Electrical and magnetic studies of \((\text{Cu/Zn})\)-bonded \(\text{Sm}_2\text{Fe}_{17}M_xN_y\) magnets \((M=\text{B or C})\)

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Interstitial nitrides \(\text{Sm}_2\text{Fe}_{17}N_y\) magnets discovered by Coey et al.\(^1\) have been extensively studied during the past few years, e.g., Refs. 1—9. It was found that the effect of nitrogen on the structure is to expand the unit cell without changing the symmetry of the 2:17 parent compound. \(\text{Sm}_2\text{Fe}_{17}N_y\) compound possesses high Curie temperature, a net magnetization, which are comparable or superior to those of \(\text{Sm}_2\text{Fe}_{17}\) bonded magnets.\(^11—15\)

Samples of \((\text{Cu/Zn})\)-bonded and unbonded \(\text{Sm}_2\text{Fe}_{17}M_xN_y\) with \(M=\text{B or C (}x=0, 0.25, \text{ and } 0.5; y<3\) were fabricated. All the samples, besides those with B, show single Curie temperature \(T_C\) and with \(\text{Sm}_2\text{Fe}_{17}\)-type crystal structure; however, multiphase structure and double \(T_C\) were observed in all the samples with B. For all the heating runs the electrical resistivity roughly above 600 K increases abruptly for all \(\text{Zn-bonded samples, and decreases abruptly for all Cu-bonded samples. After these high temperature runs, the residual electrical resistivity increases for all Zn-bonded samples, and decreases for all Cu-bonded samples. The effects of Cu segregation and Zn reaction with samples are identified by the EPMA analyses.}

Powder x-ray diffraction analyses show that the \(\text{Sm}_2\text{Fe}_{17}\) phase with the Th\(_2\)Zn\(_{17}\) crystal structure exists in our samples; however, a small amount of \(\alpha\)-Fe is always presented in most of our samples. Multiphase structure was observed in the samples with B. As an example, the powder x-ray diffraction patterns observed for \(\text{Sm}_2\text{Fe}_{17}\), \(\text{Sm}_2\text{Fe}_{17}\)C\(_{0.5}\), \(\text{Sm}_2\text{Fe}_{17}\)B\(_{0.5}\), and \(\text{Sm}_2\text{Fe}_{17}\)N\(_{2.6}\) samples are shown in Fig. 1 (a) to (d), respectively. It is clearly that the 2:17 phase peaks in (b) and (d) are shifted to lower angles in comparison with (a) for \(\text{Sm}_2\text{Fe}_{17}\); their lattice parameters \(a\) and \(b\) were roughly calculated from the powder x-ray diffraction pattern to be \(a=8.58, 8.63, 8.71\) Å, and \(b=12.41, 12.45, 12.61\) Å for \(\text{Sm}_2\text{Fe}_{17}\), \(\text{Sm}_2\text{Fe}_{17}\)C\(_{0.5}\), and \(\text{Sm}_2\text{Fe}_{17}\)N\(_{2.6}\), respectively. Curve (b) in Fig. 1 shows multiphase structure in \(\text{Sm}_2\text{Fe}_{17}\)B\(_{0.5}\).

The temperature dependence of the magnetization \(M\) at 8 kG of the samples had been studied between 4 and 1100 K. The value of the magnetization at 4 K are roughly between 100 and 120 emu/g for all the unbonded samples, and between 80 and 100 emu/g for all (Zn/Cu)-bonded samples. Typically, four kinds of behaviors have been observed; as an example, Fig. 2 presents the normalized magnetization \(M/M_0\) as functions of temperature for (a) \(\text{Sm}_2\text{Fe}_{17}\), (b) \(\text{Sm}_2\text{Fe}_{17}\)C\(_{0.5}\), (c) \(\text{Sm}_2\text{Fe}_{17}\)B\(_{0.5}\), and (d) \(\text{Sm}_2\text{Fe}_{17}\)N\(_{2.6}\). \(M_0\) is the magnetization at 4 K and 8 kG for each sample. Clearly, the magnetization roughly above 900 K increase slowly and then drop abruptly around 1040 K with increasing temperature. This suggests that \(\alpha\)-Fe is precipitated roughly above 900 K. Besides the Curie temperature \(T_C\) of \(\alpha\)-Fe around 1040 K, the curves show single \(T_C\) around 390 K for \(\text{Sm}_2\text{Fe}_{17}\), around 540 K for \(\text{Sm}_2\text{Fe}_{17}\)C\(_{0.5}\), and around 780 K for \(\text{Sm}_2\text{Fe}_{17}\)N\(_{2.6}\). However, double \(T_C\) around 400 and 600 K had

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Footnotes:
1. Coey et al.
2. Electrical and magnetic studies of (Cu/Zn)-bonded Sm\(_2\)Fe\(_{17}\)M\(_x\)N\(_y\) magnets (M=\text{B or C})
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The electrical resistivity and magnetization of these samples were measured as functions of temperatures between 4 and 1200 K. For the magnetization studies, both vibration sample magnetometer (VSM) and superconducting quantum interference device (SQUID) were used to determine the magnetization.
observed for all the Sm$_2$Fe$_{17}$B$_x$ samples. From the x-ray diffraction pattern, the electrical resistivity, and the magnetization studies, we conclude that besides the α-Fe phase, at least two major mixture phases with $T_c$ around 400 and 600 K, are coexisted in the Sm$_2$Fe$_{17}$B$_x$ magnets. We guess that they may be the Sm$_2$Fe$_{17}$ and Sm$_2$Fe$_{14}$B phases.

The electrical resistivity $\rho$ of the bulk Sm$_2$Fe$_{17}$M$_x$ (M=C or B; $x$=0, 0.25, and 0.5) samples has been studied with increasing and decreasing temperatures between 4 and 1200 K. Each resistivity curve approaches to a constant residual resistivity near 4 K; and its value decreases after the high temperature run. This indicates that the scattering centers for the conduction electrons are decreased after high temperature runs; and also suggests that α-Fe and other ordered phases may be precipitated after the high temperature runs. Typically, Fig. 3 presents the electrical resistivity data of Sm$_2$Fe$_{17}$C$_{0.25}$ sample. The open circle and cross are associated with heating and cooling runs, respectively. The derivative of the electrical resistivity with respect to temperature for the heating run is plotted by dots in Fig. 3. $T_c$ determined from the peak of $d\rho/dT$ are 480 K for Sm$_2$Fe$_{17}$C$_{0.25}$ phase and 1040 K for α-Fe phase.

FIG. 1. The powder x-ray diffraction patterns for (a) Sm$_2$Fe$_{17}$, (b) Sm$_2$Fe$_{17}$C$_{0.25}$, (c) Sm$_2$Fe$_{17}$B$_{0.5}$, and (d) Sm$_2$Fe$_{17}$N$_{2.8}$ samples.

FIG. 2. The normalized magnetization as a function of temperature for (a) Sm$_2$Fe$_{17}$, (b) Sm$_2$Fe$_{17}$C$_{0.25}$, (c) Sm$_2$Fe$_{17}$B$_{0.5}$, and (d) Sm$_2$Fe$_{17}$N$_{2.8}$ samples.

FIG. 3. The electrical resistivity and its derivative $d\rho/dT$ of the Sm$_2$Fe$_{17}$C$_{0.25}$ sample as functions of $T$ between 4 and 1200 K. (○: heating run, ×: cooling run, and ■: $d\rho/dT$ for heating run.)

FIG. 4. The electrical resistivity as a function of $T$ between 4 and 1000 K for (a) Zn-bonded Sm$_2$Fe$_{17}$N$_{2.8}$ and (b) Cu-bonded Sm$_2$Fe$_{17}$C$_{0.25}$N$_{2.6}$ (The sequence of the heating and cooling runs is indicated by arrows.)
The coercivity $H_c$ of the Zn-bonded samples can be improved to 6–14 kOe after annealing them between 620 and 720 K in N$_2$ for 2 h. However, $H_c$ of the Cu-bonded samples was only reached 1–3 kOe after annealing them between 620 and 800 K in N$_2$ for 2 h. Generally speaking, from the DSC investigations below 700 K for all the (Zn/Cu)-bonded samples, we found that an exotherm peak between 600 and 700 K for all the bonded samples, and an endothermic peak between 400 and 450 K for Cu-bonded samples only. The exotherm peak has been explained to be the onset temperature of the nitrogen absorption into Sm$_2$Fe$_{17}$. It is not clear at present about the corresponding changes correlated to the exothermic peak for all the Cu-bonded samples. However, it seems to relate the slope increase of the resistivity near 450 K with increasing temperature for all the Cu-bonded samples as shown in Fig. 4.

In general, the temperature dependence of the magnetization at 8 kG for all the (Zn/Cu)-bonded Sm$_3$Fe$_{19}$M$_x$N$_y$ samples behaves quite similarly to the curve d in Fig. 2 with $T_c$ around 780 K. However, this two bonded groups show completely different behaviors for the temperature dependence of $\rho$ with increasing and decreasing temperatures between 4 and 1000 K. The typical behaviors are that (1) for all Zn-bonded samples, the heating run $\rho$ increases abruptly roughing above 600 K, and the value of cooling run $\rho$ is always lower than that of the heating run. In Fig. 4, as an example, curve a shows the $\rho$ of Zn-bonded Sm$_3$Fe$_{17}$N$_{2.0}$ samples, and curve b shows the $\rho$ of Cu-bonded Sm$_3$Fe$_{17}$Cu$_{0.22}$N$_{2.5}$ samples. The sequence of the heating and cooling runs is indicated by arrows in the figures.

From the EPMA investigations of the SEM micrographs of the (Zn/Cu)-bonded samples, we found that in the Cu-bonded samples after the high temperature measurements the Fe-rich and Cu-rich areas are completely distinguishable. As shown in Fig. 5, (a) is the SEM micrograph of the Cu-bonded Sm$_3$Fe$_{17}$Cu$_{0.22}$N$_{2.5}$ sample after the electrical resistivity measurements; (b) is the EPMA picture of Fig. 5(a) for the Fe-rich distribution (white regions); and (c) is the EPMA picture of Fig. 5(a) for the Cu-rich distribution (white regions). However, it is difficult to separate the Fe-rich and Zn-rich regions in Zn-bonded samples. As an example, Fig. 5(d) is the SEM micrograph of the Zn-bonded Sm$_3$Fe$_{17}$N$_{2.0}$ sample after the electrical resistivity measurements; (e) is the EPMA picture of Fig. 5(d) for the Fe-rich distribution (white regions); and (f) is the EPMA picture of Fig. 5(d) for the Zn-rich distribution (white regions).

Finally, for Cu-bonded samples, the main reason for the decrease of $\rho$ after high temperature runs is due to the segregation of Cu and precipitation of Fe, so that the scattering center for conducting electrons is reduced; however, the variation of the magnetization and coercivity is small after the Cu bonding. For Zn-bonded samples, the main reason for the decrease of $\rho$ after high temperature runs is due to the chemical reactions between Zn and Sm$_3$Fe$_{17}$M$_x$N$_y$; and under proper annealing, the variation of magnetization is small, but the coercivity can be enhanced up to 14 kOe.

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