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# Experimental study of the isothermal section of the Ho–Fe–Cr system at 873 K

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ABSTRACT

The isothermal section of the Ho–Fe–Cr ternary system was investigated by means of X-ray powder diffraction (XRD), metallography and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). The ternary compound $HoFe_{12-x}Cr_x$ ($x = 2$) was characterized and the homogeneity range of the various ternary solutions was studied. It crystallizes with $ThMn_{12}$-type structure, space group $I4/mmm$ and unit parameters $a = 0.8406$ nm and $c = 0.4756$ nm. The homogeneity range in $HoFe_{12-x}Cr_x$ was determined as $x = 1.9$–$3.6$, i.e. 14.6–27.7 at.% Cr. The maximum solid solubilities of Cr in Fe, $Ho_2Fe_{17}$, $Ho_6Fe_{23}$, $HoFe_3$ and $HoFe_2$ are about 28.0 at.%, 4.0 at.%, 13.0 at. %, 3.0 at.% and 11.0 at.%, respectively.



## 1. Introduction

The properties of ternary rare earth iron-rich compounds of the type $RFe_{12-x}M_x$ and $R_3Fe_{29-x}M_x$ (R = Y, Nd, Sm, Gd, Tb, Dy, Ho, Er and Tm; M = Ti, V, Cr, Mo and Si) have been studied intensively [1–6]. Those studies have been stimulated for the possibility of using some of these materials for high performance permanent magnet applications. To further understand the formation, solubility limit and phase relations in the R–Fe–M ternary alloy systems, an investigation on the phase diagram of the relevant systems is useful. In this paper, the experimentally determined isothermal section of the Ho–Fe–Cr ternary system at 873 K is presented.

The three relevant binary systems have been assessed and collected in Refs. [7–10], together with the available crystallographic data and stability temperature ranges of all the intermediate phases. There are four compounds in the Ho–Fe system, namely $Ho_2Fe_{17}$ ($Th_2Ni_{17}$-type structure, space group $P6_3/mmc$), $Ho_6Fe_{23}$ ($Th_6Mn_{23}$-type structure, space group $Fm\bar{3}m$), $HoFe_3$ ($NbBe_3$-type structure, space group $R\bar{3}m$) and $HoFe_2$ ($MgCu_2$-type structure, space group $Fd\bar{3}m$). The lowest liquids temperature in the Ho–Fe system is 1148 K. There is one compound FeCr in the Fe–Cr binary system at 821–1097 K. No binary compound was found in the Ho–Cr system. One ternary compound $HoFe_{12-x}M_x$ has been reported in Refs. [1–3]. The compound $HoFe_{12-x}M_x$ crystallizes with $ThMn_{12}$-type structure, space group $I4/mmm$, in which there are three nonequivalent crystal positions (8i, 8f and 8j) of Mn and one (2a) for Th. Like the $Th_2Ni_{17}$-(2:17), the $ThMn_{12}$-type (1:12) can be derived from the $CaCu_5$-type structure by replacement of a fraction of the R sites in the $CaCu_5$ structure by pairs of Fe atoms (dumb-bells).

## 2. Experimental

Samples weighing 2.5 g were prepared by arc-melting in an arc furnace under high purity argon. Ho (99.95%), Fe (99.9%) and Cr (99.9%) were used as the starting materials. The samples were melted several times in order to achieve a full homogenization. The samples in the Ho–Fe–Cr ternary system with different compositions were prepared. Weight loss of the samples during arc-melting is less than 1%. Each sample was wrapped into tantalum foil, encapsulated in an evacuated quartz tube and annealed at 1073 K for 30 days, followed by lowering at a rate of 10 K/h to 873 K and keeping at the temperature for 15 days, then quenched into an ice–water mixture.

Powder X-ray diffraction (XRD) data were collected at room temperature on a Rigaku D/Max 2500 PC X-ray diffractometer with Cu Kα and graphite monochromator operated at 40 kV, 250 mA. The experimental XRD patterns were analyzed using JADE 5.0 [11] software by comparing them with the powder diffraction files and the calculated ones obtained by the powder Cell program [12]. Microstructures of selected samples were examined by electron microscope (SEM) using backscatter electron (BSE) imaging. SEM investigation was carried out in a JSM-5610LV SEM equipped with energy dispersive X-ray spectroscopy (EDS) for phase identification and composition determination. From all these results, the phase relations in the Ho–Fe–Cr system were determined.

## 3. Results and discussion

### 3.1. Phase analysis

By analyzing and comparing the X-ray diffraction patterns and metallographs of the samples, we have confirmed the existence of five binary compounds in the three relevant binary systems, i.e. $Ho_2Fe_{17}$, $Ho_6Fe_{23}$, $HoFe_3$, $HoFe_2$ and FeCr, which were in good

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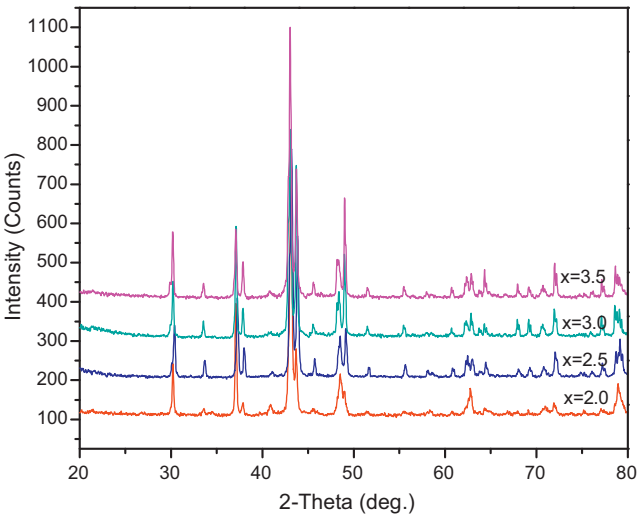


**Fig. 1.** XRD patterns of $HoFe_{12-x}Cr_x$ with different $x$.

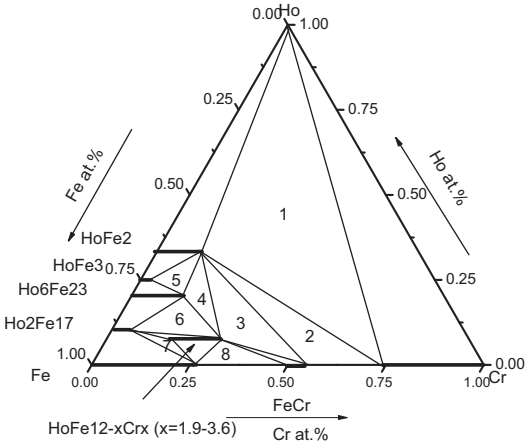


**Fig. 3.** Isothermal section of the Ho–Fe–Cr system at 873 K.

agreement with the binary phase diagrams in Refs. [7,8]. The corresponding crystal data were in agreement with those given in Refs. [9,10]. The existence of the binary compounds $HoFe_5$, which were not given in the Ho–Fe phase diagram in Refs. [7,8], was reported in Refs. [13]. The XRD patterns for the sample with composition of $HoFe_5$ (in at.%) consist of the patterns of $Ho_2Fe_{17}$ and $Ho_6Fe_{23}$ two phases. Therefore, the compound $HoFe_5$ should not existed in this isothermal section.

De Mooij et al. [1–6] reported the existence of two ternary compounds, namely $R_x(T,M)_y$ of the type 1:12 and 3:29. For the $Ho(Fe,Cr)_{12}$ compound, we prepared the alloy samples with composition of 7.69 at.% Ho, 61.5–80.0 at.% Fe and 12.31–30.81 at.% Cr. The XRD pattern of $HoFe_{12-x}Cr_x$ ($x = 2.0$, 2.5, 3.0 and 3.5) is in agreement with the data on the calculated XRD pattern of $HoFe_{10}Cr_2$, as shown in Fig. 1. The compound $HoFe_{10}Cr_2$ exhibits a linear homogeneity range along the line of 7.69 at.% Ho. Fig. 2 shows the variation of the lattice parameters $a$ and $c$ on x in $HoFe_{12-x}Cr_x$. In the single phase region, the lattice parameters increase linearly with increasing Cr content. Combining the phase-disappearing method and the lattice parameter method, the homogeneity range of the single-phase $HoFe_{12-x}Cr_x$ compound was determined to be $1.9 \le x \le 3.6$, i.e. 14.6–27.7 at.% Cr. The lattice parameters for $HoFe_{12-x}Cr_x$ with $1.9 \le x \le 3.6$ were obtained as $a = 0.8406$–$0.8464$ nm and $c = 0.4755$–$0.4772$ nm in this work. And the compound of $Ho_3Fe_{29-x}Cr_x$ is found by homogenization at 1293–1373 °C for 120 h [3–6]. In our work, we prepared some alloy samples with composition of $Ho_3Fe_{29-x}Cr_x$ ($0.5 \le x \le 4.0$). The results show that the XRD patterns of the samples with composition of $Ho_3Fe_{29-x}Cr_x$ ($0.5 \le x < 2.3$) consist of two phases. i.e. $Ho_2Fe_{17}$ and Fe, and the XRD patterns of the samples with composition of $Ho_3Fe_{29-x}Cr_x$ ($2.3 < x \le 4.0$) consist of three phases. i.e. $Ho_2Fe_{17}$, $HoFe_{10}Cr_2$ and Fe. So the compound $Ho_3Fe_{29-x}Cr_x$ is considered as a high temperature phase and below a certain temperature it decomposes into the combination of other phases. In another word, the compound $Ho_3(Fe,Cr)_{29}$ does not exist as a stable phase at 873 K, and therefore is not presented in the isothermal section.

### 3.2. Solid solubility

The homogeneity ranges of the single-phase regions were determined by X-ray diffraction technique using the phase disappearing and lattice parameter method or on the basis of the movement of the XRD pattern of the phase in the sample with different compositions. The lattice parameters of compounds Fe, $Ho_2Fe_{17-x}Cr_x$, $Ho_6Fe_{23-x}Cr_x$, $HoFe_{3-x}Cr_x$ and $HoFe_{3-x}Cr_x$ were calculated and refined from X-ray diffraction patterns by using the computer Software Jade 5.0 and the least square method to determine the solubilities of Cr in these compounds. The results showed that the solid solubilities of Cr in Fe, $Ho_2Fe_{17}$, $Ho_6Fe_{23}$, $HoFe_3$ and $HoFe_2$ were about 28.0, 4.0, 13.0, 3.0 and 11.0 at.% Cr, respectively. The solubility of Fe in Cr was about 26.0 at.%. The FeCr compound has

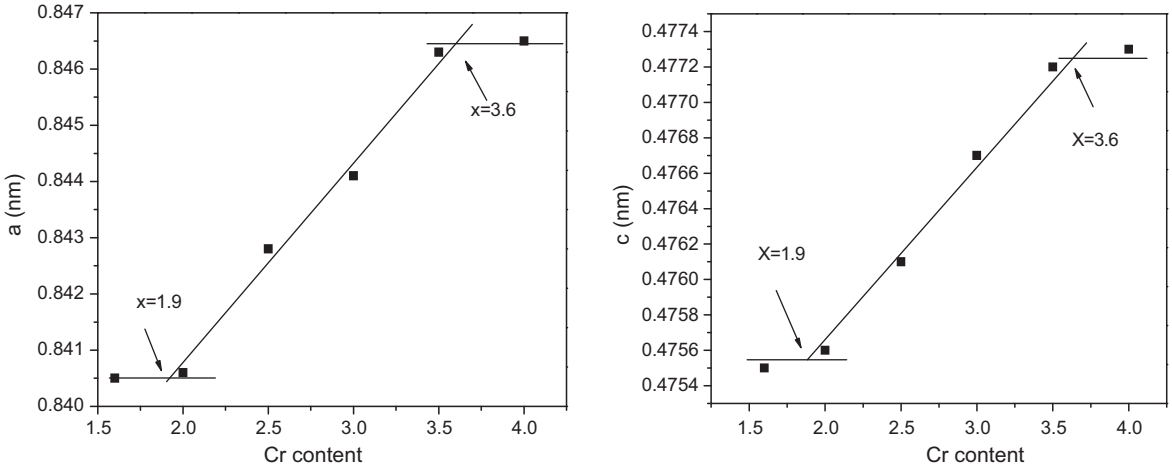


**Fig. 2.** Dependence of the lattice parameters of the $HoFe_{12-x}Cr_x$ compounds on the Cr ($x$).

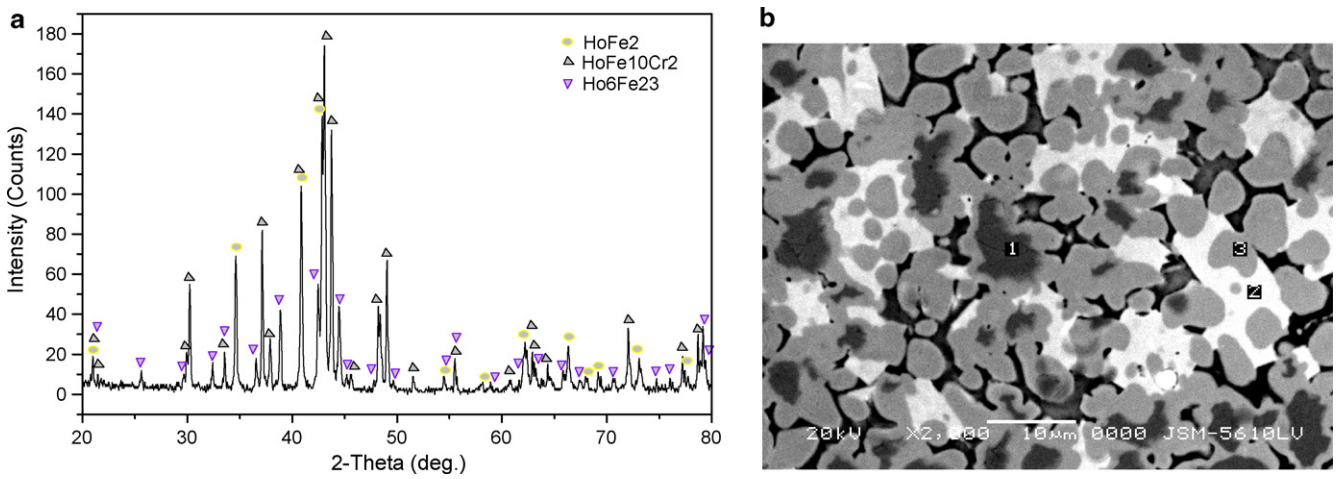


**Fig. 4.** (a) X-ray diffraction (XRD) pattern of alloy Ho0.20Fe0.62Cr0.18 situated in the three-phase region no. 4. (b) Micrograph (2000×) of sample Ho0.20Fe0.62Cr0.18, the 1 area is the phase $Ho_6Fe_{23}$, the 2 area is $HoFe_2$ and the 3 area is $HoFe_{10}Cr_2$.

**Table 1**
XRD and EDS results with the composition of Ho0.20Fe0.62Cr0.18 (in at.%) at 873 K.

| Alloy | Alloy composition (at.%) | | | Phase identified by EDS (at.%) | | | | Phase identified by XRD | Notes |
|---|---|---|---|---|---|---|---|---|---|
| | Ho | Fe | Cr | Ho | Fe | Cr | Phase | | |
| Ho0.20Fe0.62Cr0.18 | 0.20 | 0.62 | 0.18 | 21.75 | 65.22 | 13.02 | $Ho_6Fe_{23}$ | $Ho_6Fe_{23}$ | The 1 area in Fig. 4(b) |
| | | | | 33.13 | 57.02 | 9.85 | $HoFe_2$ | $HoFe_2$ | The 2 area in Fig. 4(b) |
| | | | | 7.85 | 64.26 | 27.89 | $HoFe_{10}Cr_2$ | $HoFe_{10}Cr_2$ | The 3 area in Fig. 4(b) |

a narrow homogeneity range of 50–54 at.% Cr in the binary Fe–Cr line and dissolves up to 1.0 at.% Ho.

### 3.3. Isothermal section at 873 K

From the results of XRD analysis, metallography and SEM/EDS of the alloy samples, we have identified the phase components of each sample. According to the results, the isothermal section of the Ho–Fe–Cr ternary system was determined (shown in Fig. 3). It consists of 9 single-phase regions, 16 two-phase regions and 8 three-phase regions. As shown in Fig. 4(a), the sample with the composition of Ho0.20Fe0.62Cr0.18 (in at.%) is characterized to contain three phases, namely $Ho_6Fe_{23}$, $HoFe_2$ and $HoFe_{12-x}Cr_x$, which were substantiated by the SEM/EDX microstructure and composition measurement (Fig. 4(b)). And the XRD and EDS results of the sample Ho0.20Fe0.62Cr0.18 are presented in Table 1.

## 4. Conclusion

The phase equilibria of the Ho–Fe–Cr system at 873 K had been systematically investigated by using XRD analysis, metallography and SEM/EDS composition measurement. It consists of 9 single-phase regions, 16 two-phase regions and 8 three-phase regions. The ternary phase $HoFe_{12-x}Cr_x$ (space group $I4/mmm$) was confirmed in Ho–Fe–Cr ternary system. The variation of lattice parameters with the composition was studied for the ternary solid solution phase $HoFe_{12-x}Cr_x$ and the homogeneity range was determined to be $HoFe_{12-x}Cr_x$ ($x = 1.9–3.6$). And the solid solubilities of Cr in Fe, $Ho_2Fe_{17}$, $Ho_6Fe_{23}$, $HoFe_3$ and $HoFe_2$ were about 28.0, 4.0, 13.0, 3.0 and 11.0 at.% Cr, respectively.

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