ThMn₁₂-type structure and uniaxial magnetic anisotropy in ZrFe₁₀Si₂ and Zr_{1-x}Ce_xFe₁₀Si₂ alloys

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Arc-melted (Zr_{1-x}Ce_x)_{1.1}Fe₁₀Si₂ alloys were found to crystallize into a pure or nearly pure ThMn₁₂ structure for $0 \leq x \leq 0.6$. At room temperature, the alloys exhibit ferromagnetism with an uniaxial magnetocrystalline anisotropy. Metastable ZrFe₁₀Si₂ compound possesses room-temperature saturation magnetization of at least 11 kG and Curie temperature of 325 °C; both properties slightly decrease when Ce is being substituted for Zr. The anisotropy field, on the other hand, increases with the Ce from 16.9 to 24 kOe at $x = 0.6$. These intrinsic magnetic characteristics as well as the absence of expensive rare-earths and Co make the compounds interesting for development of low-cost permanent magnets. At $0.7 \leq x \leq 0.8$, the ThMn₁₂ structure was found to co-exist with the Th₂Ni₁₇-type structure, whereas the equilibrium Th₂Zn₁₇-type structure was observed only at $x = 1$. Prepared under similar conditions Hf_{1.1}Fe₁₀Si₂ alloy does not crystallize into the ThMn₁₂-type structure.

Keywords: intermetallics; permanent magnets; crystal structure; anisotropy

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1. Introduction

Tetragonal $R(\text{Fe},\text{M})_{12}$ compounds with R standing for rare earth elements have long been of interest as permanent magnet materials [1]. In recent years, concerns about supply of the raw rare earths motivated intensifying search for the rare-earth-lean and rare-earth-free hard magnetic materials which would not necessarily surpass the $\text{Nd}_2\text{Fe}_{14}\text{B}$, but nevertheless could "bridge" the performance gap presently existing between the ferrite and Nd-Fe-B magnets [2]. The $R(\text{Fe},\text{M})_{12}$ compounds are already "rare-earth-lean" compared to the R-Fe-B and R-Co permanent magnet materials. To fully explore this advantage, a particular attention has been recently paid to synthesis of these compounds with the most abundant and least "critical" rare earth, cerium [3-5]. Although the mixed-valent state of the Ce atoms is known to have an unfavorable effect on the Curie temperature T_C of the Ce-Fe compounds, Zhou *et al.* [4] reported an unexpectedly high T_C of the 1:12 structure (the ThMn_{12} type) in $\text{CeFe}_{10}\text{Si}_2$ - together with a uniaxial, if not very strong, magnetocrystalline anisotropy. This important observation was made for the multiphase alloy prepared via melt spinning, a non-equilibrium technique. *Ab initio* calculations by Drebov *et al.* [6] had led to a tentative conclusion that the tetragonal $\text{CeFe}_{10}\text{Si}_2$ structure is stable. At the same time, the available experimental data [7-12] confirm stability of the tetragonal $R(\text{Fe},\text{Si})_{12}$ structures only for the rare-earth and actinide R having an atomic radius equal or smaller than 0.181 nm (Sc, Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu and U). Sakurada *et al.* [13] proposed a model according to which stability of the 1:12 structure in the $R(\text{Fe},\text{Si})_{12}$ alloys depends on the *average* radius of the atoms in the R sites (the 2a sites); they demonstrated stabilization of this structure when part of the larger Nd atoms in the $\text{RFe}_{10}\text{Si}_2$ was replaced with the smaller Zr atoms. The 1:12-structure-stabilizing effect of Zr is evident even in the case of the Sm atoms (the "borderline" atomic radius of 0.181 nm): unlike the $\text{SmFe}_{10}\text{Si}_2$, cast $\text{Sm}_{0.7}\text{Zr}_{0.3}\text{Fe}_{10}\text{Si}_2$ alloys were found to crystalize directly into the 1:12 structure [14]. In fact, Zr and Hf are the only non-rare-earth and non-actinide R known to form the tetragonal $R(\text{Fe},\text{M})_{12}$ compounds. However, the two such compounds reported to date, $\text{ZrFe}_{12-\delta}\text{Al}_\delta$ and $\text{HfFe}_{12-\delta}\text{Al}_\delta$, exist at large δ values (6 - 7) and they do not exhibit a room-temperature ferromagnetism [15]. As for the Zr-Fe-Si system, the available phase diagrams [16,17] feature no equilibrium 1:12 structure at 800 °C, 1000 °C and 1100 °C.

The work presented in this report began as an attempt to study Zr substitution for Ce in the $\text{CeFe}_{10}\text{Si}_2$ alloys. To the authors' surprise, the 1:12 structure was easily obtained not only in

the quaternary alloys, but also in the ternary $\text{ZrFe}_{10}\text{Si}_2$. Thus, the magnetic properties of the new $\text{Zr}_{1-x}\text{Ce}_x\text{Fe}_{10}\text{Si}_2$ series of the 1:12 compounds are reported together with discussion of their stability and application prospects.

2. Experiment

Alloys with the nominal compositions $(\text{Zr}_{1-x}\text{Ce}_x)_{8.4}\text{Fe}_{76.2}\text{Si}_{15.4}$ with $x = 0, 0.2, 0.4, 0.6, 0.7, 0.8, 1.0$ and also a $\text{Hf}_{8.4}\text{Fe}_{76.2}\text{Si}_{15.4}$ alloy were prepared as 2.5 g ingots by arc-melting the pure components on a water-cooled copper hearth. Selected alloys were additionally annealed at 1000 °C (in argon-filled quartz capsules; quenched in water). Ingot surfaces, likely to contain impurities, were machined off prior to characterization. Densities of the alloys were determined with the water-immersion techniques (the Archimedes method). Powders for X-ray diffraction (XRD) and room-temperature magnetic measurements were prepared with a hand mortar. Oriented powders were immobilized with epoxy resin (for the XRD) or with paraffin wax (for the magnetic measurements) under a magnetic field of 16 – 19 kOe. XRD determination of the crystal phases was performed with a Rigaku Ultima IV diffractometer at the $\text{CuK}\alpha$ radiation. The XRD results were analyzed with Powder Cell software [18]. Scanning electron microscopy (SEM; a JEOL JSM-6335F instrument) and energy-dispersive spectrometry (EDS; an IXRF Systems instrument) of polished unetched alloy samples were employed to clarify the nature of minority phases. The magnetic measurements were done with a Quantum Design VersaLab vibrating sample magnetometer. Thermomagnetic data were obtained at a field of 5 kOe for small (≈ 10 mg) ingot pieces. Room-temperature magnetization-vs-field data for the oriented powders were corrected for self-demagnetization using demagnetization factors determined for similarly prepared Fe powders.

3. Results

XRD spectra of the as-made alloys are presented in Fig. 1. The ternary $\text{ZrFe}_{10}\text{Si}_2$ sample features the 1:12 structure coexisting with 3 - 5 vol.% of the cubic $\text{Zr}_6\text{Fe}_{16}\text{Si}_7$ structure (the $\text{Mg}_6\text{Cu}_{16}\text{Si}_7$ type, space group $\text{Fm}\bar{3}\text{m}$, $a = 1.157$ nm). The latter phase appears as lighter inclusions in the backscattered electrons SEM image shown in Fig. 2(a). The 1:12 becomes the only detectable structure in the Ce-substituted $(\text{Zr}_{1-x}\text{Ce}_x)_{1.1}\text{Fe}_{10}\text{Si}_2$ alloys when $0.2 \leq x \leq 0.6$. Further Ce substitution results in emergence of $(\text{Ce,Zr})_2(\text{Fe,Si})_{17}$ and bcc Fe-Si phases. It is

interesting that in none of the alloys the 1:12 structure was found to be present alongside the rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type structure (2:17R) which is the equilibrium structure of the $\text{Ce}_2(\text{Fe},\text{Si})_{17}$ compounds [19]. At $0.7 \leq x \leq 0.8$, the $(\text{Ce},\text{Zr})_2(\text{Fe},\text{Si})_{17}$ phase in the arc-melted $(\text{Zr}_{1-x}\text{Ce}_x)_{1.1}\text{Fe}_{10}\text{Si}_2$ alloys adopts the hexagonal $\text{Th}_2\text{Ni}_{17}$ -type structure (2:17H) with the lattice parameters $a \approx 0.84$ nm and $c \approx 0.83$ nm. Only the Zr-free $\text{Ce}_{1.1}\text{Fe}_{10}\text{Si}_2$ alloy featured the 2:17R as the majority phase – and it showed no traces of the 1:12 structure. The quantitative XRD estimates for the phases observed on the Ce side of the alloy series are summarized in Table I; these results are corroborated by the SEM-EDS data.

Although there exist $\text{Hf}(\text{Fe},\text{Al})_{12}$ compounds isotypical to the $\text{Zr}(\text{Fe},\text{Al})_{12}$ [15], the arc-melted $\text{Hf}_{1.1}\text{Fe}_{10}\text{Si}_2$ alloy did not contain the 1:12 structure. Instead, the alloy was found to crystallize into a mixture of the bcc Fe-Si phase (60 - 70 vol. %) and the Laves phase Hf-Fe-Si (the MgZn_2 -type, $\text{P6}_3/\text{mmc}$) with $a \approx 0.486$ nm and $c \approx 0.791$ nm.

Thermomagnetic scans, some of which are presented in Fig. 3(a), confirm that the 1:12 phase is the only ferromagnetic phase present in the $(\text{Zr}_{1-x}\text{Ce}_x)_{1.1}\text{Fe}_{10}\text{Si}_2$ alloys with $0 \leq x \leq 0.6$. Its Curie temperature T_C decreases with the Ce substitution from 325 °C to 285 °C. At $x = 0.7$, the magnetization of the 1:12 phase is significantly diluted by two other ferromagnetic phases, 2:17H exhibiting a T_C of around 200 °C and Fe-Si ($T_C > 450$ °C).

The easy magnetization direction (EMD) of the tetragonal 1:12 structure in the arc-melted $(\text{Zr}_{1-x}\text{Ce}_x)_{1.1}\text{Fe}_{10}\text{Si}_2$ alloys was determined by comparing the XRD spectra recorded for randomly oriented and field-oriented powder samples (data 1 and 2 in Fig. 4). The very strong enhancement of the [002] reflections at the expense the $[hkl]$ with $h, k \neq 0$ conclusively demonstrates that the magnetocrystalline anisotropy of the $\text{Zr}_{1-x}\text{Ce}_x\text{Fe}_{10}\text{Si}_2$ compounds is uniaxial. Magnetization curves measured parallel and perpendicular to the [001] EMD [the examples are shown in Fig. 3(b)] were used to determine room-temperature values of the anisotropy field H_a ; the H_a monotonically increases with the x reaching 24 kOe at $x = 0.6$. The saturation magnetization values $4\pi M_s$ were found by extrapolating the $M(1/H^2)$ data. The value determined this way for the $\text{Zr}_{1.1}\text{Fe}_{10}\text{Si}_2$ alloy, 11.0 kG, can only be considered a low $4\pi M_s$ estimate for the 1:12 $\text{ZrFe}_{10}\text{Si}_2$ compound, because it does not account for several percent of the non-magnetic $\text{Zr}_6\text{Fe}_{16}\text{Si}_7$ phase present in this alloy. The crystallographic and magnetic data for $\text{Zr}_{1-x}\text{Ce}_x\text{Fe}_{10}\text{Si}_2$ compounds are summarized in Table II.

Based on the data for the Zr-Fe-Si equilibria [16,17], one can state with sufficient confidence that the observed $\text{ZrFe}_{10}\text{Si}_2$ compound is metastable. There is no, however, such certainty regarding the Ce-substituted compounds. Moreover, even *relative* stability during a heat treatment may be of interest for materials with application prospects. Therefore, two of the $(\text{Zr}_{1-x}\text{Ce}_x)_{1.1}\text{Fe}_{10}\text{Si}_2$ alloys, $x = 0$ and $x = 0.6$, were annealed for up to 20 h at 1000 °C. In both cases, most of the 1:12 phase (around 90%) has been preserved (see XRD spectra 3 in Fig. 4). At the same time, the Fe-Si phase has emerged in the annealed $\text{Zr}_{1.1}\text{Fe}_{10}\text{Si}_2$ alloy, and the amount of the $\text{Zr}_6\text{Fe}_{16}\text{Si}_7$ phase has increased; the corresponding SEM micrograph is shown in Fig. 2(b). In the annealed alloy $x = 0.6$, the XRD (Fig. 4) and SEM-EDS (not shown) detected, somewhat unexpectedly, a Zr-free CeFe_2Si_2 minority phase (the Al_4Ba type, $I4/mmm$, $a = 0.399$ nm, $c = 0.986$ nm). There were no indications of emergence of the bcc Fe-Si phase

4. Discussion

The findings presented in this report are reasonably consistent with the information available in the literature. The lattice parameters of the newly observed $\text{Zr}_{1-x}\text{Ce}_x\text{Fe}_{10}\text{Si}_2$ compounds agree with the values reported for $\text{CeFe}_{10}\text{Si}_2$ [4] (see Fig. 5). The agreement for the T_C values is less good, but the difference may be explained, at least in part, by the different methods of the thermomagnetic analysis. The "stabilizing" effect of Zr on the $\text{RFe}_{10}\text{Si}_2$ compounds [13,14] has been confirmed; moreover, the "stabilized" $(\text{R,Zr})_1\text{Fe}_{10}\text{Si}_2$ compounds may now be seen as an extension of the $\text{ZrFe}_{10}\text{Si}_2$.

Having a rather modest anisotropy constant $K_1 = H_a M_s / 2$ of $7.4 \cdot 10^6$ erg/cm³, the $\text{ZrFe}_{10}\text{Si}_2$ compound itself may not have a significant potential for the permanent magnet applications. However, as a new uniaxially anisotropic ferromagnet not containing rare earths or other "critical" elements [20] such as Co, it deserves attention as a possible base for low-cost permanent magnet materials superior to the barium ferrites. The Ce substitution may serve an example here; the $\text{Zr}_{0.4}\text{Ce}_{0.6}\text{Fe}_{10}\text{Si}_2$ contains as little as 11.4 wt.% of the most abundant rare earth, but its K_1 value reaches $1.03 \cdot 10^7$ erg/cm³ and its magnetic hardness parameter $(K_1 / 4\pi M_s^2)^{1/2}$ is equal to 1.05. The compound, therefore, meets the requirement proposed in [21] for a permanent magnet material to have its anisotropy energy higher than its magnetostatic energy. At the same time, the known past attempts to obtain an application-worthy magnetic

hysteresis in the $\text{UFe}_{10}\text{Si}_2$ [10] and $\text{Sm}_{0.7}\text{Zr}_{0.3}\text{Fe}_{10}\text{Si}_2$ [14] exhibiting even higher H_a values were not very successful.

Development of a permanent magnet consists essentially in creating the specific favorable microstructure, usually via mechanical and thermal processing. This may be particularly difficult if the base compound is metastable; and many of the compounds derived from the $\text{ZrFe}_{10}\text{Si}_2$ are expected to be so. It is therefore significant that the $\text{Zr}_{1-x}\text{Ce}_x\text{Fe}_{10}\text{Si}_2$ compounds were mostly preserved after a prolonged heat treatment: this may allow for more options when actually attempting the development of practical magnets.

5. Conclusion

The metastable $\text{ZrFe}_{10}\text{Si}_2$ compound synthesized via arc-melting possesses the intrinsic properties of a moderately hard magnetic material. Its derivatives such as $\text{Zr}_{1-x}\text{Ce}_x\text{Fe}_{10}\text{Si}_2$ may be of interest for the development of new low-cost permanent magnets superior to the ferrite and Alnico magnets.

Acknowledgments

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Table I. Approximate volume percentage of crystalline phases observed in arc-melted $(\text{Zr}_{1-x}\text{Ce}_x)_{1.1}\text{Fe}_{10}\text{Si}_2$ alloys with $x \geq 0.6$.

x	Structure			
	1:12	2:17H	2:17R	bcc
0.6	100	0	0	0
0.7	57	36	0	7
0.8	24	69	0	7
1.0	0	0	79	21

Table II. Lattice parameters, density, Curie temperature, room-temperature saturation magnetization and anisotropy field of $(\text{Zr}_{1-x}\text{Ce}_x)_{1.1}\text{Fe}_{10}\text{Si}_2$ alloys crystallized into the ThMn_{12} -type structure.

x	a (nm)	c (nm)	ρ (g/cm ³)	T_C (°C)	$4\pi M_s$ (kG)	H_a (kOe)
0*	0.8300	0.4721	7.26	325	11.0	16.9
0.2	0.8322	0.4724	7.30	304	11.1	18.7
0.4	0.8356	0.4740	7.34	289	10.8	21.3
0.6	0.8376	0.4741	7.36	285	10.8	24.0

* Alloy contains up to 5 vol.% of non-magnetic $\text{Zr}_6\text{Fe}_{16}\text{Si}_7$ phase.

Figure captions

Fig. 1. Powder XRD spectra of $(\text{Zr}_{1-x}\text{Ce}_x)_{1.1}\text{Fe}_{10}\text{Si}_2$ arc-melted alloys.

Fig. 2. Backscattered electrons SEM micrographs of $\text{Zr}_{1.1}\text{Fe}_{10}\text{Si}_2$ arc-melted alloy: (a) as-made, (b) additionally annealed for 20 h at 1000 °C. Lighter inclusions: $\text{Zr}_{19}\text{Fe}_{57}\text{Si}_{24}$; darker inclusions: $\text{Fe}_{88}\text{Si}_{12}$.

Fig. 3. Magnetization of selected $(\text{Zr}_{1-x}\text{Ce}_x)_{1.1}\text{Fe}_{10}\text{Si}_2$ arc-melted alloys: (a) heating alloy pieces at 5 kOe; (b) room-temperature isotherms for field-oriented powders in parallel (//) and perpendicular ($\perp$) directions.

Fig. 4. Powder XRD spectra of (a) $\text{Zr}_{1.1}\text{Fe}_{10}\text{Si}_2$ and (b) $(\text{Zr}_{0.4}\text{Ce}_{0.6})_{1.1}\text{Fe}_{10}\text{Si}_2$ arc-melted alloys: 1 – randomly oriented; 2 – field-oriented; 3 – randomly oriented after additional annealing for 20 h at 1000 °C.

Fig. 5. Effect of Ce content on lattice parameters and Curie temperatures of the 1:12 phase in $(\text{Zr}_{1-x}\text{Ce}_x)_{1.1}\text{Fe}_{10}\text{Si}_2$ arc-melted alloys as found in this work (filled symbols) and reported in [4] (open symbols).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 4