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Hydrogenation of Pd-coated Zr–Cu–Ni–Al metallic glasses and quasicrystals

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Abstract

Zr-based metallic glasses and quasicrystals might be excellent materials for hydrogen storage because of their high number of tetrahedrally coordinated sites suitable for interstitial hydrogen and their favorable hydrogen chemistry. However, hydrogen desorption at low temperatures of the amorphous as well as quasicrystalline Zr–Cu–Ni–Al alloys is hindered by a thin ZrO_2 barrier and proceeds only at higher temperatures together or even after phase transformations of the metastable alloys. Pd coating was observed to improve the absorption and in particular the desorption kinetics significantly. Hydrogen charging was performed electrochemically in a 2:1 glycerin–phosphoric acid electrolyte. Hydrogen desorption was studied by means of DSC as well as TDA, the microstructure by X-ray diffraction and TEM. In Pd-coated alloys full desorption is observed even below 300 °C, but only after hydrogenation up to about H/M=0.4; higher hydrogen contents led to irreversible microstructural changes, in amorphous as well as quasicrystalline materials. The characteristics of hydrogen desorption and the micromechanism of decomposition during annealing of the hydrogenated Pd-coated metastable alloys at higher temperatures are discussed in detail.

Keywords: Metallic glasses; Quasicrystals; Zr–Cu–Ni–Al; Hydrogenation; Desorption

1. Introduction

The high number of potential interstitial sites suitable for hydrogen and the favorable hydrogen–metal chemistry make glassy and quasicrystalline Zr–Cu–Ni–Al candidates for hydrogen storage materials. Zr-based as well as Ti-based quasicrystals [1–3] are known to store hydrogen up to a content close to the best crystalline storage materials. The Zr–Cu–Ni–Al alloys are of special interest for studying any influence of the structure, since quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ can be formed by a polymorphic reaction during annealing of the amorphous precursor ribbon [4]. As reported earlier (partially) quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ can be charged electrochemically up to a hydrogen content of H/M=2.0 [1]. The storage capacity was found to be larger and the absorption kinetics to be faster for partially quasicrystalline ribbons than for the glassy precursor material [5].

Hydrogenation of amorphous or partially quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ribbons results in significant changes of a number of physical properties; for example an increase in length accompanied by a shift of the X-ray peaks to lower angles indicating a lattice expansion [3,6]. Whereas no microstructural changes could be observed by TEM even after hydrogenation of the amorphous ribbons to very high hydrogen contents, the quasicrystalline material exhibited significant microstructural changes as indicated by the weakening of the contrast probably due to the formation of as yet unknown defects in the quasicrystalline structure as well as a disappearance of the weak diffraction spots in the corresponding diffraction pattern [1,6]. Further investigations on the hydrogenation of the icosahedral phase in $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ (a_q=0.539 nm) indicated a continuous transformation into rational approximants above a hydrogen content of H/M=0.4 and finally amorphization of the quasicrystalline Zr–Cu–Ni–Al alloy at even higher hydrogen contents [3,6].

Desorption of hydrogen as measured by TDS [5] was not observed to proceed at temperatures less than about

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450 °C probably due to thin oxide layers formed at the surfaces of the amorphous or partially quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ribbons. It was observed [3,7] that at low hydrogen concentration ($H/M \leq 0.15$) the absorption of hydrogen causes a significant increase in the thermal stability of the amorphous phase; at high hydrogen concentrations ($H/M \geq 0.9$) the formation of ε-ZrH_{2-x} and δ-ZrH_2 was revealed.

The icosahedral phase in $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ decomposes during annealing for example at 455 °C or at higher temperatures by a discontinuous transformation into tetragonal Zr_2Cu, tetragonal Zr_2Ni and hexagonal Zr_6NiAl_2 starting with a precipitation reaction of Zr_2Cu [5]. As already mentioned even mild hydrogenation leads to the formation of defects within the icosahedral structure; it can be assumed that these defects accelerate the nucleation of the stable crystalline phase. Hydrogenated quasicrystals ($H/M \leq 0.05$) decompose faster or at lower temperatures into the same phases, but with a finer microstructure. At very high hydrogen contents ($H/M \geq 1.1$) decomposition of the hydrogenated quasicrystalline phase starts with the precipitation of tetragonal ZrH_{2-x} (ε-phase: $H/Zr \sim 1.6$).

As mentioned above, Zr-oxide layers may hinder hydrogen diffusivity; oxide layers are also known to reduce the dissociative chemisorption of hydrogen on surfaces; the use of catalysts, e.g. Pd, may change this behavior significantly. Pd-coating is well known to improve the hydrogenation in crystalline metal hydrides and was also used for Ti–Zr–Ni quasicrystals [8]. The aim of this paper is to present recent results on the improved hydrogen absorption as well as desorption of $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ metallic glasses and quasicrystals after Pd-coating.

2. Experimental

The pre-alloys were prepared by melting Zr, Cu, Ni and Al in an arc furnace under argon atmosphere (~1.2 bar) on a water-cooled copper substrate. From these pre-alloys amorphous ribbons with the nominal composition of $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ were prepared by melt spinning in a He atmosphere of 300 mbar. The temperature of melt was between 1100 and 1300 °C before casting. Quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ was prepared by subsequent annealing above the glass transition temperature as described elsewhere in detail [3,4].

Pd-coating (100 nm) by vapor deposition exhibited sufficient adhesion to the amorphous and quasicrystalline ribbon. 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 and $i=5$ A/m^2 for Pd-coated alloys, respectively. The hydrogen content was measured by means of a hydrogen determinator (LECO: RH-404). Hydrogen desorption and the influence of hydrogen on the thermal stability of uncoated as well as of Pd-coated Zr-based quasicrystals was studied by means of differential scanning calorimetry (DSC: DSC Pyris 1) in Ar atmosphere during continuous heating at 20 K/min, thermal desorption analysis (TDS) as well as by microstructural investigations using X-ray diffraction and transmission electron microscopy (TEM: Philips CM200) operating at 200 kV.

3. Results and discussion

Coating the surface of $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ribbons (amorphous and quasicrystalline) with a Pd-layer (100 nm) was observed to improve the absorption as well as desorption of hydrogen significantly.

3.1. Hydrogenation

Oxide layers are known to reduce the dissociative chemisorption of hydrogen on surfaces; the use of catalysts, e.g. Pd, change this behavior significantly. As shown in Fig. 1 hydrogen absorption kinetic and storage capacity are almost identical for Pd-coated amorphous and partially quasicrystalline ($V_{qc}=50\%$) $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ribbons. After charging for 24 h a hydrogen content of $H/M=1.6$ was found for both microstructures; further charging would probably increase the hydrogen content, but could not be followed quantitatively due to deterioration of the Pd-coating. Uncoated partially quasicrystalline ($V_{qc}=50\%$) $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ was found to absorb hydrogen up to $H/M=2.0$ after a much longer charging time and even higher current density. The absorption for Pd-coated amorphous and partially quasicrystalline Zr-based alloys was accelerated by a factor of about 10.

The chemical interactions between metal and hydrogen atoms and the number, type and size of the interstitial sites in the material are main factors influencing hydrogen storage in metals. In most transition metal alloys, hydrogen prefers to occupy tetrahedrally coordinated sites. This make the amorphous [9] and the icosahedral phase which

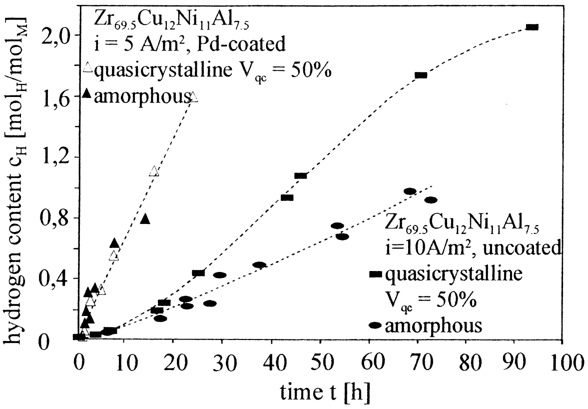

Fig. 1. Kinetics of hydrogen charging of uncoated as well as Pd-coated amorphous and partially quasicrystalline Zr–Cu–Ni–Al.

are both dominated by local tetrahedral order [10] particularly attractive. Hydrogen absorption capacity and kinetic of Pd-coated amorphous as well as quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ are almost identical, quite opposite to the behavior of the uncoated materials. This indicates that surface reactions as the rate determining steps for electrochemical hydrogen charging are responsible for the differences observed in the charging behavior.

3.2. Hydrogen desorption

TDS experiments on hydrogenated Pd-coated amorphous as well as partially quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ revealed that hydrogen desorption can proceed already in a temperature range between 150 and 400 °C, quite different to uncoated ribbons. These results were confirmed by LECO data. In addition, DSC measurements (Fig. 2a,b) exhibited clearly that partial desorption proceeds prior to any decomposition of the quasicrystalline phase. Fig. 3 shows the X-ray diffraction of hydrogenated ($H/M=0.1$, $H/M=0.6$) Pd-coated amorphous $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ribbons after DSC up to different temperatures. Formation of quasicrystals proceeds only at very low hydrogen contents. A hydrogen content of $H/M=0.1$ is known to deteriorate quasicrystal formation [7]; the Pd-coating, however, allows hydrogen desorption in order to fall short of the critical concentration, thus leading to quasicrystal formation. At higher hydrogen contents (above about $H/M=0.4$) full hydrogen desorption of the Pd-coated amorphous ribbons was not observed. In this regard it is of interest, that at a hydrogen content of about $H/M=0.35$ a sudden increase in the slope of the emf [11] as well as of the microhardness versus hydrogen content plots was observed. Pd-coated ribbons hydrogenated to $H/M=1.6$ exhibit a hydrogen content of 1.0 after heating up to 450 °C; the reason for the lack of desorption at such high hydrogen contents can probably be found in amorphous phase separation which is often mentioned as a consequence of severe hydrogenation [12]. Charging to high hydrogen contents ($H/M\geq0.6$) leads also in the Pd-coated $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ to the formation of hydrides during subsequent heating up to 550 °C. Hydride formation, however, is shifted to higher temperatures which can be explained by the partial desorption of hydrogen due to the Pd-coating.

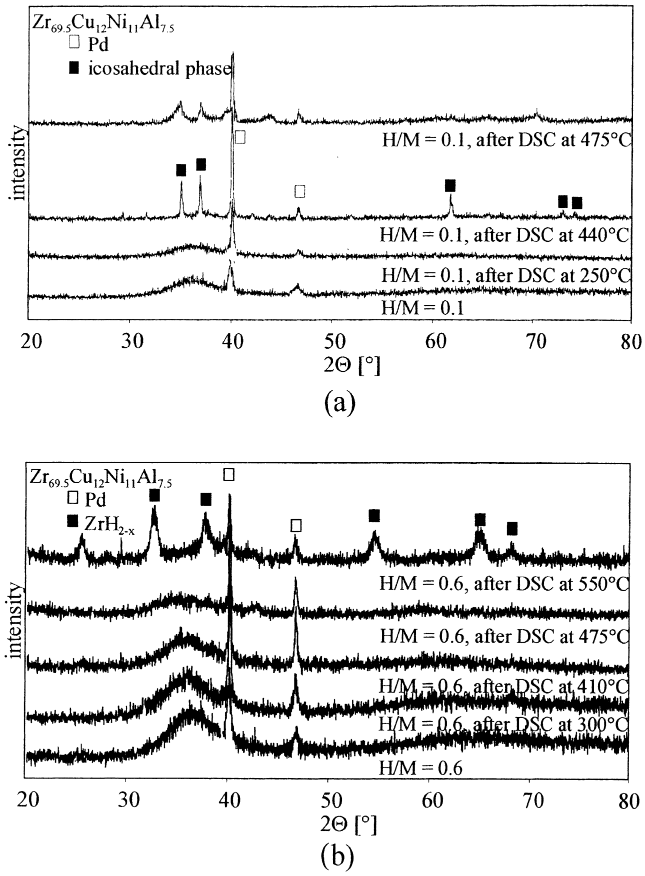

Fig. 3. X-ray diffraction of uncharged and hydrogenated Pd-coated amorphous $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ after DSC at different temperatures: (a) $H/M=0.1$; (b) $H/M=0.6$.

The X-ray diffraction of uncharged and hydrogenated ($H/M=0.34$, $H/M=0.55$) Pd-coated quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ after DSC up to different temperatures

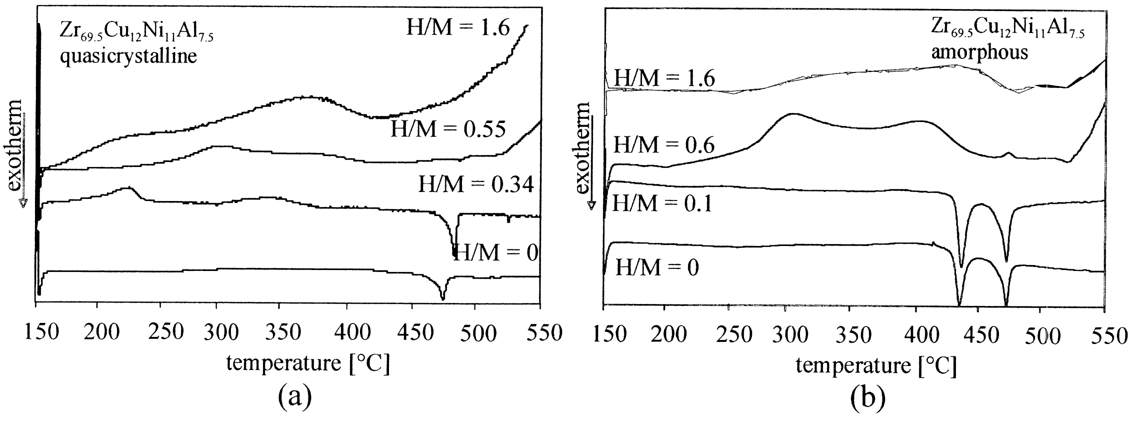

Fig. 2. DSC of uncharged and hydrogenated Pd-coated (a) quasicrystalline and (b) amorphous $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ribbons (heating rate: 20 K/min).

revealed that full desorption and recovery of the icosahedral structure could be observed only at about H/M=0.4. It is of interest that for example the microhardness of hydrogenated quasicrystalline alloys exhibits a minimum at this concentration [13]. Higher hydrogen concentrations significantly change the desorption and the recovery of the icosahedral phase, i.e. only partial desorption (for example from H/M=1.4 to 0.9 after heating up to 300 °C) and no recovery of the quasicrystalline structure. As already mentioned for hydrogenation of the uncoated partially quasicrystalline material, this behavior can be explained by a hydrogen-induced transformation of the metastable quasicrystalline phase into approximants at hydrogen contents above about H/M=0.4 [6] thus leading to a lower state of free energy of the system.

4. Conclusions

It was demonstrated that coating with Pd not only accelerates the kinetics of hydrogenation in amorphous as well as partially quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$, but in particular allows desorption of hydrogen at temperatures even below 300 °C (prior to any decomposition of the metastable amorphous or quasicrystalline phases). The similar hydrogenation behavior of amorphous and quasicrystalline alloys with Pd-coating indicates that the influence of the microstructure observed in uncoated alloys are due to surface reactions during the rate determining steps.

Full desorption and recovery of the amorphous as well as the quasicrystalline structure depends on the hydrogen content and could be observed only for $H/M \leq 0.35$ for the amorphous phase and for $H/M \leq 0.4$ for the icosahedral phase, respectively. We assume that phase separation in the amorphous material and transformation of the quasicrystals into approximants during hydrogenation led to a state of lower free energy of the hydrogenated material which does not allow full recovery into the original state. Full recovery would require phase transformations which cannot be expected due to the metastable character of the amorphous as well as the partially quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$.

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References

[1] U. Köster, D. Zander, J. Meinhardt, N. Eliaz, D. Eliezer, in: S. Takeuchi, T. Fujiwara (Eds.), Proc. 6th Int. Conf. Quasicrystals, World Scientific, Singapore, 1998, 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, Wasserstoff in metastabilen Zr–Cu–Ni–Al-Legierungen, Ph.D. thesis, Dortmund 2001, Logos Verlag, Berlin, 2001.
[4] U. Köster, J. Meinhardt, S. Roos, H. Liebertz, Appl. Phys. Lett. 69 (1996) 179.
[5] D. Zander, U. Köster, N. Eliaz, D. Eliezer, Mater. Sci. Eng. 294–296 (2000) 112.
[6] D. Zander, U. Köster, V. Khare, Quasicrystals—Preparation, Properties and Applications, in: E. Bellin-Ferré, P.A. Thiel, A.-P. Tsai, K. Urban (Eds.), MRS Symp. Proc. 643, MRS, Warrendale, 2001, p. K2.2.
[7] D. Zander, H. Leptien, U. Köster, N. Eliaz, D. Eliezer, J. Non-Cryst. Solids 250–252 (1999) 893.
[8] J.Y. Kim, P.C. Gibbons, K.F. Kelton, J. Alloys Comp. 266 (1998) 311.
[9] K. Aoki, T. Yamamoto, T. Masumoto, Sci. Rep. Res. Inst. Tohoku Univ. A33 (1986) 163.
[10] J.Y. Lee, W.-C. Choi, Y.-G. Kim, J.-Y. Lee, Acta Metall. Mater. 39 (1991) 1693.
[11] J. Bankmann, A. Pundt, R. Kirchheim, J. Alloys Comp. 2003 (in press).
[12] D. Menzel, A. Niklas, U. Köster, Mater. Sci. Eng. A133 (1991) 312–315.
[13] D. Zander, U. Köster, V. Khare, Proc. ICQ 8, Bangalore, 2002 (in press).