Hydrogenation properties of alloys based on ErNi$_2$ binary compound

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Abstract. The effect of Ni by Fe and V and Er by Y substitution on the crystal structure and hydrogenation-dehydrogenation properties of the ErNi$_2$ compound with the cubic MgCu$_2$ type structure has been studied. The ErNi$_{2-x}$T$_x$ compounds easily absorb hydrogen at room temperature under 0.12 MPa hydrogen pressure, after preliminary activation treatment by heating in vacuum. Hydrogenation of ErNi$_2$ and all ErNi$_{1.85}$V$_{0.15}$, ErNi$_{1.7}$Fe$_{0.3}$ and Er$_{0.85}$Y$_{0.15}$Ni$_2$ substituted compounds resulted in formation of the crystalline hydrides with the MgCu$_2$ type structure of the metallic sublattice and hydrogen content up to 3.3 at.H/f.u. The stability of hydrides based on ErNi$_2$ compound increases as well with substitution of Er by Y and the shift from RNi$_2$ to R$_{1-x}$Ni$_2$ stoichiometry.

1. Introduction

This paper is a part of our systematic studies of the influence of third component on the crystal structure and hydrogenation properties of RT$_2$ (R=rare earth element, T=3$d$-transition metal) compounds with Laves phases MgCu$_2$ or MgZn$_2$ type structure [1-4]. The series of RT$_2$ Laves phases are extensively investigated recently due to their hydrogen absorption capacity and particular magnetic properties. These compounds can absorb a large amount of hydrogen (up to 5 at.H/f.u.=hydrogen capacity ~ 1.67 H/M) into R$_2$T$_2$, RT$_3$ and T$_4$ interstitial tetrahedral sites of the structure. Cell volume increases up to 30%. Generally this process is accompanied by a lowering of the crystal symmetry of hydrides in comparison with the basic intermetallics.

Recently we reported the hydrogenation properties of the ErFe$_{2-x}$T$_x$ (T= Ti, V, Cr, Mn, Co, Ni, Cu, Mo) alloys [4]. Under selected hydrogenation conditions all the samples absorb a large amount of hydrogen (~3.50-4.03 at.H/f.u.) without amorphization. The hydrogenation of ErFe$_2$ and ErFe$_{2-x}$T$_x$ (T=Cr, Mn, Co, Ni, Cu) are accompanied by transformation of the cubic MgCu$_2$ type structure into the trigonal one of the TbFe$_2$ type. Substitution of Fe (r=1.26 Å) by small amounts of other 3$d$ metal with the similar atomic radius (Cr, r=1.27 Å; Co, r=1.25 Å; Ni, r=1.24 Å; Cu, r=1.28 Å) decreases the hydrogen capacity of the alloys from 3.85 at.H/f.u. for ErFe$_2$ to 3.50 at.H/f.u. for ErFe$_{2-x}$Cu$_x$. Hydrogenation of these ternary alloys is accompanied with the phase transition of the cubic structure (MgCu$_2$-type) into the trigonal one (TbFe$_2$- type) as it occurs in the case of the basic compound ErFe$_2$. Substitution of Fe by the larger d atom (Ti, r=1.46 Å; V, r=1.34 Å; Mo, r=1.39 Å) increases the hydrogen capacity of the ErFe$_{2-x}$T$_x$ compounds. Structure of the basic compounds and their hydrides remains the same.

According to [5] R$_{1-x}$Ni$_2$ compounds annealed at 650ºC crystallize with ordered R vacancies in a cubic structure derived from the MgCu$_2$ type cubic structure (Fd-3m space group) by doubling the
cell parameter resulting the symmetry lowering (F-43m space group). These R_{1-x}Ni_2 compounds form amorphous hydrides with three exceptions for R=Nd, Tb, Er which hydrides R_{1-x}Ni_2H_x are crystalline with the same structure as the initial binaries R_{1-x}Ni_2 occur.

On the investigation of thermal stability of hydrides based on RT_2 (R=rare earth, T=Fe,Co,Ni) compounds the authors [6-9] revealed the following regularities and peculiarities. The hydrogen desorption of the majority RT_2H_x hydrides lead to formation of very stable phases with residual hydrogen content ≈1-2 at.H/f.u. The hydrogen desorption of the RNi_2H_x hydrides occurs in 2 stages. On the first stage (T≈160-230°C) the largest part of hydrogen is evolved and the phases with hydrogen content 1.2-1.5 at.H/f.u. are formed. On the next stage (T≈380-440°C) an extra small fraction of hydrogen is desorbed leading to the RNi_2H_{0.4-1.0} hydrides. Only the RNi_2H_x (R=Tb,Ho,Er,Lu) hydrides totally desorb hydrogen.

This report is focused on investigation of the influence of substitution of Ni by Fe and V and Er by Y on the crystal structure, hydrogenation properties and kinetic of the hydrogenation-dehydrogenation process of the alloys based on ErNi_2 binary compound in order to find dopants T and R increasing the hydrogen absorption capacity of the cubic Laves phases ErNi_{2-x}T_x and Er_{1-y}Y_yNi_2.

2. Experimental procedure

Alloys have been prepared by arc melting of the initial components in argon atmosphere (with Ti as a getter). High purity metals (erbium, 99.9 mass %; yttrium, 99.9 mass %; iron, 99.99 mass %; nickel, 99.99 mass %; and vanadium, 99.99 mass %) were used for preparation of the alloys. During arc melting the weight losses were less than 1% of the total mass of the ingots. The alloys were annealed in quartz ampoules under vacuum at 600°C for 720 h.

Phase analysis was carried out using X-ray powder diffraction patterns obtained by the powder diffractometer DRON-2.0 (FeKα-radiation). For crystal structure determination the diffraction data were collected using a θ-2θ scan mode with steps of 0.05° 2θ and exposition time 10 sec. at every point (diffractometer DRON-3M, CuKα-radiation). Theoretical diffractograms were calculated using the PowderCell program [10]. The lattice parameters were obtained by least-squares fits using the Latcon program [11]. The crystal structure calculations were performed by the Rietveld method using the FullProf program [12].

All hydrides were synthesized at room temperature under 0.12 MPa hydrogen pressure in autoclave after preliminary activation of the samples in vacuum at 350 - 400°C. The amount of absorbed hydrogen was determined volumetrically.

Thermal decomposition of hydride phases was made with an apparatus adopting Sievert’s method in hydrogen and argon atmospheres at normal pressure. The apparatus allows to record automatically a dependency of quantities of hydrogen releasing from a hydride during its heating upon temperature.

3. Results and discussion

XRD patterns of the annealed initial alloys ErNi_2, ErNi_{1.85}V_{0.15}, ErNi_{1.7}Fe_{0.3} and Er_{0.85}Y_{0.15}Ni_2 were used for crystal structure refinement. These data are presented in Table. Formation of single-phase samples with the MgCu_2 type (Fd-3m space group) structure were observed in all cases.

The hydrogen absorption of the ErNi_2, ErNi_{1.85}V_{0.15}, ErNi_{1.7}Fe_{0.3} and Er_{0.85}Y_{0.15}Ni_2 alloys have been investigated. Under selected hydrogenation conditions all the samples absorb a large amount of hydrogen (≈3.0-3.3 at.H/f.u.) without amorphization (Table). Substitution of Ni by Fe and V increases the hydrogen capacity of the ErNi_{2-x}T_x compounds. A maximum hydrogen capacity of 3.3 at.H/f.u. was observed for the ErNi_{1.7}Fe_{0.3} alloy. Substitution of Er by Y did not change the value of hydrogen capacity of the Er_{0.85}Y_{0.15}Ni_2 compound in comparison with the ErNi_2. The X-ray powder data of the ErNi_2H_3, Er_{0.85}Y_{0.15}Ni_2H_2, ErNi_{1.85}V_{0.15}H_2, ErNi_{1.7}Fe_{0.3}H_2 hydrides have revealed the formation of hydride phases where the metallic matrix has preserved the MgCu_2 type structure with a unit cell
volume expansion up to ~21%. In addition to the main hydride phase with the MgCu₂ type structure, a small quantities of the ErH₂ (CaF₂ structure type, Fm-3m space group) have been detected (Fig.1, Table).

Figure 1. Observed (points) and calculated (line) XRD profiles of ErNi₂H₃.₀ (a), Er₀.₈₅Y₀.₁₅Ni₂H₃.₀ (b), ErNi₁.₇Fe₀.₃H₃.₃ (c), ErNi₁.₈₅V₀.₁₅H₃.₂ (d) hydrides (hydride phase with the MgCu₂ type structure (1); hydride phase with the CaF₂ type structure (2); unknown phase (?)).
Also, all the patterns exhibit some extra weak peaks allowing to index them in a space group $F-43m$ with a double cubic cell. XRD patterns of hydrogenated sample were of bad quality as they were partially amorphous. For that reason we were unable to refine a lattice parameter of doubled cubic superstructure lattice.

### TABLE

Crystallographic data and hydrogen capacity of the ErNi$_2$, ErNi$_{1.85}$V$_{0.15}$, ErNi$_{1.7}$Fe$_{0.3}$ and Er$_{0.85}$Y$_{0.15}$Ni$_2$ alloys

| Alloy          | Observed phase(s) | Structure type | Lattice parameter $a$ (Å) | $V(Å^3)$   | $ΔV/V$ (%) | Hydrogen capacity (H/M) |
|---------------|-------------------|----------------|---------------------------|------------|------------|-------------------------|
| ErNi$_2$      | ErNi$_2$          | MgCu$_2$       | 7.1249(4)                 | 361.69(4)  |            |                         |
| ErNi$_2$H$_{3.0}$ | ErNi$_2$H$_{3.0}$ | MgCu$_2$       | 7.483(1)                  | 419.01(1)  | 15.85      | 0.99                    |
| ErH$_2$       | ErH$_2$           |               | 4.983(2)                  | 123.4(1)   |            |                         |
| Er$_{0.85}$Y$_{0.15}$Ni$_2$ | Er$_{0.85}$Y$_{0.15}$Ni$_2$ | MgCu$_2$       | 7.1316(4)                 | 362.72(4)  |            |                         |
| Er$_{0.85}$Y$_{0.15}$Ni$_2$H$_{3.0}$ | Er$_{0.85}$Y$_{0.15}$Ni$_2$H$_{3.0}$ | MgCu$_2$       | 7.506(1)                  | 422.89(1)  | 16.59      | 0.98                    |
| ErH$_2$       | ErH$_2$           |               | 4.998(3)                  | 124.9(1)   |            |                         |
| Er$_{1.85}$Y$_{0.15}$Ni$_2$ | Er$_{1.85}$Y$_{0.15}$Ni$_2$ | MgCu$_2$       | 7.1293(6)                 | 362.37(5)  |            |                         |
| Er$_{1.85}$Y$_{0.15}$Ni$_2$H$_{3.2}$ | Er$_{1.85}$Y$_{0.15}$Ni$_2$H$_{3.2}$ | MgCu$_2$       | 7.487(1)                  | 419.69(1)  | 15.82      | 1.06                    |
| ErH$_2$       | ErH$_2$           |               | 4.883(6)                  | 116.4(3)   |            |                         |
| Er$_{1.7}$Fe$_{0.3}$ | Er$_{1.7}$Fe$_{0.3}$ | MgCu$_2$       | 7.1552(4)                 | 366.32(4)  |            |                         |
| Er$_{1.7}$Fe$_{0.3}$H$_{3.3}$ | Er$_{1.7}$Fe$_{0.3}$H$_{3.3}$ | MgCu$_2$       | 7.629(1)                  | 444.02(1)  | 21.21      | 1.09                    |
| ErH$_2$       | ErH$_2$           |               | 4.997(14)                 | 124.8(6)   |            |                         |

Hydrogen desorption curves for the hydride phases ErNi$_2$H$_{3.0}$, Er$_{0.85}$Y$_{0.15}$Ni$_2$H$_{3.0}$, ErNi$_{1.85}$Y$_{0.15}$Ni$_2$H$_{3.2}$ heated in hydrogen and argon atmosphere with speed of 5 K/min are presented in Figure 2. An intensive hydrogen release begins already at ~120-130°C. This temperature indicates that hydrogen desorbs from RT$_3$ interstitial tetrahedral sites of the structure. The width of the first peak on dehydorgenation curves for ErNi$_{1.85}$Y$_{0.15}$Ni$_2$H$_{3.2}$ hydride is evidence of higher hydrogen content in the RT$_3$ tetrahedral sites in this hydride in comparison with the ErNi$_2$H$_{3.0}$, Er$_{0.85}$Y$_{0.15}$Ni$_2$H$_{3.0}$ hydrides. Substitution of Ni ($r=1.24$ Å) by the larger atom V ($r=1.34$ Å) increases the dimension of the interstitial tetrahedral sites of the structure and increases the hydrogen capacity of the ErNi$_{1.85}$Y$_{0.15}$V$_{0.15}$ compound. The hydrogen desorption traces indicate two main peaks of hydrogen desorption from R$_2$T$_2$ tetrahedral sites occurring at around 200 and 400 °C. Substitution of Ni by V and Er by Y reduces the temperature of desorption of the main part of hydrogen from 198°C for ErNi$_2$H$_{3.0}$ to 189°C for ErNi$_{1.85}$V$_{0.15}$H$_{3.2}$ and to 193°C for Er$_{0.85}$Y$_{0.15}$Ni$_2$H$_{3.0}$ and increases temperatures of desorption of the remaining hydrogen from 380°C for ErNi$_2$H$_{3.0}$ to 394°C for ErNi$_{1.85}$V$_{0.15}$H$_{3.2}$ and to 393°C for Er$_{0.85}$Y$_{0.15}$Ni$_2$H$_{3.0}$. 
Figure 2. Hydrogen desorption curves for $\text{ErNi}_2\text{H}_{3.0}$ (a), $\text{Er}_{0.85}\text{Y}_{0.15}\text{Ni}_2\text{H}_{3.0}$ (b), $\text{ErNi}_{1.85}\text{V}_{0.15}\text{H}_{3.2}$ (c) hydrides.
The XRD patterns for the ErNi$_2$, ErNi$_{1.85}$V$_{0.15}$ and Er$_{0.85}$Y$_{0.15}$Ni$_2$ samples after dehydrogenation were indexed in the cubic MgCu$_2$ type structure. Structure of the initial compounds and their hydrides after dehydrogenation remains the same.

**Conclusions**

All basic alloys ErNi$_2$, ErNi$_{1.85}$V$_{0.15}$, ErNi$_{1.7}$Fe$_{0.3}$ and Er$_{0.85}$Y$_{0.15}$Ni$_2$ occur in the cubic MgCu$_2$ type structure. These compounds easily absorb hydrogen at room temperature under 0.12 MPa hydrogen pressure, after preliminary activation treatment by heating in vacuum.

Hydrogenation of ErNi$_2$ and all ErNi$_{1.85}$V$_{0.15}$, ErNi$_{1.7}$Fe$_{0.3}$ and Er$_{0.85}$Y$_{0.15}$Ni$_2$ substituted compounds resulted in the formation of crystalline hydrides with hydrogen content up to 3.3 at. H/f.u.

The stability of hydrides based on ErNi$_2$ compound increases as well with substitution of Er by Y and the shift from RNi$_2$ to R$_{1-x}$Ni$_2$ stoichiometry. The ErNi$_2$H$_{3.0}$, Er$_{0.85}$Y$_{0.15}$Ni$_2$H$_{3.0}$, ErNi$_{1.85}$V$_{0.15}$H$_{3.2}$ hydrides totally desorb hydrogen at temperature ~380-394°C. After dehydrogenation these samples remain the structure of the initial compounds.

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