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Structure and the Magnetic Properties of $RFe_{6-x}Si_x$ ($R = Y, Gd, Dy, Ho$) Alloys

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Abstract

In this work we report our first efforts to prepare and characterize a series of intermetallic compounds of the type $RFe_{4.48}Si_{1.52}$ ($R = Y, Gd, Ho$), and $DyFe_{6-x}Si_x$ ($x = 1, 1.2, 1.4$). From X-ray analysis it was found that the compounds are mixed phases, mainly of the $R(Fe, Si)_{17}$, (Rhombohedral Th_2Zn_{12} or Hexagonal Th_2Ni_{17} structure type), the RFe_4Si_2 , ($ZrFe_4Si_2$ structure type), the $RFeSi$ ($PbClF$ structure type) and the RFe_2Si_2 ($CeAl_2Ga_2$ structure type). From magnetization data and Curie temperature measurements we attempted to further characterize these phases and preliminary data are presented in this work.

Keywords: Intermetallic compounds, Rare earth, Structure, Curie temperature.

Introduction

The modern permanent magnets are based in intermetallic compounds of rare earth and transition metals and especially in Sm-Co and Nd-Fe-B systems. The sintered Sm-Co magnets dominated the market in the beginning of the seventies and today are integrated in multiphase alloys of $SmCo_5$ (1:5) and Sm_2Co_{17} (2:17) compounds. The Sm-Co magnets were displaced by the Nd-Fe-B system, which was discovered in 1983 [1,2]. The discovery of the $Nd_2Fe_{14}B$ (2:14:1), a compound with exceptional magnetic properties, has dramatically increased the application field of permanent magnets. The quest for novel magnetic materials suitable for the fabrication of novel permanent magnets is based on studies of the ternary R-T-X systems, where R is a rare-earth, T is a transition metal, and X is a post-transition element. At first, crystal data and a discussion of the crystal chemistry of ternary rare-earth intermetallics were made by Parthé and Chabot [3]. An updated compilation of ternary phase equilibria and crystal chemistry in ternary rare-earth systems was presented by Rogl [4], Gschneidner and al [5], etc and lately by S. Gupta and K. Suresh [6]. The total number of known ternary phases increases every year.

The iron-rich regions of the R-Fe-T system ($R = \text{rare earth}$, $T = \text{transition metal}$) have been intensively studied with the aim to investigate for new magnetic materials with hard magnetic

properties even better than those of $SmCo_5$. Numerous studies have been obtained in rare earth - transition metals metastable phases for new magnetic materials development [7-10]. An approach how to find new phases is following the Stadelmaier scheme [11], i.e., taking $m RT_5$ unit cells and replacing $n R$ atoms by T-T pairs one can get intermetallic series described by the general formula $R_{m-n}T_{5m+2n}$. The other way to find new phases or to improve the old ones is by partial substitution of Fe atoms with the magnetic Co or even by non magnetic atoms, like a post-transition metal Ga and Bi or a metalloid like Si [12]. The last approach is based on the Pettifor theory, a semi-empirical approach that has been successfully employed for the stabilization of the $RFe_{12-x}T_x$ [13]. Taking in to account that a few works on the system R-Fe-Si have been reported and these concern the magnetic phase diagram for Gd [14], the phase diagram of Dy [15], the structure of RFe_4Si_2 for Dy and Tm [16] and the magnetic properties for Ho [17], we undertaken a systematic study of this system. In this work we study the off-stoichiometric composition $RFe_{4.48}Si_{1.52}$ ($R = Y, Gd, Ho, Lu$), and $DyFe_{6-x}Si_x$ ($x = 1, 1.2, 1.4$) presented firstly in the early 80s [2] and advanced lastly by Bardin and al [16], in order to evaluate its structural and magnetic properties as a novel permanent magnet.

Experimental

R-Fe-Si ingots were prepared by arc-melting elemental constituents of high purity (99.9%), with the starting composition $RFe_{4.48}Si_{1.52}$ ($R = Y, Gd, Ho$), and $DyFe_{6-x}Si_x$ ($x = 1, 1.2, 1.4$) subsequently followed by annealing (wrapped in tantalum foil) in vacuum at 973 K for thirty days and then fast quenching in water. X-ray diffraction (XRD) data of powder samples were obtained with the SIEMENS D500 diffractometer using Cu-K α radiation, diffracted beam monochromator and the following combination of slits 1.0°/1.0°/1.0° as aperture diaphragms, 0.15° and 0.25° as detector and diffracted beam monochromator diaphragms respectively. Thermomagnetic measurements (TMA) were carried out in a range 300-1200 K using DTA/TGM Perkin Elmer device, applying a magnetic field of 150 Oe and heating rate of 5°C/min under Ar flow; the apparent magnetic force was measured, therefore the magnetic units are arbitrary given. The minimum of the first derivative of the magnetization curve was used for the

determination of T_c . Differential thermal analysis curves (DTA) were recorded simultaneously with TMA curves, providing data on phase transformations or other transformations that have been occurred. Magnetization isothermal measurements at 10 and 300 K were recorded by VSM and Squid magnetometer. Zero field cooled (ZFC) and field cooled (FC) measurements are performed under a magnetic field of 200 Oe using a Squid magnetometer. The morphology and composition of samples were determined using scanning electron microscopy (SEM) and dispersive X-ray microanalyses (EDX).

Results and discussions

Structural data analysis of the XRD diffraction patterns shows that all the studied compounds are multiphase. All prepared samples contain different phases in variable composition. These phases are: the silicon doped R(Fe,Si)₁₇ [18, 19] (Rhombohedral Th₂Zn₁₂ or Hexagonal Th₂Ni₁₇ structure type), the RFe₄Si₂ [16] (ZrFe₄Si₂ structure type), the RFeSi [20] (PbClF structure type) and the RFe₂Si₂ [21] (CeAl₂Ga₂ structure type).

In Table 1 the phase composition, the structural parameters and the weight percentage for each one phase and for all studied samples are given. In Figure 1 the XRD diagrams for all studied samples are shown. In Figure 2 the Rietveld diagram for sample DyFe₅Si₁ is also given. The crystallographic analysis was performed using the Fullprof Rietveld analysis Program [22].

Figure 1: XRD diagrams for all studied samples. With the (*), (^) (+) and (-) symbols the main Bragg peaks for the corresponding ReFe₄Si₂, Re(Fe,Si)₁₇ (rhombohedral or hexagonal), ReFeSi and the ReFe₂Si₂ are indicated

Figure 2: XRD diagram for the DyFe₅Si₁ sample refined by the Rietveld method. (o) experimental points, the continuous line

bottom indicate the position of the Bragg peaks for each phase. The first, second and third series of bars correspond to the 2:17, DyFe₄Si₂ and DyFeSi phases. The continuous line at the bottom is the difference between the experimental intensity values and the calculated one

In Table 2 the Curie temperatures and the magnetization values for all studied samples at 10 K and at 300 K (RT) are given. Representative curves of magnetization variation versus temperature are shown in the Figure 3. The thermomagnetic data (TMA) curves for samples containing Ho, Dy, Gd and Y respectively, present almost one magnetic transition in the interval 298-1150 K.

Figure 3: Magnetizations versus temperature curves for HoFe_{4.48}Si_{1.52}, GdFe_{4.48}Si_{1.52}, DyFe₅Si₁, R(FeSi)₆ and YFe_{4.48}Si_{1.5}

ZFC and FC measurements (Figure 4) for the Gd containing sample show a magnetic transition at 139 K (Figure 4) which correspond to the phase GdFeSi, in agreement with ref. [23]. It is worthy to mention that the GdFe₂Si₂ phase is antiferromagnetic (AFM) with Neel point at 8.4 K [24, 25], therefore it was not detected in the TMA curve. The respective curves (ZFC and FC) for Dy samples barely show a magnetic transition at 117 K (Figure 5, point 2) when the temperature decreases from RT to 10 K, which corresponds to the phase DyFeSi, near the value 110 K as have been observed in ref. [23]. The DyFeSi phase is one of seven possible phases given in the Dy-Fe-Si phase diagram [15].

Figure 4: ZFC and FC curves of HoFe_{4.48}Si_{1.52} and GdFe_{4.48}Si_{1.52} sample

The respective ZFC and FC curves (Figure 4) for Ho does not show any magnetic transition which could correspond to the phase HoFeSi, although, XRD analysis indicates that this phase is present in the system in small quantity. Taking in consideration

Table 1: Crystallographic data, a, b, c (Å), Space Group (S.G) and the volume cell V (Å³) of samples according the Rietveld analysis.

Sample	Phase	a(Å)	c(Å)	V(Å ³)	Weight	S.G
GdFe _{4.48} Si _{1.52}	2:17R	8.4767(5)	12.4260(8)	773.23(8)	65%	R -3 m
	RFe ₂ Si ₂	3.9331(3)	9.9930(9)	154.58(2)	30%	I 4/m m m
	RFeSi	4.0008(5)	6.843(2)	109.53(3)	5%	P 4/n m m
DyFe ₅ Si ₁	2:17	8.4443(4)	12.3677(8)	763.75(7)	38%	R -3 m
	RFe ₄ Si ₂	7.1751(3)	3.7852(2)	194.87(1)	56%	P 42/m n m
	RFeSi	3.9639(5)	6.752(2)	106.10(3)	6%	P 4/n m m
DyFe _{4.8} Si _{1.2}	2:17	8.4559(9)	12.449(2)	771.0(2)	58%	R -3 m
	RFe ₄ Si ₂	7.1727(9)	3.7822(6)	194.60(5)	33%	P 42/m n m
	RFeSi	3.9802(6)	6.753(2)	106.99(4)	10%	P 4/n m m
DyFe _{4.6} Si _{1.4}	2:17	8.4559(9)	12.449(2)	771.0(2)	58%	R -3 m
	RFe ₄ Si ₂	7.1727(9)	3.7822(6)	194.60(5)	33%	P 42/m n m
	RFeSi	3.9791(7)	6.754(2)	106.94(4)	9%	P 4/n m m
HoFe _{4.48} Si _{1.52}	2:17	8.4378(4)	8.2257(5)	507.18(5)	47.2%	P 6 ₃ /m m c
	RFe ₄ Si ₂	7.1589(4)	3.7852(2)	193.99(2)	44.4%	P 42/m n m
	RFeSi	3.9413(5)	6.801(2)	105.64(3)	8.4%	P 4/n m m
YFe _{4.48} Si _{1.52}	2:17	8.4505(5)	12.3596(5)	764.4(1)	49%	R -3 m
	RFe ₄ Si ₂	7.1800(5)	3.7856(3)	195.2(2)	47%	P 42/m n m
	RFeSi	3.959(1)	6.759(3)	105.9(1)	4%	P 4/n m m

that the HoFeSi phase has a ferromagnetic transition at 29 K and an antiferromagnetic at 20 K [6], this would explain why it is not found a transition in the narrow range of 20-29 K, except a slope-change of curve at ~20 K (point 2, Figure 4). The increase of Si amount in the DyFe_{6-x}Si_x (x=1, 1.2, 1.4) samples, has little effect in the Curie temperature, as is shown in the Table 2.

From X-Ray data, all samples presented in Table1 contain three phases. All samples contain 2:17 and RFeSi phases. As has been already mentioned and discussed in [23] the RFeSi (R= Gd, Dy) compounds exhibit ferromagnetic ordering of the R sublattices at

Table 2: Magnetic properties of R(FeSi)₆ samples (Curie temperatures and magnetization at 10 and 300 K)

Alloys	Curie Temperature (K)	Magnetization (Am ² /kg)	
		10 K	300 K
GdFe _{4.48} Si _{1.52}	T _{c1} =139, T _{c2} =544.8 (5)	59.7	45.8
DyFe ₅ Si ₁	T _c =483(5)	51.8	29.5
DyFe _{4.8} Si _{1.2}	T _c =485 (5)	52.9	44.3
DyFe _{4.6} Si _{1.4}	T _c =487 (5)	52.87	35.2
HoFe _{4.48} Si _{1.52}	T _c =475 (5)	49.96	34.1
YFe _{4.48} Si _{1.52}	T _c =457(5)	70.03	55.9

low temperatures, having their Curie temperature below the RT. Therefore we didn't expect a magnetic transition of these phases in the temperature range of 298-1200 K. So, for Gd the observed two T_c values [Table2], as has been discussed, are attributed to

2:17 at 544.8 K in agreement with ref. [18] and GdFeSi at 139 K. For the other samples, from XRD analysis it was found the third phase is the RFe₄Si₂ and it is contained in considerable quantity (30-60% weight). Although investigation on magnetic properties of Fe-based RFe₄Si₂ compounds was until now limited, a investigation for RFe₄Si₂ (R=Y, Lu) system was communicate in two conferences, which states that all compounds with a trivalent rare earth exhibit clear evidence for AFM Fe-order associated with a structural distortion, with Neel temperatures in the range from 30 to 75 K [26] and has not a magnetic transition in the temperature range of 298 K to 1200 K. In this view it is understandable the presence of only one Curie point in TMA curves mentioned above (Figure 3), and this comes from 2:17 phase. The Curie temperature for samples shown in the Figure 3 reaches a maximum of 544.8K for the Gd-sample as is expected for Si doped R₂Fe₁₇ phases [18].

The FC curve for Gd is quasi-reversible with the respective ZFC curve, while in the case of Dy and Ho the FC and ZFC curves start to diverge at 250 and 125 K respectively. It can be supposed that the curvature change of ZFC curve at point 1 as the temperature increases (Figure 4) for Ho or at point 1 (Figure 5) for Dy sample, is due to the Neel's transition of RFe₂Si₄ type phase [26, 27]. However, more TMA measurements at different field and low temperature, as well as measurements of magnetic susceptibility and other methods are required to explain the overall contribution of two FM phases and the other AFM phase. Only domain wall motion of FM phases could not explain the characteristics of ZFC and FC curves.

Figure 5: ZFC and FC curves of DyFe₅Si₁

Differential thermo analysis curves for RFe_{4.48}Si_{1.52} show no phase transition in the interval temperature 300-1150 K when the temperature increases (Figure 6). Therefore, the only magnetic transition observed on TMA curves (Figure 3) in this range was not caused by any phase transition. The temperature-dependent magnetic measurements (TMA) are quite reversible in the range 300-900 K; a representative curve is given in the Figure 7 for Gd. The respective DTA curve is shown also at the same figure where the only small transition is due to the ferromagnetic-paramagnetic transition at ~544 K.

Figure 6: DTA curves for R-Fe-Si (R=Y, Gd, D, Ho)

Figure 7: TMA and DTA curves for GdFe_{4.52}Si_{1.48}

Representative, demagnetization curves measured at 10 K and at RT are shown for Gd and Ho (Figure 8, 9). Magnetization values for all samples are given in Table2 at 10 K and at RT. The room temperature magnetization of samples increases from 29.5 for Dy to 55.9 Am²/kg for Y-sample, while the magnetization at 10 K reach a value of 70.03 Am²/kg for Y. The Ho samples have a coercive field H_c of 3.2 kOe at 10 K (Figure 7).

Figure 8: Demagnetization curves at 10 and 300 K for GdFe_{4.48}Si_{1.52}-sample

Figure 9: Demagnetization curves at 10 and 300 K for HoFe_{4.48}Si_{1.52}-sample

Finally from the EDAX analysis it was found that all the studied alloys had compositions very close to the nominal one, i.e. ~RFe_{4.5}Si_{1.5}. Figure 10a shows the SEM image of GdFe_{4.48}Si_{1.52}-sample. No variation of stoichiometry was detected in different large areas (with magnification x 5000), indicating a homogeneous sample and no phase precipitation. The EDAX analysis by spotting in a smaller area (with magnification x 40000) gives that the dominant phase is the 2:17 in agreement with XRD analysis. Grains with composition close to Gd_{10.77}Fe_{62.26}Si_{26.97} or Gd₂Fe_{11.4}Si₅ corresponds to the doped Gd₂(Fe_{1-x}Si_x)_{16.4} (x=0.304) (see Figure 10b). EDAX analysis on polished samples, which are in progress, could give information for two other phases.

Figure 10a: SEM image of cross-sections for a piece of GdFe_{4.48}Si_{1.52}-sample (x5000)

Figure 10b: SEM image of cross-sections for a piece of GdFe_{4.48}Si_{1.52}-sample (x40.000)

Conclusion

The research on the intermetallic silicon based ternary system R(FeSi)₆ (R =Y, Gd, Ho), and DyFe_{6-x}Si_x (x=1, 1.2, 1.4) shows that mixture samples are produced. All studied samples contain different known phases in variable composition like the silicon doped R(Fe,Si)₁₇ (Rhombohedral Th₂Zn₁₂ or hexagonal Th₂Ni₁₇ structure type), the RFe₄Si₂, (ZrFe₄Si₂ structure type), the RFeSi (PbClF structure type) and the RFe₂Si₂ (CeAl₂Ga₂ structure type). The different magnetic behavior of the different phases at different temperature ranges gives the possibility to interpret the experimental observations. The room temperature magnetization of samples increases from 29.5 for Dy to 55.9 Am²/kg for Y-sample, while the magnetization at 10 K reach a maximum value of 70.03 Am²/kg for Y. The Ho sample has a coercive field H_c of 3.2 kOe at 10 K. Work is continuing in order to eliminate the co-existing phases and fully characterize them.

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