

**SOLUBILITY OF MANGANESE IN THE BINARY  
La–Zn AND Gd–Zn INTERMETALLICS**

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Intermetallic compounds remain the basis of promising materials for different fields of modern technics and industry. The accumulation of experimental data on phase diagrams of the metallic systems, stability ranges of new phases, their crystal structure, physical and chemical properties promotes the purposeful synthesis of the functional materials with the desired properties.

Previous research showed that binary phases containing rare earth and 3d-transition metal and having the composition AB, AB<sub>2</sub>, AB<sub>3</sub>, AB<sub>5</sub> or A<sub>2</sub>B<sub>17</sub> can reversibly accumulate hydrogen. The sorption ability and electrochemical properties of the accumulators constructed on their basis can be improved by doping the binary compounds with other elements.

Here we report the solubility of Mn in La–Zn and Gd–Zn binary compounds as a part of systematic study of {La,Gd}–Mn–Zn systems and investigation of the influence of the third element on the effectiveness of the electrochemical hydrogenation of the binary phases.

The alloys were synthesized by arc melting of pure metals (> 99.9 wt. %, commercial) under a purified argon atmosphere with further annealing at 500 °C for two month. X-ray phase analysis of the samples was carried out using the XRD powder diffraction data collected on the diffractometer DRON-2.0M (Fe K $\alpha$ -radiation). The quantitative composition of the alloys was studied by X-ray fluorescent (ElvaX Pro analyser) and energy dispersive X-ray spectroscopy (scanning electron microscope TESCAN Vega3 LMU, Oxford Instruments AZTEC ONE system).

{La,Gd}–Zn systems are characterized by the formation of binary phases with stoichiometry 1:1, 1:2, 1:5, 2:17 (for both systems) at 500 °C [1–2]. The phases with stoichiometry 1:4, 1:5, 1:11 and 1:13 are typical for La–Zn system, while for the Gd–Zn system the phases GdZn<sub>3</sub>, Gd<sub>3</sub>Zn<sub>11</sub>, Gd<sub>13</sub>Zn<sub>58</sub>, Gd<sub>3</sub>Zn<sub>22</sub> and GdZn<sub>12</sub> are formed. Atomic radii of rare-earth element ( $r_{La} = 1.86 \text{ \AA}$ ,  $r_{Gd} = 1.79 \text{ \AA}$ ) influences on the type of formed compounds. X-ray analysis of the ternary alloys showed the formation solid solutions of substitution with Mn. A small difference between the atomic radii of Mn and Zn ( $r_{Mn} = 1.28 \text{ \AA}$ ,  $r_{Zn} = 1.34 \text{ \AA}$ ) promotes substitution however different physical and chemical characteristics causes the formation limited solid solutions.

The homogeneity ranges of the solid solutions were determined based on the changes of lattice parameters with the increasing Mn-concentration obtained from X-ray data. For the zinc-rich alloys the solubility of Mn in the binary compounds was confirmed by energy dispersive X-ray analysis. At the experimental conditions, the largest homogeneity ranges have the solutions based on the phases LaZn (4.4 at.% Mn), LaZn<sub>5</sub> (6 at.% Mn), La<sub>2</sub>Zn<sub>17</sub> (3.9 at.% Mn) and LaZn<sub>11</sub> (2.9 at.% Mn) in the system La–Mn–Zn, and based on the phases GdZn (4.5 at.%), GdZn<sub>2</sub> (4.6 at.% Mn), Gd<sub>3</sub>Zn<sub>11</sub> (3.7 at.% Mn) and Gd<sub>2</sub>Zn<sub>17</sub> (3.5 at.% Mn). The solubility of Mn in other binary compounds does not exceed 2 at. %.

[1] Dychko N., Andrash V., Kordan V., Zelinska O., Zelinskiy A., Pavlyuk V. Crystal structure and electrochemical hydrogenation of LaZn<sub>5-x</sub>Mn<sub>x</sub> solid solution. Visn. Lviv Univer. Ser. Chem. 2018, Iss. 59(1). P. 107-114 (in Ukrainian).

[2] Dychko N.O., Andrash V.V., Porodko O.Yu., Zelinska O.Ya., Pavlyuk V.V. Phase equilibria in the {La,Gd}–Mn–Zn ternary systems at 0-70 at.% Zn. XIII Int. Conf. Cryst. Chem. Int. Compd. (September 25-29, 2016). Lviv, Ukraine. 2016. P. 66.