7-2013

HfCo7-Based Rare-Earth-Free Permanent-Magnet Alloys

Bhaskar Das
University of Nebraska-Lincoln, bhaskar.das@huskers.unl.edu

Balamurugan Balamurugan
University of Nebraska-Lincoln, balamurugan@unl.edu

Pankaj Kumar
Kendriya Vidyalaya, panksamrat@gmail.com

Ralph Skomski
University of Nebraska-Lincoln, rskomski2@unl.edu

Shah R. Valloppilly
University of Nebraska-Lincoln, svalloppilly2@unl.edu

See next page for additional authors

Follow this and additional works at: http://digitalcommons.unl.edu/physicsskomski

Das, Bhaskar; Balamurugan, Balamurugan; Kumar, Pankaj; Skomski, Ralph; Valloppilly, Shah R.; Shield, Jeffrey E.; Kashyap, Arti; and Sellmyer, David J., "HfCo7-Based Rare-Earth-Free Permanent-Magnet Alloys" (2013). Ralph Skomski Publications. 76.
http://digitalcommons.unl.edu/physicsskomski/76

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Ralph Skomski Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.
HfCo$_7$-Based Rare-Earth-Free Permanent-Magnet Alloys

B. Das$^{1,2}$, B. Balamurugan$^{1,2}$, Pankaj Kumar$^3$, R. Skomski$^{1,2}$, V. R. Shah$^1$, J. E. Shield$^{1,4}$, A. Kashyap$^3$, and D. J. Sellmyer$^{1,2}$

$^1$Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, NE 68588 USA
$^2$Department of Physics and Astronomy, University of Nebraska, Lincoln, NE 68588 USA
$^3$School of Basic Sciences, Indian Institute of Technology, Mandi 175 001, India
$^4$Department of Mechanical and Materials Engineering, University of Nebraska, Lincoln, NE 68588 USA

This study presents the structural and magnetic properties of melt-spun HfCo$_7$, HfCo$_{7-x}$Fe$_x$ (0.25 $\leq x \leq$ 1), and HfCo$_7$Si$_x$ (0.2 $\leq x \leq$ 1.2) alloys. Appreciable permanent-magnet properties with a magnetocrystalline anisotropy of about 9.6–16.5 Merg/cm$^3$, a magnetic polarization $J_s \approx$ 7.2–10.6 kG, and coercivities $H_c = 0.8$–3.0 kOe were obtained by varying the composition of these alloys. Structural analysis reveals that the positions of x-ray diffraction peaks of HfCo$_7$ show good agreement with those corresponding to an orthorhombic structure having lattice parameters of about $a = 4.719$ Å, $b = 4.278$ Å, and $c = 8.070$ Å. Based on these results, a model crystal structure for HfCo$_7$ is developed and used to estimate the magnetic properties of HfCo$_7$ using density-functional calculations, which agree with the experimental results.

Index Terms—Doping, magnetocrystalline anisotropy, permanent magnets, rare-earth-free alloys.

I. INTRODUCTION

RECENTLY, the search for rare-earth-free alloys with magnetocrystalline anisotropy $K_1 \geq 10$ Merg/cm$^3$ and magnetic polarization $J_s \geq 10$ kG ($J_s \approx 4\pi M_s$, $M_s$ is saturation magnetization) has become the thrust area of permanent-magnet research, which is aimed at satisfying the rapidly growing demand for rare-earth elements and reducing the cost of the permanent magnets for bulk applications [1]–[3]. In this regard, the HfCo$_7$ intermetallic phase has shown high Curie temperature $T_c$ (∼600 K) and $J_s$ (∼10 kG), and is reported to form a non-cubic crystal structure, which can cause a high $K_1$ suitable for permanent-magnet applications [4]–[8]. However, according to Co-Hf binary phase diagram, the HfCo$_7$ phase forms only at a single composition (12.5 at. % of Hf) and temperatures above 1000°C under thermal equilibrium conditions [9]; thus it is challenging to control the phase purity and crystal structure, which is important to obtain permanent-magnet properties in HfCo$_7$. These limitations presumably restricted earlier studies on bulk HfCo$_7$ alloys, which do not provide a detailed structural analysis and other vital information such as magnetic anisotropies and coercivities [4]–[8].

In particular, the crystal structure of HfCo$_7$ is insufficiently known, with conflicting reports on unit cells (tetragonal, hexagonal or orthorhombic) and without information about individual atomic positions [4]–[7]. Recently, stoichiometric HfCo$_7$ nanoparticles were produced using a gas-aggregation-type cluster-deposition system. These nanoparticles have shown permanent-magnet properties with a $K_1 \approx 10$ Merg/cm$^3$ and $H_c \approx 4.4$ kOe at 300 K and their x-ray diffraction peaks could be indexed with an orthorhombic structure [10]. In the present study, we have investigated the structural and magnetic properties of melt-spun HfCo$_7$, HfCo$_{7-x}$Fe$_x$ and HfCo$_7$Si$_x$ bulk alloys, and also proposed a model crystal structure for HfCo$_7$, which provides an opportunity to estimate the magnetic properties using density-functional calculations and new insights in understanding the underlying magnetic properties of HfCo$_7$-based alloys. Note that the rapid cooling during the melt-spinning process is advantageous in obtaining the phase purity and desired crystal structure in these alloys.

II. EXPERIMENTAL AND THEORETICAL METHODS

Ribbons of HfCo$_7$, HfCo$_{7-x}$Fe$_x$ (0.25 $\leq x \leq$ 1), and HfCo$_7$Si$_x$ (0.2 $\leq x \leq$ 1.2) were fabricated by melt spinning. For this, alloys with the above-mentioned nominal compositions were made from high purity (>99.95%) elements using conventional arc melting followed by melt spinning in high-purity argon atmosphere at a tangential wheel velocity of 40 m/s. Bulk ribbons were characterized using a superconducting quantum interference device (SQUID) magnetometer, energy dispersive x-ray spectroscopy (EDX, JEOL JSM 840A scanning electron microscope), and x-ray diffractometer (XRD, Rigaku D/Max-B diffractometer).

For model calculations, we use frozen-core full-potential projector-augmented-wave method as implemented in the Vienna Ab-Initio Simulation Package (VASP) within the framework of density-functional theory (DFT) [11], [12]. The exchange and correlation effects are described by the method of Perdew, Burke and Ernzerhof using the generalized-gradient approximation (GGA) [13].

III. EXPERIMENTAL RESULTS

XRD patterns for HfCo$_7$, HfCo$_{5.5}$Fe$_{0.5}$, and HfCo$_7$Si$_{0.4}$ are shown in Fig. 1. We have carried out the peak indexing analysis on the XRD pattern of HfCo$_7$ (curve i in Fig. 1) using TOPAS (Total Pattern Analysis Solution, Bruker AXS) by assuming all the reported crystal structures such as hexagonal, tetragonal or orthorhombic. The positions of the experimental XRD peaks of HfCo$_7$ (curve i in Fig. 1) show good agreement with the diffraction-peak positions determined using TOPAS (vertical lines in Fig. 1(a)) for an orthorhombic structure having lattice parameters of about $a = 4.719$ Å, $b = 4.278$ Å, and $c = 8.070$ Å.
Fig. 1. X-ray diffraction patterns for HfCo7, HfCo5.5Fe0.5, and HfCo5Si0.4, where the XRD peak positions determined using TOPAS for orthorhombic structure are shown as vertical lines. A shift in the XRD peak positions of HfCo6.5Fe0.5 as compared to those of HfCo7 is guided by a vertical dotted line.

Fig. 1 also reveals that HfCo7−xFe and HfCo7Si4 alloys have XRD patterns similar to HfCo7 (curve i) as shown in the case of HfCo6.5Fe0.5 (curve ii) and HfCo5Si0.4 (curve iii). In addition, HfCo5.5Fe0.5 exhibits a shift in the angular position of the diffraction peaks towards lower angle side (for example, as indicated by a dotted line in the case of (202) peak of HfCo6.5Fe0.5 as compared to HfCo7 and this result reveals a lattice expansion on the substitution of Fe for Co in HfCo7−xFe. In the case of HfCo5Si0.4, the position of XRD peaks does not show considerable shift with respect to that of HfCo7, presumably due to the interstitial occupation of Si in HfCo7 lattice. Interestingly, alloying of HfCo7 with Si improves the crystallinity of these alloys as revealed by the sharp diffraction peaks in the case of HfCo7Si1.4, as compared to HfCo7 and HfCo5.5Fe0.5.

The magnetic properties of the HfCo7, HfCo7−xFe, and HfCo7Si1.4 alloys were investigated by measuring the magnetization (M) curves at 300 K as a function of applied magnetic field H from −70 to 70 kOe and show two important features. First, the expanded room-temperature M − H curves from H = −25 to 25 kOe for HfCo7, HfCo5.5Fe0.5, and HfCo7Si1.4 show high Hc as shown in Fig. 2(a), as compared to Hc ≈ 0.09 kOe for bulk hcp Co (not shown in Fig. 2(a)). Second, M does not attain complete saturation even at H = 70 kOe as shown by the M − H curves in the high-field region (Fig. 2(b)) and this behavior indicates a large value of magnetic anisotropy in HfCo7-based alloys. The magnetic anisotropy constant K1 was estimated from the high field region of the experimental M − H curves (H > 30 kOe) using the law of approach to saturation method, widely used for randomly oriented magnets [14]–[16].

\[
M = M_s \left(1 - \frac{A}{H^2}\right) + \chi H \tag{1}
\]

In (1), \(\chi\) is the high-field susceptibility and the constant \(A\) depends on the anisotropy constant \(K_1\) as given by

\[
A = \frac{4}{15} \frac{K_1^2}{M_s^2} \tag{2}
\]

The experimental M (solid spheres) in the high-field region (H > 30 kOe) is fitted as represented by solid lines using (1) to estimate \(K_1\) as shown in Fig. 2(b). This evaluation reveals high magnetic anisotropies of about 10 Merg/cm³ in HfCo7—based alloys as indicated in Fig. 2(b). Note that the law of approach to saturation method yields \(K_1 = 4.7\) Merg/cm³ for bulk hcp Co (not shown here), but the magnetization of HfCo7-based alloys is considerably reduced as compared to 1438 emu/cm³ of bulk hcp Co (not shown in Fig. 2(b)).

\(K_1\) and \(J_x\) of HfCo7−xFe and HfCo7Si1.4 as a function of x are summarized in Fig. 3. These results show that \(J_x\) improves on substituting Fe for Co in HfCo7−xFe, but \(K_1\) exhibits a slight decrease for high x ≈ 0.75 and 1. In the case of HfCo7Si1.4, both \(K_1\) and \(J_x\) decrease on increasing x. In brief, these results reveal that permanent-magnet properties of HfCo7-based alloys can be tailored by varying the composition of these alloys.

IV. MODEL STRUCTURE AND ANISOTROPY CALCULATIONS

Our XRD analysis indicates that HfCo7 has an orthorhombic unit cell with lattice parameters of \(a = 4.719\) Å, \(b = 4.278\) Å, and \(c = 8.074\) Å. Based on these lattice parameters, the metallic radii of dense-packed Hf and Co atoms suggest two formula units in the unit cell, and thus this structure can be realized by an
atomic hardcore model in which Hf atoms are coordinated with Co atoms as shown in Fig. 4(a). DFT was used to relax the structure inside the unit cell, and Fig. 4(b) shows the corresponding atomic positions in HfCo7. Note that Fig. 4(b) is a model structure aiming at an approximate description of the alloy during quenching, as monitored by XRD. Very likely, the equilibrium structure of HfCo7 is different from Fig. 4(b), with complicated stackings of simple units such as that in Fig. 4(b). Further experimental and theoretical research is necessary to clarify these points.

The structure of Fig. 4(b) is used to calculate the magnetization and the magnetic anisotropy of HfCo7, in the latter case using the energy difference method by including spin-orbital coupling in noncollinear mode [17], [18].

A rather unusual feature of the anisotropy and micromagnetism of orthorhombic crystals is the existence of two lowest-order anisotropy constants, $K_1$ and $K'_1$, defined by the anisotropy energy [19]

$$
\frac{E_{100}}{V_{\text{atom}}} = K_0 + K_1 + K'_1 \quad (\theta = 90^\circ, \phi = 0^\circ)
$$

(5)

$$
\frac{E_{010}}{V_{\text{cell}}} = -K_0 + K_1 - K'_1 \quad (\theta = 0^\circ, \phi = 90^\circ)
$$

(6)

$\theta$ and $\phi$ are the magnetization angles with respect to $c$ and $a$ axes, respectively. The energy values $E_{100} = 0.00$ meV/f.u., $E_{010} = 1.67$ meV/f.u., and $E_{001} = 1.78$ meV/f.u. obtained from the DFT calculations make it possible to extract the anisotropy constants from (4)–(6) as $K_1 = -16.46$ Mergergs/cm$^3$ and $K'_1 = -18.53$ Mergergs/cm$^3$, which are in the range of the experimentally measured $K_1 \approx 14.0$ Mergergs/cm$^3$ at 300 K for HfCo7. Note that the two anisotropy constants give rise to a small rotational anisotropy (around $c$), but it is predominantly in-plane. The negative value of $K_1$ and $K'_1$ also suggests that HfCo7 possibly has easy plane anisotropy. However, DFT calculations somewhat overestimate $J_\perp$ (11.4 kG), as compared to the experimentally room-temperature value of 7.9 kG. This difference can be attributed to the following facts: (i) the theoretical calculations are relevant to zero-temperature and (ii) the experimental magnetization does not saturate even for a field $H \approx 70$ kOe.

In addition, Hf atoms are coupled anti-ferromagnetically with the neighboring Co atoms. The spin and orbital moments of Hf in HfCo7 are $-0.32$ and $0.011 \mu_B/\text{atom}$, respectively. This coupling reduces the average spin moment of Co in HfCo7 to $1.08 \mu_B/\text{atom}$ as compared to $1.6 \mu_B/\text{atom}$ of bulk Co.

V. CONCLUSIONS

In conclusion, HfCo7, HfCo7-xFe$_x$, and HfCo7Si$_4$ alloys were prepared using melt-spinning method and their structural and magnetic properties were investigated. X-ray diffractions of HfCo7-based alloys were indexed with an orthorhombic structure having lattice parameters of about $a = 4.719$ Å, $b = 4.278$ Å and $c = 8.670$ Å. These studies show that high magnetic anisotropies ($K_1 > 10$ Mergergs/cm$^3$) and coercivities ($H_c \approx 3$ kOe) at 300 K can be obtained in HfCo7-based alloys as compared to bulk hcp Co ($K_1 = 4.7$ Mergergs/cm$^3$ and $H_c = 0.09$ kOe). In addition, these alloys also exhibit appreciable magnetic polarization in the range of 7.2 to 10.8 kG. This study indicates that HfCo7-based alloys are promising alternative alloys for permanent-magnets, from the view point of mitigating the critical material aspects of rare-earth permanent magnets.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy/BREM (Grant No. DE-AC02-07CH11358, B.D., J.E.S.), Advanced Research Projects Agency-Energy (Grant No. DE-AR 0000046, B.B), US Department of Energy (Grant No. DE-FG02-04ER46152, D.J.S.), NSF-Materials Research Science and Engineering Center (Grant No. DMR-0820521, R.S), the Indo-European (PKS, AK), and Nebraska Center for Materials and Nanoscience, V.R.S, X.Z.L.). Thanks are due to P. Manchanda for help in the DFT calculations, and to C.-Z. Wang and K.-M. Ho for helpful discussions regarding the structural determination of HfCo7.
REFERENCES