MECHANICALLY-INDUCED HYDROGEN ABSORPTION IN Zr-BASED QUASICRYSTALS

G.Mulas[1], C.Pistidda[1], G.Cocco[1], S.Scudino[2] and J.Eckert[2]

[1]Department of Chemistry, University of Sassari, Via Vienna 2, I-07100 Sassari, Italy
[2]FB 11 Material- und Geowissenschaften, FG Physikalische Metallkunde, Technische Universität Darmstadt, Petersenstraße 23, D-64287 Darmstadt, Germany

Abstract. We report on hydrogen sorptive properties of Zr-Ti-Nb-Cu-Al-Ni icosahedral alloys under different mechanical activation conditions. Two compositions were investigated, $Zr_{67}Ti_{6.14}Nb_{1.92}Cu_{10.67}Ni_{8.52}Al_{5.75}$ and $Zr_{57}Ti_8Nb_{2.5}Cu_{13.9}Ni_{11.1}Al_{7.5}$ prepared respectively by partial crystallization from mechanically alloyed amorphous powders, and by copper mold casting. In the former, independently by the milling conditions, the gaseous absorption took place with loss of the icosahedral symmetry and precipitation of a δ-$ZrH_{1.66}$-type nanocrystalline hydride which accompanied the formation of an amorphous hydride. Annealing treatments did not permit to restore initial structural conditions, so hindering the process reversibility. In the latter system, conversely, hydrogen absorption, activated by mechanical agitation in absence of milling ball, occurred by retaining the quasiperiodic features, just swelling the icosahedral structure. Thermally activated desorption preserved the QC symmetry and further successful hydrogenation indicated cycling possibility, at least partial, of the process. Hydriding kinetics, studied under isobaric conditions, followed sigmoidal trends, with specific characteristics depending on the alloy stoichiometry and the activation conditions.

1. INTRODUCTION

In the last years the development of advanced materials for hydrogen storage has continuously received increasing attention in view of their use for mobile applications. Key requirements for such materials are high hydrogen capacity combined with light weight, fast sorption kinetics and cycling performances [1]. The large free volume associated with quasi-periodicity and the high density of tetrahedral interstitial sites displayed by metallic alloys with quasicrystalline structure make such materials of potential technological interest in the field. Such structural features may indeed result in improved hydrogen storage capabilities [2-6].

Along this line, this work deals with hydrogen absorption processes on Zr-Ti-Nb-Cu-Al-Ni alloys consisting of icosahedral quasicrystals in the meta-stable micrometer size range [7,8]. Absorption was carried out under mechanical treatment in order to improve the sorption kinetics by exploiting the enhancement of gas-solid reactivity due to mechanochemical effects [9,10].

2. EXPERIMENTAL

Commercial powders with at least 3N purity level were used. Powder handling procedures were performed inside an Ar-filled MBraun M150 glove box, with O_2 and H_2O content below 1 ppm.

Two quasicrystalline (QC) alloys of composition $Zr_{67}Ti_{6.14}Nb_{1.92}Cu_{10.67}Ni_{8.52}Al_{5.75}$ and $Zr_{57}Ti_8Nb_{2.5}Cu_{13.9}Ni_{11.1}Al_{7.5}$ were studied. The former was prepared by controlled crystallization of the amorphous phase obtained by mechanical alloying. The latter was prepared by copper mold cast-

Corresponding author: Gabriele Mulas, e-mail: mulas@uniss.it

ing as a rod and successively comminuted. Details are reported in previous works [7,8]. The XRD patterns of the as-prepared QC alloys are shown in Fig. 1, curves (a) and (d) respectively. The different positions of the two (100000) and (110000) main peaks are related to the different stoichiometry. The broadened haloes underlying the diffraction profiles highlights the presence of an amorphous fraction, more evident in the Zr-richer alloy, accompanying the icosahedral phases.

The mechanochemical hydriding tests were carried out by employing a Spex Mixer Mill, mod. 8000, and hardened-steel milling media. The reactor was an appositely manufactured vial, 41.5 mm in height and 15.8 mm in diameter. It was properly allocated within a larger steel cylinder the covers of which were equipped with gas valves and filters. Teflon pipes were used for the connection to a volumetric apparatus. Isobaric conditions were kept constant inside the reactor at 0.1 MPa over atmospheric pressure and absorption was monitored by registering the pressure drop in the gas reservoir. 0.7 g of powders were introduced in the mechanochemical reactor together with a single milling ball. Balls of different mass were used in each test to obtain different impact energy values. The structure was investigated by X Ray Diffraction (XRD), performed with a Rigaku DMax diffractometer equipped with CuK_α radiation. The thermal stability of the powder was evaluated by Differential Scanning Calorimetry (DSC) in a Perkin Elmer power compensation PE DSC7 apparatus. Characterization was completed by Transmission Electron Microscopy (TEM) coupled with Energy Dispersive Analysis [7,8].

3. RESULTS AND DISCUSSION

Hydriding tests initially focused on the $Zr_{67}Ti_{6.14}Nb_{1.92}Cu_{10.67}Ni_{8.52}Al_{5.75}$ alloy. Sorptive properties were studied at different impact energies [9,11,12]. No reactivity was observed under static conditions, i.e. with the mill at rest. Conversely, all the mechanical treatments were effective in activating the absorption process, with kinetic features and structural evolution depending by the specific milling conditions. The XRD pattern (b) in Fig. 1, relevant to a sample treated with a 3.5-g ball, shows the loss of icosahedral symmetry and the formation of a δ-$ZrH_{1.66}$-type nanocrystalline hydride (JCPDS 34-649). An amorphous hydrided phase with a depleted Zr fraction is also observed. The maximum of its halo is located at $2\theta \approx 35.55$, a diffraction angle smaller than the ones pertaining,
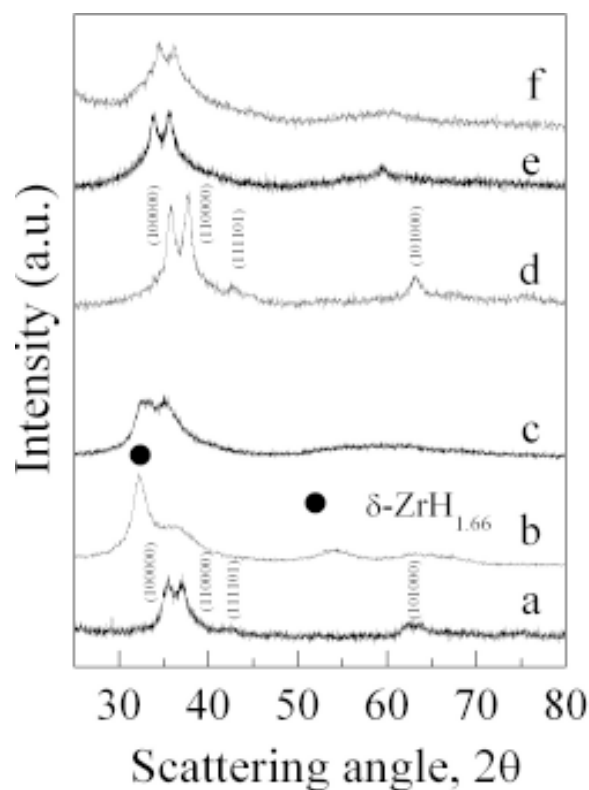

Fig. 1. CuK_α XRD patterns relevant to the Zr_{67}- and Zr_{57}-based alloys, in the as prepared QC state, curves a and d respectively, and after mechanically induced hydrogen absorption, traces b, c, and e. The pattern f refers to the Zr-poorer sample after the thermally activated hydrogen desorption.

respectively, to the original amorphous alloy, $2\theta \approx 36.15$, and to the amorphous fraction associated with the QC phase, $2\theta \approx 36.2$. The occurrence of an hydride amorphous phase was also confirmed by thermal desorption measurements: a progressive shift-back of the above cited value towards its original angular position was observed in the XRD of the sample annealed up to 629K. These results suggest that in this case, once the maximum hydrogen concentration available in the QC phase is overcome, the hydriding process determines the formation of hydrides with different thermodynamic stability. As indicated by curve (a) in Fig. 2, the kinetics of such process follows a sigmoidal trend with an initial increase of the reaction rate up to a maximum value of $4.3 \cdot 10^{-6}$ mole g^{-1}s^{-1} and a progressive decrease when the saturation limit of 1.95 H/M weight % is approached. Curves (b) and (c) of
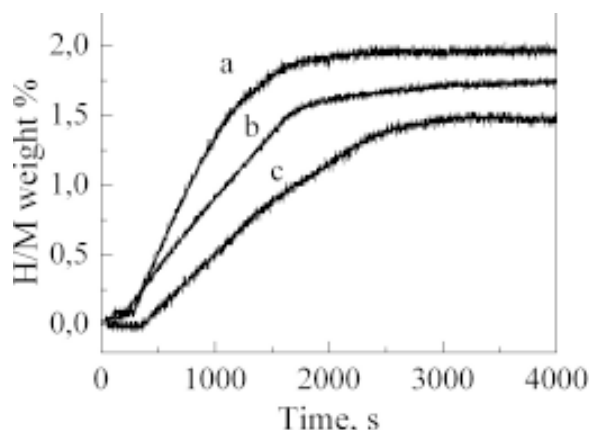
Fig. 2. Absorption kinetic curves pertaining to mechanically induced hydrogen absorption in $Zr_{67}Ti_{6.14}Nb_{1.92}Cu_{10.67}Ni_{8.52}Al_{5.75}$ QC powders under different impact energy conditions (using different colliding ball masses), 3.5 g, 2 g, and 1 g respectively in the trace a, b, and c.

Fig. 3. DSC thermograms relevant to mechanochemically hydrogenated samples. From the bottom: (a) $Zr_{67}Ti_{6.14}Nb_{1.92}Cu_{10.67}Ni_{8.52}Al_{5.75}$ powders milled with a 3.5 g mass sphere, (b) sample of Zr_{67}-based alloy after mechanochemical process without milling sphere, (c) sample of Zr_{57}-based alloy treated as the previous one.

Fig. 2 were instead obtained by using one 2-g and one 1-g ball respectively. The sigmoidal behaviour is retained but the maximum rate decreased to $3.24 \cdot 10^{-6}$ and $2.33 \cdot 10^{-6}$ mole $g^{-1}s^{-1}$. The final H/M values also decreased, probably due to the slightly smaller fraction of precipitated crystalline hydride.

The observed kinetics is quite common in solid-state thermally-activated processes proceeding at reactant interface [13] and has also been observed in mechanochemical processes involving either solid or gas-solid systems [10-12, 14]. The possibility of interpreting the mechanochemical conversion in terms of nucleation-and-growth mechanisms is however still questioned [14]. Another aspect related to mechanical activation can be instead underlined. Previously developed experimental procedures indicate that the mechanical energy dose D_M ($J \cdot g^{-1}$) delivered to the powders during the treatment represents a physical parameter more meaningful than the milling time [9]. The key role played by D_M in the activation step is strongly suggested by the satisfactory overlap, not shown here for sake of brevity, of the three curves of Fig. 2 obtained by plotting the conversion data versus D_M. Such result agrees then with previous findings for amorphous and nanostructured phases [9,11,12,14]. It is further noteworthy that the simple mechanical agitation of powders without a milling ball was still able to activate the hydriding process.
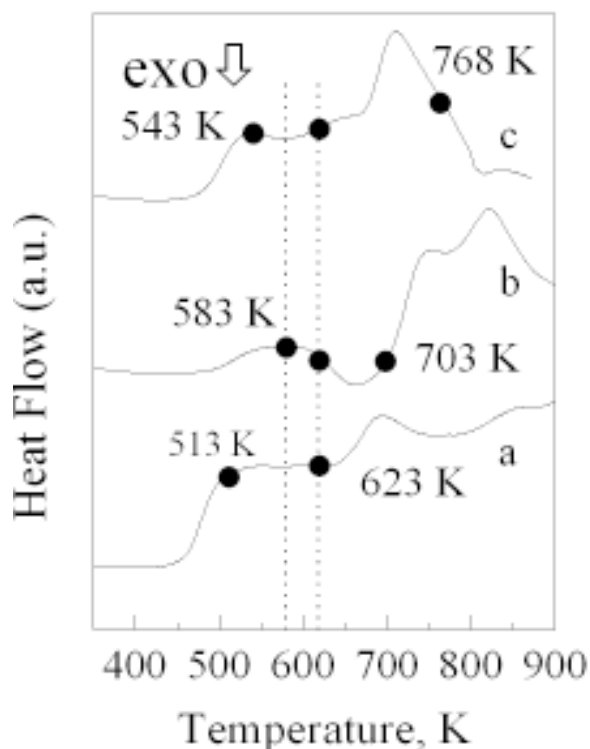
In this latter case, a different structural evolution was observed. As shown by curve (c) in Fig. 1, the main peaks characteristic of the QC phase are still present with a shift to smaller angles due to an increase of about 9% of the quasilattice constant from 0.478 to 0.52 nm consequent to hydrogen absorption. The shoulder on the left side of the (100000) peak is due to the precipitation of the d-$ZrH_{1.66}$ phase, as can be also gained from the comparison with the lower (b) trace.

The DSC thermograms of the (b) and (c) samples of Fig. 1 are shown in Fig. 3 by curves (a) and (b), respectively. The broad, overlapping, endothermal signals with onset at about 450K which characterize trace (a) suggest the existence of several sites of different stability from which H_2 can evolve. The hydrogen desorption from the amorphous hydride is activated by annealing the sample

at 513K and 623K (see Fig. 3a). The latter is however accompanied by the growth of the stable crystalline hydride, as confirmed by XRD analyses following the thermal treatment. In the curve (b) the endothermic features are spaced by an exothermal signal with onset at about 600K, corresponding to the crystallization and growth of the more stable δ-ZrH$_{1.66}$-type hydride phase. Even at 583K, below the exothermal peak, the thermal treatment did not activate the desorption from the quasicrystalline hydride. Conversely the growth of the δ-ZrH$_{1.66}$ is observed. Therefore it appears that the formation of such thermodynamically stable crystalline hydride limits the hydriding process reversibility.

In the case of the QC Zr$_{57}$Ti$_8$Nb$_{2.5}$Cu$_{13.9}$Ni$_{11.1}$Al$_{7.5}$ alloy prepared by copper mold casting, no absorption was observed under static conditions. On the other hand, the mechanical action without milling balls was again able to activate the absorption process. The XRD patterns of the as-prepared and hydrided QC alloy, pertaining to this latter case, are presented in the curves (c) and (d) of Fig. 1. Both of them are characterized by signals relevant to the (100000) and (110000) peaks indicating that the quasiperiodic structure is retained after hydrogenation.

The hydrogenation kinetics of this last sample is again sigmoidal and the maximum absorption rate, $1.75 \cdot 10^{-6}$ mole g^{-1}s^{-1}, is slightly smaller than the ones cited above. The asymptotic value of *H/M* weight %, 1.55, is also about 10% lower than the one corresponding to the Zr-richer sample. The quasilattice parameter increases of about 5% from 0.472 to 0.497 nm and the precipitation of the δ-ZrH$_{1.66}$ phase no longer takes place. This is probably a consequence of the different Zr content in the two alloys. The higher Zr fraction of the previous composition seems to permit the absorption of a larger amount of H$_2$. After the saturation of the amorphous fraction has been attained, the stored hydrogen promotes Zr segregation and the successive precipitation of the crystalline δ-ZrH$_{1.66}$ phase.

In addition, the evidence that hydrogenation proceeds under mechanical processing even without a milling body clearly demonstrates the occurrence of mechanical energy transfer events simply promoted by the dynamics of the granular body. The study of the behaviour of a granular body under mechanical agitation has been already performed [15] and the quantification of the energy involved in powder grain collision events will be the subject of future work.

The DSC analysis of the quasicrystalline hydride, illustrated by thermogram (c) in Fig. 3, shows a convolution of endothermic signals starting at about 473K. No exothermic peak was observed. The thermal stability of the sample was investigated by annealing at 543, 623, and 768K. The thermal treatment at 623K was able to activate the precipitation of the crystalline δ-ZrH$_{1.66}$ hydride. Conversely hydrogen desorption occurred preserving the quasicrystal features after 3 h of isothermal treatment at 543K. The pattern (f) in Fig. 1 indicates a decrease of the quasilattice constant of about 2%. A second hydrogenation of the annealed sample was carried out by repeating the mechanical treatment under hydrogen atmosphere in the same working conditions previously specified. A renewed swelling of the QC matrix was observed, the main XRD peaks regaining the same angular position occupied after the first hydrogenation. The amount of hydrogen absorbed in the second cycle was about 20% of that absorbed in the first cycle, indicating a process cycling ability, at least at a partial extent.

It is also interesting to note that using different hydrogenating pressures, in the range between 0.05 and 0.30 MPa, under isobaric conditions as well as milling with either 0.5 or 1 g balls do not affect the kinetic features of the hydriding process. In particular, the structural evolution and the final *H/M* value remained unchanged.

4. CONCLUSIONS

The present preliminary work, confirmed the effectiveness of reactive milling to activate hydrogen absorption in quasicrystal phases, while, depending on the alloy composition, highlighted the occurrence of hysteretical cycles in the hydrogen absorption-desorption processes. The observed kinetic trends as well as their dependence on the impact energy, could suggest that a key role is played by the D_M parameter in starting the process, as it was reported in previous works for Zr-based amorphous and nanostructured systems. Many points are expected to be clarified in the prosecution of this research work, among which the role of passivating oxygen in triggering the surface phenomena under mechanical treatment as well as the existence of a truly mechanochemical effect distinct from a simple increase of surface area available to sorptive steps.

ACKNOWLEDGEMENTS

REFERENCES

[1] Proc. 9th Int. Symp. on Metal Hydrogen Systems, Fundamentals and Applications (MH2004), ed. by. Henryk Figiel, Olgierd Żogał and Volodymyr Yartys // *J. Alloys Comp.* **404-406** (2005).

[2] Xiao Dong Wang, Min Qi, Patricia A. Thiel and Chuang Dong // *Philosophical Magazine* **84** (2004) 825.

[3] A. Takasaki and K.F. Kelton // *International Journal of Hydrogen Energy* **31** (2006) 183.

[4] J.Y. Kim, R. Hennig, V.T. Huett, P.C. Gibbons and K.F. Kelton // *Journal of Alloys and Compounds* **404-406** (2005) 388.

[5] V.T. Huett, D. Zander, L. Jastrow, E.H. Majzoub, K.F. Kelton and U. Koster // *Journal of Alloys and Compounds* **379** (2004) 16.

[6] D.Zander, U.Koster and V.Khare // *Journal of Non-Crystalline Solids* **334-335** (2004) 247.

[7] S. Scudino, C. Mickel, L. Schultz, J. Eckert, X.Y. Yang and D.J. Sordelet // *Applied Physics Letters* **85** (2004) 4349.

[8] U. Kuhn, J. Eckert, N. Mattern and L. Schultz // *Applied Physics Letters* **77** (2000) 3176.

[9] G. Mulas, L. Schiffini and G. Cocco // *J. Mater. Res.* **19** (2004) 3279.

[10] P.Yu. Butyagin // *Reactivity of Solids* **1** (1986) 345.

[11] G. Mulas, L. Schiffini, G. Tanda and G. Cocco // *Journal of Alloys and Compounds* **404-406** (2005) 343.

[12] G. Mulas, S.Scudino and G. Cocco // *Materials Science and Engineering A* **375-377** (2004) 961.

[13] E.N. Yeremin, *The Foundation of Chemical Kinetics* (Mir, Moscow, 1979).

[14] G. Mulas, L.Schiffini, S.Scudino and G. Cocco // Journal of Alloys and Compounds 455 (2008) 106.

[15] G.Manai, F.Delogu, L.Schiffini and G.Cocco // *Journal of Materials Science* **39** (2004) 5319.