

# Influence of hydrogen on formation and stability of Zr-based quasicrystals

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## Abstract

Hydrogenation of quasicrystalline  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  was performed electrochemically in a 2:1 glycerine–phosphoric acid electrolyte. Hydrogen absorption/desorption as well as the influence of hydrogen on the formation and stability was studied by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermal desorption spectroscopy (TDS). In comparison to amorphous Zr–Cu–Ni–Al the absorption kinetics in quasicrystalline Zr–Cu–Ni–Al were found to be faster. Desorption is hindered in both materials probably due to the formation of thin  $ZrO_2$  layers. Only partial desorption of hydrogen was observed by means of TDS to occur prior to the decomposition of the quasicrystalline phase. The observed increase in length during hydrogen charging indicates an interesting new result. Instead of the continuous increase of the specific volume per hydrogen atom at very low hydrogen concentration typical for the filling up of larger trapping sites, a decrease from a rather high value is observed. This means that not only the site for the hydrogen atom is expanded, but also the neighboring still empty ones.

Above a hydrogen content of  $H/M=0.05$  the formation of Zr–Cu–Ni–Al quasicrystals is replaced by tetragonal  $Zr_2Cu$ , tetragonal  $Zr_2Ni$  and hexagonal  $Zr_6NiAl_2$ . At high hydrogen contents (about  $H/M=1.0$ ) phase separation is assumed to take place followed by the formation of nanocrystalline  $ZrH_2$ . Icosahedral  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  was found to decompose through a discontinuous transformation by complex precipitation reactions; it transforms mainly into tetragonal  $Zr_2Cu$ , tetragonal  $Zr_2Ni$  and hexagonal  $Zr_6NiAl_2$ . Hydrogenation of quasicrystals at low concentrations does not change the phases formed during decomposition. At hydrogen contents higher than  $H/M=1.1$  decomposition of quasicrystals starts with the precipitation of tetragonal  $ZrH_{2-x}$ . © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Quasicrystal; Hydrogenation; Zr–Cu–Ni–Al

## 1. Introduction

The high number of potential interstitial sites for hydrogen and the favorable hydrogen–metal chemistry make quasicrystalline alloys candidates for hydrogen storage applications. Zr as well as Ti-based quasicrystals have been observed recently to store hydrogen up to a content close to the best crystalline materials [1,2].

Hydrogen was observed to exhibit a significant effect not only on the stability of the Zr–Cu–Ni–Al quasicrystals, but also on their formation from the glassy precursor material. Formation of Zr-based quasicrystals could be observed only if the hydrogen content of the glassy precursor is less than 5 at.% [3]. The objective of this paper is to present our recent results on the specific volume per hydrogen atom, the reversibility of hydrogen charging as well as the effect of hydrogen on the formation of  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$

quasicrystals from glassy precursor material and on their stability at higher hydrogen contents.

## 2. Experimental procedure

Quasicrystalline  $i-Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  ribbons were prepared by melt spinning and subsequent annealing above the glass transition temperature as described elsewhere in detail [4]. Cathodic hydrogenation was carried out in a 2:1 glycerine–phosphoric acid electrolyte at 25°C and a current density of  $i=10 A/m^2$ . The hydrogen content was measured by a microbalance (Mettler Toledo MT5) with an accuracy of  $\pm 1 \mu g$ . Volume changes of the alloys caused by hydrogen were calculated from length changes measured with an inductance strain-gauge device (HBM-W5TK). This sensitive technique developed by Stolz et al. [5] allows to measure length changes of  $\Delta l=0.01 \mu m$ . Hydrogen desorption was investigated by thermal desorption spectroscopy (TDS); experimental details are given elsewhere [6]. Electrochemical charging for these experiments was done in an elec-

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trolyte which contains  $D_3PO_4$  instead of  $H_3PO_4$  in order to reduce the background noise. Crystallization and the influence of hydrogen on the thermal stability were studied by microstructural investigations using X-ray diffraction (Cu  $K\alpha$  radiation) and transmission electron microscopy (Philips CM200 operating at 200 kV).

### 3. Results and discussion

Quasicrystalline  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  can be charged electrochemically up to a hydrogen to metal ratio  $H/M$  of 1.6 [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 [3]. The improved storage capacity may result from the large number of adjacent tetrahedral sites assumed for the icosahedral structure. Moreover, if hydrogen transport is dominated by hopping, the large number of adjacent tetrahedral sites may also qualitatively explain the faster absorption kinetics in the quasicrystalline structure. The increase of length during hydrogenation of the quasicrystalline Zr-based alloy is associated with an increase of the quasilattice constant. It could be observed, however, that the quasilattice constant does not expand up to a hydrogen concentration of about  $H/M=0.1$  while the length change increases very fast in this concentration region. One explanation of this behavior could be that the first hydrogen atoms occupy only sites for interstitial hydrogen in the remaining amorphous matrix, thus causing a significant expansion of the material. At higher hydrogen contents the quasicrystalline phase also seems to be responsible for hydrogen absorption. From the length change during hydrogenation, one can calculate the specific volume per hydrogen atom  $\Delta V_H$ . As shown in Fig. 1 the specific volume per hydrogen atom versus charging time is accompanied with an increase of the quasilattice constant indicated by the  $d_{(110000)}$  value for the quasicrystalline  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ .

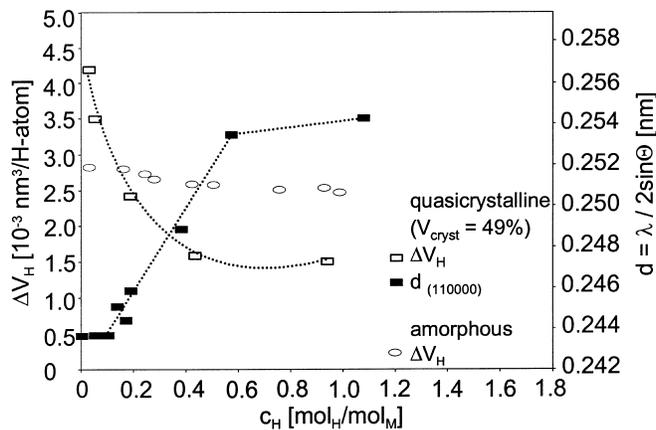


Fig. 1. Change of the specific volume per hydrogen atom  $\Delta V_H$  and  $d_{(110000)}$  in quasicrystalline and amorphous  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  during hydrogenation.

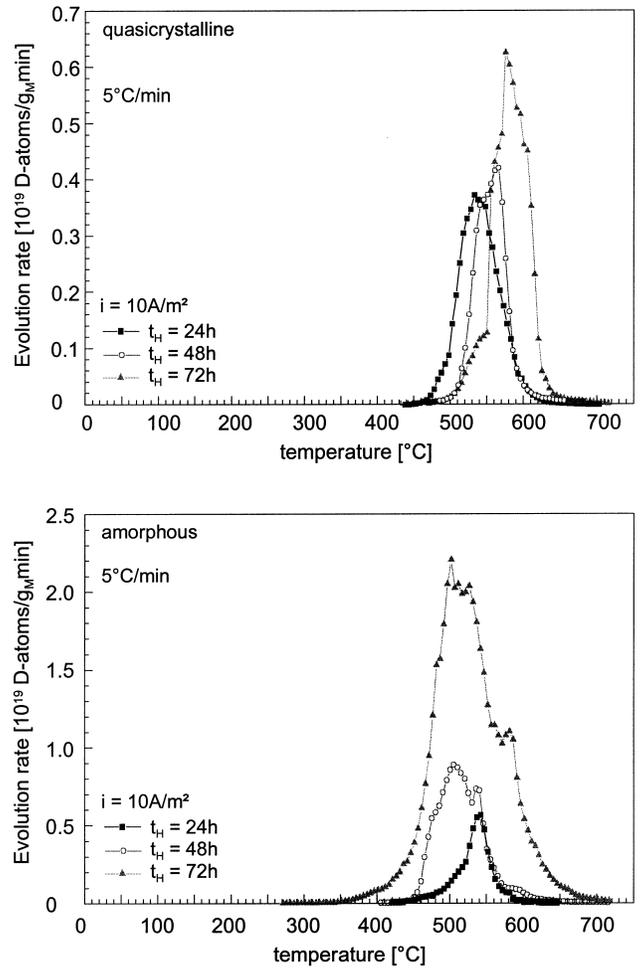


Fig. 2. Thermal desorption analysis of deuterium charged quasicrystalline and amorphous  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  ( $t_H$ =charging time).

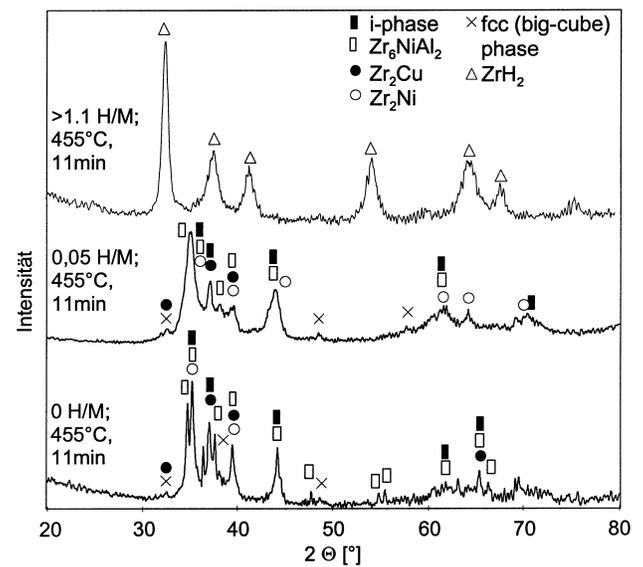


Fig. 3. X-ray diffraction of uncharged as well as hydrogenated quasicrystalline  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  after annealing for 11 min at  $455^\circ C$ .

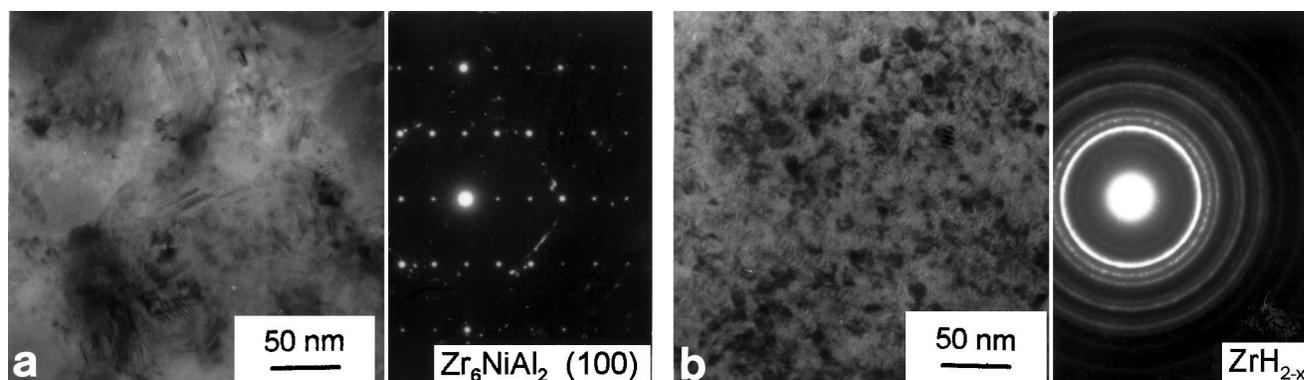


Fig. 4. Electron micrograph and diffraction pattern of (a) uncharged and (b) highly charged ( $H/M > 1.1$ ) quasicrystalline Zr–Cu–Ni–Al after annealing for 11 min at  $455^\circ\text{C}$ .

While  $\Delta V_H$  of the amorphous alloy seems to be constant during charging up to high concentrations,  $\Delta V_H$  for the quasicrystalline alloy was observed to decrease from  $4.25 \times 10^{-3} \text{ nm}^3/\text{H-atom}$  at the lowest hydrogen content measured to  $1.5 \times 10^{-3} \text{ nm}^3/\text{H-atom}$  at  $H/M=0.4$ . These results of the change of length, the quasilattice constant and the  $\Delta V_H$  of quasicrystalline Zr–Cu–Ni–Al indicate that the first hydrogen atoms expand not only their interstitial sites, but also the neighboring still empty ones. This means that during the following charging the occupation of these already expanded sites becomes easier. This would also explain the very small value for  $\Delta V_H$  at higher hydrogen contents.

Fig. 2 shows desorption of hydrogen as observed by means of TDS. Whereas the onset temperature for the hydrogen desorption in the amorphous material decreases slightly with higher hydrogen contents, an opposite effect is observed for the quasicrystal not understood as yet. Comparing these onset temperatures with crystallization temperatures measured by DSC of as-cast as well as hydrogenated Zr–Cu–Ni–Al metallic glasses and quasicrystalline Zr-based alloys [7,8] one can realize that desorption of larger amounts of hydrogen did not take place prior to the formation or decomposition of the quasicrystalline phase. This made it very easy to investigate the influence of hydrogen on the formation as well as the decomposition of the quasicrystalline phase. Investigations on the thermal stability of hydrogenated amorphous  $\text{Zr}_{69.5}\text{Cu}_{12}\text{Ni}_{11}\text{Al}_{7.5}$  showed that with increasing hydrogen content up to  $H/M=0.05$  the formation of icosahedral quasicrystals is shifted to higher temperatures and then replaced by the formation of tetragonal  $\text{Zr}_2\text{Cu}$ , tetragonal  $\text{Zr}_2\text{Ni}$  and hexagonal  $\text{Zr}_6\text{NiAl}_2$ . At hydrogen contents of more than  $H/M=0.6$  the amorphous state seems to be destabilized due to phase separation. Higher concentrations of about  $H/M=1.0$  lead to the formation of nanocrystalline  $\text{ZrH}_{2-x}$ . The quasicrystals decompose through a discontinuous transformation at higher temperature or longer annealing times mainly into the tetragonal  $\text{Zr}_2\text{Cu}$  phase, the tetragonal  $\text{Zr}_2\text{Ni}$  and the hexagonal  $\text{Zr}_6\text{NiAl}_2$  (Fig. 4a). X-ray diffraction (Fig. 3) of hydrogenated quasicrystals showed that hydrogenation does not change the phases formed during decom-

position at low hydrogen contents ( $H/M < 0.05$ ), but leads to the formation of a finer microstructure due to defects formed during the hydrogenation. These defects which lead to a weakened contrast of the quasicrystals [1] can probably accelerate the nucleation of the stable crystalline phase. At high hydrogen contents about  $H/M=1.1$ , decomposition of quasicrystals starts with the precipitation of tetragonal  $\text{ZrH}_{2-x}$  (Fig. 4b). As compared to the lattice parameters of  $\text{ZrH}_2$ , an increase of the lattice parameter  $a_0$  and a decrease of the lattice parameter  $c_0$  are observed. It is well known that the lattice parameters of the stable body-centered tetragonal  $\epsilon$ -hydride depend strongly on the hydrogen content, i.e.  $a_0$  increases and  $c_0$  decreases with increasing hydrogen concentration [9]. The observed lattice parameters of the  $\epsilon$ -phase formed during decomposition of the hydrogenated quasicrystals correspond to an atom ratio  $H/\text{Zr}$  of about 1.6. This is in good agreement with the measured hydrogen content after charging and with the fact that only a small amount of hydrogen was desorbed around  $500^\circ\text{C}$ .

#### 4. Conclusion

The length increase observed during hydrogenation of quasicrystalline  $\text{Zr}_{69.5}\text{Cu}_{12}\text{Ni}_{11}\text{Al}_{7.5}$  indicates an interesting new result. Instead of the continuous increase of the specific volume per hydrogen atom at very low hydrogen concentration, a decrease from a rather high value is observed. It is assumed that the first hydrogen atoms not only expand their own sites, but also the neighboring still empty ones.

At a hydrogen content  $H/M=0.05$ , the formation of quasicrystalline  $\text{Zr}_{69.5}\text{Cu}_{12}\text{Ni}_{11}\text{Al}_{7.5}$  is replaced by the formation of tetragonal  $\text{Zr}_2\text{Cu}$ , tetragonal  $\text{Zr}_2\text{Ni}$  and hexagonal  $\text{Zr}_6\text{NiAl}_2$ . At even higher hydrogen contents, phase separation is assumed to be followed by the formation of nanocrystalline  $\text{ZrH}_{2-x}$ .

Quasicrystals decompose mainly into tetragonal  $\text{Zr}_2\text{Cu}$ , tetragonal  $\text{Zr}_2\text{Ni}$  and hexagonal  $\text{Zr}_6\text{NiAl}_2$  by complex precipitation reactions. Hydrogenation of quasicrystals up to  $H/M=0.05$  does not change the phases formed during hydro-

drogenation. At hydrogen contents higher than  $H/M=1.1$ , the decomposition of quasicrystal was observed to start with the precipitation of tetragonal  $ZrH_{2-x}$  ( $\varepsilon$ -phase:  $Zr/H\sim 1.6$ ).

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### References

- [1] U. Köster, D. Zander, J. Meinhardt, N. Eliaz, D. Eliezer, in: S. Takeuchi, T. Fujiwara (Eds.), Proceedings of the Sixth International Conference on Quasicrystals, Tokyo 1997, World Scientific, Singapore, 1996, p. 313ff.
- [2] A.M. Viano, R.M. Stroud, P.C. Gibson, A.F. McDowell, M.S. Conradi, K.F. Kelton, *Phys. Rev. B* 51 (1995) 12026.
- [3] D. Zander, H. Leptien, U. Köster, N. Eliaz, D. Eliezer, *J. Non-Cryst. Solids* 250-252 (1999) 893.
- [4] U. Köster, J. Meinhardt, S. Roos, H. Liebertz, *Appl. Phys. Lett.* 69 (1996) 179.
- [5] U. Stolz, U. Nagorny, R. Kirchheim, *Scripta Metall.* 18 (1984) 347.
- [6] E. Abramov, D. Eliezer, *Metal. Trans.* 25A (1994) 949.
- [7] U. Köster, D. Zander, H. Leptien, N. Eliaz, D. Eliezer, Bulk metallic glasses, in: W.L. Johnson, C.T. Liu, A. Inoue (Eds.), Proceedings of Materials Research Society Symposium, Vol. 554, Warrendale, 1999, p. 287ff.
- [8] D. Zander, U. Köster, N. Eliaz, D. Eliezer, D. Plachke, Quasicrystals, in: J.M. Dubois, P.A. Thiel, A.P. Tsai, K. Urban (Eds.), Proceedings of Materials Research Society Symposium, Vol. 553, Warrendale, 1999, p. 49ff.
- [9] H.J. Goldschmidt, *Interstitial Alloys*, Butterworths, London, 1967, p. 477.