The Nucleus, **45** (1-2) 2008: 39-43

The Nucleus
A Quarterly Scientific Journal of Pakistan Atomic Energy Commission
NCLEAM, ISSN 0029-5698

STRUCTURAL AND MAGNETIC PROPERTIES OF SmCoCu PERMANENT MAGNETS

*M.S. AWAN, U. MANZOOR and A.S. BHATTI

Department of Physics, COMSATS Institute of Information Technology, Park Road, Islamabad, Pakistan

(Received June 16, 2008 and accepted in revised form July 16, 2008)

The effect of composition and heat treatment on the intermetallic alloy $SmCo_5$ has been carried out to improve the magnetic properties. The base composition ($SmCo_5$) was modified by substitution of cobalt (Co) with copper (Cu) and annealing the samples under argon atmosphere. Annealed and cast samples revealed mixed-phase microstructure responsible for improved magnetic properties. X-ray diffraction (XRD) confirmed the hexagonal crystal structure of the base alloys. Optical and scanning electron microscopy (SEM) was used to study the formation and effect of annealing on the different phases and was related to the magnetic properties. Energy dispersive X-ray (EDX) was carried out to determine the composition of different phases. Precipitation of copper-rich phase acts as the pinning centers for the domain wall motion. This restriction on domain wall motion improves the magnetic hardening of the base alloy. It was found that Cu diffusion plays a major role in determining the magnetic properties of these magnetic alloys.

Keywords: Magnetiocrystalline anisotropy, Magnetic hardening, Saturation magnetization, Domain-wall pinning, $SmCo_5$.

1. Introduction

High magnetocrystalline anisotropy and low saturation magnetization are the key features of $SmCo_5$ metallic compound for the fine particle permanent magnets. The hard magnetic properties of this compound are one of the major hindrances in its application as a permanent magnet in the as-cast state. Due to its hexagonal crystal structure and combination of the rare-earth Sm with the transition metal Co, $SmCo_5$ exhibits a high uniaxial anisotropy and large Curie temperature [1]. This made $SmCo_5$ a potential candidate for high temperature applications [2]. Large magneto-crystalline anisotropy in rare-earths originates from interaction of the crystal field and asymmetry of the charge cloud of the 4f electrons. Interaction of the magnetic moments of 3d electrons with the magnetic moments, associated with the rare-earth elements constitutes the basis of magnetic ordering and the magnetic crystal anisotropy. This combination can yield well defined intermetallic compounds with superior magnetic properties, e.g., RCo_5 and R_2Co_{17} (R is lighter rare-earth element, such as Sm) compounds are of great interest. The $SmCo_5$ compound has moderate value of saturation magnetization but extremely large value of magnetiocrystalline anisotropy constant whereas Sm_2Co_{17} compound exhibits higher saturation magnetization but considerably smaller value of magnetiocrystalline anisotropy constant [3].

The microstructure of optimally heat-treated Sm(CoCuFeZr)z magnets plays an important role in magnetic properties. It consists of rhombohedral $Sm_2(CoFe)_{17}$ cells surrounded by a hexagonal $Sm(CoCu)_5$ cell boundary phase [4-6]. Also a Zr-rich lamellar phase parallel to c-axis exists in these magnets with high coercivity [7]. It is believed that Cu may be the critical element for such type of magnets [8]. It is mainly concentrated at the 1:5 cell boundary phases [2, 8] and causes the dilution of its intrinsic magnetic properties including the anisotropy field and Curie temperature [9]. Additionally, the Zr-rich phase helps to form the uniform cell boundary phase by providing easy diffusion paths for Cu segregation [7]. This further dilutes the magnetic properties of 1:5 phase and causing a large domain wall energy gradient at the interface between the 2:17 and 1:5 phases [9-10]. As a result high coercivity is obtained.

Keeping in view the key role of 1:5 phase in 2:17 type magnets, the dependence of the specific coercivity mechanism on heat-treatment,

* Corresponding author : sss_awan@yahoo.com

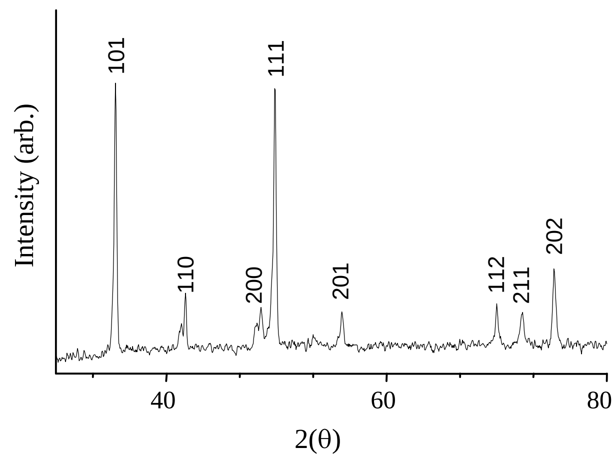

Figure 1. XRD pattern of as-cast $SmCo_5$ alloy.

microstructure and substitution of Co by Cu in the $SmCo_5$ phase is studied for the cast samples.

2. Experiment

A number of cylindrical samples (ϕ=8.8mm) of binary and ternary compositions $SmCo_5$ and $Sm(Co_{5-x}Cu_x)$ with ($3.0 \geq x \geq 0$) were prepared from Sm, Co and Cu metals with purity of 99.99%. Ingredient components were weighed according to the stoichiometric formula. Casting of the alloy was performed in an arc melting apparatus with chilled water cooled hemispherical copper hearth. Due to rapid solidification and large surface area being cooled, control of the process was relatively easy. The loss of Sm was overcomed by adding Sm (optimized to be 6%) in a little more fraction than stoichiometric ratios [1]. Melting was carried out in an inert atmosphere (Ar) to avoid oxidation. Furthermore to minimize the oxidization some pieces of activated calcium (Ca) were put in the small cavity located nearby the melting atmosphere. Ingots were prepared and weighed about 10 grams each. The samples, sealed in a quarts tube under Ar atmosphere, were annealed and then furnace cooled. Annealing of the cast samples was carried out at 800^{o}C for three hours.

For surface morphology and metallographic studies, samples were mold mounted, ground, polished and finally etched in a solution containing (3:1:1) glycerin, acetic acid and nitric acid (HNO_3) respectiely. Surface studies and chemical analysis were performed on digital Olympus optical and Jeol JSM-5910LV scanning electron microscope (SEM)-equipped with Oxford EDX-system. For structural analysis XRD measurements were taken on bulk samples using Siemens D-500 X-ray diffractometer equipped with four-circle goniometry. Co-Ka radiations were used for scanning. Magnetic measurements were performed on a Riken Denshi DC-BHU-30 B-H curve tracer. During measurements the maximum attainable magnetic field strength was limited to 20KOe.

3. Results and Discussion

Figure 1 is the X-ray diffraction pattern of the as-cast alloy of $SmCo_5$. The highest peak was obtained for the (111) reflection. The analysis of the diffraction pattern shows the alloy is single-phase (1:5) with hexagonal crystal structure. The lattice parameters of the unit cell are found to be a= 4.996 Ǻ and c = 3.985 Ǻ while structural analysis of the ternary alloy ($SmCo_{3.5}Cu_{1.5}$) shows the same crystal structure with lattice parameters a = 4.980 Ǻ and ***c*** = 4.040 Ǻ. The slight increase in the c-axis of the unit cell is due to the substitution of copper atoms at the sites of Co in the unit cell [12].

Figure 2(a, b) shows representative scanning and optical images of the as-cast $SmCo_5$ sample. The alloy is brittle with cracks visible in the SEM image shown in Figure 2a while, danderitic structures are visible in the optical micrograph (Figure 2b). Energy dispersive X-ray (EDX)

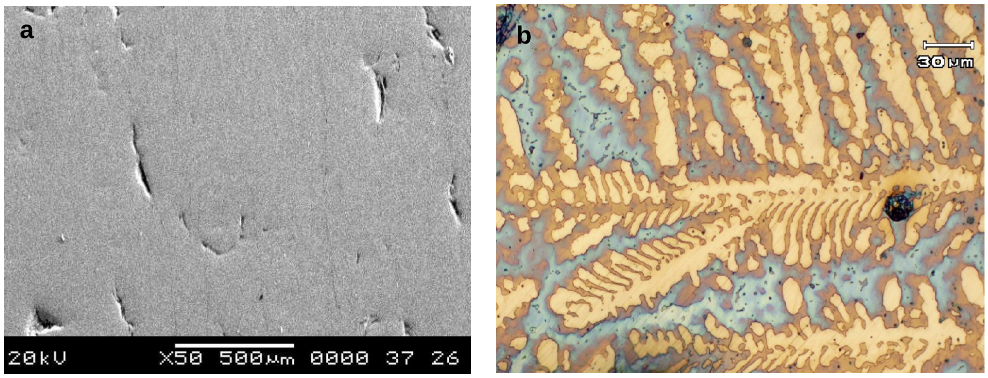

Figure 2. SEM and optical micrographs of as cast samples of Samarium-Cobalt ($SmCo_5$). After polishing and etching shows (a) single phase microstructure (b) typical dendratric structure.

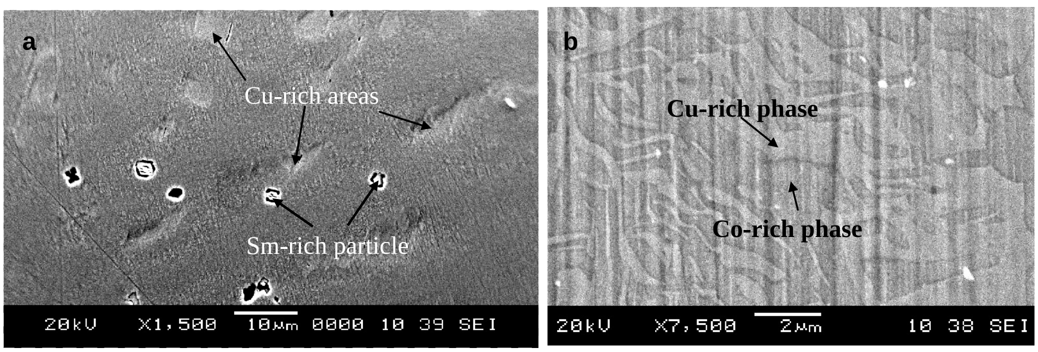

Figure 3. SEM micrographs of the sample $SmCo_{1-x}Cu_x$ with x = 1.5 after polishing and etching. Samples reveal two-phase structures (a) as-cast (b) annealed at 800^{o}C for 3hrs.

analysis shows that the alloy is single-phase with average chemical composition (Sm = 16.73 at.%, Co = 83.27 at.%).

Figure 3(a-b) shows the SEM micrographs of the (a) as-cast and (b) annealed sample in which cobalt was partially substituted by copper (x = 1.5). After etching both the samples show two–phase microstructure. Interestingly, three distinct regions of interest can be observed in Figure 3 (a), i.e., (1) randomly distributed bright patches, (2) plane surfaces and (3) particles imbedded in the cavities. EDX-analysis was employed to determine the composition of these three distinct areas. It was found that the bright patches are the copper-rich areas, plane surfaces are the cobalt-rich areas and particles imbedded in cavities are the samarium-rich particles. The detailed elemental analyses of different species in different regions are given in the Table 1. The copper rich areas contain double the copper content compared to plane matrix surface. Excess oxygen was found in the Sm-rich particles compared to other areas due to its high affinity for oxygen especially at high temperature. The copper-rich areas acting as relatively nonmagnetic phase and may serve as pinning centers for the domain wall motion. Figure 3(b) is the microstructure of the same sample when it was annealed at 800^{o}C for three hours under the argon atmosphere. Pronounced differences in the structural and magnetic properties were observed after annealing. The annealed sample showed two-phase microstructure with different microchemistry and samarium rich particle like cast structure disappeared. EDX analysis of the annealed sample shows that most of the copper during annealing diffused from Co-rich phase to Cu-rich phase. This makes the Cu-rich phase even more nonmagnetic and enhances magnetic nature Co rich areas. Diffusion of Cu in copper rich area may give better pinning effect for the domain wall motions.

Table 1. EDX analysis of as-cast and annealed samples.

Element	As-cast Sample ($SmCo_{3.5}Cu_{1.5}$)			Annealed Sample ($SmCo_{3.5}Cu_{1.5}$)	
	Bright patches	Plane surfaces	Sm-rich particles	Cu-rich phase	Co-rich phase
Sm	33.75	30.01	78.18	31.53	23.99
Co	30.03	51.85	3.14	43.06	66.60
Cu	29.47	14.18	6.20	25.41	9.41
O	0.22	0.33	7.43		
C	6.53	3.63	5.06		

Table 2. Magentic properties as a function of Cu-contents.

X (Cu)	Br (KG)	Mmax (kG)	iHc (KOe)	(BH)max (MGOe)
0.0	1.011	4.989	0.4027	0.1
0.5	1.678	4.807	1.035	0.3
1.0	2.625	4.448	1.995	0.97
1.5	3.65	3.669	3.839	2.12
2.0	2.374	2.81	9.256	1.04
2.5	2.042	2.207	7.92	0.9
3.0	1.865	1.845	6.432	0.7

A series of samples $SmCo_{5-x}Cu_x$ with varied Cu-contents (x=0, 0.5, 1, 1.5, 2, 2.5 and 3.0) were prepared and their magnetic properties were determined and plotted in Figure 4. For comparision the data for magnetic properties is shown in Table 2. This shows that as-cast alloy (x=0) with composition $SmCo_5$ exhibits poor hard magnetic properties having Br=1011 gauss, iHc=402.7 Oe and $(BH)_{max}$ = 0.1 MGOe, respectively. Copper addition introduces the two phase structure which influences the magnetic properties. Increase in Cu contents has a non-monotonic effect on magnetic properties and maxima is observed at around x=1.5. This increase in magnetic properties is supported by the microstructure of as-cast samples shown in Figure 3(a). Copper addition introduces the nonmagnetic pinning barriers in the form of bright patches for domain wall motion. These barriers seem to restrict the motion of the domain walls hence improving the magnetic properties. Although Cu addition favors the magnetic properties but at the same time maximum magnetization (M_{max}) of the samples almost decreases linearly shown in Figure 4. This may be due to the increase in the size of Cu rich areas competing with Co rich areas. As copper is non-magnetic, it may be the cause of reduction in M_{max}. Here it seems that x=1.5 is the limit for Cu-contents. Further Cu replacement with Co dilutes the magnetic properties drastically. Heat treatment modified the microstructure and microchemistry of the two-phase cast alloy. When the samples were annealed at 800^{o}C for three hours most of the copper diffuses from Co-rich phase to Cu-rich phase. This diffusion further dilutes the intrinsic magnetic properties of the Cu-rich phase. According to the pinning mechanism [11], the coercivity is proportional to the difference between the domain-wall energy for the two phases. As in the Cu substituted $SmCo_{5-x}Cu_x$, Cu mainly goes into the Cu-rich phase during annealing, leading to further dilution of its intrinsic magnetic properties and causing a large domain–wall energy gradient at the interface between the two phases. Therefore, heat treatment influences both the microstructure and magnetic properties of the alloy. The magnetic data for x= 1.5 alloy is presented after anealing at 800^{o}C for three hours. The two phase alloy (x=1.5) after annealing exhibits Br=3045 gauss, iHc=10290 Oe and (BH)max= 2.65 MGOe.

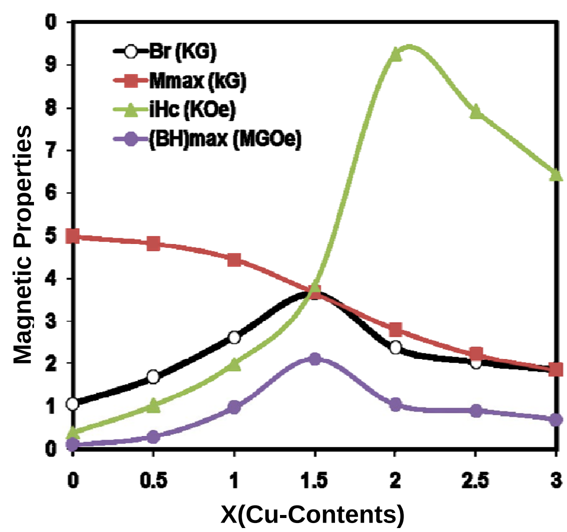

Figure 4. Magnetic properties of $SmCo_{1-x}Cu_x$ as a function of copper contents.

4. Conclusions

The partial replacement of Co with Cu in the $Sm(Co_{5-x}Cu_x)$ system results in a two-phase microstructure which yields magnetically stronger alloy. Annealing the as-cast samples modifies the microstructure and microchemistry of the alloys. During annealing diffusion of Cu from Co-rich phase to Cu-rich phase creates a large domain-wall energy gradient which magnetically isolate the two phases and improves the magnetic properties. Due to introduction of nonmagnetic phase maximum magnetization of the samples decreases almost linearly with increasing Cu contents. Lower Cu contents $1.5 = x > 0$ favors the magnetic properties.

Acknowledgement

The author is grateful to M/s M.A. Yar, S.A. Marth and Afzal Hussain for their cooperation and fruitful discussion.

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