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An investigation of the Ho–Ni phase diagram

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Abstract

The phase diagram of the Ho–Ni binary system was investigated by X-ray diffraction, differential thermal analysis, optical microscopy and electron probe microanalysis techniques. The existence of eight intermediate phases has been confirmed: Ho_3Ni, Ho_3Ni_2, HoNi, $HoNi_2$, $HoNi_3$, Ho_2Ni_7, $HoNi_5$ and Ho_2Ni_{17}. The homogeneity region of the $HoNi_2$ phase extends from 65.6 to 66.7 at.% Ni. The other phases are line compounds. No appreciable solid solubility of holmium in nickel or of nickel in holmium was observed. Ho_3Ni_2 exists in two structural modifications depending on the temperature. HoNi and $HoNi_5$ melt congruently at 1060 and 1370 °C respectively. There are seven peritectic reactions and three eutectic reactions in this system.

1. Introduction

Many intermetallic compounds exist in the binary systems consisting of rare earth metals and nickel. They are of scientific and technical interest because of their hydrogen sorption and magnetic properties [1–3]. No equilibrium Ho–Ni diagram was found in the literature although most of the phase diagrams of the R–Ni binary systems have been reported [4–9]. In this investigation the phase diagram of the Ho–Ni binary system is studied.

The intermetallic compounds of the Ho–Ni system have been reported by various authors. These data have been summarized by Iandelli and Palenzona [10] and Taylor [11] and show the existence of eight intermetallic compounds: Ho_3Ni, Ho_3Ni_2, HoNi, $HoNi_2$, $HoNi_3$, Ho_2Ni_7, $HoNi_5$ and Ho_2Ni_{17}. Their crystallographic data are listed in Table 1.

2. Experimental details

The starting materials nickel and holmium used for the experiments were of 99.99% and 99.9% purity respectively. The alloy buttons, prepared in an argon atmosphere in a high frequency induction furnace, had smooth surfaces and uniform compositions. A total of 43 samples were prepared.

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TABLE 1

Crystallographic data of Ho–Ni binary system

Phase	Composition (at.% Ni)	Structure type	Space group	Lattice parameters (nm)			Reference
				a	*b*	*c*	
Ho_3Ni	25.0	Al_3Ni	*Pnma*	0.683	0.954	0.625	[11]
				0.678	0.945	0.619	This work
HoNi	50.0	FeB	*Pnma*	0.7022	0.4140	0.5435	[15]
		CrB	*Cmcm*	0.5432	0.7016	0.4143	[14]
		FeB	*Pnma*	0.7018	0.4141	0.5433	This work
$HoNi_2$	66.7	$MgCu_2$	*Fd3m*	0.7136			[16]
		$MgCu_2$	*Fd3m*	0.7132			This work
$HoNi_3$	75.0	$PuNi_3$	$R\bar{3}m$	0.4953		2.431	[19]
Ho_2Ni_7	77.78	Gd_2Co_7	$R\bar{3}m$	0.492		3.604	[21]
$HoNi_5$	83.3	$CaCu_5$	*P6/mmm*	0.488		0.396	[17]
		$CaCu_5$	*P6/mmm*	0.4873		0.3963	This work
Ho_2Ni_{17}	89.5	Th_2Ni_{17}	$P6_3/mmc$	0.8298		0.8027	[24]
		Th_2Ni_{17}	$P6_3/mmc$	0.8295		0.8018	This work

The weight loss of the alloys in the melting process was found to be less than 0.3%.

The samples were sealed in evacuated quartz tubes. Conditions of the homogenization treatment were 900 °C, 720 h for the alloys with more than 50 at.% Ni and 650 °C, 1080 h for the others. After annealing, the samples were cooled slowly to room temperature at a rate of less than 10 °C h^{-1}. The powders used for X-ray diffraction (XRD) analysis were annealed at 500 °C for 96 h in vacuum and then cooled slowly to room temperature.

The XRD analysis was carried out using a Debye–Scherrer camera of diameter 114.6 mm and a Rigaku (3015) X-ray diffractometer. Cu Kα radiation and nickel filters were used. Differential thermal analysis (DTA) was carried out in a CR-G-type analyser using tin, copper, aluminium, silver, nickel and manganese as standards. The rate of heating and cooling was controlled within 10 °C min^{-1} in an argon atmosphere.

3. Results and discussion

3.1. Equilibrium diagram

Melting points and phase transformation temperatures were obtained by DTA. The determination of the phase boundaries at room temperature was performed using the disappearing phase method based on X-ray diffraction. Eight intermetallic compounds were observed in this system. They are Ho_3Ni, Ho_3Ni_2, HoNi, $HoNi_2$, $HoNi_3$, Ho_2Ni_7, $HoNi_5$ and Ho_2Ni_{17}. The results are in good agreement with those reported in ref. 10.

DTA of the 40.0 at.% Ni specimen revealed two peaks at 760 and 970 °C. This indicates that Ho_3Ni_2 exists in two structural modifications depending on the temperature. It decomposes peritectically at 970 °C and undergoes a polymorphic transformation at 760 °C. Electron probe microanalysis (EPMA) of the alloy with 35.0 at.% Ni shows that the microstructure of the specimen is obviously of eutectic nature and consists of the Ho_3Ni and Ho_3Ni_2 phases. This is in good agreement with the results of XRD analysis.

There are seven peritectic reactions in the binary Ho–Ni system:

$$Ho + L \rightleftharpoons Ho_3Ni \quad (750\ °C) \tag{1}$$

$$HoNi + L \rightleftharpoons \alpha\text{-}Ho_3Ni_2 \quad (760\ °C) \tag{2}$$

$$HoNi + L \rightleftharpoons \beta\text{-}Ho_3Ni_2 \quad (970\ °C) \tag{3}$$

$$HoNi_3 + L \rightleftharpoons HoNi_2 \quad (1195\ °C) \tag{4}$$

$$Ho_2Ni_7 + L \rightleftharpoons HoNi_3 \quad (1285\ °C) \tag{5}$$

$$HoNi_5 + L \rightleftharpoons Ho_2Ni_7 \quad (1320\ °C) \tag{6}$$

$$HoNi_5 + L \rightleftharpoons Ho_2Ni_{17} \quad (1290\ °C) \tag{7}$$

and three eutectic reactions:

$$L \rightleftharpoons Ho_3Ni + \alpha\text{-}Ho_3Ni_2 \quad (30.0\ \text{at.\% Ni},\ 720\ °C) \tag{1}$$

$$L \rightleftharpoons HoNi + HoNi_2 \quad (54.0\ \text{at.\% Ni},\ 975\ °C) \tag{2}$$

$$L \rightleftharpoons Ni + Ho_2Ni_{17} \quad (93.0\ \text{at.\% Ni},\ 1280\ °C) \tag{3}$$

No appreciable solid solubility of nickel in holmium or of holmium in nickel was observed.

The phase diagram of the Ho–Ni binary system shown in Fig. 1 resembles that of the R–Ni (R≡Gd, Er, Dy, Y) systems [4, 5, 8].

3.2. Intermetallic compounds

3.2.1. Ho_3Ni

Lemaire and Paccard [12] reported that Ho_3Ni has the orthorhombic, Fe_3C-type structure with space group *Pnma*. Taylor [11] reported that this phase belongs to the Al_3Ni type. Our results confirmed that this compound exists and that it decomposes peritectically at 750 °C.

3.2.2. Ho_3Ni_2

The compound Ho_3Ni_2 was reported to form with the Dy_3Ni_2-type and Er_3Ni_2-type structure [10], but no crystallographic data were given. In the present work, DTA, micrographic and microprobe analysis revealed the formation of a compound (existing in two structural modifications) close in composition to 40.0 at.% Ni, *i.e.* Ho_3Ni_2. The powder pattern of the α-Ho_3Ni_2 phase at room temperature was obtained from the 40.0 at.% Ni sample which contained mainly the α-Ho_3Ni_2 phase and only a small amount of the HoNi phase. It was indexed using an analytical method on the basis of a tetragonal lattice with $a = 0.719$ nm and $c = 0.831$ nm.

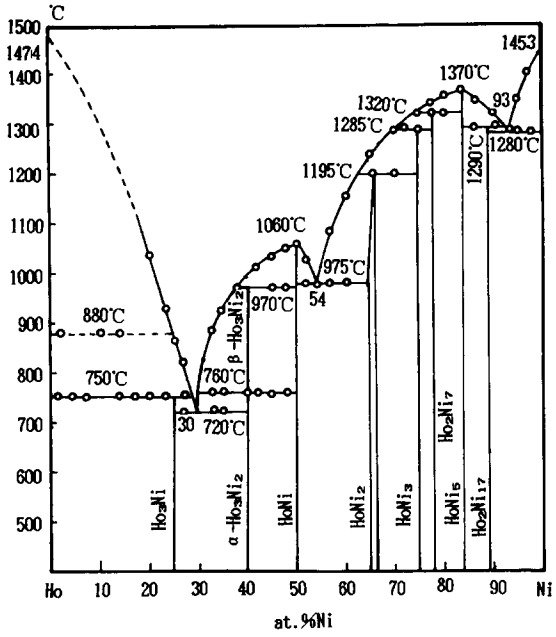

Fig. 1. Phase diagram of the Ho–Ni binary system.

3.2.3. HoNi

Walline and Wallace [13] examined the structure of HoNi by X-ray diffraction and found an orthorhombic, FeB-type structure with $a = 0.531$ nm, $b = 0.428$ nm and $c = 0.649$ nm. Abrahams *et al.* [14] reported that HoNi belongs to the CrB type, with $a = 0.5432$ nm, $b = 0.7016$ nm and $c = 0.4134$ nm. Finally, Dwight *et al.* [15] determined the crystal structure of this compound and suggested that it forms with FeB-type structure, but the lattice parameters reported were rather different from those given in ref. 13. Our results show that HoNi is a congruently melting compound with a melting point of 1060 °C.

3.2.4. $HoNi_2$

This compound was investigated by Wernick and Geller [16] and Nassau *et al.* [17] using XRD analysis. A cubic (C15) Laves phase was found. The same conclusion was obtained in ref. 18. $HoNi_2$ is formed peritectically at 1195 °C. On the basis of the change in lattice parameter, we found that this phase was of slightly variable composition and the single-phase range at room temperature was approximately between 65.6 and 66.7 at.% Ni.

3.2.5. $HoNi_3$

Dwight [19] suggested that $HoNi_3$ has the rhombohedral, $PuNi_3$-type structure on the basis of his X-ray patterns of an alloy button homogenized at 1000 °C for 3 days. This was confirmed by Buschow and Van Der Goot [20]. We found that $HoNi_3$ decomposes peritectically at 1285 °C.

3.2.6. Ho_2Ni_7

It is debatable whether an RNi_4 compound exists in the R–Ni systems in the range 77.0–80.0 at.% Ni. It was suggested that the compounds $GdNi_4$, $SmNi_4$ and $DyNi_4$ exist [5, 6, 8, 9], but no single-phase samples were obtained in these studies. Iandelli and Palenzona [10] and Taylor [11] have collected all the crystallographic data concerning the compositions and structure types of the intermetallic compounds which are formed in the R–Ni systems. Their results show that no RNi_4 compound is formed except $GdNi_4$. For most of the R–Ni systems the formation of R_2Ni_7 was confirmed. In the present work we have confirmed the existence of Ho_2Ni_7, but no $HoNi_4$ was found. Ho_2Ni_7 decomposes peritectically at 1320 °C. It has the rhombohedral, Gd_2Co_7-type structure [21]. Buschow and Van Der Goot obtained the same conclusion.

3.2.7. $HoNi_5$

Nassau *et al.* [17] determined the structure of $HoNi_5$ by XRD and found a hexagonal, $CaCu_5$-type structure. This was confirmed by Nesbitt *et al.* [22] and Buschow [23]. We confirmed that $HoNi_5$ melts congruently at 1370 °C and its lattice parameters are in agreement with those given in ref. 23.

3.2.8. Ho_2Ni_{17}

Buschow [24] has investigated intermetallic compounds of the form R_2Ni_{17}, R_2Co_{17} and R_2Fe_{17} and found that the structure of these compounds depends on the size of the rare earth component and on the temperature. The structure of Ho_2Ni_{17} is hexagonal, Th_2Ni_{17} type. Its lattice parameters are similar to those of Ho_2Co_{17} and Ho_2Fe_{17}. Laforest *et al.* [25] reported the same structure with $a = 0.829$ nm and $c = 0.802$ nm. In the present investigation we found that Ho_2Ni_{17} decomposes peritectically at 1290 °C.

4. Conclusions

The phase diagram of the Ho–Ni system has the following features.

(1) Eight intermediate phases exist: Ho_3Ni, Ho_3Ni_2, HoNi, $HoNi_2$, $HoNi_3$, Ho_2Ni_7, $HoNi_5$ and Ho_2Ni_{17}. HoNi and $HoNi_5$ melt congruently at 1060 and 1370 °C respectively. The homogeneity region of the $HoNi_2$ phase at room temperature extends from 65.6 to 66.7 at.% Ni. The polymorphic transformation of Ho_3Ni_2 occurs at 760 °C.

(2) There are seven peritectic reactions and three eutectic reactions. Eutectics are formed between Ho_3Ni and α-Ho_3Ni_2 at 720 °C (30.0 at.% Ni), between HoNi and $HoNi_2$ at 975 °C (54.0 at.% Ni) and between Ho_2Ni_{17} and nickel at 1280 °C (93.0 at.% Ni). Ho_3Ni, α-Ho_3Ni_2, β-Ho_3Ni_2, $HoNi_2$, $HoNi_3$, Ho_2Ni_7 and Ho_2Ni_{17} decompose peritectically at 750, 760, 970, 1195, 1285, 1320 and 1290 °C respectively.

(3) No appreciable solid solubility of holmium in nickel or of nickel in holmium was observed.

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