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The isothermal section phase diagram of the Sm-Fe-Ni ternary system at 800 °C

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ABSTRACT

Isothermal section at 800 °C of the ternary Sm-Fe-Ni system was established in the whole concentration range, by means of powder X-ray diffraction and scanning electron microscopyenergy dispersive X-ray spectroscopy (SEM/EDS). All measured compositions and unit-cell refinements were performed at room temperature from quenched samples annealed at 800 °C for one week. Ten binary compounds and $\alpha(Fe_{1-x}$ Nix) (Im−3m-W type structure) have been confirmed.

The $SmNi_{5-x}Fe_x$ ($P6/mmm$-$CaCu_5$ type structure) was found to have a solubility range from 0 to 50 at% Fe. The maximum solubility at 800 °C of Fe in $Sm_2Ni_{7-x}Fe_x$ ($P6_3/mmc$-Ce_2Ni_7 type structure), $SmNi_{3-x}Fe_x$ ($R\overline{3}m$-$PuNi_3$ type structure) and $SmNi_{2-x}Fe_x$ ($Fd-3m$-$MgCu_2$ type structure) are about 2.7 at% Fe, 40 at% Fe and 6.66 at% Fe, respectively. The homogeneity domain of $Sm_2Fe_{17-x}Ni_x$ ($R\overline{3}m$-Th_2 Zn_{17} type structure) ranges from 0 to 21.05 at% Ni. The XRD and the SEM/EDS analysis show that there are no solubility of Fe in the Sm_2 Ni_{17}, Sm_5Ni_{19} and SmNi. The same analysis show that there are no solubility of Ni in the $SmFe_2$ and $SmFe_3$ and no ternary compound was found in all ternary alloy samples. The addition of Ni in the Sm-Fe system did not stabilize the $ThMn_{12}$ type structure.

1. Introduction

The present paper is a part of systematic investigation of the Sm-Fe-Ni system, which we are studying with the purpose to find compounds with important magnetic properties. The ternary phase diagram is an important basis for this materials research and materials application. The assessment of the isothermal section is a valuable tool to improve the synthetic route of high purity samples, especially those not yet magnetically characterized. For the RE-Fe-Ni ternary phase diagrams, the phase relations have not been investigated systematically until now, except a partially isothermal section at 25 °C with a Ho contents up to 33.3 at% of the Ho-Fe-Ni system [1].

In the literature, we found tow partial La-Fe-Ni isothermal section, studied by H. Zhou et al. [2] at Ni and La-low concentration annealing at 550 °C and at 400 °C, respectively. The partial isothermal section of the phase diagram of the ternary system Nd-Fe-Ni (Nd < 35%) was determined at 510 °C [3]. Recently, Sh. Pan et al. have investigated the isothermal section of Pr-Fe-Ni at 500 °C [4]. Within the limited SmFeNi ternary compositions synthesized in the literature, there are two pseudo-binaries systems studied, exhibiting interesting magnetic properties. The first is the $Sm_2Fe_{17-x}Ni_x$ ($x = 1.7$; 3.4) [5]. The second is the $SmNi_{5-x}Fe_x$ ($x = 0.2$; 0.5 and 1) [6].

Moreover, the Sm-Fe-Ni ternary system has not been studied until now, for this reason we have decided to investigate the phase diagram of this system at 800 °C. The choosing of this annealing temperature is in order to assure a good atomic diffusion for the formation of potentially novel phases, to explore the solid solutions extension and their magnetic and magnetocaloric properties. Among the desired objectives, is to determine the solid phase equilibrium at this temperature and finally to provide the phase relationship in this system. We present, in this work, the results of the systematic investigation of the isothermal section at 800 °C of the Sm-Fe-Ni phase diagram, in the whole concentration range.

2. Experimental

Each sample with a total weight of 0.5 g starting from the pure

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Table 1
Sm-Fe-Ni unary and binary boundary systems: solid phases stables at 800 °C.

Phase composition	Structure type	Space group	Lattice parameters (Å)			References
			a	b	c	
$Sm_2 Ni_{17}$	Th_2Ni_{17}	$P6_3/mmc$	8.341 (4)		8.062 (4)	[11]
$Sm_2 Ni_{17}$	Th_2Ni_{17}	$P6_3/mmc$	8.4122 (2)		7.9960 (3)	This work
$SmNi_5$	$CaCu_5$	$P6/mmm$	4.924 (5)		3.974 (5)	[12]
$SmNi_5$	$CaCu_5$	$P6/mmm$	4.9203 (1)		3.9662 (1)	This work
$Sm_5 Ni_{19}$	Ce_5Co_{19}	$R\bar{3}m$	5.000		49.0000	[13]
$Sm_5 Ni_{19}$	Ce_5Co_{19}	$R\bar{3}m$	4.9966 (2)		49.1011 (3)	This work
$Sm_2 Ni_7$	Ce_2Ni_7	$P6_3/mmc$	4.969		24.35	[14]
$Sm_2 Ni_7$	Ce_2Ni_7	$P6_3/mmc$	4.9690 (2)		24.3500 (3)	This work
$SmNi_3$	$PuNi_3$	$R\bar{3}m$	5.00		24.59	[15]
$SmNi_3$	$PuNi_3$	$R\bar{3}m$	5.07 (1)		24.74 (2)	This work
$SmNi_2$	$MgCu_2$	$Fd\bar{3}m$	7.2326 (2)			[16]
$SmNi_2$	$MgCu_2$	$Fd\bar{3}m$	7.2368 (3)			This work
SmNi	TlI	$Cmcm$	3.776 (1)	10.358 (1)	4.291 (1)	[17]
SmNi	TlI	$Cmcm$	3.7760 (2)	10.3580 (1)	4.2910 (2)	This work
$SmFe_2$	$MgCu_2$	$Fd\bar{3}m$	7.415 (4)			[18]
$SmFe_2$	$MgCu_2$	$Fd\bar{3}m$	7.4208 (2)			This work
$SmFe_3$	$PuNi_3$	$R\bar{3}m$	5.180		24 0.789	[19]
$SmFe_3$	$PuNi_3$	$R\bar{3}m$	5.1815 (2)		25.015 (1)	This work
Sm_2Fe_{17}	$Th_2 Zn_{17}$	$R\bar{3}m$	8.57		12.44	[20]
Sm_2Fe_{17}	$Th_2 Zn_{17}$	$R\bar{3}m$	8.5796 (3)		12.4624 (2)	This work
α(FeNi)	W	$Im-3m$	2.8704			[21]
α($Fe_{0.6}Ni_{0.4}$)	W	$Im-3m$	2.8777 (2)			This work
Fe	W	$Im-3m$	2.4855			[22]
Ni	Cu	$Fd\bar{3}m$	2.5116			[23]
Sm	Sm	$R\bar{3}m$	3.611 (4)		26.22 (3)	[24]

components (Sm: 99.99%, Fe: 99.99%, and Ni: 99.99%) was prepared by arc melting on a water-cooled copper tray with a non-consumable tungsten electrode under the protection of a pure argon atmosphere. The samples were turned over and re-melted four times to ensure adequately homogeneity.

A total of 140 alloys buttons were prepared. Only those samples with less than 1 wt.% weight losses were used for phase analysis. During melting process, a piece of zirconium was used as an oxygen getter. The bulk was wrapped in a tantalum sheet. As-cast samples were sealed in vacuum quartz tubes and annealed at temperature 800 °C for one week in order to reach a good homogenization and to improve the atomic diffusion kinetics.

Phase analysis was carried out using the Powder-cell program package [7] and/or Rietveld refinement [8–10] on an X-ray powder diffraction pattern recorded on a Bruker D8 diffractometer (monochromatic Cu Kα radiation $\lambda = 1.5406$ Å) with data collected by 0.015°step width for 13.5 s over a 2θ range from 20°to 80°.

The microstructure of the samples was studied on polished surfaces using a Merlin Scanning Electron Microscope (SEM) equipped with Silicon Drift Detector (SDD)-X-Max 50 from Oxford Instrument employed for the elemental analysis of the various phases. Elemental compositions were obtained by averaging the values of at least three EDS analyzed zones, from different regions of the sample. An estimated deviation from the mean value is about 0.5 at%. The agreement between the targeted and the sample compositions was checked by measuring a large zone of the sample surface.

3. Results and discussion

3.1. Phase binary analysis and solid solubility

From the analysis of X-ray diffraction patterns of the samples, we have confirmed the existence of ten binary phases and α(FeNi) solid solution in the boundary systems Sm-Fe, Sm-Ni and Fe-Ni. In the SmNi system, seven compounds were reported in literature, namely, Sm_2Ni_{17} (Th_2Ni_{17} type structure), $SmNi_5$ ($CaCu_5$-type structure), $Sm_5 Ni_{19}$ ($Ce_5 Co_{19}$-type structure), Sm_2Ni_7 (Ce_2Ni_7-type structure), $SmNi_3$ ($PuNi_3$-type structure), $SmNi_2$ ($MgCu_2$-type structure) and SmNi (TlI type structure) [11–24].

Three binaries phases in the Sm-Fe section, namely, Sm_2Fe_{17} (Th_2Zn_{17} type structure), $SmFe_2$ ($MgCu_2$ type structure) and $SmFe_3$ ($PuNi_3$ type structure) and the solid solution α(Fe_xNi_{1-x}) with $0 < x < 0.95$ (W type structure) in the Fe-Ni section. Data can be found in literature concerning the intermetallic phases. These intermetallic compounds and their structural description are listed in Table 1 and confirmed by our results. Rietveld analysis for Sm_2Fe_{17}, α($Fe_{0.6}Ni_{0.4}$) and $SmNi_3$ phases shown in Fig. 1, as examples, demonstrate the obtaining of pure single phases in the three binary sections. Fe and Ni can substitute each other because they have the same dimension but this behavior is limited and only certain single binary regions present extension in the ternary Sm-Fe-Ni system. Five binaries extensions in the Sm-Fe-Ni ternary diagram have been observed for Sm_2Fe_{17}, $SmNi_5$, Sm_2Ni_7, $SmNi_3$ and $SmNi_2$ phases. There is no extension for the $SmFe_3$, $SmFe_2$, Sm_2Ni_{17}, Sm_5Ni_{19} and SmNi.

By using microprobe analysis, Rietveld refinement and disappearing-phase method, the solid solutions, the homogeneity ranges and the maximum solid solubility of the Fe/Ni in the binary Sm-Fe and Sm-Ni compounds were determined.

The 2/17 binary phase exists in both the Sm-Fe and Sm-Ni boundary systems with a rhombohedral Th_2Zn_{17} structure-R-3m and a hexagonal Th_2Ni_{17} structure-$P6_3/mmc$, respectively. In the Fe region, the Th_2Zn_{17}-type structure is stable within a significantly large homogeneity range for the solid solution $Sm_2 Fe_{17-x}Ni_x$. The limit composition of this solid solution is pointed to the chemical formula $Sm_2Fe_{13}Ni_4$. This was also observed by BO-Ping et al. [5], while they estimated the extension of the solid solution of $Sm_2 Fe_{17-x}Ni_x$ at $x = 3.4$. In the literature, the maximum extension of $SmNi_{5-x}Fe_x$ ($P6/mmm$) is about 16.66 at% of Fe ($SmNi_4Fe_1$) [6], in