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Journal of Alloys and Compounds 275–277 (1998) 6–9

Journal of ALLOYS AND COMPOUNDS

On synthesis and magnetic properties of $YFe_{10}Si_2Z_x$ (Z=H and N)

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Abstract

A single phase of the ternary intermetallic compound, $YFe_{10}Si_2$, has been synthesized by a reduction–diffusion process with superfine iron metal, Y_2O_3 and silicon as the starting materials. All of the compounds, $YFe_{10}Si_2$, $YFe_{10}Si_2H_{0.3}$ and $YFe_{10}Si_2N_{0.5}$, show the easy magnetization *c*-axis. For the nitrogen interstitial compound, the Curie temperature increases from 540 to 673 K and the anisotropy field decreases from 27 to 23 KOe. © 1998 Elsevier Science S.A.

Keywords: Reduction-diffusion; $YFe_{10}Si_2$; Magnetic property

1. Introduction

Recently, it was discovered that the introduction of interstitial nitrogen or carbon atoms into the ternary intermetallic compounds *Ln*(Fe,M)$_{12}$ may dramatically improve their intrinsic magnetic property [1], which stimulated a worldwide study on these materials. Regarding to the phase diagrams of rare earth and iron, the binary phases of *Ln*Fe$_{12}$ do not exist. However, this compound can be stabilized by partial substitution of early transition metals or some main group elements, such as Ti, V, Cr, Mo. W or Si, to the iron sites [2,3]. All of these compounds crystallize in the tetragonal $ThMn_{12}$ structure, but the occupation preference in three iron sites (8f, 8i and 8j) varies from the transition metal to the main group elements. For the silicon substituted *Ln*Fe$_{10}$Si$_2$, Buschow [3,4] and Stefanski and Wazeciono [5] have extensively studied the structure and magnetic properties and indicated that the silicon atoms prefer to occupy the 8j and 8f positions in the structure. It is known that the iron at the 8i site has the largest moment for the $ThMn_{12}$ structure, so the *Ln*Fe$_{10}$Si$_2$ shows a higher saturation magnetization and Curie temperature than other substituted analogue. However, the properties of the nitrogen interstitial compound *Ln*Fe$_{10}$Si$_2$N$_x$ has not been well established. This may be largely due to the fact that only the heavy later rare earth elements R=Y, Gd, Tb, Dy, Ho, Er and Tm can form this compound and, unfortunately, these heavy rare earth compounds do not have application potential as permanent magnetic materials. Nevertheless, the study of the structure and magnetic properties of the interstitial compounds *Ln*Fe$_{10}$Si$_2$ may provide some insights into these materials. Furthermore we have recently synthesized *Ln*Fe$_{10}$Mo$_2$ [6] and *Ln*$_2$Fe$_{17}$ [7] by a reduction–diffusion reaction, with the superfine precursors as starting materials. The intermetallic materials synthesized with this method have been proved to possess promising particle sizes and crystalline integrity. In this paper we describe the synthesis of the $YFe_{10}Si_2$ by this route, as well as some magnetic properties of the nitrogen and hydrogen interstitial compounds.

2. Experimental

Y_2O_3 and $Fe(NO_3)_3 \cdot 9H_2O$ were used as starting materials for the synthesis of superfine oxide precursors by a polymer–network gel method [8,9]. The polymer gel obtained was first treated at 250°C for 3 h in oxygen atmosphere to remove all of the organic and other volatile components. The temperature was, then, increased to 500°C to convert the gel into oxide. A preliminary reduction treatment at 700°C under Ar–H_2 for 2 h, was applied to reduce Fe_2O_3 to the metallic states. The starting materials, i.e. superfine iron powder, Y_2O_3, silicon and calcium hydride, were mixed in a glove box and transferred into a stainless steel crucible. For compensation of yttrium loss during the reaction, about 2% excess Y_2O_3 was used. The starting mixture was first heated at 950°C for 2 h under purified argon, then at 1100°C for 2.5 h. After being quenched with water, the product was washed with dilute acetic acid and subsequently with water several times to remove the calcium and calcium oxide.

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PII: S0925-8388(98)00263-1

The charging of $YFe_{10}Si_2$ with hydrogen and nitrogen gas was carried out in a closed thermopiezic system. The hydrogen or nitrogen contents were calculated from pressure variation before and after charging. X-ray powder diffraction was measured with a Rigaku D/max-2000 diffractometer. The temperature dependence of the magnetization was measured with the Faraday method. The Curie temperatures T_c were determined from σ^2–T plots by extrapolating σ^2 to zero. The magnetization curves were measured with a CF-1 extracting sample magnetometer.

3. Results and discussion

Buschow [3] has examined several intermetallic compounds, $LnFe_{12-x}T_x$ for T=Ti, Mo, Cr, V, Si and, found that the range of the solid solution for T=Ti and Mo is very small, whereas for the T=V and Cr the solid solutions of $LnFe_{12-x}T_x$ can exist in a wide range from $x=1$ to $x=4$. We have examined the range of the solid solution of $YFe_{12-x}Si_x$ from $x=1$–4 for the samples prepared with the reduction–diffusion process, and found that only $YFe_{10}Si_2$ can be obtained as a single phase. The samples with other compositions always contain considerable amounts of α-Fe and other binary compounds, suggesting that the solid solution of $YFe_{12-x}Si_x$ is very limited.

The reduction–diffusion process with superfine precursors as the starting materials is one of the promising synthetical routes for the rare earth intermetallic compounds, by which single phases could be conveniently obtained at relatively lower temperature. However, the surface of the alloys obtained in this way may be contaminated by oxides. This is particularly true when the products have been washed with dilute acetic acid and water. The contamination of the surface prevents the alloys from further interstitial reaction. Therefore, all of the alloys obtained from a reduction–diffusion process have to be treated with hydrogen in order to increase the reactivity of the samples. Generally, the rare earth transition metal compounds could react with hydrogen at relatively lower temperature. The formed hydrides may further decompose to the binary rare earth hydride if the temperature goes higher. The activated treatment of the samples should be performed at a temperature which is slightly lower than the decomposition temperature of the hydrides. From our experiences, the activated treatment in hydrogen can significantly reduce the temperature of the nitrogenation reaction.

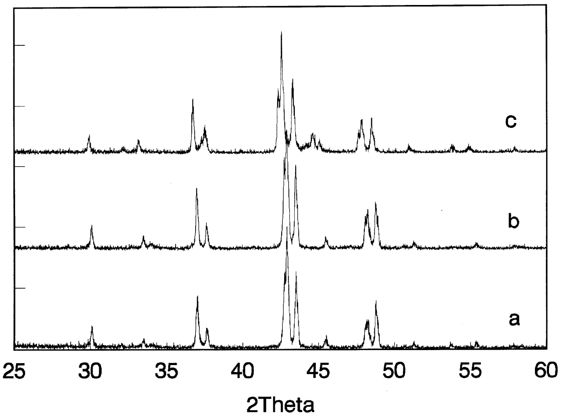

Fig. 1. X-ray powder diffraction patterns of the $YFe_{10}Si_2Z_x$ compounds: (a) $YFe_{10}Si_2$, (b) $YFe_{10}Si_2H_{0.3}$ and (c) $YFe_{10}Si_2N_{0.5}$.

Fig. 1 shows the X-ray diffraction patterns of the $YFe_{10}Si_2$, as well as hydrogen and nitrogen interstitial compounds. $YFe_{10}Si_2$ crystallizes in tetragonal $ThMn_{12}$ structure, with the lattice constants $a=8.439$ Å, $c=4.746$ Å. The $YFe_{10}Si_2$ sample prepared with the reduction–diffusion process is almost a pure single phase. After the nitrogenation, considerable amounts of the $YFe_{10}Si_2$ were decomposed resulting in the formation of α-Fe in the products. We have tried to eliminate α-Fe by carrying out the nitrogenation reaction at lower temperatures, but this was not successful. The hydrogen content determined from pressure variation during the activation treatment is about $x=0.3$ for the underlying sample. While the obtained nitrogen content is about 0.5. The trial of increasing the nitrogen content always leads to the further decomposition of $YFe_{10}Si_2N_x$. It seems that the silicon-substituted compound, $YFe_{10}Si_2$, unlike the other transition-substituted compounds, is not very stable against the nitrogenation reaction. The reason for this instability may relate to the smaller unit volume of the $YFe_{10}Si_2$, so further introduction of the nitrogen atoms in this compound may expand the structure too much, resulting in the collapse of the structure. Table 1 lists the lattice constants refined with FINAX for these samples. From Table 1 one can see that the unit volume of the hydrogen interstitial compound does not change very much. However, lattice constants do change anisotropically due to the insertion of the hydrogen atoms, i.e. the lattice expands in the *a*–*b* plan, and shrinks in the *c* direction. Furthermore significant increase of the unit volume (2.4%) has been obtained for the nitrogen interstitial compound $YFe_{10}Si_2N_{0.5}$.

The temperature dependence of the saturation magnetization of the $YFe_{10}Si_2Z_x$ samples is plotted in Fig. 2. The introduction of the hydrogen atoms in $YFe_{10}Si_2$ compound does not change the Curie temperature, but slightly increases the saturation magnetization at room temperature. Meanwhile a significant increase of the Curie temperature is observed (400°C) for the $YFe_{10}Si_2N_{0.5}$. From Fig. 2 the presence of α-Fe can be clearly seen. After subtracting the contribution of the α-Fe, the saturation magnetization of the $YFe_{10}Si_2N_{0.5}$ at room temperature only shows a slight increase as compared with that of $YFe_{10}Si_2$.

X-ray diffraction patterns of the aligned powder samples are shown in Fig. 3. It has been known that the easy magnetization direction is along the *c*-axis for the

Table 1
Structure and magnetic properties of the $YFe_{10}Si_2Z_x$

Sample	a (Å)	c (Å)	V ($Å^3$)	V/V_0 (%)	T_c (K)	M_s (emu/g)
$YFe_{10}Si_2$	8.439(2)	4.764(1)	339.2(1)		540	98.2
$YFe_{10}Si_2H_{0.3}$	8.488(1)	4.746(1)	341.9(1)	0.8	536	113.0
$YFe_{10}Si_2N_{0.5}$	8.523(1)	4.782(1)	347.3(1)	2.4	673	102.0

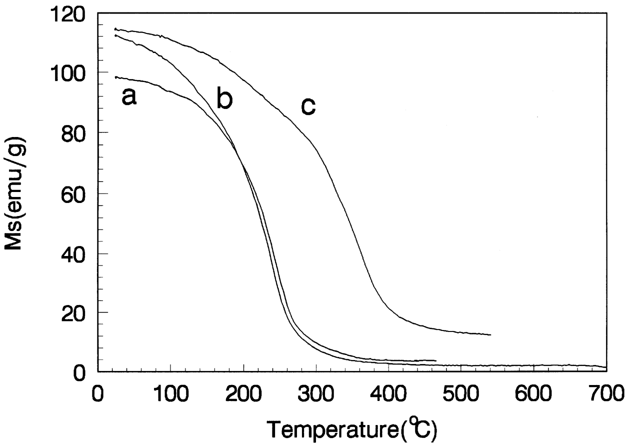

Fig. 2. Temperature dependence of the magnetization of the $YFe_{10}Si_2Z_x$ compounds: (a) $YFe_{10}Si_2$, (b) $YFe_{10}Si_2H_{0.3}$ and (c) $YFe_{10}Si_2N_{0.5}$.

$YFe_{10}Si_2$. The magnetization direction does not change for the hydrogen and nitrogen interstitial compounds, so that the (001) reflection of all $YFe_{10}Si_2Z_x$ samples becomes dominant for the samples aligned in magnetic field. Stefanski and Wazeciono [5] have measured the magnetization curve of the $YFe_{10}Si_2$ at room temperature and found that the anisotropy field is about 27 KOe for the $YFe_{10}Si_2$. To find out the influence of the interstitial nitrogen atoms on the anisotropy field for this material, we have performed the measurement of the magnetization curves for the nitrogen interstitial compound $YFe_{10}Si_2N_{0.5}$. Fig. 4 shows the magnetization curves of the oriented $YFe_{10}Si_2N_{0.5}$ samples parallel and perpendicular to the magnetic field at 1.5 K and room temperature. The anisotropy fields H_A obtained from the intersection of the magnetization curves are about 23 KOe at room temperature and about 40 KOe at 1.5 K. The yttrium is a non-magnetic element, so the magnetic anisotropy of the $YFe_{10}Si_2Z_x$ compounds depends mainly on the sublattice of the iron atoms. This results in a relative lower anisotropy field than the other magnetic rare earth compound. Interestingly, the insertion of the nitrogen atoms in $YFe_{10}Si_2$ reduces the anisotropy field from 27 to 23 KOe. Moreover the higher anisotropy at lower temperature suggests that the iron atoms at different sites may contribute to the bulk anisotropy in the some direction.

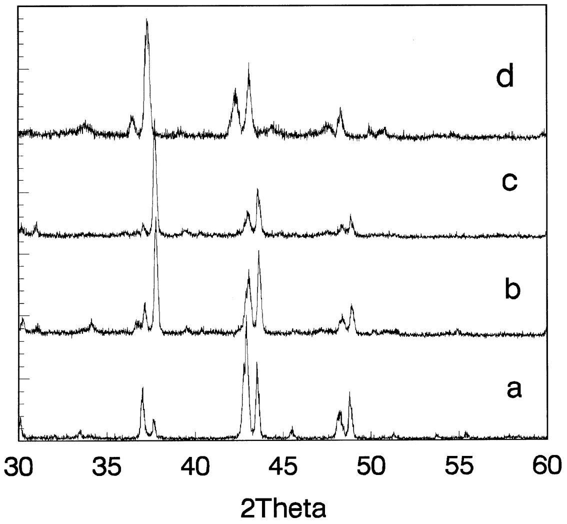

Fig. 3. X-ray powder diffraction patterns of aligned $YFe_{10}Si_2Z_x$ samples: (a) $YFe_{10}Si_2$, (b) aligned $YFe_{10}Si_2$, (c) aligned $YFe_{10}Si_2H_{0.3}$, (d) aligned $YFe_{10}Si_2N_{0.5}$.

Acknowledgements

This project (No. 296527701) is supported by the National Science Foundation of China.

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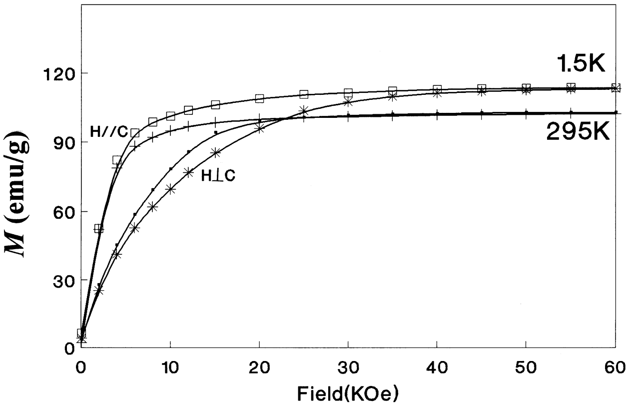

Fig. 4. Magnetization curves of the $YFe_{10}Si_2N_{0.5}$ at 1.5 K and room temperature.

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