Directional Magnetic Properties and Structures in the SmCo₅-SmCu₅ System Alloy*

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The coercive force BH_C of the intermetallic compound SmCo₅ is not sufficient for its application as a permanent magnet in the cast state. This study deals with increasing of the coercive force of the SmCo₅ alloy system. Specimens are melted in an arc melt furnace which has the tungsten electrode and inactive gas Ar.

The directional magnetic properties are observed in the SmCo₅-SmCu₅ system alloy, as a result of freezing in a direction normal to the cold surface of the copper hearth. The maximum energy product, $(BH)_{\max}$, of the 65 wt% SmCo₅-35 wt% SmCu₅ alloy has 5.78 MGOe in the as-cast state, when the measurement is carried out in a direction perpendicular to the chill plane. By annealing at 300°C for 1 hour, the $(BH)_{\max}$ value increases to 7.73 MGOe with B_r 6450 G and BH_C 3400 Oe. The magnetic properties in the direction perpendicular to the chill plane are superior to those in other directions and the chill plane shows a weak texture, (0001). These alloys have the easy direction of magnetization, which is the c-axis of the hexagonal crystal as in the case of SmCo₅.

The lattice constants of both a- and c-axes of the hexagonal crystal enlarge linearly with increasing copper content in alloy. The value of lattice constant ratio c/a keeps approximately 0.802 in all the alloys investigated.

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I. Introduction

The study of ferromagnetism of rare earth metals combined with iron group elements has been developed since a pioneer work on GdCo₅⁽¹⁾ in 1959. The intermetallic compounds of rare earth-cobalt have been extensively investigated. In recent papers⁽²⁾⁽³⁾, it is reported that the $(BH)_{\max}$ value is 18.5 or 20 MGOe. The excellent magnetic properties in rare earth-cobalt compounds originate in the magnetic crystal anisotropy constant (K). In MnBi or MnAl which is well known as a fine powder magnet, K is approximately 10^7 erg/cc, but K is between $5 \sim 8 \times 10^7$ erg/cc in compounds RCo₅, where R is the rare earth element. In view of such a superior K value, their application as a permanent magnet may be in the form of a fine powder magnet, but a high level technique is needed in order to obtain the above-mentioned superior value. In this connection, an attempt was made to produce a high-coercivity magnet by a conventional casting technique. The results show a remarkable directional structure in the cast alloy. Nesbitt et al. also studied SmCo_{5-x}Cu_x alloy⁽⁴⁾⁽⁵⁾ and found that replacement of cobalt with copper in some of these rare-earth compounds resulted in solid materials having substantial permanent magnet properties.

II. Experimental Procedure

99.9% pure samarium, 99.99% pure cobalt and 99.95% pure copper were used as the alloying materials. The specimens were melted using an arc-melt furnace in

purified argon gas atmosphere. In order to prevent segregation, alloy buttons were crushed and remelted repeatedly.

As shown in Table 1, 9 specimens are classified by weight percent of SmCo₅ and SmCu₅. Magnetic measurements were made with a self-recording magnetic flux-meter. Microstructures were investigated by means of optical and electron microscopy and X-ray measurements.

Table 1 Composition of specimens

Sample No.	100	101	102	103	104	105	106	107	108
SmCo ₅ (wt%)	100	90	80	70	65	60	55	50	40
SmCu ₅ (wt%)	0	10	20	30	35	40	45	50	60

Photo. 1 shows the cleavage structure of specimens 104 and 106 in the as-cast state. The bottom in the photograph is a freezing plane which contacts with cold copper hearth, and the columnar crystal elongates linearly in the center to the upper part from the bottom part and is curved at the edge. This structure resembles structure of the chilled zone in Alnico magnet alloys. The specimen cut off from the alloy button is shown in Fig. 1, and the specimen selected from the linear part of the columnar crystal (Photo. 1) indicates a directional structure. The dimension of the specimen is approximately 5 (high) × 8 × 5 mm and the alloy button is 30 mm dia. × 9 mm high.

III. Experimental Results and Discussion

I. Magnetic properties

In the intermetallic compound, Strnat et al. found that

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Photo. 1 Microstructure (a) is cleavage structure of 70 wt% SmCo_5 -30wt% SmCu_5 and (b) is same structure of 55wt% SmCo_5 -45 wt% SmCu_5 ($\times 10 \times \frac{2}{3}$)

Fig. 1 A pattern of the specimen in bottom ingot. An arrow indicates each direction of measurement. (A) and (B) planes are perpendicular to the Easy and Hard directions, respectively

the magnetization field strongly affected the magnetic properties⁽⁶⁾. Magnetic measurements were carried out using the usual electromagnet and the maximum measuring field was between 14~18 kOe. Fig. 2 shows the variation in magnetic properties of the as-cast specimens with SmCu_5 contents. As shown in the figure, in the range of 30 to 35 wt% SmCu_5 the magnetic values increase remarkably. For example, the magnetic values of specimen 104 observed parallel to the easy direction are $B_r = 6300$ G, $BH_C = 3000$ Oe and $(BH)_{\max} = 5.78$ MGOe. On the other hand, the values observed parallel to the hard (H) direction are considerably inferior to the easy (E) direction for all the specimens and the $(BH)_{\max}$ value is less than 1 MGOe in all cases.

After annealing from 200° to 1000°C for 1 hr in vacuum, the magnetic values for both directions vary as shown in Figs. 3 and 4. A significant magnetic difference between the E and H directions for specimens 100 to 102 cannot be recognized, but it is shown clearly for specimen 103 in Fig. 3. Remanence B_r to the easy direction hardly changes but coercive force BH_C has a maximum at 700°C. Therefore a maximum of $(BH)_{\max}$ exists at 700°C and its value is 6.55 MG Oe with $B_r = 6100$ G and $BH_C = 3900$ Oe.

In Fig. 4 specimens 104, 105, and 106 exhibit directional magnetic properties during the annealing treatment. The highest magnetic values by the annealing are obtained with the 65 wt% SmCo_5 -35 wt% SmCu_5 ; $B_r = 6450$ G at 300°C, $BH_C = 4000$ Oe at 400°C, are $(BH)_{\max} = 7.73$ MGOe at 300°C. In the SmCo_5 - SmCu_5 system alloy, remarkable improvements owing to annealing are found only in specimens 103 and 104. Both specimens can be

Fig. 2 Magnetic properties obtained on each specimen in SmCo_5 - SmCu_5 alloys in the as-cast state

rewritten in the form of molecular formulae as $\text{SmCo}_{3.55}\text{Cu}_{1.45}$ and $\text{SmCo}_{3.3}\text{Cu}_{1.7}$, respectively. Fig. 5 substantiates the above and suggests that the optimum composition for magnetism exists in the range of 65 wt% SmCo_5 -35 wt% SmCu_5 .

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Fig. 3 Magnetic properties vs. annealing temperature for $\text{SmCo}_5\text{-SmCu}_5$ alloys Fig. 4 Magnetic properties vs. annealing temperature for $\text{SmCo}_5\text{-SmCu}_5$ alloys

Photo. 2 Microstructure of SmCo_5 - SmCu_5 alloys in as-cast state ($\times 100$)

Each specimen in this system was magnetized at 25°C in a field of 17 kOe, held at each temperature for 30 minutes and then returned to 25°C . Flux changes in the specimens were measured by the gauss meter using Hall element InSb. The flux losses of the specimens are shown in Fig. 6.

The flux loss from 25°C to -170°C (liquid nitrogen) can hardly be observed, but at 25°C to 250°C , the loss increases with the rise of temperature.

The flux density after heat treatment at 250°C is almost half of the value at 25°C , but is completely reversible to the initial value at 25°C by remagnetizing. For this reason, it is considered that magnetic anisotropy constant K in this system is reduced at temperatures above 25°C as in the case of YCo_5 ⁽⁷⁾.

2. Microstructure

Photo. 2 shows optical microstructures of specimens

100, 103, 105, and 107 in the as-cast state. The basal plane of the cellular structure is shown in the (A) plane of each specimen and the side plane (perpendicular to the basal plane) of this structure in the (B) plane. Side and basal patterns of the cellular structure exist in both the (A) and (B) planes of specimen 100 in the as-cast state. It is well understood that in specimens 103, 105, and 107 the crystal arrangement on the (A) plane is different from the (B) plane.

After annealing at 300°C for 1 hr, the change in microstructure appears as shown in Photo. 3. The area of the black structure on the (B) plane becomes complicated as compared with that in the as-cast state. The diameter of a certain part of the cellular structure on the (A) plane becomes smaller in specimen 103, and in specimen 105 this tendency is observed over the whole area. This insignificant change in the structure suggests that the coercive force attains a maximum value at approximately 400°C .

Photo. 4 shows microstructures of specimens 103, 105,

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Photo. 3 Microstructure of $\text{SmCo}_5\text{-SmCu}_5$ alloys after annealing at 300°C for 1 hr ($\times 100$)

Photo. 4 Microstructure of $\text{SmCo}_5\text{-SmCu}_5$ alloys after annealing at 300°C for 1 hr ($\times 8000$)

and 107 by an electron-microscope. Fine particles which cannot be observed by an optical microscope are shown and their sizes become smaller with increasing of SmCu_5 content. The shape of the fine particles in specimens 103 and 105 is angular, but those in specimen 107 are round-shaped. The mean diameter of these fine particles is approximately $5000 \text{ \AA}$, $4000 \text{ \AA}$ and $2500 \text{ \AA}$, respectively. The X-ray diffraction patterns are shown in Figs. 7 and 8. In Fig. 7 on specimen 104, the (A) plane has the diffraction of $(00\cdot2)$ but the diffraction of $(20\cdot0)$ exists on the (B) plane. In Fig. 8 specimen 106 has the same $(00\cdot2)$ diffraction on the (A) plane, but the diffraction on the (B) plane is $(11\cdot0)$ instead of $(20\cdot0)$. Since fiber texture may be expected in both specimens from the

above results, pole figures of the above specimens are made out. In spite of the clear directional structure on magnetism, an indistinct fiber texture is obtained. Namely, on the (A) plane of specimen 104 a weak texture of $(00\cdot2)$ can be observed in the as-cast state. The cast textures of cadmium and zinc has a hexagonal structure, and the outer skin seems to have (0001) parallel to the surface. In the columnar zone, the skin seems to have (1010) parallel to the developing direction, with the coexistence of both planes⁽⁸⁾. As $\text{SmCo}_5\text{-SmCu}_5$ alloys have a hexagonal structure and also a columnar structure by the chill effect, it is reasonable that the weak texture

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Fig. 5 The best value obtained on each specimen in the $\text{SmCo}_5\text{-SmCu}_5$ alloys

Fig. 6 Flux loss in $\text{SmCo}_5\text{-SmCu}_5$ alloys after heating at $50^\circ\sim 250^\circ\text{C}$ or cooling at $0^\circ\sim -170^\circ\text{C}$

Fig. 7 Diffraction patterns of 65 wt % $\text{SmCo}_5\text{-35 wt % SmCu}_5$ alloys in the as-cast state

of (00·2) is observed⁽⁸⁾.

The lattice constants calculated from the diffraction chart are shown in Fig. 9 and both a- and c-parameters increase linearly with increasing copper content, while the axial ratio c/a stands at approximately 0.802. These results suggest the formation of solid solution in this system.

Fig. 10 shows powder diffraction patterns of specimens

Fig. 8 Diffraction patterns of 55 wt % $\text{SmCo}_5\text{-45 wt % SmCu}_5$ alloys in the as-cast state

Fig. 9 Lattice parameter vs. copper content curves for $\text{SmCo}_5\text{-SmCu}_5$ alloys

Fig. 10 X-ray powder pattern traces for oriented and random samples of $\text{SmCo}_5\text{-SmCu}_5$ alloys

104 and 106 of less than 325 mesh, which were buried in dissolved paraffin and solidified with or without a

magnetic field of less than 1000 Oe. The X-ray irradiated plane is perpendicular to the magnetic field. A strong diffraction of $(00\cdot2)$ is recognized in both specimens. The above fact suggests the magnetic easy axis coincides with the c -axis of the hexagonal crystal as in the case of the SmCo_5 compound.

The inversion of composition occurs in the white and black areas of the cellular structure with increasing copper content. X-ray microanalysis of specimens 102 and 107 are shown in Fig. 11 and the fine lines in the figure are

Fig. 11 X-ray microanalysis patterns for $\text{SmCo}_5\text{-SmCu}_5$ alloys the in as-cast state

the mean value of each metallic element. The convex part for cobalt corresponds to the concave part for copper. This concave-convex relation can be explained by the micro-structure in Photo. 2. That is, the convexed part for cobalt corresponds to the black cellular structure rich in cobalt. Therefore, the white area in specimen 102 is copper-rich. This relation is reversed in specimen 107. It is observed that the inversion occurs between the compositions 40 to 50 wt% SmCu_5 in this alloy system. An assumption may be drawn from the above fact that this alloy system has a congruent point or an eutectic point on a quasi-binary diagram.

In the $\text{SmCo}_5\text{-SmCu}_5$ alloys, the optimum composition for magnetism existed around $\text{SmCo}_{3.3}\text{Cu}_{1.7}$ and 7.73 MGOe of $(BH)_{\text{max}}$ was obtained. The theoretical $(BH)_{\text{max}}$ value for this system alloys would be 11 MGOe on the assumption that the packing factor is 70%.

IV. Summary

The alloy button shows directional magnetic properties and the direction perpendicular to the chill plane. The optimum composition of this system is $\text{SmCo}_{3.3}\text{Cu}_{1.7}$ and the magnetic values are measured to be $(BH)_{\text{max}} = 7.73$, $BH_C = 3400$ Oe and $Br = 6450$ G. Improvement of magnetic properties by annealing from 300° to 700°C is attained in the compositions of $\text{SmCo}_{3.5}\text{Cu}_{1.5}$ to $\text{SmCo}_{3.0}\text{Cu}_{2.0}$. The lattice constants of the alloys, a - and c -parameters increase linearly with increasing SmCu_5 content, and the axial ratio c/a stands at approximately 0.802. The phase diagram of this system has not been made out, but X-ray microanalysis suggests the presence of a congruent point or an eutectic point on a quasi-binary diagram.