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Journal of Alloys and Compounds 281 (1998) 1–5

Journal of ALLOYS AND COMPOUNDS

Structure and magnetic properties of $SmCo_{5-x}Cu_x$ alloys

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Abstract

The magnetic properties of polycrystalline $SmCo_{5-x}Cu_x$ (x=1, 1.5, 2, 2.5, 3, 4) samples were studied in the as-cast state as well as after annealing. The Curie temperature decreases whereas the lattice constant increases with increasing Cu content. The hysteresis loop was measured between 10 and 900 K using a pulsed-field system. The coercivity field shows strong time dependence. The temperature dependence of the coercivity and the time dependence are analysed using common models for the magnetic aftereffect. The results strongly support the major effect of the number of Cu atoms acting as local defects on the concentration, time and temperature dependence of the coercivity.

Keywords: Aftereffect; Hard magnetic materials; Pulsed-field measurements; Structure; Time dependence

1. Introduction

In $Sm(Co,Fe,Cu,Zr)_z$ permanent magnets, $7.0 \leq z \leq 8.5$, an hexagonal $Sm(Co,Cu)_{5-7}$ phase was found which is precipitated predominantly at the cellular walls surrounding the $Sm_2(Co,Fe)_{17}$ matrix grains [1]. The domain walls are pinned at different phase boundaries between the $Sm_2(Co,Fe)_{17}$ matrix, the $Sm(Co,Cu)_{5-7}$ boundary phase and the Zr-rich platelet phase [2–4]. The magnetic properties of this precipitated Sm(Co,Cu) phase, which are important for the understanding of the magnetization process in these magnets, are not well known. Magnets of a composition close to $Sm(Co,Cu)_5$ show giant intrinsic magnetic hardness irrespective of mode of preparation [5]. Microprobe and metallographic analysis of $SmCo_{5-x}Cu_x$ indicate spinodal decomposition in as-cast material [6]. The resulting components are still of $CaCu_5$-type structure, but exhibit a randomly varying transition metal composition. Subsequent annealing at 1073–1273 K removes this variation in stoichiometry. The coercive field of these magnets is in the as-cast state based on domain-wall nucleation with subsequent weak pinning at the grain boundaries, whereas in the annealed alloy a domain-wall pinning process occurs [7,8]. Electron microscopy of as-cast samples (x=1.25, 1.75 and 2.25) showed the existence of three phases: a so-called ''1–5 Co'' phase, a so-called ''1–5 Cu'' phase (these phases show slightly different Co–Cu concentrations) and between the grains a Cu-rich ''5–19'' phase [9]. Generally, the coercive field was ascribed to the precipitation of a copper-rich phase, the result of a solid-state miscibility gap in the $SmCo_5$–$SmCu_5$ section. However, no experimental evidence is available to identify this copper-rich phase. In the present paper, our main emphasis is on a systematic study of the properties of $Sm(Co,Cu)_5$ magnets over a large temperature range.

2. Experimental details

Polycrystalline $SmCo_{5-x}Cu_x$ (x=1, 1.5, 2, 2.5, 3, 4) were prepared by induction melting appropriate amounts of the raw materials of a purity of at least 99.9 wt.%. The as-cast ingot was embedded in a Ta foil and placed in a quartz tube, which was evacuated prior to filling with purified Ar gas. In order to compensate for Sm loss at high temperature, a small piece of metallic Sm was placed in the quartz tube. The annealing was performed at 1273 K for three weeks. The obtained samples were subsequently subjected to X-ray powder diffraction analysis, indicating that the samples are of single phase with the hexagonal $CaCu_5$-type structure. For the diffraction experiment, Ge powder was added to the sample using the (111) and (220) reflexes for calibrating the pattern. For the magnetic measurements, small cylinders 3 mm in diameter and about 9 mm in height were cut from the samples.

The Curie temperatures and also possible magnetic phase transitions were investigated by measuring the temperature dependence of the ac susceptibility in the temperature range from 4.2 to 900 K. The hysteresis loops of the as-cast and annealed $SmCo_{5-x}Cu_x$ compounds were

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0925-8388/98/$ – see front matter
PII: S0925-8388(98)00760-9

measured from 4.2 to the Curie temperature by using a pulsed-field magnetometer with a maximum field of 24 MA m^{-1}. The field strength of the system was calibrated by Ba-ferrite which has an anisotropy field of 1.32 MA m^{-1} at room temperature. The value of the coercive field H_{CJ} is determined as the field at which the dJ/dH versus H curve has a maximum in the demagnetization curve. dH/dt was varied by changing the capacitance of the condensator battery between 8 mF (pulse duration about 4 ms) and 24 mF (pulse duration about 7.5 ms) and by varying the amplitude of the field.

3. Results and discussion

3.1. Structure and Curie temperature

Similarly as reported in Refs. [10–12], the lattice constants a and c of $SmCo_{5-x}Cu_x$ increase monotonically with increasing Cu concentration (see Fig. 1), indicating that Cu enters into the $SmCo_5$ lattice.

Table 1 lists the lattice constants a and c together with the calculated volumes of the unit cells V. It was found that $SmCo_3Cu_2$ is a single hexagonal $CaCu_5$ phase. Due to the heat treatment the lattice constant and the volume of the unit cell increase slightly (see Fig. 1 for $x=2$ and 2.5). From Fig. 2 one can see that the Curie temperature T_C of annealed $SmCo_{5-x}Cu_x$ decreases with increasing x, which is in agreement with Ref. [13]. Both results also indicate that the Cu substitutes the Co. It is interesting to note that the T_C of as-cast material is generally higher (see Fig. 2). Comparing the volume dependence of the unit cell of the system in the as-cast state and after heat treatment with the behaviour of T_C, one can conclude that in the as-cast state not all Cu entered into the $SmCo_5$ lattice, therefore the lattice constant is smaller and the ordering temperature higher.

Table 1
Lattice parameters and Curie temperatures of $SmCo_{5-x}Cu_x$ compounds after holding at 1273 K for three weeks and subsequent quenching. The error in the last position of the lattice constant is given in parentheses

	a (nm)	c (nm)	V (nm^3)	T_C (K)
$SmCo_5$	0.49957(2)	0.39726(5)	0.08586 (1)	
$SmCo_4Cu$	0.50083(2)	0.39924(2)	0.086724(8)	774
$SmCo_{3.5}Cu_{1.5}$	0.50184(9)	0.3998(2)	0.08720(4)	706
$SmCo_3Cu_2$	0.5023(2)	0.40054(2)	0.087667(7)	624
$SmCo_{2.5}Cu_{2.5}$	0.5025(2)	0.4025(2)	0.08801(9)	506
$SmCo_2Cu_3$	0.50347(5)	0.40382(5)	0.08865(2)	387
$SmCoCu_4$	0.50410(9)	0.4054(1)	0.08922(3)	134

3.2. Coercivity

The coercivity was determined in a pulsed-field magnetometer by measuring the first derivative of the magnetic polarization dJ/dt versus the external field and by measuring the hysteresis loop $J(H)$ giving the same value. The as-cast samples already have a relatively high coercive field but, after the heat treatment, it becomes stronger. It should be mentioned that the loops for the samples with $x=1.5$, 2, 2.5 and 3 show indications of either a second hard magnetic phase or the existence of two different pinning fields. Fig. 3 gives the concentration dependence of the coercivity measured at room temperature in the as-cast state and after the heat treatment.

The coercivity reaches its maximum value for the sample $SmCo_{2.5}Cu_{2.5}$ showing a coercive field of 1.2 MA m^{-1} (as-cast state). After annealing and subsequent quenching, the coercive field of this compound is enhanced to 2.08 MA m^{-1}. The concentration behaviour is in agreement with that estimated at 4.2 K [5]. Measuring the hysteresis loop in a static field generally delivers lower H_{CJ} values (for $x=1.5$, 2, 2.5 and 3), however the concentration dependence is similar. The coercive field decreases

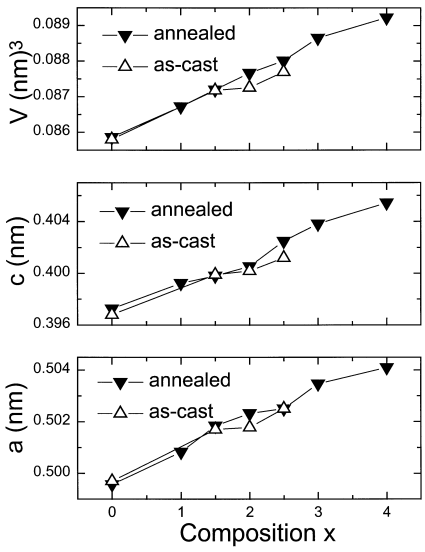

Fig. 1. The composition dependence of the lattice parameters a and c and volume of the cells of $SmCo_{5-x}Cu_x$ alloys determined at room temperature.

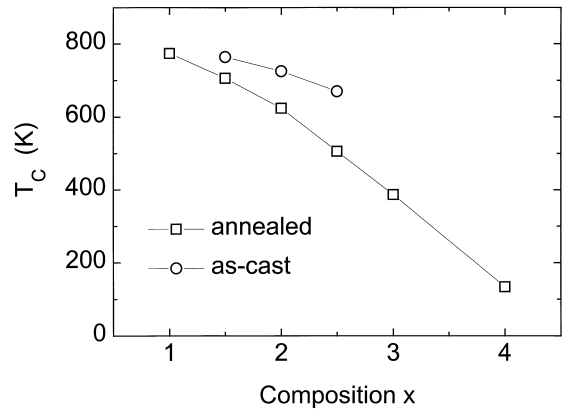

Fig. 2. Concentration dependence of the Curie temperature of $SmCo_{5-x}Cu_x$ compounds.

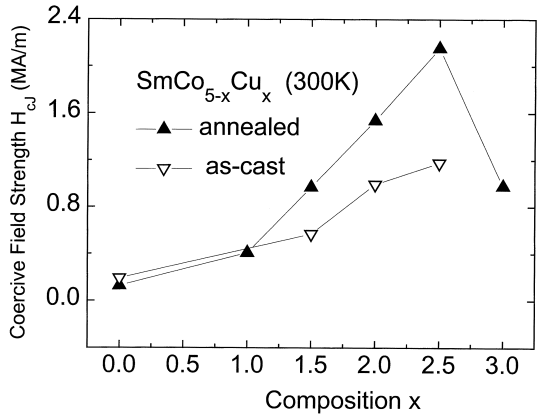

Fig. 3. Coercive force at room temperature as a function of the chemical composition of $SmCo_{5-x}Cu_x$ alloys in the as-cast state and after heat treatment at 1273 K for three weeks and subsequent quenching. H_{cJ} was measured in a pulsed field (pulse duration 4 ms, field amplitude 12 MA m^{-1}).

monotonically with increasing temperature, as shown in Fig. 4. For annealed $SmCo_{2.5}Cu_{2.5}$ at low temperatures coercive field strength above 8 MA m^{-1} were found.

3.3. Analysis

A large time dependence of the coercivity of $SmCo_{5-x}Cu_x$ has been reported [8]. For the time dependence of the remanence J_r of hard magnetic materials a formula of the following type has been deduced [14]:

$$|J_r(t)| = J_0 \exp\left(-\frac{E_a}{kT}\right)$$

where E_a is the activation energy. Because in hard magnetic materials the domain wall represents a rather extended but thin sheet, the jump over the potential hills by one unique coherent motion of the whole domain wall area requires a rather large activation energy. Therefore, Egami [15] proposed a partial bowing of the domain walls. Within the framework of this model the thermally activated motion of the domain wall is initiated by so-called domain wall kinks. According to this model the necessary activation energy can be written as

$$E = \frac{\pi\sigma^2}{2M_s}\frac{1}{H}$$

where σ is the kink energy by unit length, which is proportional to $\sqrt{AK}$ (A is the exchange energy and K the anisotropy energy). Using a general law describing thermal activation of the type

$$\tau^{-1} = \tau_0^{-1}\exp\left(-\frac{E_a}{kT}\right), \text{ and } \tau^{-1} = \frac{1}{M_s}\frac{dM}{dt} \text{ and } \frac{dM}{dt} = \alpha\frac{dH}{dt}$$

it can be written as

$$\frac{dH}{dt} = \frac{M_s}{\tau_0\alpha}\exp\left(-\frac{E_a}{kT}\right)$$

and introducing for E_a that it is proportional to σ^2/H leads with

$$\ln\left(\frac{dH}{dt}\right) = \ln\left(\frac{M_s}{\tau_0\alpha}\right) - \frac{1}{kT}\frac{\pi\sigma^2}{2MH}$$

to the idea of plotting $\ln(dH/dt)$ versus $1/H_{CJ}$ ($1/H \rightarrow 1/H_{CJ}$) as shown in Fig. 5. As can be expected from the above formulas this delivers a linear relation. The slope is proportional to σ^2/M_s. In the above theory, the numbers of defects (N), dislocations or kinks are not considered. Because the interaction between the domain walls and the defects (local distortions) play the dominant role, it can be assumed that E_a will be replaced by NE_{al}, where E_{al} now represents the local activation energy. This activation energy depends on the local anisotropy (K) and on the exchange energy A. In the work of Barbara et al. [8] such a plot was produced for temperature dependent measurements of $SmCo_{3.5}Cu_{1.5}$. There, the slope decreases sys-

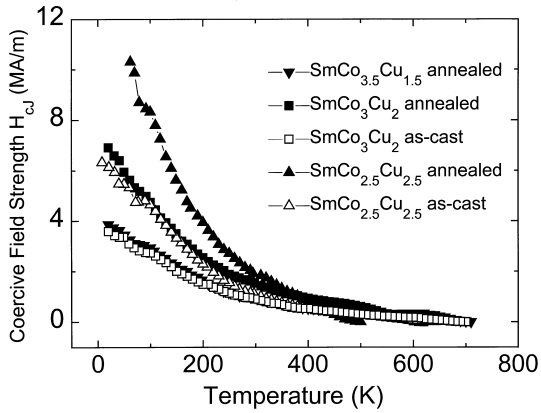

Fig. 4. Temperature dependence of the coercive field strength of as-cast and annealed $SmCo_{5-x}Cu_x$ compounds ($x = 1.5$, 2, 2.5) after holding at 1273 K for three weeks and subsequent quenching.

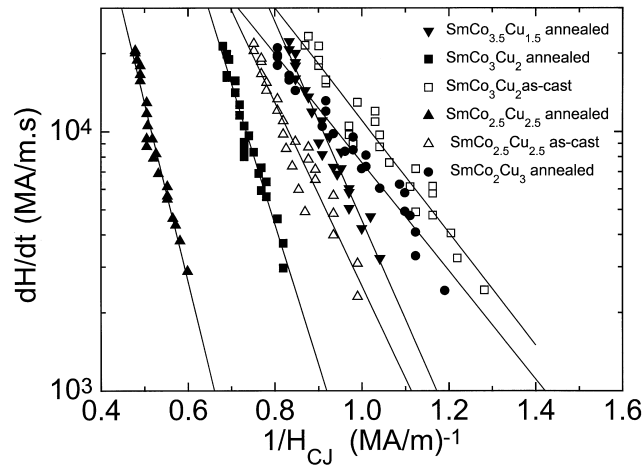

Fig. 5. $\ln(dH/dt)$ versus $1/H_{CJ}$ (room temperature values) of as-cast and annealed $SmCo_{5-x}Cu_x$ ($x = 1.5$, 2, 2.5, 3).

tematically with increasing temperature due to the decreasing anisotropy (N = constant). In the present work the slope of $\ln(dH/dt)$ versus $1/H_{CJ}$ is proportional to NE_{al}.

In the case of $SmCo_{5-x}Cu_x$ the magnetization M_s, the anisotropy K and the exchange A generally decrease with increasing Cu content. This should cause a decrease of E_{al}, which is, according to Egami [15], proportional to AK/M_s. Fig. 5 demonstrates that for the annealed samples the slope first increases with Cu content to the highest value for $x=2.5$ and then decreases ($x=3$). For $x=2$ and $x=2.5$ the slope in the annealed state is higher than in the as-cast state. All this coincides with the concentration behavior of the coercivity of as-cast and annealed material (see Fig. 3). Because the slope is also proportional to N this analysis shows that the number of defects which can be due to the very narrow domain walls set proportional to the amount of Cu dissolved in the $SmCo_5$ lattice determines the time dependence and also the slope of these plots. In the annealed state the Cu is more homogeneously dissolved in the $SmCo_5$ lattice (which also became evident in the concentration dependence of the lattice constant and the Curie temperature) and the number of ''active Cu-defects'' also increases.

The temperature dependence of the coercivity can be analyzed using the same model. Starting from the formula for the relaxation time τ and using the expression for σ gives

$$\ln\left(\frac{\tau}{\tau_0}\right)=\frac{\pi NAK}{8kTM_s}\frac{1}{H}$$

which can be rewritten to give

$$\frac{1}{H}=\frac{8M_sk}{\pi NAK}\ln\left(\frac{\tau_0}{\tau}\right)T$$

which finally leads to

$$HT^2=\frac{\pi}{8k\ln(\tau_0/\tau)}\frac{NAK}{M_s}T$$

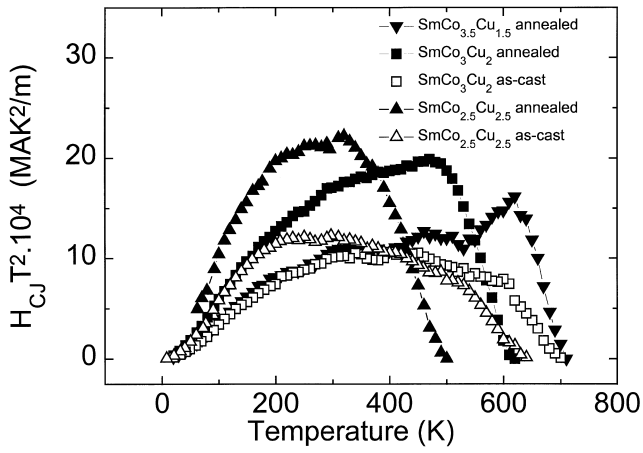

Fig. 6. $H_{CJ}(T)T^2$ versus temperature of as-cast and annealed $SmCo_{5-x}Cu_x$ compounds ($x=1.5$, 2, 2.5).

Now taking this formula at $H=H_{CJ}$ leads to the plot $H_{CJ}T^2$ versus T as given in Fig. 6. The idea of this plot is that at low temperatures M_s and K can be assumed to be constant, therefore the slope should be proportional to K (see also Ref. [8]). In fact, the slope for $T<200$ K of the annealed samples increases systematically with increasing Cu concentration, indicating that for a comparison of different samples K is not important but N which has a maximum for $x=2.5$. Also, the slope increases for $x=2$ and $x=2.5$ due to the annealing, indicating again that N increases due to the more homogenous distribution of the Cu in the Co lattice. At higher temperatures the decreasing anisotropy is responsible for the decreasing $H_{CJ}(T)T^2$ behavior.

4. Conclusion

Bulk $Sm(Co,Cu)_5$ shows an increasing coercivity which is also time dependent with increasing Cu content (up to $x=2.5$). A coercive field of 2.08 MA m^{-1} at room temperature was obtained for $SmCo_{2.5}Cu_{2.5}$ after annealing at 1273 K for three weeks and subsequent water-quenching. The results strongly support the major effect of the number of Cu atoms acting as local defects on the concentration, time and temperature dependence of the coercivity. In order to estimate the activation energy from these data, intrinsic parameters such as the temperature dependence of the anisotropy and the magnetization have to be known. Such measurements are therefore in progress.

Acknowledgements

This work was supported by the Jubiläumsfond of the Austrian National Bank under project number 5661. J.C. Téllez-Blanco thanks ÖAD for financial support. The authors appreciate the very helpful discussion with Drs. Alma Valor-Reed and Giselle Fernández-Soto.

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