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Journal of Non-Crystalline Solids 250–252 (1999) 893–897

JOURNAL OF
NON-CRYSTALLINE SOLIDS

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Hydrogenation of Zr-based metallic glasses and quasicrystals

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Abstract

Zr-based metallic glasses and quasicrystals were electrochemically charged with hydrogen. Hydrogen absorption/desorption as well as the influence of hydrogen on the formation and stability of quasicrystals were studied by means of X-ray diffraction, electron microscopy, differential scanning calorimetry (DSC) and thermal desorption analysis (TDA). In $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ absorption kinetics and storage capacity were found to be better for the quasicrystalline than for the associated amorphous phase. Dissolved hydrogen was observed to play an important role not only in the stability of the quasicrystals, but also in their formation from glassy precursor material. Even hydrogen contents as low as 5 at.% changed the formation as well as the decomposition of the icosahedral quasicrystals: the formation was shifted to higher temperatures whereas decomposition temperatures were lowered. At larger hydrogen contents, changes in both transformations were observed, yet not fully understood. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The high number of tetrahedrally coordinated sites for interstitial hydrogen and the favorable hydrogen–metal chemistry make glassy as well as quasicrystalline Zr–Cu–Ni–Al alloys candidates for hydrogen storage applications. In addition, the greater ductility of metallic glasses compared to those of crystalline materials reduces hydrogen embrittlement [1]. Zr- as well as Ti-based quasicrystals [2,3] and metallic glasses have been observed to store hydrogen up to a content close to the best crystalline materials.

Quasicrystals are often regarded as Hume-Rothery phases stabilized at a particular electron concentration. Concentration changes during the hydrogenation are expected to displace the electron concentration out of the stability range [4],

thus leading to a decomposition of the quasicrystalline phase. On the other hand, hydrogenation of a glassy precursor is expected to hinder the formation of quasicrystals.

The aim of this paper is to study the absorption kinetics and storage ability as well as the stability of hydrogenated glassy and quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ alloys to provide information on a new class of material for hydrogen storage.

2. Experimental procedure

Amorphous and quasicrystalline Zr–Cu–Ni–Al alloys were prepared by melt spinning and subsequent annealing above the glass transition temperature, as described elsewhere [5]. The microstructure was studied by X-ray diffraction as well as transmission electron microscopy (Philips CM200 electron microscope operating at 200 kV).

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Amorphous and quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ribbons were ground and then electrolytically charged with hydrogen in a 2:1 glycerine–phosphoric acid electrolyte at 25°C and a current density of $i = 10 \text{ A/m}^2$. The hydrogen content was measured by a microbalance with an accuracy of $\pm 1 \mu\text{g}$. Hydrogen desorption was investigated by thermal desorption analysis (TDA), thermal stability by means of differential scanning calorimetry (Perkin Elmer DSC7).

3. Results

Quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ can be charged electrochemically up to a maximum hydrogen to metal ratio H/M of 1.6 [3] before failure of the ribbon. This hydrogen content is larger than the maximum hydrogen content of H/M = 0.9 in the associated amorphous phase, as well as related binary Zr-based glasses [6]. As shown in Fig. 1 the storage capacity was found to be larger and the absorption kinetics to be faster for the quasicrystalline phase than for the amorphous one.

Hydrogen absorption of Zr-based alloys might be hindered even by a very thin layer of ZrO_2 . Pd plating, often used to overcome this barrier, showed insufficient adhesion to the glassy or quasicrystalline ribbons. However, alloying with

small amounts of Pd (e.g., 3–5 at.% Pd replacing part of the Ni) was found to improve the absorption kinetics significantly, probably due to Pd segregation at the surface of the ribbon. Since such Pd additions, however, destroy the ability to transform the glass into the quasicrystalline state, this method could not be used for this comparative study.

Thermal stability was investigated by DSC measurements of hydrogenated Zr–Cu–Ni–Al metallic glasses and quasicrystals (see Fig. 2(a) and b). In both materials desorption of hydrogen, as measured by TDA, was not observed to proceed at temperatures less than about 500°C. This allowed us to investigate the effect of hydrogen on the formation as well as on the decomposition of quasicrystals.

The DSC shows a two-step reaction in glassy $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ (see Fig. 2(a)): formation of icosahedral quasicrystals followed by decomposition of the quasicrystals into stable crystalline phases [7]. With increasing hydrogen content, the temperature for quasicrystal formation is shifted to higher temperatures. Decomposition of the quasicrystals, however, is moved to lower temperatures with increasing hydrogen content. In addition we observe the crystallization of a small amount of the oxygen-stabilized f.c.c. (big-cube) phase which itself transforms around 460°C (third peak) into the stable Zr_2Ni phase.

Fig. 3 exhibits the X-ray diffraction pattern after annealing glassy ribbons with differing hydrogen contents for 420 s at 400°C. Hydrogen contents of H/M < 0.05 were found to reduce the number of quasicrystals formed during annealing. In the X-ray diffraction pattern all peaks of the icosahedral phase became weaker, thus indicating a smaller amount of quasicrystals. TEM investigations confirm that this change is due to a smaller number of quasicrystals; growth seems not to be affected. At slightly larger hydrogen contents instead of the quasicrystalline phase a tetragonal one with lattice parameters close to Zr_2Ni is formed as shown by X-ray diffraction (see Fig. 3) and TEM investigations. At even larger hydrogen contents up to about H/M = 0.6, the amorphous state seems to be stabilized and the number of nucleated crystals had decreased.

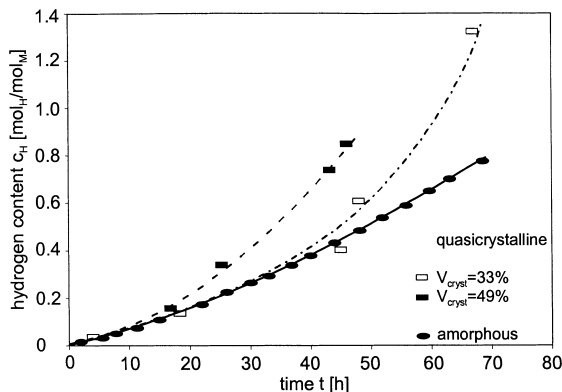


Fig. 1. Hydrogen charging of amorphous and quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ alloys (10 A/m^2 , electrolyte: 2:1 glycerine–phosphoric acid, 25°C). Lines are drawn as guides for the eye.

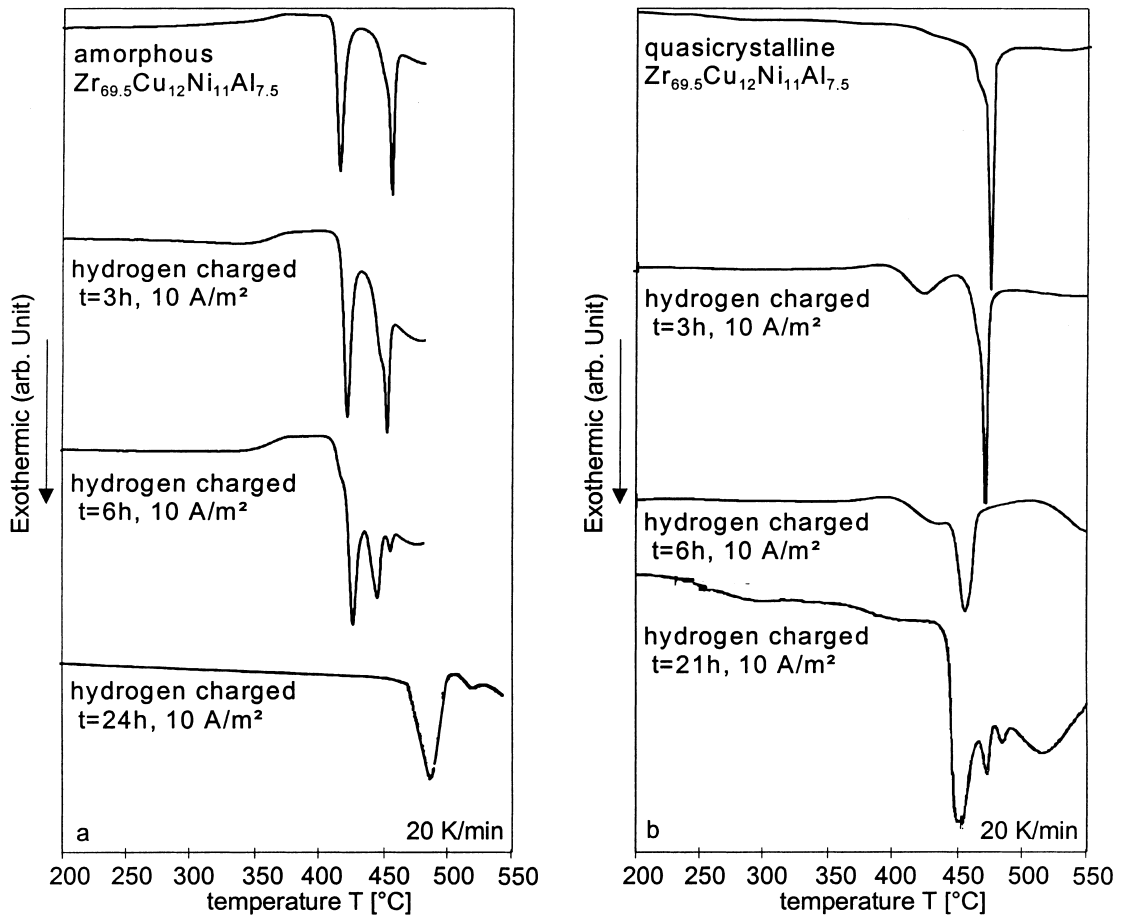


Fig. 2. DSC of uncharged and hydrogenated $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ribbons: (a) amorphous; (b) quasicrystalline.

Hydrogen contents of about $H/M=1.0$, on the other hand, have been observed to lead to nanocrystallization at temperatures as low as $300^{\circ}C$.

The influence of hydrogen on the stability of the Zr–Cu–Ni–Al quasicrystals was also investigated by DSC (see Fig. 2(b)). The X-ray diffraction pattern of uncharged as well as hydrogenated quasicrystalline samples after annealing at $455^{\circ}C$ are shown in Fig. 4. Since TDA indicated that hydrogen will not be desorbed at temperatures below $500^{\circ}C$, the broad first peak in the DSC has to be associated with the transformation of the remaining amorphous matrix into a quasicrystalline structure. We can observe the same shift with

hydrogen content to higher temperatures known from the fully amorphous ribbons (see Fig. 2(a)). The main peak can be associated with the decomposition of the icosahedral quasicrystals.

The X-ray data show that uncharged quasicrystals decompose mainly into hexagonal Zr_6Al_2Ni as well as tetragonal Zr_2Ni and Zr_2Cu ; in addition we found small amounts of the oxygen-stabilized f.c.c. big-cube phase ($a=1.228$ nm). Based on the X-ray data after hydrogen charging of the quasicrystals ($H/M=0.05$) the phases formed are the same, but the microstructure changed. As indicated by X-ray diffraction or shown by TEM, much smaller crystals (about 10 nm in diameter) are formed.

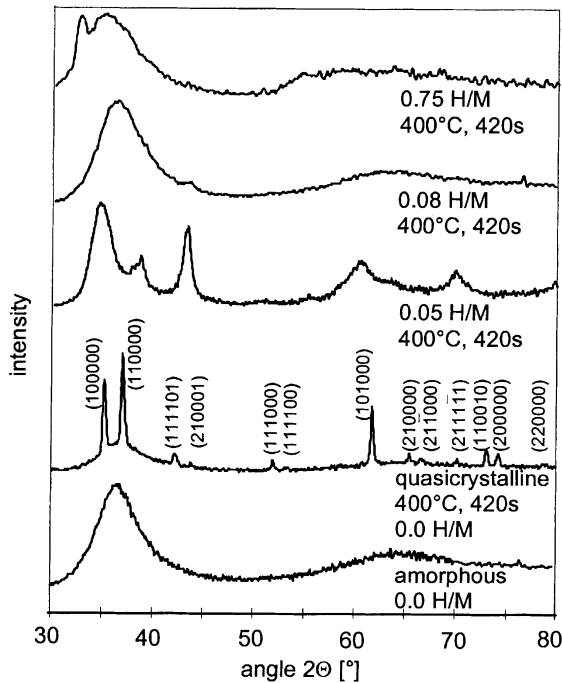


Fig. 3. X-ray diffraction of melt-spun as well as hydrogenated glassy $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ribbons after annealing at 400°C.

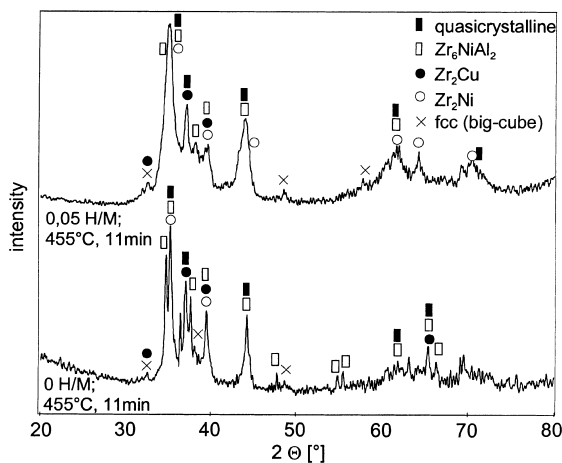


Fig. 4. X-ray diffraction of uncharged as well as hydrogenated quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ after annealing for 11 min at 455°C.

Even larger hydrogen contents were found to change the transformation of quasicrystals dramatically as indicated by the DSC plot in Fig. 2(b) which we do not understand as yet.

4. Discussion

The chemical interactions between metal and hydrogen atoms and the number, type and size of the interstitial sites in the material are the two main factors influencing hydrogen storage in metals. In most transition metal alloys, hydrogen prefers to sit in tetrahedrally coordinated sites. This makes the amorphous [8] and the icosahedral phase which are both dominated by local tetrahedral order [9] particularly attractive.

The larger storage capacity and faster absorption kinetics of the Zr–Cu–Ni–Al quasicrystals as compared to the amorphous phase can be qualitatively associated with differing site-energies for hydrogen and increased diffusion in the quasicrystalline structure. The number of tetrahedrons in the icosahedral phase may explain the improved storage capacity. Moreover, if hydrogen transport is dominated by hopping, the number of adjacent tetrahedral sites might also explain the kinetics.

With increasing hydrogen content first the formation of icosahedral quasicrystals is shifted to higher temperatures due to a smaller number of quasicrystals formed. This might result from destabilization of the quasicrystalline structure by the hydrogen or more probably by the destruction of the quenched-in nucleation sites for the quasicrystals. At larger hydrogen contents instead of the quasicrystalline a tetragonal phase with lattice parameters close to Zr_2Ni is formed. At hydrogen contents up to about $H/M = 0.6$, the amorphous state seems to be stabilized as the number of nucleated crystals decreased. This might result from phase separation into two amorphous phases which leads first to elimination of quenched nucleation sites. The DSC (see Fig. 2(a)) also differs as compared to less hydrogenated glasses. Further charging to much larger H/M led probably to a progressive phase separation, followed by easy nanocrystallization of ZrH_2 and phases with reduced Zr-content at relative low temperatures. A similar destabilizing phase separation was reported for binary Ti-based metallic glasses [10].

The decomposition of Zr–Cu–Ni–Al quasicrystals into the stable neighboring phases was found to move to lower temperatures with increasing hydrogen content. The phases formed

through decomposition of the hydrogen charged ($H/M = 0.05$) are the same as those in uncharged quasicrystals, but the microstructure becomes much finer. This means that the number of nucleation sites for the transformation increased, which is consistent with the observed shift of the DSC-peak to lower temperatures. It is known that hydrogenation leads to the formation of defects whose structure is still unknown [7] within the icosahedral structure. We assume that these defects influence the nucleation of the stable crystalline phases.

5. Conclusions

We have shown that in $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ absorption kinetics and storage capacity are larger in the quasicrystalline than in the precursor glassy phase.

With increasing hydrogen content the formation of icosahedral quasicrystals in amorphous $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ is shifted to higher temperatures and then replaced by the formation of a tetragonal phase with lattice parameters close to Zr_2Ni . At even higher hydrogen contents phase separation is assumed to be followed by the formation of nanocrystalline ZrH_2 and other phases with reduced Zr-content.

The decomposition of the quasicrystals is shifted to lower temperatures with increasing hydrogen content due to an increased number of nucleation sites formed by the hydrogenation.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG Ko 668/22-1). One of us (N.E.) is grateful to the Israel Ministry of Science for the financial support through Eshkol Grant no. 2206-0587 for Scientific Infrastructures. The authors are indebted to cand.ing. H. Torwesten for his help in the hydrogenation experiments.

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