em>{50}$Zr$</em>{50}$</td>
<td>720</td>
<td>4.6</td>
<td>A</td>
</tr>
<tr>
<td>Ni$<em>{60}$Zr$</em>{50}$</td>
<td>730</td>
<td>4.0</td>
<td>A</td>
</tr>
<tr>
<td>Ni$<em>{60}$T$</em>{12}$</td>
<td>750</td>
<td>2.4</td>
<td>TC</td>
</tr>
<tr>
<td>Ni$<em>{64}$T$</em>{12}$Zr$_9$</td>
<td>835</td>
<td>2.4</td>
<td>A</td>
</tr>
<tr>
<td>Ni$<em>{64}$Zr$</em>{56}$</td>
<td>840</td>
<td>3.5</td>
<td>A</td>
</tr>
<tr>
<td>Ni$<em>{60}$Nb$</em>{40}$</td>
<td>930</td>
<td>3</td>
<td>A</td>
</tr>
<tr>
<td>Ni$<em>{60}$Nb$</em>{60}$</td>
<td>940</td>
<td>4</td>
<td>A</td>
</tr>
</tbody>
</table>

![Fig 1. X-ray diffractogram of Ni$_{50}$Zr$_{50}$ in the as-quenched state and after hydrogen sorption.](image1)

![Fig 2. P-C isotherms of amorphous Ni$_{64}$Zr$_{56}$.](image2)

![Fig 3. P-C isotherms of crystalline Ni$_{64}$Zr$_{36}$.](image3)
line 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$_3$Zr$_2$ also the 433 K and 333 K isotherms of these compounds were measured (fig. 4).

![Graph showing P-C Isotherms of intermetallic compounds Ni$_{10}$Zr$_7$ and Ni$_3$Zr$_2$.](image)

The isotherms of crystalline Ni$_{64}$Zr$_{36}$ closely approximate a weighted average of the isotherms of Ni$_3$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 coworkers (3-5). Only the values for Ni$_3$Zr$_2$ differ widely, probably due to the low amount of hydrogen absorbed by this compound. These results will be discussed in detail elsewhere.

### Table 2

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Enthalpy of formation (kJ/mol H$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$Zr$_2$</td>
<td>-39 ± 4</td>
</tr>
<tr>
<td>Ni$<em>{64}$Zr$</em>{36}$</td>
<td>-41 ± 4</td>
</tr>
<tr>
<td>Ni$<em>{64}$Zr$</em>{36}$ amorph.</td>
<td>-44 ± 6</td>
</tr>
<tr>
<td>Ni$<em>{64}$Zr$</em>{36}$ Cryst.</td>
<td>-47 ± 5</td>
</tr>
</tbody>
</table>

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).

![Graph showing DSC and hydrogen desorption scan of hydrided Ni$_{64}$Zr$_{36}$.](image)
As-quenched samples of Ni$_{64}$Zr$_{36}$ 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 Ni$_{64}$Zr$_{36}$. 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 LaNi$_5$ Schlapbach 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), Cu$_{62}$Zr$_{38}$, Ni$_{60}$Zr$_{30}$ and Ni$_{61}$Ti$_{39}$, the first two crystallize during hydrogen sorption. The amount of crystalline material present in Ni$_{61}$Ti$_{39}$ does not increase.
- The alloys with a relatively high crystallization temperature (835 K or higher), Ni$_{67}$Ti$_{12}$Zr$_{11}$, Ni$_{64}$Zr$_{36}$, Ni$_{60}$Nb$_{24}$ and Ni$_{60}$Nb$_{30}$, do not crystallize during hydrogen sorption.
- Under Ar amorphous Ni$_{64}$Zr$_{36}$ desorbs hydrogen at lower temperatures than amorphous NiTi- and NiNb-alloys of comparable composition.
- The isotherms of amorphous Ni$_{64}$Zr$_{36}$ 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 Ni$_{64}$Zr$_{36}$ segregation of Ni found place.

LITERATURE


ACKNOWLEDGEMENTS

The authors are very grateful to E. Kuipers for performing magnetization measurements. Participating students were K. Blok, W. Classen, E. Hendriks, M. Kramer, R. Wevers and G. Winkels.