SYNTHESIS AND PHASE COMPOSITION OF THE HIGH ENTROPY AB_5 ALLOYS (A = La, Zr; B = Ni, Mg, Al or Ga)

Kalytovskyi I. V., Zelinska O. Ya., Zelinskiy A. V., Pavlyuk V. V.
Department of Inorganic Chemistry, Ivan Franko National University of Lviv,
Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
ihor.kalytovskyi@lnu.edu.ua

Intermetallic compound $LaNi_5$ with hexagonal $CaCu_5$-type structure is well known for hydrogen sorption properties because it has sufficient interatomic space (octahedral and tetrahedral voids) to incorporate hydrogen atoms. Multicomponent alloys based on it are widely used in hydrogen storage devices and nickel-metal hydride energy sources. Hydrogen storage devices and nickel-metal hydride energy sources are the most popular applications of materials based on this phase. To improve sorption and electrochemical behaviour, increase life cycle and corrosion resistance and lower the cost, it is usually doped by other rare-earth and transition metals as well as main group metals and metalloids. Here we present the results of alloying $LaNi_5$ with zirconium, magnesium, aluminium and gallium, focusing on the synthesis and the phase composition of alloys.

The synthesis of two alloys, $La_{11.67}Zr_5Ni_{73.33}Mg_5Al_5$ and $La_{11.67}Zr_5Ni_{73.33}Mg_5Ga_5$, was carried out by melting pure metals with a content of the main component not lower than 99.9 wt. % in an arc furnace under an argon atmosphere. An excess of magnesium of up to 10 wt.% was added to the samples to cover its losses during the melting procedure. To ensure the homogeneity the obtained alloys were sealed in a silica ampule under vacuum and annealed at 400°C for two weeks. After that, they were quenched in cold water without breaking ampoules. Phase analysis of the samples was carried out on data sets obtained by powder X-ray diffraction (XRD) using a powder diffractometer DRON-2.0M (Fe$K\alpha$-radiation, $20° \leq 2\theta \leq 120°$). Experimental powder patterns were compared with theoretical ones calculated using the PowderCell-2.4 program. Refinement of the crystal structure of observed phases was performed according to the Rietveld procedure using the WinPLOTR software. The qualitative and quantitative composition of the phases was confirmed by energy-dispersive X-ray spectroscopy using an electron microscope TescanVega3 LMU with Oxford Instruments EDX system.

The major phases observed in both samples, as well as the binary prototype, crystallize in the $CaCu_5$-type structure (space group *P6/mmm*, Pearson code *hP6*). The atoms of lanthanum in their structures are partially substituted by the atoms of zirconium and the atoms of nickel are partially substituted by the atoms of magnesium and aluminium or gallium. The lattice parameters (a =0.50297(10) nm, c = 0.40279(10) nm, V = 0.08824(3) nm^3 for (La,Zr)(Ni,Mg,Al)$_5$ and a = 0.50122(3) nm, c = 0.40317(3) nm, V = 0.08771(1) nm^3 for (La,Zr)(Ni,Mg,Ga)$_5$) correlate well with atomic radii of aluminium and gallium (r_{Al} = 0.143 nm; r_{Ga} = 0.139 nm). In addition to the main phase, minor reflections from the cubic $ZrNi_5$ derivative phase ($AuBe_5$-type structure, space group F-43m) were present on the powder patterns of the samples. The EDX analysis confirmed the average compositions of the samples and the composition of each phase observed by XRD in particular. Further research will be devoted to the study of the effectiveness of the electrochemical hydrogenation of synthesised alloys.