Proceedings of IX International Conference "Hydrogen Material Science and Chemistry of Metal Hydrides", Ukraine, September 5-11, 2005, http://www.ichms.org

PECULIARITIES OF HYDROGENATION OF Ti-Zr-Ni ALLOYS, CONTAINING THE APPROXIMANT PHASE

Karpets M.V.*, Solonin Yu.M., Velikanova T.A., Fomichev A.S., Karpets F.M., Homko T.V.

Frantsevich Institute for Problems of Materials Sciences,
3, Krzhyzhanovsky str., Kyiv-142, 03680, Ukraine,
E-mail address: karp@ipms.kiev.ua

Exhaustions of natural resources of oil and gas do the problem of search of alternative energy-storage mediums, foremost environmentally clean, more substantial. Among such materials, hydrogen is the most perspective material, because hydrogen power engineering - absolutely ecologically clean technological processes. One of the main problems of hydrogen energetic is development of hydrogen-absorbing and hydrogen-storing materials. Key requirements for such substances are: ability to the as full as possible loading of significant hydrogen quantities; ability to give back accumulated hydrogen at the acceptable values of pressure and temperature within the limits of reasonable time; ability to repeat this cycle nonexpendable without material properties degradation.

Possibility of application of hydrogen in the energy-accumulating systems becomes in more widespread since discovery and further development of extremely disordered materials, which contained new phase, named quasicrystals and approximants. In contrast to ordinary crystalline phases, quasicrystals have not translational periodicity, but, in the same time, unlike amorphous phases, they, as well as ordinary crystals, have long-range order. One of the most useful properties of such extremely disordered materials is their ability to absorb significant quantities of hydrogen

Ti-based quasicrystals are the second large group of quasicrystals, next after the Al-based quasicrystals. Many metastable quasicrystals have been found in rapidly quenched $Ti_2(Mn,Fe,Co,Ni)$ binary alloys and in the multicomponent Ti-alloys. More stable quasicrystals was found in rapidly quenched Ti-Zr-Ni ribbons [1] and also in arc-melted bulk samples of this system after certain annealings. Ti-Zr-Ni quasicrystalline materials got considerable advantage before others due to: 1) capability of hydrogen absorption up to two hydrogen atom per metal atom [2], 2) comparative easiness of obtaining this materials in the stable state, 3) cycling of hydrogen loading-unloading at the low values of pressure and temperature [3].

Thermodynamically stable icosahedral quasicrystal (i-phase) and its approximant (W-phase) were found in the Ti-Zr-Ni system. Structure of the stable W-phase with lattice constant a=1,4317 nm, consists of icosahedral clusters and closely related as to Frank-Kasper approximant R-phase ($Al_{56}Li_{32}Cu_{12}$) and to Bergman-phase ($Al_{40}Mg_{40}Zn_{20}$). It have BCC-packed Bergman-type icosahedral clusters of atoms.

Phase identifications were performed by X-Ray diffractometer DRON-UM1 with Bragg-Brentano geometry (R_g=192 mm) using Cu-Kα monochromatic radiation. The graphite-monocrystal was used for monochromatization of diffracted beam. High-temperature X-Ray diffraction investigation have been carried out with using of UVD-2000 chamber. During X-ray heating experiments the samples were kept flowing helium at a positive pressure of 20 kPa over atmosphere. The data treatment of X-Ray experiment was carried out using the program Powder Cell 2.4.

Samples were prepared by two methods: 1) arc melting in a water-cooling Cu crucible under an Ar atmosphere; 2) mixing, compacting and sintering of initial powder components at 800-900°C in a vacuum. The maximal loss of mass during ingots melting was not higher than 0,1 % mas. As-cast and sintered samples were annealed at 500-600°C in a vacuum during 48-100 hours. Hydrogenation of the annealed samples was carried out at 260°C and 41 atmospheres.

The reflections of hexagonal C14 Laves phase and α – (Ti,Zr) solid solution appeared on the diffractograms of the cast-alloys. As the content of zirconium in the alloys increases the volume of hexagonal cell of α – (Ti,Zr) solid solution raises. It can be explained by a greater atomic radius of the Zr-atom (0,160 nm) comparatively with an Ti-atom (0,145 nm). Phase composition of initial sintered samples differs from one of cast ingots. In addition to reflexes of C14 Laves phase the peaks of Ti_2Ni-type cubic phase are registered (Fig.1). The peaks of nickel are registered on the diffraction patterns of sintered at 800°C samples also. However, reflexes of α – (Ti,Zr) solid solution are not appeared at all temperatures of sintering.

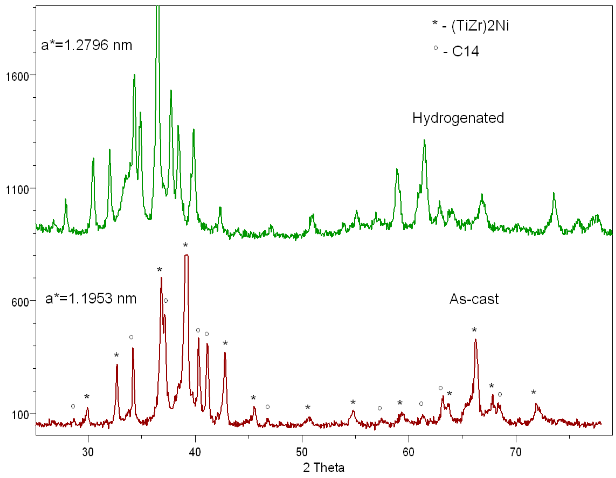

Fig.1. Comparison of the XRD patterns of the as-sintered $Ti_{41}Zr_{41}Ni_{18}$ alloy in initial state and after hydrogen loading from the gas phase

Annealing of the as-cast samples at 500-600°C changes its phase composition, at the same time, annealing of the sintered samples have not large an influence on its phase composition. Soaking of $Ti_{42}Zr_{42}Ni_{16}$ alloy in the high-temperature chamber during 50 hours results to appearance of approximant cube phase W(TiZrNi) (a=1,4356(2) nm) as a dominant phase(Fig.2).

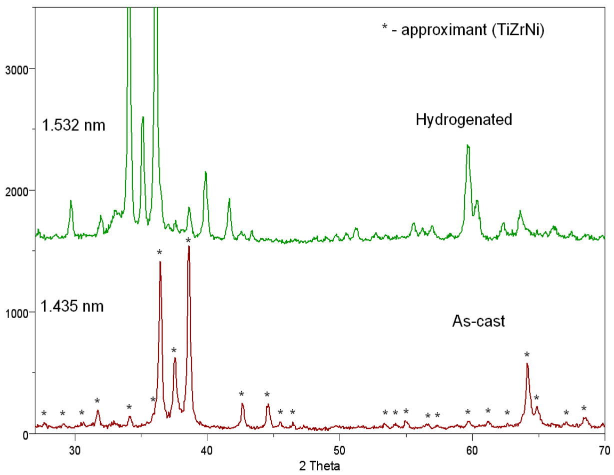

Fig.2. Change of the XRD patterns of the annealed $Ti_{44}Zr_{40}Ni_{16}$ alloy before and after its hydrogenation from the gas phase.

The results of the profiles refinement method for diffraction patterns of the sintered powders are satisfactorily described within the bounds of two structures: hexagonal C14 Laves phase C14 (a=0,5238 nm, c=0,8578 nm) and cube $(TiZr)_2Ni$ phase (a=0,1953 nm) that is of the Ti_2Ni-type (Fig.1). Hydrogen loading of the sintered alloys from the gas phase results in absorption of hydrogen by the sintered $Ti_{41}Zr_{41}Ni_{18}$ alloy up to 2,47 % mas. It gives rise to the shifting of diffraction peaks to the smaller angles (Fig.1). At that the lattice parameters are growing to the values a=0,595 nm, c=0,9103 nm for the C14 Laves phase and a=1,2796 nm for the cube $(TiZr)_2Ni$ phase that fit with cell volume rising 21,1 and 22,7 %, accordingly.

Hydrogen loading from the gas of the melted annealed alloys results in absorption of hydrogen by the approximant phase up to 2,4-2,5 % mas. At that it does not take place the change of alloys phase composition. It gives rise to the shifting of peaks of the approximant phase to the smaller angles (Fig.2), that indicates on the increasing of the cube cell parameter during hydrogen loading. So, for an $Ti_{44}Zr_{40}Ni_{16}$ alloy the lattice parameter changes from a=1,4351(2) nm to a=1,5320(3) nm (Fig.2). Calculations show that such increasing of linear sizes of cell is accompanied by a volume rising 13,9 %.

Conclusions

Thus, forming of the quasicrystalline or approximant phases in the Ti-Zr-Ni alloys allows to accumulate up to 2,5 % mas. of hydrogen at considerably less volume effect comparatively with f samples, in which C14 Laves phase or cube $(TiZr)_2Ni$ phase of Ti2Ni-type are present.

References

1. Molokanov V., Chebotnikov V. J. Quasicrystals and amorphous alloys in Ti-Zr-Ni system. Glassforming ability, Structure and properties // Non-Cryst. Solids. –1990. –V.117/118. – P. 789 - 792.

2. Wehner B.I., Meinhardt J., Koster U., Alves H., Eliaz N., and Eliezer D. Oxidation and hydrogenation of quasicrystals // Mat. Sci. & Eng. A.–1997. –V.226-228. –P. 1008 –1011.

3, Kim J.Y., Gibbons P.C. and Kelton K.F. Hydrogenation of Pd-coated samples of the Ti-Zr-based icosahedral Phase and related crystalline phases // J. Alloys and Compounds. –1998. – V.266. –P.311.

4. Kelton K.F. Ti/Zr-Based quasicrystals-formation Structure and Hydrogen storage properties // Mat. Res. Soc. Symp. Proc.-1999. -V.553. -P. 471-482.