Phase Composition and Magnetic Properties of Fast-Quenched Co-Sm-La and Co-Sm-Ce Alloys

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Abstract. The intermetallic compounds of rare-earth metals (REM) and iron triad metals have unique properties that are increasingly exploited in cutting-edge technology both as individual materials and as phase components that give the alloy its desired properties. Of greatest interest are the intermetallic compounds (IMC) of cobalt based on light REMs. Proper processing imbues these compounds with considerable coercivity on the order of $10^4$. Thus, spinning that is used for the superfast quenching of melts ($v=10^6$ K/s) can produce intermetallic compounds in microcrystal state, in which crystals have distorted crystal lattices. In such cases, phases have high coercivity. Experimentally obtained magnetization and coercivity values of fast-quenched alloys (FQA) in the $\text{Sm}_2\text{Co}_{17}$ plane of Co-Sm-La and Co-Sm-Ce systems are significantly higher than the equilibrium values.

1. Phase Composition of Fast-Quenched Co-Sm-La and Co-Sm-Ce Alloys

Alloys based on the intermetallic compounds (IMC) of samarium and cobalt in a 1:5 ratio are already in use for making permanent magnets; they have high temperatures of transitioning to a magnetically ordered state; they also feature high magnetization of saturation and a coercivity far higher than that of the popular iron-cobalt and platinum-cobalt magnets. However, it is on today’s agenda to make such magnetic materials cheaper by replacing the expensive samarium with cheaper mischmetal. The basic components of mischmetal are cerium and lanthanum. This is why it seems appropriate to analyze how cerium and lanthanum could affect the phase composition and magnetic properties of the ferromagnetic phases in a samarium-cobalt compound.

Fast-quenched Co-Sm-La and Co-Sm-Ce alloys were produced by spinning on a VChI-100 machine by quickly cooling the melt jet on the outer surface of a high-speed (30 m/s) rotary copper cylinder with a disk diameter of 296 mm. The quenching rate was found from the calibration curve in coordinates: sample thickness (mm) and quenching rate (K/s); it turned out to be $v=10^6$ K/s [1]. The produced samples (2 mm wide and 0.01 to 0.02 mm thick scales) were subjected to X-ray diffraction analysis. Phases in the fast-quenched alloys were identified before and after annealing by visual inspection of the diffractograms produced by a Drone-1 diffractometer using CoKα radiation. Magnetization of Saturation was measured at room temperature in a magnetic field of up to 30 kOe using a vibration magnetometer.

Notably, alloys of cobalt and samarium, cerium, lanthanum are microcrystalline rather than amorphous, which distinguishes them from the alloys of many d metals. The phase composition of Co-Sm-La and Co-Sm-Ce systems in the $\text{SmCo}_5$ and $\text{Sm}_2\text{Co}_{17}$ plane is nearly identical in fast-quenched state and in equilibrium [2,3], see Table 1. There are exceptions, though. Thus, in such alloys as Co-
At 91 at.%, Sm-at.7%, La-2at.% and Co-91at.%, Sm-at.7%, Ce-2at.%, the crystallizing phase has a low-temperature modification $\text{Th}_2\text{Zn}_{17}$ rather than high-temp $\text{Th}_2\text{Ni}_{17}$[4,5].

Table 1. Phase composition of alloys in the $\text{Sm}_2\text{Co}_{17}$ plane of Co-Sm-La and Co-Sm-Ce systems in equilibrium and fast-quenched state.

| Alloy No. | Composition, at.% | Phase composition | Structural type |
|-----------|-------------------|-------------------|----------------|
|           | Co    | Sm | Ce | La | Equilibrium | Fast-quenched | Equilibrium | Fast-quenched |
| 1         | 88    | 12 | -  | -  | $\text{Sm}_2\text{Co}_{17}$ | $\text{Sm}_2\text{Co}_{17}$ | $\text{Th}_2\text{Ni}_{17}$ | $\text{Th}_2\text{Ni}_{17}$ |
| 2         | 88    | 9  | -  | 3  | $\text{R}_2\text{Co}_{17}$ | $\text{R}_2\text{Co}_{17}$ | $\text{Th}_2\text{Ni}_{17}$ | $\text{Th}_2\text{Ni}_{17}$ |
| 3         | 88    | 7  | -  | 5  | $\text{R}_2\text{Co}_{17}$ | $\text{R}_2\text{Co}_{17}$ | $\text{Th}_2\text{Ni}_{17}$ | $\text{Th}_2\text{Ni}_{17}$ |
| 4         | 91    | 9  | -  | -  | $\text{R}_2\text{Co}_{17} + \text{Co}$ | $\text{R}_2\text{Co}_{17} + \text{Co}$ | $\text{Th}_2\text{Ni}_{17}$ | $\text{Th}_2\text{Ni}_{17}$ |
| 5         | 91    | 7  | -  | 2  | $\text{R}_2\text{Co}_{17} + \text{Co}$ | $\text{R}_2\text{Co}_{17} + \text{Co}$ | $\text{Th}_2\text{Ni}_{17}$ | $\text{Th}_2\text{Zn}_{17}$ |
| 6         | 88    | 9  | 3  | -  | $\text{R}_2\text{Co}_{17}$ | $\text{R}_2\text{Co}_{17}$ | $\text{Th}_2\text{Ni}_{17}$ | $\text{Th}_2\text{Ni}_{17}$ |
| 7         | 88    | 7  | 5  | -  | $\text{R}_2\text{Co}_{17}$ | $\text{R}_2\text{Co}_{17}$ | $\text{Th}_2\text{Ni}_{17}$ | $\text{Th}_2\text{Ni}_{17}$ |
| 8         | 91    | 7  | 2  | -  | $\text{R}_2\text{Co}_{17} + \text{Co}$ | $\text{R}_2\text{Co}_{17} + \text{Co}$ | $\text{Th}_2\text{Ni}_{17}$ | $\text{Th}_2\text{Zn}_{17}$ |

Apparently, adding cerium and lanthanum stabilizes the low-temperature modification $\text{Th}_2\text{Zn}_{17}$ in fast-quenched alloys.

2. Magnetic Properties of Fast-Quenched Co-Sm-La and Co-Sm-Ce Alloys

Research of physical and chemical interaction in triple Co-Sm-La and Co-Sm-Ce systems [2,3,4] shows that rich-in-cobalt intermetallics form continuous series of solid solutions as the samarium atoms are statistically substituted with cerium and lanthanum atoms, which is expected to alter many of the alloy’s magnetic properties: magnetization of saturation, coercivity, and Curie temperature.

Table 2. FQA saturation magnetization and coercivity values for the $\text{Sm}_2\text{Co}_{17}$ plane of Co-Sm-La and Co-Sm-Ce systems.

| Alloy No. | Composition, at.% | Magnetization $\sigma$, (A·m$^2$/kg) | Coercivity $H_c$, (kOe) |
|-----------|-------------------|--------------------------------------|------------------------|
|           | Co | Sm | Ce | La | FQ | Equilibrium | FQ | Equilibrium |
| 1         | 88 | 12 | -  | -  | 117 | 123 | 17.5 | 13.0 |
| 2         | 88 | 9  | -  | 3  | 122 | 122 | 19.0 | 13.8 |
| 3         | 88 | 7  | -  | 5  | 125 | 121 | 19.8 | 14.0 |
| 4         | 91 | 9  | -  | -  | 126 | 117 | 20.5 | 14.2 |
| 5         | 91 | 7  | -  | 2  | 148 | 120 | 22.5 | 16.2 |
| 6         | 88 | 9  | 3  | -  | 112 | 87  | 17.0 | 4.2  |
| 7         | 88 | 7  | 5  | -  | 116 | 102 | 19.2 | 8.0  |
| 8         | 91 | 7  | 2  | -  | 124 | 108 | 19.0 | 8.2  |
Fast-quenched alloys feature higher saturation magnetization and coercivity. This is due to the fact that fast quenching distorts the crystal lattice and makes it considerably more defective. In such cases, phases have higher coercivity. Table 2 presents FQA saturation magnetization and coercivity values for the Sm₂Co₁₇ plane of Co-Sm-La and Co-Sm-Ce systems.

As can be seen in Table 2, the highest saturation magnetization is featured by the Co-91at.%, Sm-7at.%, La-2at.% alloy, for which it is \( \sigma_m = 148 \text{ A} \cdot \text{m}^2/\text{kg} \), which is distinguished from the equilibrium state by the fact that it crystallizes the metastable phase, the low-temperature modification Th₂Zn₁₇. This alloy also has the highest coercivity \( H_c = 22.5 \text{ kOe} \). Alloying the intermetallic compound Sm₂Co₁₇ with cerium results in the Co-88at.%, Sm-9at.%, Ce-3at.% alloy having a 28% higher magnetization in microcrystalline state, while the coercivity of this alloy is 75% higher than that of the equilibrium alloy of the same composition, see Table 2.

Magnetization testing of the alloys in the Sm₂Co₁₇ plane shows that the magnetization of the Co-88at.%, Sm-7at.%, Ce-5at.% is \( \sigma_m = 103 \text{ A} \cdot \text{m}^2/\text{kg} \), rising further at greater cerium concentrations to \( \sigma_m = 117 \text{ A} \cdot \text{m}^2/\text{kg} \). The emergence of a non-collinear magnetic structure is what explains this analogy of concentration correlation of saturation magnetization as samarium and cerium atoms substitute each other in the structure of R₆Zn₁₇. Such modification of the magnetic structure in case of statistical substitution of atoms has been detected multiple times in the compounds of the homological series of Laves phases [7,8,9]. Saturation magnetization in the domain of the solid RCo₃ solution changes gradually, whereby increasing the cerium content lowers its value from 120 A·m²/kg to 105 A·m²/kg while raising coercivity from 10.5 kOe to 18 kOe.

3. Conclusions
Fast-quenching of Co-Sm-La and Co-Sm-Ce alloys results in a microcrystalline state, in which the phase components of some samples differ from those of the equilibrium-state samples.

Sm₂Co₁₇-based FQAs with lanthanum additives feature both higher coercivity (+36%) and higher saturation magnetization (+23%).

4. References
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