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NEUTRON DIFFRACTION STUDIES OF $ErNi_{5-x}Co_x$ (x=0.68, 1.68, 2.26) ALLOYS

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ABSTRACT

$ErNi_{5-x}Co_x$ alloys were prepared by RF induction melting and analyzed using neutron powder diffraction. Rietveld analysis of the neutron diffraction data indicates that the unit cell volume increases with Co content while the *a* and *c* lattice parameters show different dependencies on the composition. The Co atoms show higher affinity for the 3g sites than for the 2c sites. The Co sublattice tends to couple antiferromagnetically to the Er sublattice. The easy magnetization direction is along the c axis.

INTRODUCTION

It was recognized[1,2,3] that the 1:12, 2:17 and the newly-discovered 3:29 phases are all derived from the well-known 1:5 ($CaCu_5$) phase, with differing degrees of transition metal pair replacement for the rare-earth atoms. Some other possible 1:5 derived phases, such as 3:22, 4:41, ..., have been predicted[2]. These facts, as well as intense interest in $LaNi_5H_x$ based batteries[4], motivated the research on the parent 1:5 phase in more detail. This paper reports the results of neutron diffraction studies on $ErNi_{5-x}Co_x$ alloys.

EXPERIMENT

Three samples of $ErNi_{5-x}Co_x$ with x equal 0.68, 1.68 and 2.26 were prepared by RF induction melting of the constituent elements of purity 99.9-99.995% in a water-cooled copper boat under flowing argon at the Graduate Center for Materials Research, University of Missouri-Rolla. The ingots were annealed at 980°C for one week. The ingots were then crushed and ground in an acetone bath. Neutron diffraction data were collected at the University of Missouri Research Reactor using the linear position sensitive detector diffractometer at room temperature on approximately 2g samples in about 24 hours. The neutron wavelength is 1.4783Å. The data were measured from 5 to 105° in 2θ. The neutron diffraction powder patterns were analyzed by the Rietveld method using the FULLPROF[8] program for multiphase refinement including magnetic structure refinement.

RESULTS AND DISCUSSIONS

From the powder neutron diffraction data refinements, all three samples were confirmed to have the $CaCu_5$-type structure. No second phase was recognized for any sample. We also saw no evidence of the structure distortion from the 1:5 structure to 1:(5+δ) or 1:(5-δ) (0<δ<2) structure which was reported previously on some other 1:5 compounds such Tb-Co compounds [5] and Y-(Co/Fe) compounds [6]. The refinement results are given in Table 1. In this Table, μ is the site magnetic moment. R-factor is the conventional crystallographic agreement factor, R_w-factor is the weighted-R-factor and R_m-factor is the magnetic-R-factor. They are defined as

$$R=\Sigma|F_{obs}-F_{cal}| \,/\, \Sigma F_{obs}$$

$$R_w=\{[\Sigma\, w_i(F_{obs}-F_{cal})^2\,] \,/\, \Sigma w_i F_{obs}^2\}$$

$$R_m=\Sigma|\, F(M)_{obs}-F(M)_{cal}\,| \,/\, \Sigma F(M)_{obs}.$$

Where F_{obs} is the observed nuclear structure factor, F_{cal} is the calculated nuclear structure factor, $F(M)_{obs}$ is the observed magnetic structure factor, $F(M)_{cal}$ is the calculated magnetic structure factor, w_i is the weight assigned to the ith reflection and is directly related to its standard deviation. Fig. 1 shows the compositional dependence of *a* and *c* lattice parameters and the *c/a* ratio in the $ErNi_{5-x}Co_x$ alloys. It was found that the *a* parameter increases linearly as the Co content increases, while *c* decreases at low Co content but increases at high Co content. The *c/a* ratio was found to decrease at low Co content, reaching a minimum at x=1.68 and then increases slightly.

Table 1. Refinement results for $ErNi_{5-x}Co_x$

parameter	x=0.68	x=1.68	x=2.26
a, Å	4.8730(1)	4.8819(1)	4.8964(1)
c, Å	3.9785(1)	3.9729(1)	3.9858(1)
c/a	0.8164	0.8138	0.8140
V, Å**3	81.815	82.003	82.755
%Co, 2c	1.2	24.0	36.0
%Co, 3g	16.8	43.2	55.9
R-factor	3.73	4.36	3.30
Rw-factor	4.82	5.50	4.30
Rm-factor	--	5.96	10.90
Chi**2	1.32	0.94	1.87
μ, Er,1a	--	0.3(2)	- 2.6(1)
μ, Co/Ni,2c	--	- 0.0(2)	0.8(1)
μ, Co/Ni,3g	--	1.2(2)	0.5(1)

Fig. 2 displays the compositional dependence of the unit cell volume in the $ErNi_{5-x}Co_x$ alloys. It can be seen that the unit cell volume increases slowly at low Co content but more rapidly at high Co content. Fig. 3 shows the percentage of Co found on the two transition metal sites in the $ErNi_{5-x}Co_x$ alloys. The dependence which would be expected for random occupancies of Co on the transition metal sites is also given in this figure. Because the 3g site has a larger Wigner-Seitz cell volume [6], the bigger Co atoms [7] show a higher affinity for the 3g sites than for the 2c sites. The volume expands significantly only after the smaller 2c site begins to fill with Co.

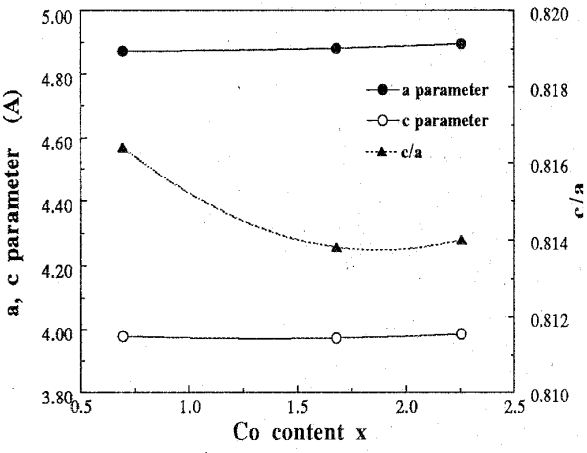

Fig. 1 The compositional dependence of the *a*, *c* parameters and the c/a in the $ErNi_{5-x}Co_x$ alloys.

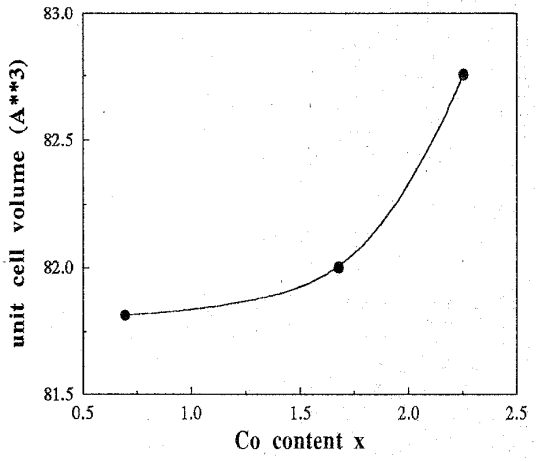

Fig. 2 The compositional dependence of the unit cell volume in the $ErNi_{5-x}Co_x$ alloys.

The Curie temperatures of these samples have not been measured. However, when testedwith a permanent magnet, we found that only the lowest x (0.68) sample is not magnetically ordered at room temperature, which is in agreement with our neutron data refinements (Table 1). This behavior can be related to the unit cell expansion and the *c/a* ratio change in this series alloys. As we can see

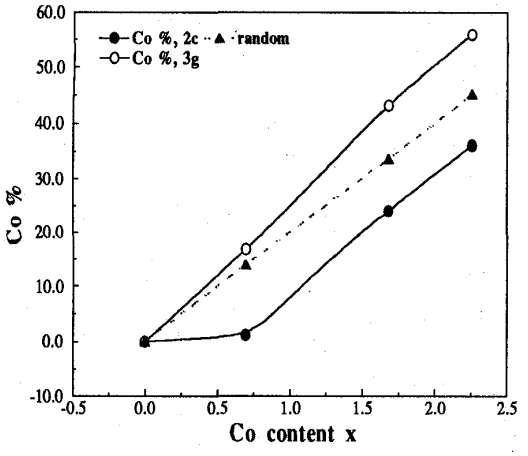

Fig. 3 The percentage Co found on the two transtion metal sites in the $ErNi_{5-x}Co_x$ alloys.

from fig. 2, the unit cell volume of $ErNi_{5-x}Co_x$ increases as the Co content x increases. It is usually accepted that the increase of the unit cell volume in the rare earth-transition metal compounds could enhance the magnetic properties of the compounds [9]. We also found (Table 1 and fig. 1) that the *c/a* ratio decreases significantly from x=0.68 to x=1.68. Because the magnetocrystalline anisotropy is somewhat related to the anisotropy of the crystal structure, the decrease in *c/a* ratio indicates an increase in the anisotropy of the crystal structure, which will have a positive effect on the magnetocrystalline anisotropy, and in turn, will enhance the magnetic properties of those compounds. The refinement results also show that for x=2.26, the transition metal sublattice couples antiferromagnetically to the Er sublattice, as we usually see for the heavy rare earth-transition metal compounds, with the site moments along the *c* axis. For x=1.68, refinement indicates that the transition metal sublattice may couple ferromagnetically to the Er sublattice, but the refined Er moment is within 2σ of zero.

CONCLUSIONS

The unit cell volume of $ErNi_{5-x}Co_x$ increases as the Co content increases while the *a* and *c* lattice parameters show different dependence on the composition. The Co atoms show higher affinity for the 3g sites than than for the 2c sites. The easy magnetization direction (for sample with x=1.68 and x=2.26) is along the *c* axis.

ACKNOWLEDGMENTS:

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