Journal of Magnetics 8(3), 124-127 (2003)

Feasibility Study of HDDR and Mechanical Milling Processes for Preparation of High Coercivity $SmCo_5$ Powder

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(Received 9 June 2003)

HDDR (hydrogenation, disproportionation, desorption, recombination) and mechanical milling processes have been applied to the $SmCo_5$ alloy in an attempt to produce a highly coercive powder. The $SmCo_5$ alloy had very high structural stability under the hydrogen atmosphere and the 1:5 phase was only partially disproportionated under up to 10 kgf/cm^2 hydrogen gas. The partially disproportionated material was recombined not into 1:5 phase after the HDDR, but rather into multi-phase mixture consisting of 1:5, 2:17, 2:7 and 1:7 phases. The $SmCo_5$ alloy HDDR-treated with hydrogen up to 10 kgf/cm^2 had poor coercivity. For a useful HDDR to prepare a high coercivity $SmCo_5$ alloy powder, much higher hydrogen pressure well exceeding 10 kgf/cm^2 would be required. The $SmCo_5$ alloy lump was amorphized by an intensive mechanical milling, and it was crystallised ultra-finely by a subsequent optimum annealing. The optimally annealed material had very high coercivity, and it was found that the mechanical milling followed by an annealing was an effective way of producing highly coercive $SmCo_5$ alloy powder.

Key words : $SmCo_5$, HDDR, hydrogenation, disproportionation, desorption, recombination, mechanical milling

1. Introduction

HDDR [1-5] and mechanical milling techniques [6, 7] have been effectively utilised as a useful means of producing magnetically coercive powder of rare earth transition metal permanent magnetic alloys. In the HDDR process a pre-alloy lump is heated under hydrogen gas to disproportionate the hard magnetic phase and then the absorbed hydrogen gas is desorbed under a vacuum. During the desorption step disproportionated phases are recombined together into the original magnetic phase with very fine grain structure. Meanwhile, in the mechanical milling technique, a pre-alloyed lump with desired composition is milled intensively to become an amorphous and subsequently annealed to crystallize the hard magnetic phase. Through these HDDR or mechanical milling processes the pre-alloy lump with coarse grain structure is converted into a powder with extremely fine grain structure. The fine grain structure leads to high coercivity. In this article, the HDDR and mechanical milling processes have been applied to the $SmCo_5$ alloy in an attempt to produce a highly coercive $SmCo_5$ powder, and feasibility of the HDDR and mechanical milling processes for the preparation of $SmCo_5$ powder was investigated.

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2. Experimental Work

$SmCo_5$-type alloy with composition 16.37 at% Sm and 83.63 at% Co was prepared by an induction melting, and the prepared alloy ingot was annealed at 1050 °C for 2 days under argon gas. The annealed ingot was crushed and pulverised. The crushed coarse particles (average size = 2~3 mm) were used for an HDDR-treatment. For the HDDR, the crushed material was heated up to 800 °C and held for 60 min under hydrogen gas with various hydrogen pressures. After that the atmosphere was changed to vacuum keeping the sample at various temperatures for a required periods and then the sample was cooled down to room temperature. For a mechanical milling, the pulverized powder with particle size less than 100 μm was used. The pulverized alloy powder was charged into a hardened steel vial together with hardened steel balls. The mass ratio between the charged material powder and milling balls was 1:10. The charged vial was evacuated and then filled with a high purity argon gas. The material was then milled for 36 hrs using a shaker mill. The milled powder was annealed in vacuum. Phase analysis of the material under various conditions was undertaken using an XRD (x-ray diffraction) with Cu K_α radiation. DTA (differential thermal analysis) was used to investigate the crystallisation of mechanical milled alloy. Magnetic properties of the material were measured by VSM (vibrating sample magnetometer). Prior to the VSM measurement, the sample was magnetised by applying pulsing field of 6 Tesla.

3. Results and Discussion

Fig. 1 shows the XRD spectra of the $SmCo_5$ alloy heated above 800 °C under various hydrogen pressures. Also included in Fig. 1 is the XRD spectrum of the as-annealed $SmCo_5$ alloy for comparison. As can be seen, in the alloy heated under 1 kgf/cm^2 hydrogen gas, most of the material remains in intact and still exists as an 1:5 phase although some evidence for the presence of Co and 2:17 phase is also observed. The appearance of the Co and 2:17 phases in this sample is thought to result from a partial disproportionation of the $SmCo_5$ under hydrogen gas. This result suggests that the $SmCo_5$ alloy has been only partially disproportionated by the heating up to 800 °C under 1 kgf/cm^2 hydrogen gas. In the $SmCo_5$ alloy heated under 5 kgf/cm^2 hydrogen, in addition to the 1:5, 2:17 and Co phases the SmH_x hydride and 1:7 phase are also clearly found. Needless to say, the phases except the 1:5 phase are believed to have resulted from the disproportionation of $SmCo_5$ phase. Obviously, however, the presence of 1:5 phase indicates that the disproportionation is not complete even under the increased hydrogen pressure of 5 kgf/cm^2. In the $SmCo_5$ alloy heated up to 800 °C under even higher hydrogen pressure of 10 kgf/cm^2 hydrogen gas, a trace of 1:5 phase is still observed together with SmH_x hydride, Co and 2:17 phases. This is also a solid evidence for an incomplete disproportionation of the 1:5 phase even under the high hydrogen pressure of 10 kgf/cm^2. The 1:7 phase existed in the alloy heated under 5 kgf/cm^2 hydrogen is no longer found. The findings from the above XRD results lead us to conclude that the $SmCo_5$ alloy has very high structural stability under the hydrogen atmosphere up to 10 kgf/cm^2 and during the heating only partial disproportionation has occurred. For an effective HDDR-treatment the 1:5 phase has to be fully disproportionated by heating under hydrogen and the disproportionation product should be a mixture of SmH_x and Co, which has not been achieved in the present study. It would seem that much higher hydrogen pressure well exceeding 10 kgf/cm^2 is required to get a full disproportionation of the $SmCo_5$ alloy. Fig. 2 shows XRD spectra for the HDDR-treated $SmCo_5$ alloy. The alloy was heated up to 800 °C for 30 min under different hydrogen pressure of 1 and 10 kgf/cm^2 for a hydrogenation and disproportionation, and then subjected to a desorption and recombination at 800 °C for 30 min under vacuum. As can be seen in Fig. 2, the material HDDR-treated with 1 kgf/cm^2 hydrogen gas stays in 1:5 structure form. This 1:5 phase is believed not to have passed the HDDR steps because of the high structural stability of 1:5 phase under 1 kgf/cm^2 hydrogen gas as can be expected from Fig. 1. Meanwhile, the material HDDR-treated with 10 kgf/cm^2 hydrogen gas has a very complicated phase structure consisting of multiphase of 1:5, 2:17, 2:7 and 1:7 phases. It seems that the partially disproportionated $SmCo_5$ alloy has been recombined not into its original 1:5 phase, but rather into a multiphase mixture.

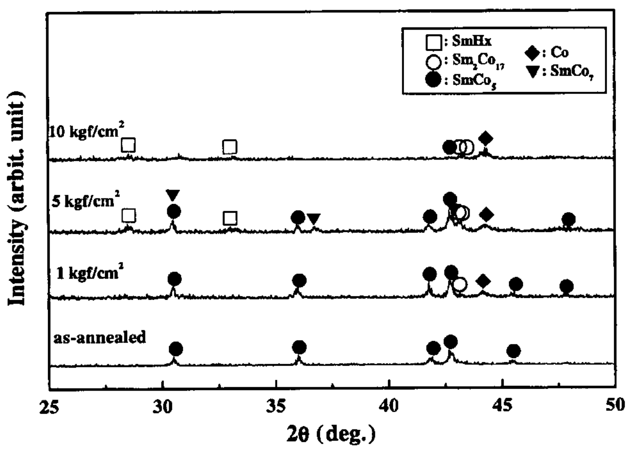

Fig. 1. XRD spectra of the $SmCo_5$ alloy heated up to 800 °C under various hydrogen pressures.

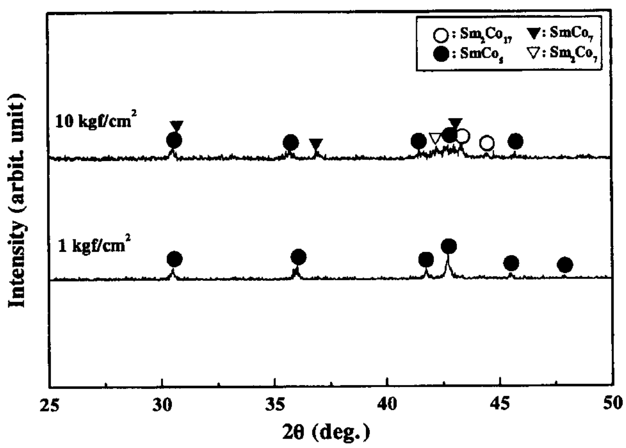

Fig. 2. XRD spectra of the $SmCo_5$ alloy HDDR-treated with different hydrogen pressures.

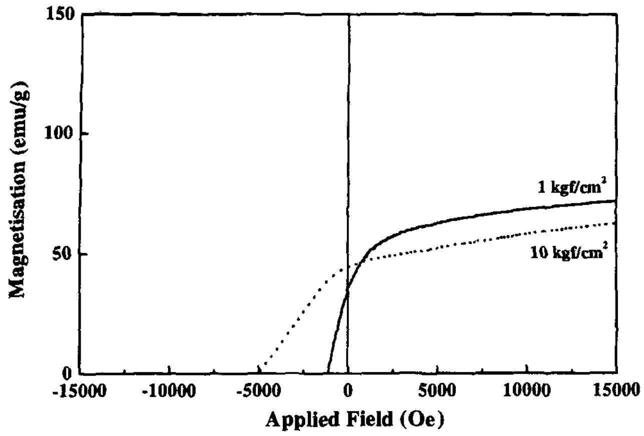

Fig. 3. Demagnetisation curves of the $SmCo_5$ alloy HDDR-treated with different hydrogen pressures.

Fig. 3 shows demagnetisation curves of the $SmCo_5$ alloy HDDR-treated with hydrogen pressure of 1 kgf/cm^2 and 10 kgf/cm^2. The material HDDR-treated with 1 kgf/cm^2 exhibits poor coercivity, and this may be attributed to the incomplete disproportionation. As discussed above, the 1:5 phase has not been HDDR-processed, and thus the material may still have the same coarse grain structure as that in as-annealed condition. The coarse grain structure may lead to a poor coercivity. Meanwhile, the material HDDR-treated with 10 kgf/cm^2 exhibits a somewhat enhanced coercivity of 5 kOe. As discussed above, the material HDDR-treated with 10 kgf/cm^2 hydrogen gas has been HDDR-processed significantly and has a multi-phase of 1:5, 2:17, 2:7 and 1:7 phases. These recombined phases may have fine grain structure, thus an enhanced coercivity may be obtained. However, the obtain coercivity is still fairly low when considering the high anisotropy field ($H_A \approx$ 440 kOe) of the $SmCo_5$ compound [8]. This may be attributed to the magnetically less hard 2:17 phase ($H_A \approx$ 65 kOe [9]) included in the material after the HDDR. The coexistence of magnetically less hard phases may act as a nucleation site for a reverse domain under the demagnetising field, thus leads to the lower coercivity.

Fig. 4 shows the dependence of coercivity on the recombination temperature for the $SmCo_5$ alloy HDDR-treated with 10 kgf/cm^2 hydrogen gas. Hydrogenation and disproportionation of this material was carried out by heating up to 800 °C for 30 min under 10 kgf/cm^2 hydrogen gas, and the disproportionated material was recombined for 30 min at various temperatures. As can be seen, the obtained coercivities are fairly low. The poor coercivity is due to the incomplete disproportionation in HDDR reactions even under 10 kgf/cm^2 hydrogen gas. It is suggested, therefore, that for a useful HDDR-treatment for preparing a high coercivity $SmCo_5$ alloy powder much higher

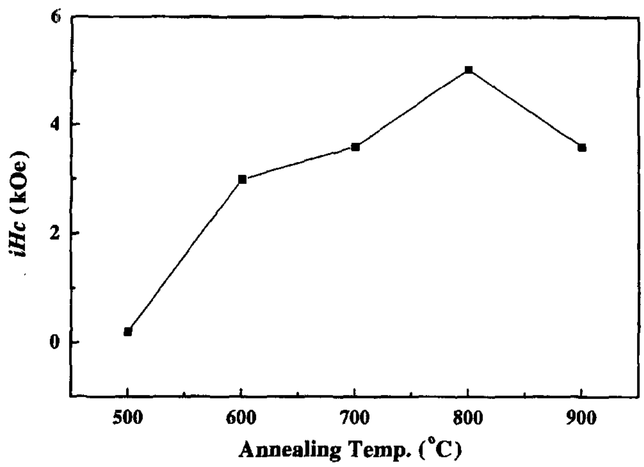

Fig. 4. Dependence of coercivity of the HDDR-treated $SmCo_5$ alloy on the recombination temperature.

hydrogen pressure is definitely required, which is not available in the present study due to a limitation of the used HDDR rig.

Fig. 5 shows the XRD spectra of the $SmCo_5$ alloy after mechanical milling for 36 hrs and annealing at an elevated temperature (900 °C for 20 min). It can be seen that the pre-alloy lump has been decomposed into an amorphous state after the mechanical milling (a), and the subsequent annealing causes a crystallisation of the amorphous material (b). It appears that the annealed material has two-phase structure consisting of 1:5 and 2:17 phases rather than the initial 1:5 single-phase structure.

Fig. 6 shows demagnetisation curves of the mechanically milled (36 hrs) $SmCo_5$ alloy after annealing at different temperatures for 20 min. Also included is the demagnetisation curve of the as-milled material. The as-milled amorphous material has some coercivity, and this is not

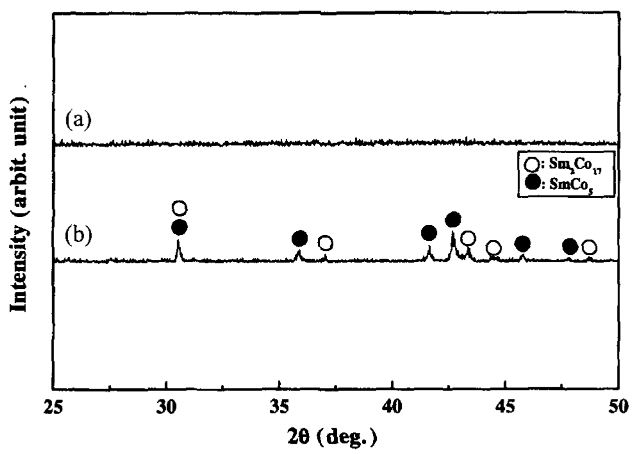

Fig. 5. XRD spectra of the $SmCo_5$ alloy after (a) mechanical milling for 36 hrs and (b) annealing at 900 °C for 20 min.

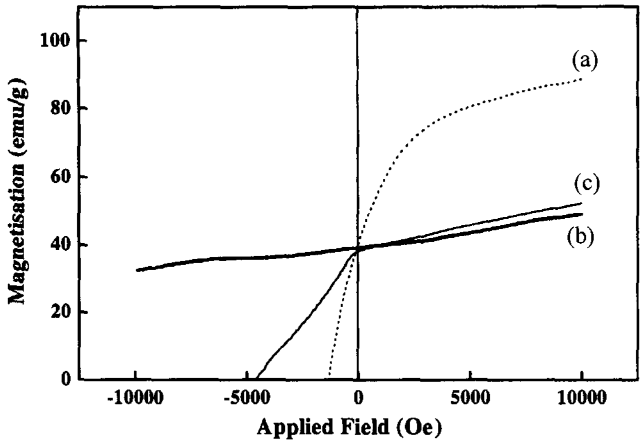

Fig. 6. Demagnetisation curves of the mechanically milled $SmCo_5$ alloy. (a) As-milled, (b) annealed at 600 °C for 20 min, and (c) annealed at 1000 °C for 20 min.

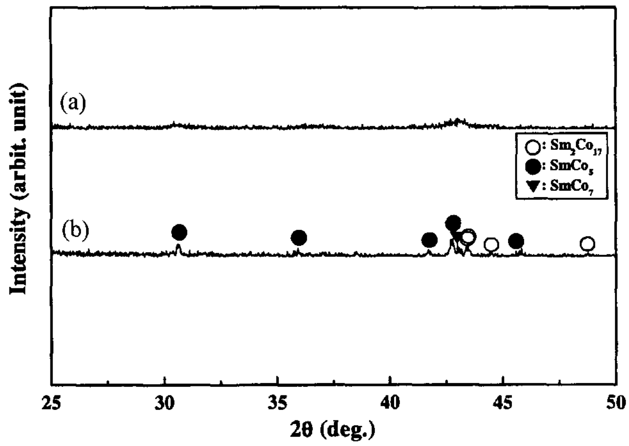

Fig. 7. XRD spectra of the mechanically milled $SmCo_5$ alloy after annealing (a) at 600 °C for 20 min and (b) at 1000 °C for 20 min.

surprising as some amorphous rare-earth - Co alloy systems have been reported to have a significant magnetic anisotropy [10]. The material annealed at 600 °C shows very high coercivity, and this is due to the ultra finely crystallized Sm-Co compounds. As can be seen in Fig. 7(a), the milled amorphous has been crystallised and the reflections are heavily broadened, which indicates ultra-fine grain structure. Meanwhile, the material annealed at 1000 °C has a radically reduced coercivity compared to that annealed at 600 °C. XRD spectra of the material annealed at 1000 °C for 20 min showed that the phase structure consisted of 1:5, 2:17 and 1:7 phases (Fig. 7(b)). The reduced coercivity may, therefore, be interpreted by an over grown grain structure and the presence of less hard phase (2:17 phase).

4. Conclusion

The $SmCo_5$ alloy had very high structural stability under the hydrogen atmosphere and the 1:5 phase was only partially disproportionated under up to 10 kgf/cm^2 hydrogen gas. The partially disproportionated material was recombined not into the 1:5 phase after the HDDR, but rather into a multi-phase mixture consisting of 1:5, 2:17, 2:7 and 1:7 phases. The $SmCo_5$ alloy HDDR-treated with hydrogen up to 10 kgf/cm^2 had poor coercivity. For a useful HDDR to prepare high coercivity $SmCo_5$ alloy powder, much higher hydrogen pressure well exceeding 10 kgf/cm^2 would be required. The $SmCo_5$ alloy lump was amorphized by an intensive mechanical milling, and it was crystallised ultra-finely by a subsequent optimum annealing. The optimally annealed material had very high coercivity, and it was found that the mechanical milling followed by annealing was an effective way of producing highly coercive $SmCo_5$ alloy powder.

Acknowledgement

The author would like to acknowledge that the present work was supported by the KOSEF (Korea Science and Engineering Foundation) under Grant No. R02-2000-00238.

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