Journal of Magnetics 12(1), 45-48 (2007)

Study of Coercivity Origin in Mechanically Alloyed Co-Zr System

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(Received 16 February 2007)

$Co_{100-X}Zr_X$ (x=10-40) alloys were prepared by using a mechanical alloying technique. Phase constitution of the crystallised material depended on the annealing temperature. The $Co_{82}Zr_{18}$ alloy crystallised at lower temperature around 550°C consisted of $Co_{23}Zr_6$, Co_5Zr and fcc-Co phases, while the alloy crystallised at higher temperature around 800°C consisted of $Co_{23}Zr_6$ and fcc-Co phases. Phase constitution of the crystallised material also depended on the chemical composition of the alloy. The material with lower Zr content less than 10 at% Zr consisted of $Co_{23}Zr_6$ and fcc-Co, and the material with higher Zr-content over 30 at% consisted of Co_2Zr phase. The material containing 15-20 at% Zr consisted of $Co_{23}Zr_6$, Co_5Zr and fcc-Co. Only the material containing Co_5Zr phase exhibited substantial coercivity, and it was confirmed that coercivity in the mechanically alloyed Co-Zr alloy was originated from the Co_5Zr phase.

Keywords : Co-Zr alloy, coercivity, mechanical alloying

1. Introduction

Since the discovery of the Nd-Fe-B-type material over two decades ago, a great demand for a new and superior hard magnetic phase has been increased. Through the intensive research works many promising candidate materials for an application of permanent magnet have been developed, and these include $Sm_2Fe_{17}N_x$ [1], $Sm_3Fe_{29}N_X$ [2] $Nd_2Fe_{14}B/Fe(Fe_3B)$ nanocomposite materials [3]. More recently, the Co-Zr phase has also been investigated as a candidate for an application of permanent magnetic material. In the Co-Zr alloy system, there are several equilibrium phases, and those phases are known to be a non-hard magnetic phase. It has been known, however, that in the Co-Zr alloys processed in a non-equilibrium way such as melt-spinning, some non-equilibrium metastable phases can be formed in the alloy system. Some of the metastable phases have been known to have hard magnetic properties suitable for the application of permanent magnet [4-8]. Although some intensive research works have been made, the hard magnetic properties of the Co-Zr phase is not yet quite promising for the permanent magnet application. Further systematic studies are yet needed to understand the magnetic properties of the hard phase and to exploit this phase as a promising permanent magnetic material. Even the coercivity origin of the non-equilibrium processed Co-Zr alloy is not fully understood. In the present study, a mechanical alloying technique has been used to prepare a non-equilibrium material and the phase constitution and origin of coercivity in the mechanically alloyed Co-Zr system were investigated.

2. Experimental Work

$Co_{100-X}Zr_X$ (x=10-40) (at%) alloys were prepared by a mechanical alloying technique using the high purity component elements. The elemental powders were put into a milling pot together with hardened steel balls. The mass ratio of steel balls and the elemental materials was 20:1. The milling pot was evacuated and then filled with a high purity argon gas. The charged material was milled for 20 hrs in a shaker mill. The milled powder was retrieved in a glove box filled with high purity argon gas. The retrieved milled powder was annealed in a vacuum at the temperature range of 500°C-1000°C. Magnetic characterization of the materials at various conditions was carried out using a vibrating sample magnetometer (VSM) with maximum magnetic field of 15 kOe. Prior to the VSM measurement, the specimen was pre-magnetized using a pulsing field of 4.5 T. Phase study of the materials at various conditions was performed using an X-ray diffractometer (XRD) (Cu $K\alpha$ radiation). Thermomagnetic analyzing technique (TMA) was also used for the phase study of the annealed material.

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The TMA was performed in swift mode with high enough heating rate (150°C/min) to avoid causing unnecessary phase change in the course of heating. The magnetic transition temperature of a phase measured by the swift TMA may appear to be higher than the true value due to the thermal lag in the sample. In order to measure the precise magnetic transition temperature the temperature in the swift TMA was corrected by using high purity Ni and Fe with same heating rate.

3. Results and Discussion

Fig. 1 shows the coercivity variation of the mechanically alloyed $Co_{82}Zr_{18}$ alloy as a function of the annealing temperature. As can be seen, the material annealed at lower temperature (500°C) showed negligible coercivity. However, the material annealed above 550°C exhibited substantial coercivity. It showed peak coercivity at 550°C and then decreased gradually with increasing the annealing temperature. Fig. 2 shows the demagnetization curves of the mechanically alloyed $Co_{82}Zr_{18}$ alloy annealed at various temperatures. Also included in Fig. 2 is the demagnetisation curve of the as-milled amorphous material. As can be seen, the as-milled material and material annealed at 500°C exhibited magnetically soft feature. The material annealed at 500°C showed slightly low magnetisation, compared with the as-milled material. This may be due to the fact that although the material had not been fully crystallised at 500°C a slight structural modification towards crystallised form had been caused. The negligible coercivity in the material annealed at 500°C may be due to the material form near amorphous state, which had magnetically soft feature. XRD phase analysis result supported this interpretation. As can be seen in Fig. 3, the material annealed at 500°C still showed near amorphous form. The material showing peak coercivity at 550°C was fully crystallized and consisted of $Co_{23}Zr_6$, Co_5Zr and fcc-Co phases as can be seen in Fig. 3(b). Phase constitution of this material was also examined by a TMA. The TMA for this material was undertaken in swift mode. As can be seen in Fig. 4(a), there were two magnetic transitions occurring at around 575°C and 665°C. The magnetic transition occurring at lower temperature may be corresponding to the $Co_{23}Zr_6$ phase and the one at higher temperature to the Co_5Zr phase. The magnetisation increase occurring above 700°C is due to an oxidation of the sample. The magnetic transition of the fcc-Co phase, which was identified in XRD result, is not observed in this TMA tracing, and the transition temperature is beyond the measuring range. Among the three phases, the $Co_{23}Zr_6$ and fcc-Co phases are known to be magnetically soft [9]. Therefore, it can be concluded that

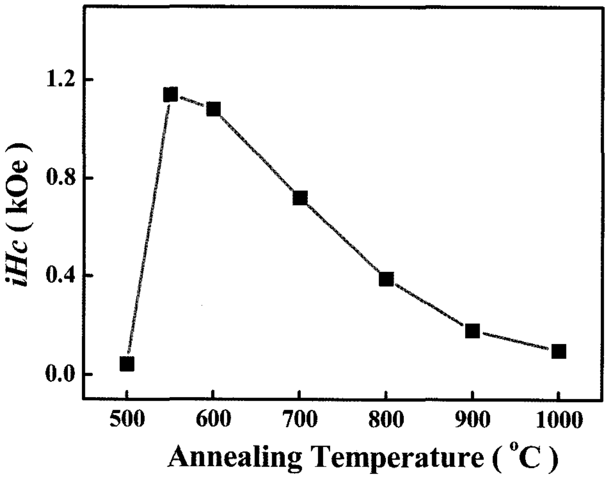

Fig. 1. Coercivity variation of the mechanically alloyed $Co_{82}Zr_{18}$ alloy annealed for 20 min as a function of annealing temperature.

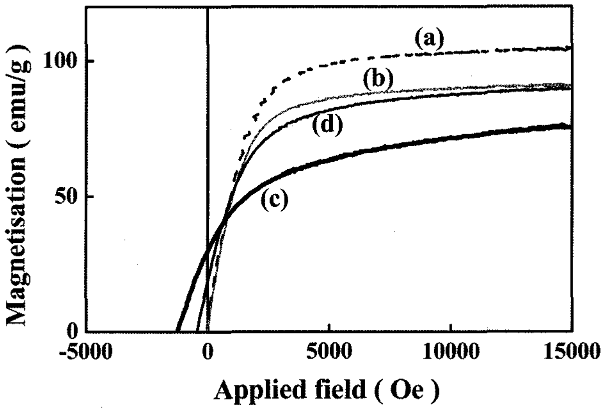

Fig. 2. Demagnetization curves of the mechanically alloyed $Co_{82}Zr_{18}$ alloy annealed for 20 min at various temperatures. (a) as-milled, (b) 500°C, (c) 550°C, and (d) 800°C.

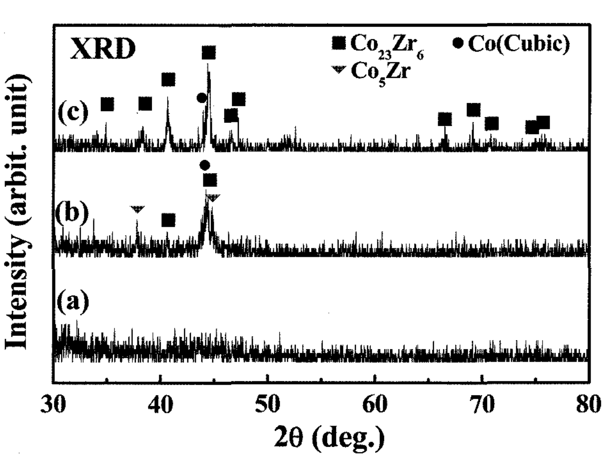

Fig. 3. XRD patterns of the $Co_{82}Zr_{18}$ alloy annealed for 20 min at (a) 500°C, (b) 550°C, and (c) 800°C.

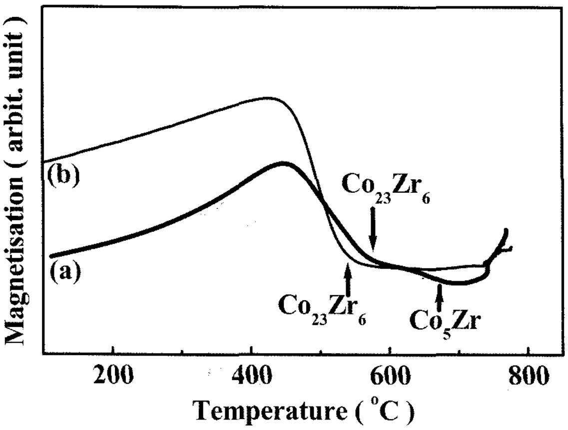

Fig. 4. Swift TMA tracings of the $Co_{82}Zr_{18}$ alloy annealed for 20 min at (a) 550°C, and (b) 800°C.

the high coercivity observed in the sample annealed at 550°C is originated from the Co_5Zr phase. The intrinsic magnetic properties of the Co_5Zr phase have not been studied yet in detail. However, it is supposed that the Co_5Zr phase may be magnetically hard phase with a significant magnetocrystalline anisotropy.

Meanwhile, the material annealed at higher temperature of 800°C consisted of $Co_{23}Zr_6$ and fcc-Co phases as can be seen in Fig. 3(c) with absence of Co_5Zr phase. The absence of Co_5Zr phase in the material annealed at 800°C is also confirmed by the TMA tracing. As seen in Fig. 4(b), there was only one magnetic transition occurring at around 535°C, and this was corresponding to the $Co_{23}Zr_6$ phase. Comparing the phase study results by the XRD and TMA for the materials annealed at 550°C and 800°C, it can be seen that the phase constitution is different depending on the annealing temperature. The material crystallised at lower temperature consisted of $Co_{23}Zr_6$, Co_5Zr and fcc-Co phases, and the relative amounts of the Co_5Zr phase, which is responsible for coercivity, decreased with increasing the crystallisation temperature, and it finally disappeared in the material annealed at sufficiently high temperature. Therefore, the coercivity deterioration in the material annealed at higher temperatures may be closely related to the variation of the relative amount of the Co_5Zr phase. As the crystallisation temperature increases the amount of the magnetically soft $Co_{23}Zr_6$ phase increases and the amount of magnetically hard Co_5Zr phase decreases. The plenty of the magnetically soft $Co_{23}Zr_6$ phase may act as a nucleation site for a reverse magnetic domain under a reverse magnetic field, thus leading to a lower coercivity. But other factor can come in to play for the degraded coercivity in the material annealed at higher temperature. As the annealing temperature increases, the grain size of the Co_5Zr phase may increases. The excessive grain growth of the Co_5Zr phase may be partly contributing to the degradation of the coercivity.

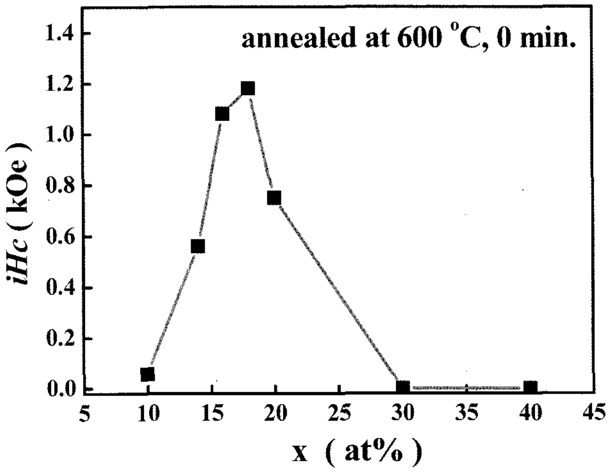

Fig. 5. Coercivity variation of the mechanically alloyed $Co_{100-x}Zr_x$ alloy as a function of the Zr-content.

It is noted that the Curie temperature of the $Co_{23}Zr_6$ phase is somewhat different in the materials annealed at different temperatures. The $Co_{23}Zr_6$ phases in the material annealed at 550°C and 800°C have Curie temperature at around 575°C and 535°C, respectively. The Curie temperatures of the $Co_{23}Zr_6$ phase measured in the present work seem to be different from the previously reported temperature (around 500°C) [9, 10]. This may be due to the different chemical composition of the phase and different processing route used in the present work from the previous one. The different Curie temperature of the $Co_{23}Zr_6$ phase in the material annealed at different temperatures suggests that the precise chemical composition of the $Co_{23}Zr_6$ phase in the materials annealed at 550°C and 800°C may be different within the compositional range of the $Co_{23}Zr_6$ phase.

Fig. 5 shows the coercivity variation of the mechanically alloyed $Co_{100-x}Zr_x$ alloy as a function of the Zr-content. The annealing at 600°C for 0 min means that the sample was cooled down as soon as it reached 600°C. As can be seen in Fig. 5, the materials containing 10 at% Zr or higher Zr-content over 30 at% had negligible coercivity. However, the material containing 15-20 at% Zr had considerable coercivity. The poor coercivity in the material with 10 at% Zr may be due to the absence of the magnetically hard Co_5Zr phase. As can be seen in Fig. 6(a), the material with 10 at% Zr contained $Co_{23}Zr_6$ and fcc-Co, and no firm evidence for the presence of the Co_5Zr phase was observed. The present two phases of $Co_{23}Zr_6$ and fcc-Co are soft magnetic and there is no hard magnetic phase in the material, thus leading to negligible coercivity. The poor coercivity in the material with higher Zr-content

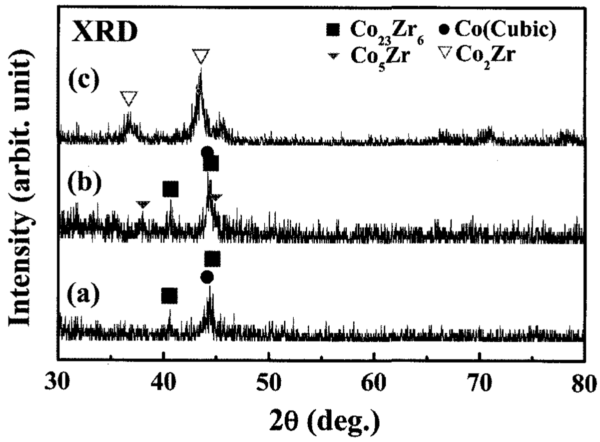

Fig. 6. XRD patterns of the mechanically allotted $Co_{100-x}Zr_x$ alloy annealed for 0 min at 600°C. (a) x=10, (b) x=18, (c) x=30.

over 30 at% may also be due to the absence of the Co_5Zr phase. As can be seen in Fig. 6(c), the material with 30 at% Zr consisted mainly of Co_2Zr phase. The Co_2Zr phase is known to be a non-magnetic [7]. The material containing 15-20 at% Zr consisted of $Co_{23}Zr_6$, Co_5Zr and fcc-Co as can be seen in Fig. 6(b). The considerable coercivity in these materials may, therefore, be attributed to the presence of the Co_5Zr phase. This result leads us again to conclude that the coercivity in the mechanically alloyed Co-Zr alloy is originated from the Co_5Zr phase.

4. Conclusion

Phase constitution of the $Co_{82}Zr_{18}$ alloy crystallised at lower temperature around 550°C consisted of $Co_{23}Zr_6$, Co_5Zr and fcc-Co phases, while the alloy crystallised at higher temperature around 800°C consisted of $Co_{23}Zr_6$ and fcc-Co phases. The material with lower Zr content less than 10 at% Zr consisted of $Co_{23}Zr_6$ and fcc-Co, and the material with higher Zr-content over 30 at% consisted of Co_2Zr phase. The material containing 15-20 at% Zr consisted of $Co_{23}Zr_6$, Co_5Zr and fcc-Co. Only the material containing Co_5Zr phase exhibited substantial coercivity. Coercivity in the mechanically alloyed Co-Zr alloy was originated from the Co_5Zr phase.

Acknowledgements

This work was supported by the Pukyong National University Research Foundation (Project No.: PK-2005-052).

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