Composition design, preparation techniques and hydrogen storage properties of high entropy alloys

Semen Klyamkin[1], Vladislav Zadorozhnyy[2], Elena Berdonosova[1], Mikhail Zadorozhnyy[2], Korol Artem[2], Ivan Savvotin[1]

[1] Lomonosov Moscow State University, Chemistry Department, Leninskie Gory 1/3, Moscow, 119991 Russia

[2] National University of Science and Technology "MISIS", Leninsky prospect 4, 119049 Moscow, Russia

Since the mid-2000s, alloys composed of five or more elements in equiatomic ratios have been allocated to a separate group, so called high entropy (HEA) or multi-principal element (MPE) alloys [1, 2]. Special interest in these alloys was first associated with their peculiar crystal structure and exceptional mechanical properties that has been considered in review [3].

As it was reported recently in [4], transition metal HEA can demonstrate outstanding hydrogen absorption capacity and form hydride phases with an unusual H/M ratio of 2.5 that is higher compared with individual metals and their binary intermetallic compounds. Crystall lattice strain owing to the presence of metals with very different atomic radii was considered as the main reason for this phenomenon. Later, hydrogen storage performance was studied for HEA of various compositions [5, 6].

Herein, we discuss fundamental approaches to composition design of multicomponent single-phase alloys. Based on these thermodynamic principles, we prepared a series of new HEA, for which the structure and interaction with hydrogen were characterized. A special attention was paid to the preparation techniques. Along with conventional arc melting, mechanochemical synthesis in a high-energy ball mill, electron beam melting and pendant drop melt extraction were used. Effect of the synthesis methods on the crystal structure of as-prepared alloys and their hydrides was examined by means of scanning and transmission electron microscopy, X-ray and neutron diffraction.

Hydrogen and deuterium interaction with the alloys was studied by volumetric measurements. Maximum hydrogen capacity was close to 2 H/M. The hydride formation is not completely reversibly because of high thermal stability of the hydride phases.

For $Ti_{20}Zr_{20}V_{20}Nb_{20}Ta_{20}$ BCC to FCC structure transformation upon hydrogenation was detected. Although all the methods used allowed us to obtain single-phase alloys, only the latter, resulting in formation of microwire samples, prevents the formation of secondary phases after hydrogenation.

A detailed structure analysis of the deuterides will be reported in a separate presentation by A. Korol et al.

Aknowledgment

This work was performed according to the Development program of the Interdisciplinary Scientific and Educational School of Lomonosov Moscow State University «The future of the planet and global environmental change» and was supported by Russian Science Foundation, project No. 19-13-00207.

References

[1] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent. Mater. Sci. Eng. A 375-377 (2004) 213-218.

[2] J.W. Yeh, S.K. Chen, S.-J. Lin, J.-Y. Gan, T.-S. Chin, C.-H. Tsau and S.-Y. Chang. Adv. Eng. Mater., 6 (5) (2004) 299-303.

[3] D.B. Miracle, O.N. Senkov. Acta Materialia 122 (2017) 448-511

[4] M. Sahlberg, D. Karlsson, C. Zlotea, U. Jansson. Sci.Rep., 6 (2016) 36770.

[5] B. Sarac, V. Zadorozhnyy, E. Berdonosova, et al. RSC Advances, 10 (2020) 24613–24623.

[6] V. Zadorozhnyy, B. Sarac, E. Berdonosova, et al. Int. J. Hydrogen Energy, 45 (2020) 5347–5355.

Semen Klyamkin is a professor at the Chemistry Department at Lomonosov Moscow State University. He obtained PhD degree in inorganic chemistry (1987) and Doctor of Sciences in solid state chemistry (2014). In 1993-1994 he worked in *Laboratoire de Chimie Métallurgique des Terres Rares, CNRS, France*. He has published over 100 articles in international scientific journals. His research activity covers hydrogen storage materials, metal hydrides, gas adsorption in porous matrices (MOFs, carbons) with emphasis on high pressures, mechanochemistry, gas separation membranes.

Presentating author: Semen Klyamkin, e-mail: klyamkin@highp.chem.msu.ru, tel: +7-495-9394576