



MAGNETIC PROPERTIES AND INTERACTION OF Er_3Ni WITH HYDROGEN AND NITROGEN

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Abstract—The interaction of Er_3Ni with hydrogen was studied in the temperature range of 293–243 K. The reaction at room temperature and hydrogen pressure of 20 atm leads to formation of amorphous hydride phase. Hydriding Er_3Ni at the low temperature (253–243 K) and low pressure (<1 atm) leads to synthesis of individual hydride with formula Er_3NiH_8 and structure of initial intermetallic compound. Hydride, formed in this condition has a high degree of crystallization. It is indexed orthorhombically and the lattice constants have been measured. The exposure to vacuum of formed hydride for a few hours at the temperature of 873 K does not recover of initial intermetallic phase, but it is characterized by disproportionation to ErNi and ErH_2 . The interaction of Er_3Ni with nitrogen was studied at the pressure up to 40 atm in the temperature range of 873–1073 K.

The magnetic properties of the crystalline Er_3Ni and Er_3NiH_8 in the paramagnetic region are reported. Copyright © 1997 International Association for Hydrogen Energy

INTRODUCTION

The binary system Er–Ni is an interesting one in the field of the investigation of the magnetic materials, because the intermetallic compounds from this system exhibit some anomalous electrical, magnetic and structural properties [1].

In this connection the peculiarities of the interaction of the Er–Ni intermetallic compounds with hydrogen and nitrogen, in particular the problem of thermal stability of hydrides formed in this system, obtain importance. However the most of Er-rich compounds from system Er–Ni have been investigated insufficiently and influence of hydrogen and nitrogen on its magnetic properties have not been investigated in general.

In the present paper we report on investigation of the richest Er-compound from the Er–Ni system.

EXPERIMENTAL PART

The samples used in the present investigation were obtained by arc melting the constituent metals together on the copper water cooling hearth in a purified argon atmosphere at the pressure of 20 atm. The purity of the erbium and nickel was 99.9 and 99.98%, respectively. The X-ray investigation was carried out on a “DRON-2” diffractometer with the lattice constants measurement accuracy of $\pm 0.05\%$. The samples were not annealed because X-ray diffraction patterns showed that as-cast samples consisted of a single phase.

For investigation of the Er_3Ni interaction with hydrogen and nitrogen an apparatus was employed as described in Ref. [2]. Hydrogen was purified in the LaNi_5 -hydride accumulator ($10^{-4}\%$ impurity). Nitrogen was a commercial grade purity. The concentration of adsorbed hydrogen and nitrogen in the samples was calculated using the van-der-Waals equation and additionally was measured by full burning method. Magnetic measurements were made on the powder samples using the pendulum magnetometer.

RESULTS AND DISCUSSION

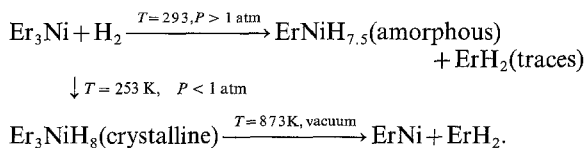
The interaction of Er_3Ni with hydrogen was studied in the temperature range of 293–243 K. The reaction at room temperature and hydrogen pressure of 20 atm leads to formation of hydride phase which contains 7.5 atoms of hydrogen per mole of initial intermetallic ($\text{H}/\text{Me} = 7.5$). X-ray diffraction pattern showed the appearance of the amorphous properties of that hydride phase, formed at the conditions described above. Furthermore, some quantity of ErH_2 was uncovered in the hydriding reaction product.

It is a known fact that the hydriding reaction for many of intermetallic compounds can be realized in the different directions that depend on the conditions of the reaction. Hydriding Er_3Ni at the low temperature 253–243 K and low pressure (>1 atm) afforded possibilities to synthesize individual ternary hydride with a structure of

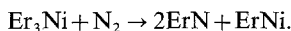
initial intermetallic compound. However, the volume of the lattice cell increased by 26%, but it is only one difference between structures of initial intermetallic and formed hydride. The reaction at low temperature and pressure is characterized with the long induction period and very low rate. The hydride with formula Er_3NiH_8 was obtained and it is distinguished in high degree of crystallization from the sample obtained at room temperature conditions.

The powder diagram of the Er_3Ni and Er_3NiH_8 could be indexed orthorhombically with the lattice constants summarized in Table 1, and it is close to that expected from literature. The compound Er_3Ni is isotropic with R_3Co [3] and belongs to the Fe_3C structure type. The reaction condition was changed in such a manner that the reaction started at the low temperature but finished at room temperature when $\text{H}/\text{Me} = 7.5$ was achieved. It leads to the marked difference in degree of crystallization because of some amorphous phase is formed.

The exposure to vacuum formed hydrides for a few hours at the temperature of 873 K does not lead to recovery of initial intermetallic phase, but is characterized by its disproportionation with formation of ErNi and ErH_2 . Thus the interaction of Er_3Ni with hydrogen may be represented in the following way:



The interaction of Er_3Ni with nitrogen was studied at pressure up to 40 atm with exposure of 50–100 h in the temperature range of 873–1073 K. At the temperature 873 K Er_3Ni did not interact with nitrogen. At the temperature 1073 K the reaction between Er_3Ni and nitrogen may be described by the following equation:



The intermetallic compound ErNi formed at the disproportionation does not interact with nitrogen in these conditions.

Recently, Talik [4] reported data on the resistivity and the magnetic susceptibility of R_3Ni single crystal (R = Y, Gd, Tb, Dy, Ho and Er). It was found that Y_3Ni is a Curie–Weiss paramagnet with $\mu_{\text{eff}} = 0.68 \mu_B$ in the temperature range of 50–420 K. Er_3Ni is a Curie–Weiss paramagnet above 400 K with $\mu_{\text{eff}} = 10.06 \mu_B$ and $\Theta = 8$ K. Indeed, there is an inflexion point on the curve $\chi^{-1}(T)$

Table 1. Lattice constants, effective paramagnetic moment and paramagnetic Curie temperature

Compound	a	b	c	μ_{eff}	Θ
	Å	Å	Å	μ_B	K
Er_3Ni	6.79	9.45	6.23	10.2	−3.5
Er_3NiH_8	7.37	10.3	6.62	9.0	−4

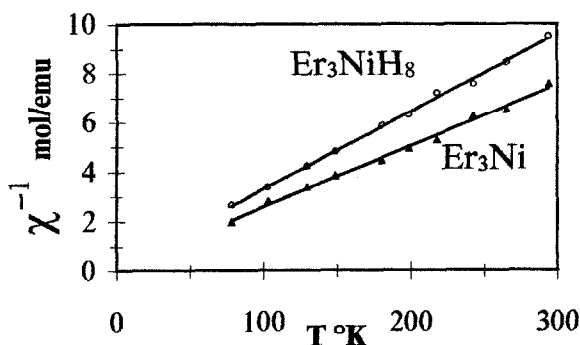


Fig. 1. Reciprocal susceptibility vs temperature for Er_3Ni and Er_3NiH_8 .

near 350 K. Earlier Gignoux *et al.* [5] reported that Er_3Ni is a Curie–Weiss paramagnet in the range of 10–300 K. XPS investigations of Y_3Ni and Gd_3Ni [6] show that there is a strong 3d–5d hybridization.

We report the data on the magnetic properties of the crystalline Er_3Ni and Er_3NiH_8 in the paramagnetic region. Magnetic measurements were made on the powder samples in the temperature range of 77–300 K and magnetic fields up to 1.2 T using the pendulum magnetometer. The temperature dependence of the reciprocal magnetic susceptibility for Er_3Ni and Er_3NiH_8 is shown in Fig. 1.

The susceptibility of both samples exhibits Curie–Weiss behaviour. The data was fitted by the relations:

$$\chi(T) = \frac{N_A \mu_{\text{eff}}^2}{3k_B} \times \frac{1}{T - \Theta}$$

where $\mu_{\text{eff}}^2 = 3\mu_{\text{Er}}^2 + \mu_{\text{Ni}}^2$ and Θ is a paramagnetic Curie temperature.

The calculations were made under assumption that $\mu_{\text{Ni}} = 0$. The results are collected in Table 1.

From value of Θ it may be deduced that the magnetic interaction is small and rather antiferromagnetic for both compounds. There are no marked changes in Θ upon hydrogen absorption. The paramagnetic moment decrease from about $10.2 \mu_B$ to about $9.0 \mu_B$. The latter value is smaller than usually adopted for Er^{3+} [7]. It is hardly possible to explain by CEF splitting.

It is of interest that paramagnetic moments of the heavy rare earth trihydrides are smaller than for pure elements and paramagnetic moments of the light rare earth trihydrides are higher than for pure elements [8]. It allows one to conclude that the value of μ_{eff} depends on antiferromagnetic coupling between the spins of 4f electrons and the magnetic moment of s and d electrons. When s and d electrons are localized they are correlated with 4f electrons and “screen” magnetic moment. The conductivity of Er_3Ni compounds is mainly due to R-element and so the metal–insulator transition may occur upon hydrogenation. In addition, the partial decomposition of samples may lead to conductivity decrease.

We suppose that in our Er_3NiH_8 s and d-electrons are localized and μ_{eff} is anomalously small because of such

“screening” 4f moments and non-magnetic behaviour of Ni sublattice. Unfortunately, data on the transport properties of R₃Ni hydrides are absent and so the investigations on electrical properties are needed.

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