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Magnetic states and structural transformations in $Sm(Co,Cu)_5$ and $Sm(Co,Fe,Cu)_5$ permanent magnets

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Abstract

We have studied the stability of $RCo_{5-x}Cu_x$ (R = Y, Sm) compounds with respect to phase separation. First principles density functional calculations imply that (i) decomposition into two phases having different x is energetically favourable and (ii) both the stable x values and the Cu atomic site preferences depend on the magnetic state of the alloys. Guided by this result, we studied the structure and magnetic properties of different $Sm(Co,Cu)_5$ and $Sm(Co,Fe,Cu)_5$ alloys. Separation into two chemically dissimilar $Sm(Co,Cu)_5$ phases is typical for the as-made $Sm(Co,Cu)_5$ alloys. We also observed in different alloys a universal correlation between the room-temperature coercivity and the magnetic state at the temperature of annealing. The coercivity increases significantly if annealed 100–140˚C below the Curie temperature; in particular, for $SmCo_{2.25}Fe_{0.75}Cu_2$, the room-temperature coercivity increases from 12.3 to 37.3 kOe. The possibility of different magnetic state-dependent structure transformations is discussed. The experimental results do not support the spinodal decomposition theory, so we suggest that the coercivity increase might be caused by a change in preferred atomic site occupancies.

1. Introduction

In spite of many experimental studies, the large coercivity in bulk $Sm(Co,Cu)_5$ alloys discovered more than three decades ago [1] is still not completely understood. According to Oesterreicher *et al* [2] the magnetic hardness in these pseudobinary compounds may be of an intrinsic nature, resulting from site disorder and the high magnetic anisotropy. On the other hand, the well-known increase of coercivity in $Sm(Co,Cu)_5$ alloys upon annealing at relatively low temperatures of about 300–500˚C has been associated with spinodal decomposition into Co- and Cu-rich $Sm(Co,Cu)_5$ phases [3–5]. In the later studies [6], however, the spinodal decomposition in the $Sm(Co,Cu)_5$ alloys has been questioned. In the model by Mitchell and McCurrie [7], the Co and Cu microsegregation formed during alloy casting evolves with annealing into a sort of cellular structure, which is responsible for the coercivity. Recently Yamashita [8] even suggested that the coercivity in $Sm(Co,Cu)_5$ can be caused by the Co precipitates along the grain boundaries.

Though $Sm(Co,Cu)_5$ compounds do not have a direct practical application because of their relatively low magnetization, it is well established that $Sm(Co,Cu)_5$ plays a critical role in the coercivity of Sm_2Co_{17}-based magnets—the hard magnetic materials of great practical importance. Typically, when modelling coercivity in the 2 : 17 magnets, the $Sm(Co,Cu)_5$ cell-boundary constituent is considered as a single phase with a certain set of physical properties [9]. However, some experimental results [10] may be interpreted in favour of a two-phase structure.

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In this work, we tried to examine the structural transformations in Sm(Co,Cu)$_5$ and their relevance to the magnetic hardness of these alloys. We started with theoretical calculations and used their results (the predicted phase separation and possible effect of magnetic states of the alloys on their structure) to guide our experimental efforts. The latter, therefore, were focused on the structure and magnetic properties of the as-made alloys, homogenized alloys and the alloys annealed in the vicinity of their Curie temperature.

2. Calculation and experimental details

Density functional calculations for $RCo_{5-x}Cu_x$ compounds with R = Y and Sm have been performed with the full-potential, linearized augmented plane wave (LAPW) method [11] using the WIEN2k code [12] and the linearized muffin-tin orbital method [13] within the atomic sphere approximation (LMTO-ASA) using the STUTTGART-4.7 package [14]. The former method is very accurate but somewhat slow, while the latter is approximate but very fast. Details of the calculations are available elsewhere [15].

Experimental results were obtained for $SmCo_{5-x}Cu_x$ with x = 1, 1.5, 2 and also for $SmCo_{2.25}Fe_{0.75}Cu_2$. The alloys were prepared from pure components by arc-melting on a water-cooled copper hearth under an argon atmosphere. Excess of Sm was added to compensate the evaporation loss of this element. The ingots were re-melted several times to ensure homogeneity; some of them (particularly those with Fe) were additionally homogenized at 1050°C for 50 h. Alloy samples were annealed at the temperature T_A ranging from 350°C to 550°C for 50 h (unless some other time is specified). The homogenization and annealing treatments were followed by quenching in water. X-ray diffraction (XRD) data were collected with the Cu-Kα radiation. Microstructure was studied for non-etched samples by scanning electron microscopy (SEM) with a JEOL JSM-6330F instrument. The room-temperature magnetic hysteresis loops were measured for coarse powders with a Quantum Design MPMS magnetometer and a vibrating sample magnetometer (VSM). The powder samples were magnetically aligned, except those used for measuring initial magnetization curves. Thermomagnetic analysis at the field of 0.1 kOe was performed with the VSM for 100–120 mg alloy pieces.

3. Theoretical stability analysis for Sm(Co,Cu)$_5$

The stability of the Sm(Co,Cu)$_5$ compounds has been analysed as follows: consider a graph of the total energy of $RCo_{5-x}Cu_x$ as a function of x with a straight line connecting the energy values of pure RCo_5 and RCu_5. This line represents the energies of mechanical mixtures of the two binary phases. Subtracting these values from the energies calculated for $RCo_{5-x}Cu_x$, we obtain $\Delta E(x)$, the difference between the energy of $RCo_{5-x}Cu_x$ and that of the $(1/5)[(5-x)RCo_5 + xRCu_5]$ mixture for every given x. Figure 1 shows $\Delta E(x)$ calculated by different techniques for R = Sm and Y in a magnetic state where the Cu atoms prefer to occupy the 2c atomic sites [16]. LAPW calculations are much more costly in terms of computer time than those for LMTO-ASA; Sm calculations require special treatment for f-electrons [15]

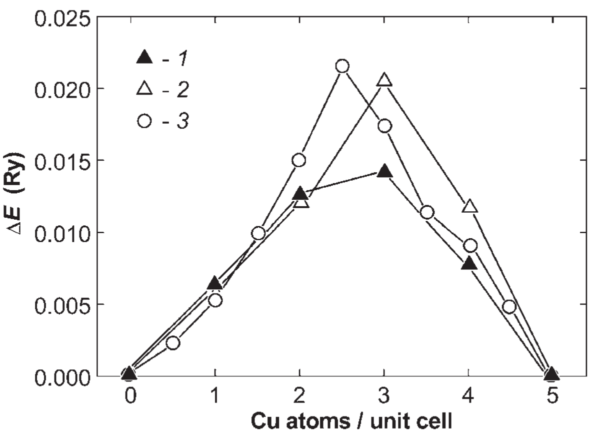

Figure 1. Deviation of the $RCo_{5-x}Cu_x$ energy from that for the $RCo_5 + RCu_5$ mixture calculated (1) by LAPW for R = Sm, (2) by LAPW for R = Y and (3) by LMTO-ASA for R = Y. All the compounds are magnetic and the Cu atoms prefer the 2c sites.

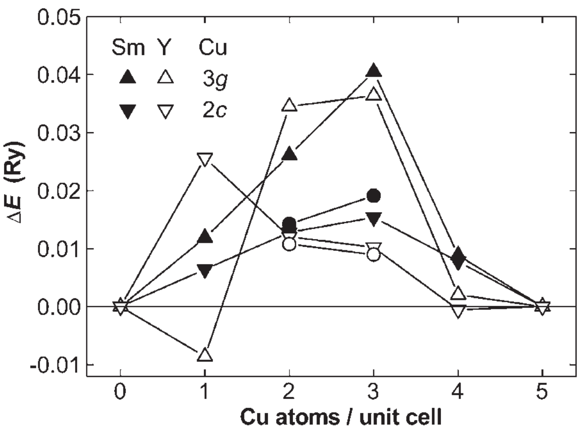

Figure 2. Deviation of the $RCo_{5-x}Cu_x$ energy from that for the $RCo_5 + RCu_5$ mixture calculated by LAPW for magnetic $SmCo_{5-x}Cu_x$ (●,▲,▼) and non-magnetic $YCo_{5-x}Cu_x$ (○,△,▽) with the Cu atoms preferring 3g sites, 2c sites (▲,△), or having no preferential site occupancies (●,○).

and, therefore, are even slower. Fortunately, the differences among all three sets of calculations are not qualitatively important, which allows us to use the faster method for further analysis.

The energy associated with the 3d magnetism of Co is substantial. Non-magnetic calculations are not meaningful in the Sm compounds since the Sm 4f shells retain local magnetic moments at any temperature. However, the similarity of the $\Delta E(x)$ curves for Y and Sm in the magnetic calculations suggests that the f-shell magnetism, as opposed to the Co d-shell magnetism, is not important for structural stability. Figure 2 shows the calculated $\Delta E(x)$ for magnetic $SmCo_{5-x}Cu_x$ and non-magnetic $YCo_{5-x}Cu_x$ for different preferred occupancies of the atomic sites. According to the calculations, in the magnetic regime (figures 1 and 2 for Sm) all the intermediate $RCo_{5-x}Cu_x$ compounds have total energies higher than that of a mixture of RCo_5 and RCu_5 and, therefore, are unstable upon decomposition into RCo_5 and RCu_5. In the non-magnetic regime (figure 2 for Y), the most stable compositions are RCo_4Cu_1 and RCo_1Cu_4. Interestingly, according to the calculations, the structure may

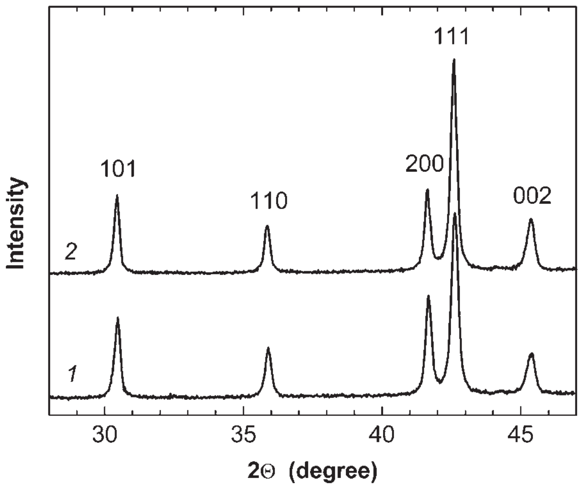

Figure 3. Powder XRD spectra of $SmCo_3Cu_2$ alloy: both as-made (1) and annealed at 350˚C (2) samples have the $CaCu_5$-type structure.

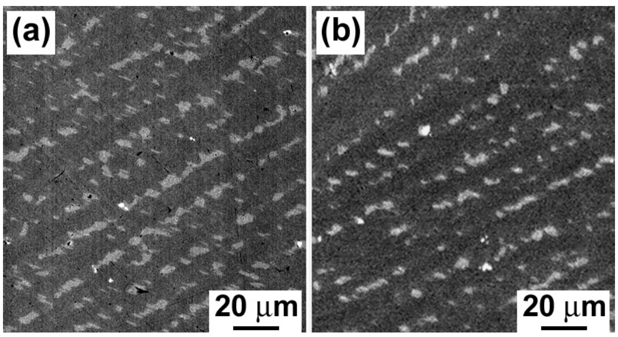

Figure 4. SEM backscattered electron images of $SmCo_3Cu_2$ samples: (*a*) the as-made alloy and (*b*) alloy annealed at 350˚C have a two-phase structure.

depend on whether annealing was done below or above the Curie temperature. For instance, the RCo_4Cu_1 alloy is expected to be a single phase if annealed above the Curie temperature but a mixture of RCo_5 and RCu_5 if annealed below the Curie temperature. The calculations also suggest that atomic site preferences depend on the magnetic state of the alloy. As can be seen from figure 2, calculations in the magnetic regime suggest that the Cu atoms prefer the $2c$ sites for any x value, while in the non-magnetic regime the $3g$ sites become more preferable for $0 < x < 2$ with disordered occupancies for $2 \leqslant x \leqslant 3$.

4. Microstructure and magnetic properties of as-made and homogenized alloys

XRD characterization of the as-made $SmCo_{5-x}Cu_x$ alloys with $x = 1$, 1.5 and 2 clearly shows the presence of a single structure, identified as $CaCu_5$ (space group $P6/mmm$). The representative part of the XRD spectrum for $SmCo_3Cu_2$ is shown in figure 3 (curve 1). However, the SEM image of the backscattered electrons reveals what appears to be a two-phase structure (figure 4(*a*)). This is consistent with the reports [3, 5, 7] about a strong tendency of the as-cast $Sm(Co,Cu)_5$ alloys for microsegregation. The

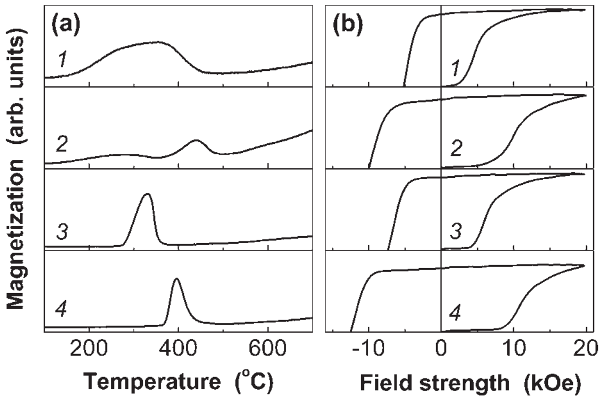

Figure 5. (*a*) Thermomagnetic curves and (*b*) magnetization curves of the $SmCo_3Cu_2$ alloy: as-made (1); annealed at 350˚C (2); homogenized at 1050˚C (3); homogenized at 1050˚C and annealed at 350˚C for 200 h (4).

resulting Co- and Cu-enriched areas have the same crystal structure and cannot be distinguished with powder XRD [7]. Homogenization at 1050˚C eliminates this segregation (the corresponding SEM image is not shown), again in good agreement with [3]. The heating thermomagnetic curves shown in figure 5(*a*) illustrate the emergence of a uniform magnetic phase (curve 3) from a set of phases with a broad range of Curie temperatures (curve 1).

It is interesting to compare the effects of low-temperature annealing on the as-made and homogenized alloys. As can be seen in figures 3 and 4, XRD and TEM show no changes in the non-homogenized $SmCo_3Cu_2$ sample after annealing at 350˚C. However, considerable changes can be observed in the magnetic measurements (figure 5, curves 1 and 2). As a result of annealing, the coercivity H_c increases two times and the thermomagnetic analysis suggests a split in the Curie temperatures. The highest observed Curie temperature T_C increases with annealing. Similarly, in the homogenized sample, both H_c and the only observed T_C increase with annealing (figure 5, curves 3 and 4). Note the difference in annealing times for the as-made and homogenized alloys—this reflects the fact that H_c of the as-made $Sm(Co,Cu)_5$ alloys reached its maximum with annealing in a shorter time than the H_c of the homogenized alloys.

It appears that the increase of coercivity in $Sm(Co,Cu)_5$ during the low-temperature annealing is independent of microsegregation within the single 1 : 5 structure. In our detailed examination of the effect of annealing temperature, we used non-homogenized $Sm(Co,Cu)_5$ alloys following the pattern of earlier works on the subject [3, 7]. In contrast to $Sm(Co,Cu)_5$, the as-made $SmCo_{2.25}Fe_{0.75}Cu_2$ alloy was non-uniform both chemically and structurally: in addition to the 1 : 5 phase it contained significant amounts of the Fe-enriched 2 : 17 phase and the Cu-enriched 2 : 7 phase. After homogenization of the $SmCo_{2.25}Fe_{0.75}Cu_2$ alloy at 1050˚C TEM and XRD showed a chemically uniform 1 : 5 structure, while thermomagnetic analysis revealed a sharp $M(T)$ peak at the Curie temperature of the only magnetic phase. This homogenized $SmCo_{2.25}Fe_{0.75}Cu_2$ alloy was the one subjected to the low-temperature annealing.

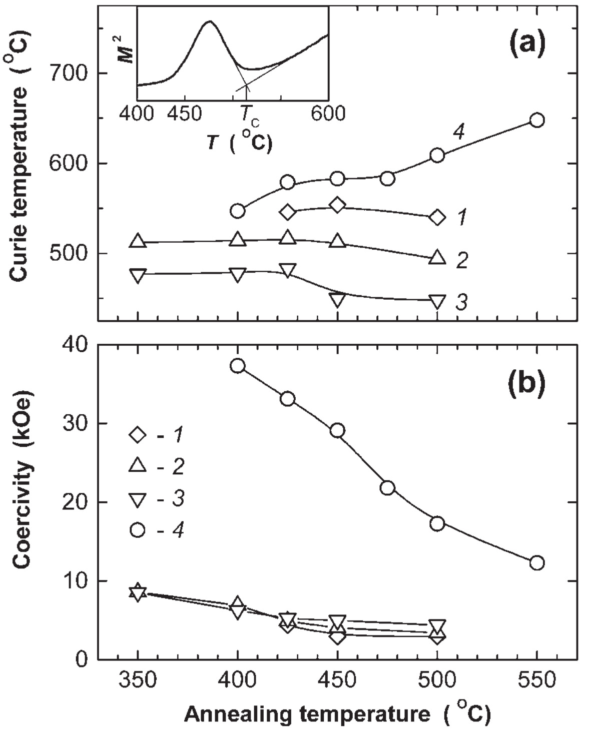

Figure 6. Effect of annealing temperature on (*a*) Curie temperature and (*b*) room-temperature coercivity for (1) $SmCo_4Cu_1$, (2) $SmCo_{3.5}Cu_{1.5}$, (3) $SmCo_3Cu_2$ and (4) $SmCo_{2.25}Fe_{0.75}Cu_2$. The inset shows an example of T_C evaluation ($SmCo_{3.5}Cu_{1.5}$, $T_A = 400$°C).

5. Effect of annealing temperature on the coercivity

Figure 6 shows the Curie temperatures and room-temperature intrinsic coercivities measured for three $SmCo_{5-x}Cu_x$ alloys ($x = 1, 1.5, 2$) and the $SmCo_{2.25}Fe_{0.75}Cu_2$ alloy after annealing treatments at different temperatures, T_A. The effect of T_A on T_C for $Sm(Co,Cu)_5$ alloys is opposite to that for $Sm(Co,Fe,Cu)_5$: in the Fe-free alloys the higher T_A results in a somewhat lower T_C, while in the Fe-added alloy T_C strongly increases with T_A. This difference may arise from the more complex metallurgical behaviour of $Sm(Co,Fe,Cu)_5$, which includes the emergence of the $Sm_2(Co,Fe)_{17}$ phase at higher annealing temperatures. A more detailed report on the structure and magnetic properties of $SmCo_{2.25}Fe_{0.75}Cu_2$ will be the subject of a separate publication; this study focuses on the annealing temperatures around T_C. In this temperature range, the coercivity of all the alloys studied changes significantly with T_A. In particular, H_c of $SmCo_{2.25}Fe_{0.75}Cu_2$ increases from 12.3 to 37.3 kOe when T_A decreases from 550°C to 400°C.

In figure 7, H_c/H_c^* (H_c^* and H_c are, respectively, the room-temperature coercivities before and after annealing) is plotted versus both T_A and the deviation of T_A from T_C. The latter plot seems to reveal a universal behaviour in all samples with the reduced coercivities increasing in a similar way, if annealed at 100–140°C below T_C. This may suggest that the magnetic states of the $Sm(Co,Cu)_5$ and $Sm(Co,Fe,Cu)_5$ influence the structural transformations, particularly those responsible for the increase in H_c. Figure 8 shows parts of the XRD scans for the $SmCo_{5-x}Cu_x$ alloys with $x = 1$, 1.5 and 2 annealed above and below the Curie temperatures. All the scans show what seems to be the uniform $CaCu_5$-type structure with neither a splitting nor broadening of the peaks, which could be associated with a phase separation.

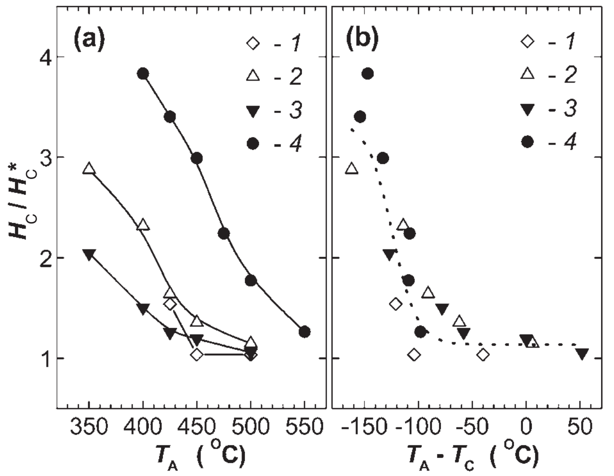

Figure 7. Reduced coercivities of (1) $SmCo_4Cu_1$, (2) $SmCo_{3.5}Cu_{1.5}$, (3) $SmCo_3Cu_2$ and (4) $SmCo_{2.25}Fe_{0.75}Cu_2$ after annealing versus (*a*) annealing temperature T_A and (*b*) deviation of T_A from the Curie temperature T_C. H_c^* is the coercivity before annealing.

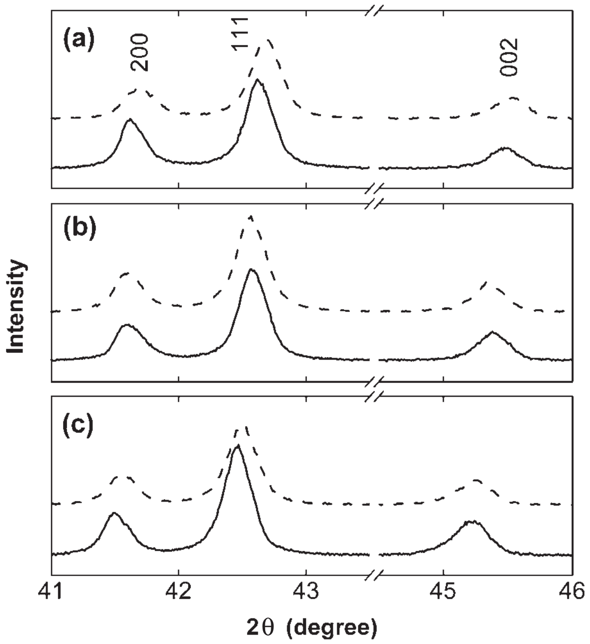

Figure 8. Experimental XRD spectra for (*a*) $SmCo_4Cu_1$, (*b*) $SmCo_{3.5}Cu_{1.5}$ and (*c*) $SmCo_3Cu_2$, annealed at 350°C (——) and at 500°C (- - - -).

6. Discussion

The electronic structure calculations predict a separation of $SmCo_{5-x}Cu_x$ into the $SmCo_4Cu_1 + SmCo_1Cu_4$ mixture or the $SmCo_5 + SmCu_5$ mixture, for the non-magnetic and magnetic states, respectively. This is consistent with the two-phase structure of the as-made alloys reported in this paper and in a number of earlier works [3, 5, 7]. However, it seems unlikely that such a separation is responsible for the magnetic hardness of alloys, as was suggested by Mitchell and McCurrie [7]. On the contrary, the magnetic measurements data for $SmCo_3Cu_2$ summarized in figure 5 (and similar data for the other Sm–Co–Cu alloy studied in this work) show that homogenization treatment actually increases the coercivity.

The very low initial susceptibility observed in all thermally demagnetized samples (see, e.g. curves in figure 5(*b*)) indicates that domain walls are not free to move through the grains. This, in particular, rules out the hypothesis by Yamashita [8] that the magnetic hardness is caused by coherent precipitates of pure Co at the $Sm(Co,Cu)_5$ grain boundaries via increase in the magnetocrystalline anisotropy of the edge Sm ions. The initial magnetization curves suggest that the coercivity of the alloys is caused by a uniform domain wall pinning *inside* the $Sm(Co,Cu)_5$ grains.

One possible mechanism generating multiple pinning sites inside a grain is a spinodal decomposition into two $SmCo_{5-x}Cu_x$ phases with different x values, similar to that observed in as-made alloys, but of a submicrometre scale. The fact that we do not see signs of such decomposition with XRD (figure 8) does not necessarily mean that it does not occur during annealing. The phase separation in the as-made alloys was also not seen by XRD. However, the thermomagnetic analysis, which appears to be more sensitive to the phase separation than XRD (as can be seen from a comparison of curves 1 and 3 in figure 5(*a*)), also does not reveal any signs of this transformation. In the energy calculations, which predicted the decomposition, we considered only chemical energy, while in the real alloy the transformation might be suppressed due to positive changes of the elastic strain energy.

The calculations also suggested different preferred site occupancies for the Cu atoms in $SmCo_{5-x}Cu_x$ with $x = 1$, 1.5 and 2. In the magnetic state, Cu should always prefer to occupy the $2c$ sites (figure 2), while in the non-magnetic state, Cu should prefer the $3g$ sites for $x = 1$ and random occupancies for $x = 2$. It is interesting that after annealing at 350˚C, the alloys with $x = 1$ and 2 have a lattice parameter a 0.14% larger than that after annealing at 500˚C (for $x = 1$ those parameters are the same). It is conceivable that this difference reflects the expansion of the atomic layer, which contains the $2c$ transition-metal sites, when it is preferred by the larger Cu atoms. In the model proposed by Oesterreicher *et al* [2], the magnetic hardness in the single phase $Sm(Co,Cu)_5$ compound was explained by domain wall pinning at the local fluctuations of the exchange energy due to weakly coupled Co atoms. If this is the case, the supposed reordering of the Cu and Co atoms upon annealing below the Curie temperature may be responsible for the observed increase in the room-temperature coercivity.

7. Summary

(1) According to our first principle density functional calculations, the $RCo_{5-x}Cu_x$ compounds with R = Y, Sm are unstable against decomposition into two phases of the same structure with different x values. The calculations also suggest that the magnetic state of the alloys affects the stable x values and the Cu atomic site preferences.

(2) SEM and thermomagnetic studies confirm the two-phase structure of the as-made $Sm(Co,Cu)_5$ alloys. The high-temperature homogenization eliminates the chemical microsegregation and slightly increases the coercivity of the alloys.

(3) A more significant increase in the coercivity (in both the as-made and homogenized alloys) can be achieved by low-temperature annealing. The low initial susceptibility observed in all the samples studied implies that the coercivity is always caused by a uniform domain wall pinning inside the $Sm(Co,Cu)_5$ grains.

(4) The coercivity of different $Sm(Co,Cu)_5$ and $Sm(Co,Fe,Cu)_5$ alloys increases significantly if annealed 100–140˚C below their Curie temperature. Of the two theoretically predicted effects of the alloy magnetic state on the alloy structure—phase separation and change in preferred atomic site occupancies—the latter seems to be more consistent with the results of XRD and especially thermomagnetic studies.

Acknowledgments

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