HYDROGEN STORAGE PROPERTIES OF THE LOW-DIMENSIONAL SYSTEMS BASED ON Ti-Zr AND Al-Mg ALLOYS

Rud A.D.*, Lakhnik A.M, Zelinskaya G.M., Perekos A.E., Uvarov V.N.*, Kolbasov G.Ya.(1), Danilov M.A.(1), U. Schmidt(2)

Institute for Metal Physics of NASU, 36 Academician Vernadsky blvd., 03142, Kiev, Ukraine

(1)Institute of General and Inorganic Chemistry of NASU, 32/34 Academician Palladin ave., 03142, Kiev, Ukraine

(2)Department of Physics, Martin-Luther-University, Hoher Weg 8, 06120 Halle, Germany

* *Fax: 38 (044) 424 2561 E-mail: rud@imp.kiev.ua*

Introduction

The Ti-Zr and high-concentrated Al-Mg based alloys have ability to considerable hydrogen accumulation and its subsequent controllable reactivation. This property evidently is strongly affected by the structural state of the alloys. The Ti-Zr alloys have a number of structural states depending on the chemical composition: from complex Laves phases to the quasicrystals and amorphous states. At the same time the amorphous state was observed for a silicon concentration of one order of magnitude less than that, given in [1]. The structural state of the melt-spunned Ti-Zr and Al-Mg ribbons, as well as its stability after hydrogenating has been investigated. It has been found the structural state of the ribbons depend on the fabrication conditions (surface wheel velocity, or hardening rate) and presence of microimpurities.

The $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$, $Al_{78}Mg_{22}$ at.% alloys were prepared by induction melting in Ar gas atmosphere from pure elements (99.9 %).

Ribbons of 50 μm thick and 10 mm width were produced by the melt-spinning technique at the different wheel surface velocity (44 m/s and 30 m/s).

X-ray diffraction analysis was performed on a diffractometer using Bragg-Brentano geometry (monochromatic Mo K_α and Cu K_α radiation).

The study of the electrochemical characteristics of the alloys was performed in an electrolytic cell with nickel oxide electrode. A 5M KOH + 1.5M LiOH electrolyte was used.

The hydrogenating was performed in the electrolytic cell during 8 hour under 5 mAh/cm^2 current density and voltage of 1.68 V. The ribbons surface has been neither etched nor coated by Pd.

Results and discussion

The X-ray diffraction experiments held within several clocks after hydrogenating, have revealed a significant modification in a structural state of a free surface of the ribbon. A geometrical factor *i*(s) and RDF for ribbons in an initial state and after hydrogenating calculated with using of the software package [3]. There are structural state modifications in the ribbons during hydrogenating process: magnification of interatomic distance and diminution of a degree of the short-range order.

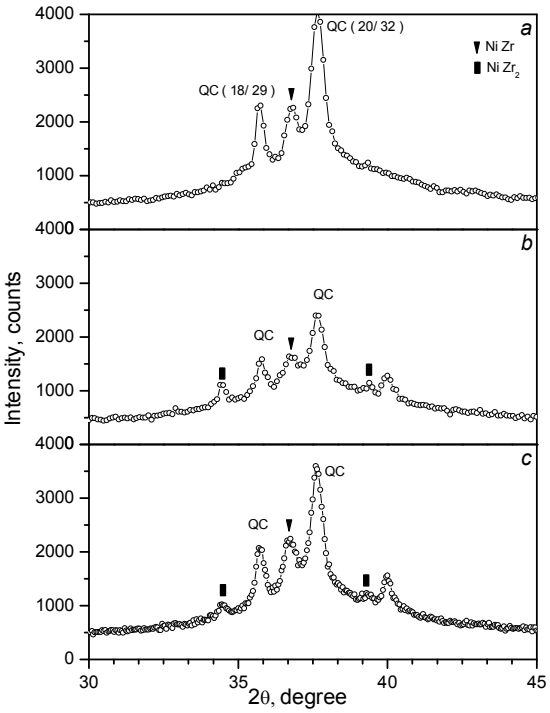


Fig. 1.

The XRD study reveals that the relaxation processes in the ribbons appear during the 1st day after hydrogenation. The fragments of the XRD patterns for the cases of the initial state, in a day after hydrogenation and in a week after hydrogenation are presented in Fig. 1 for ribbons with hardening velocity of 30 m/s. As it is seen from Fig. 1, the intensity of quasicrystalline peaks practically amounts to the initial value in a week after hydrogenation. It seems to be a result of an interaction between amorphous and quasi-crystalline subsystems. XRD study of the freshly hydrogenated samples testifies amorphous state for

the 44 m/s velocity ribbon. At the same time, there are essential changes in the structure states of the free side of 30 m/s velocity ribbon (Fig. 1a, b): namely, the intensity of the quasicrystalline peaks decreased, but their positions did not change, which is in an agreement with [2]. At that, additional peaks from Laves phases appeared.

Fig. 2. shows the discharge curve for 8 cycle after hydrogenating. Solid line on the plot corresponds to a changing of the $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ electrode potential vs nickel oxide electrode.

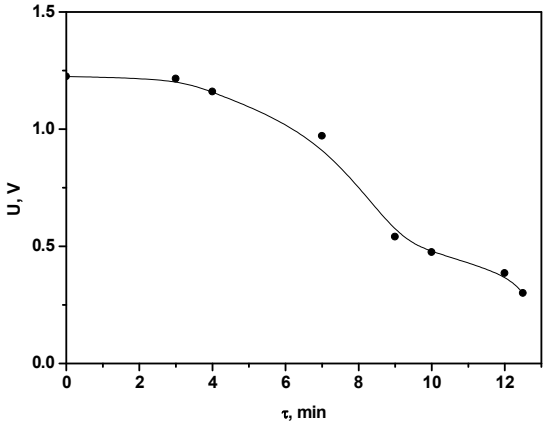


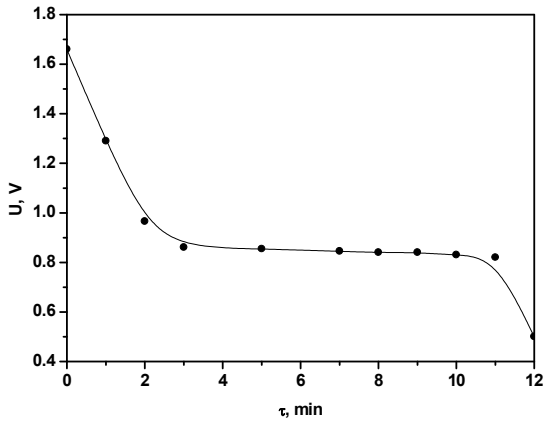
Fig. 2.

The Al-Mg alloy system, in comparison with the other systems, generally has some advantages such as light mass, lower cost and good quality of absorption.

The highest value of discharge capacity achieved for the $Al_{78}Mg_{22}$ electrode is 21 mAh/g under current of 1 mA/cm^2.

The specific capacity decreasing to 10 mAh/g after 37 charge-discharge cycles and strong electrode corrosion has been observed. The test on a storage in a charged state during 3 days have shown a residual capacitance of 7 % from that, which was obtained at discharge at once after a charge.

The data of this alloy is shown on the Fig. 3. The plateau on the discharge capacity curve at low voltage (0.85 V) indicates about the electrode dissolution. The examinations of Al-Mg alloys were held in the electrolyte containing glycerine and phosphoric acid (2:1) and in the salt electrolyte



composition of 5M NH_4Cl and 2M $ZnCl_2$. The plateau was observed on the curve under voltage of 1,15 V. The discharge capacity in these electrolytes was low (10-15 mAh/g).

Fig. 3.

Conclusions

The hydrogen concentration of 0.5 H/M was achieved by means of the electrochemical method in the $Ti_{37.1}Zr_{38.8}Ni_{23.9}Si_{0.2}$ ribbons. At that, the structural changes are observed in both the amorphous and quasicrystalline subsystems. This phenomenon has a reversible character: the ribbon structure state reverts almost entirely to the initial state after natural dehydrogenation.

The alloys $Al_{78}Mg_{22}$ have a small discharge capacity in contrast to Ti-Zr ones. As the alloys $Al_{78}Mg_{22}$ are diluted in electrolytes, the searching of the Al-Mg based alloys inconvertible in aqueous mediums with an acceptable discharge capacity is indispensable.

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References

1. J.Y. Kim, P.C. Gibbons, K.F. Kelton, J. Alloys Comp. 266 (1998) 311.
2. J.W. Cahn, D. Shechtman, D. Gratias, J. Mater. Res. 1 (1986)
3. A. G. Ilinskii, *ilin@imp.kiev.ua*