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Contributed Paper

Ferromagnetism and Magnetoresistance of Cobalt-Silicon Alloy in Early Stages of Ball Milling

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ABSTRACT

The potential applications in hydrogen storage and giant magnetoresistance (GMR) devices have led to investigation of cobalt-silicon (Co-Si) alloys. By ball-milling amount fractions of 40 % cobalt (Co) and 60 % silicon (Si) powders for 1-3 h, crystalline fcc and hcp Co as well as fcc Si phases were detected without impurity phase. All three samples exhibited ferromagnetism with increasing magnetizations with increasing milling time due to the reduction in magnetocrystalline anisotropy. The 0.4% decrease in an electrical resistance of the pressed 3 h-milled powders under an 11 kOe-magnetic field was attributed to the GMR effect. Since the GMR mainly arises from the spin-dependent scattering across magnetic Co/semiconducting Si interfaces, the room temperature GMR ratio was reduced with increasing grain sizes in the case of 2 and 1 h. From these results, this functional material is attractive for its combination of electromagnetic with electrochemical properties.

Keywords: cobalt-silicon alloys, ball-milling, magnetic hysteresis, magnetoresistance

1. INTRODUCTION

Ball-milling is a versatile technique for producing a variety of functional alloys and composites from elemental powders [1-3]. In addition to all magnetic metals, mechanical milling of semiconducting silicon (Si) with ferromagnetic iron (Fe) has been a topic of interest because of their soft magnetic properties [4-6]. The inclusion of Si reduces the magnetic anisotropy and the eddy current loss in Fe [6]. Mechanical alloying of cobalt-silicon (Co-Si) powders has also received increasing attention since their hydrogen storage properties were reported [7-9]. Since the ball-milling eventually gives rise to the undesirable Co_2Si phase [9], the evolution of phases during the early stage of milling has to be examined.

By milling with the ball-to-powder weight ratio around 15:1 at 595 rpm for up to 8 h [10], silicide and amorphous phases were not significantly induced in Co-60 at.% Si. However, the reduction in particle size as well as accumulations of strain and defect after milling for 8 h results in enhanced coercive field and magnetic squareness. The change in the early stage of ball-milled Co involves the allotropic transformation from face-centered cubic (fcc) to hexagonal closed packed (hcp) phase due to the defect accumulation [11]. The prolonged milling, however, turns the highly distorted hcp back to the fcc structure as a result of stacking faults from plastic deformation [12]. In the case of ball-milled Fe-Co-Si [13] and Fe-Al-Si [14] powders, the morphology and magnetic properties were modified by the elemental composition as well as the milling time. When Si micropowders for anode materials in lithium-ion batteries were exclusively milled [15, 16], its particle size was substantially reduced during the first hour of high energy ball-milling.

In this study, magnetoresistance (MR) in Co-60 at.% Si after milling for 1-3 h are reported. This aspect has seldom been investigated since the hydrogen storage becomes the main interest in this system. It is well known that the giant magnetoresistance (GMR) effect is observed in Co-Cu mechanical alloys with severe plastic deformations at room temperature [17-19]. The milling time, speed and ball-to-powder weight ratio were kept at minimal to prevent the third phase which is detriment to GMR and hydrogen storage capacities.

2. MATERIALS AND METHODS

Elemental crystalline cobalt powder (99.8% purity with average particle size less than 2 microns) and silicon powder (99% purity with average particle size less than 44 microns) were mixed with an atomic ratio 40:60 in a steel vial containing steel balls. The ball-to-powder ratio was 10:1. The sealed vial was then spun at 30 rpm on a ball-mill. After milling for 1, 2 and 3 h, phases and hysteresis loops of the Co–Si powders were characterized by X-ray diffraction (XRD) and vibrating sample magnetometry (VSM). The MR was measured with the four-point-probe technique at room temperature. Samples in forms of pressed powders were installed between an electromagnet and their electrical resistance was recorded as a function of the applied magnetic field up to 11 kOe. The MR ratio is defined as;

$$MR = \frac{R(H) - R(0)}{R(0)} \times 100 \tag{1}$$

where $R(0)$ and $R(H)$ is the resistance in zero and in the maximum 11 kOe field, respectively.

3. RESULTS AND DISCUSSION

According to XRD patterns in Figure 1, all major peaks are sharp indicating a high degree of crystallinity whereas impurity and amorphous phases are not observed. The fcc Si phase is detected whereas Co exists in both hcp and fcc phases. Unlike the previous reports using higher milling intensity and time [10, 13], our 30 rpm milling for up to 3 h does not lead to allotropic transformation. In this early stage of milling, the broadening of Co and Si peaks due to the refinement of crystallite size and the increase of internal strain is not obviously detected. Nevertheless, the XRD peaks are slightly shifted to higher angles indicating the interdiffusion between Co and Si as the milling is progressed [4, 6].

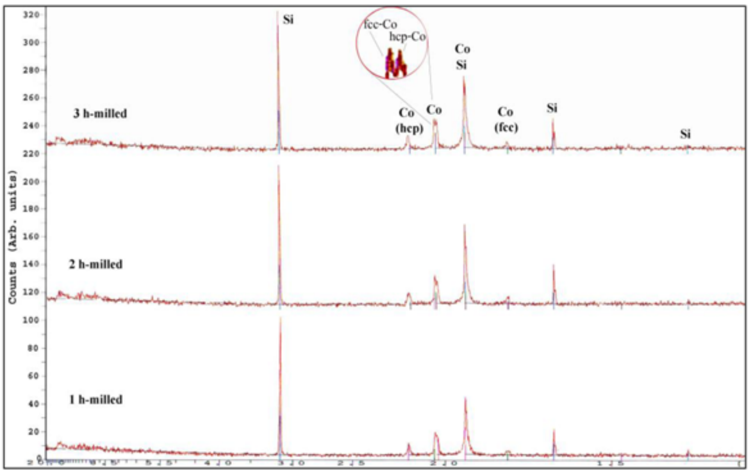

Figure 1. XRD patterns of Co - 60 at.% Si powders after milling for 1, 2 and 3 h.

It is known that the milling modifies the particle size by virtue of fracturing and cold welding [1]. The fracturing reduces the particle size but the cold welding tends to increase the particle size. Each process dominated in different stages of milling and the welding between particles should be dominant in the early stage of milling [13]. In addition to, the prolonged milling with elemental Si powder does not only homogenize particle size and shape but also leads to silicide compounds and amorphous phases [9]. However, our XRD patterns from the milling for 1-3 h show neither amorphous nor other secondary phases. These ball-milled powders may then be modeled as the dispersion of the Co clusters in Si matrix with only small fractions of silicide and oxide phases at the interfaces.

Ferromagnetic hysteresis loops are shown in Figure 2 for all Co-Si alloys and their magnetic parameters are summarized in Table 1. Similar to granular Co-Cu alloys [18-20], the magnetization is not saturated under the magnetic field as high as 10 kOe. The values are predictably lower than those of Fe-Co-Si powders with 10-20 at.% Si [13] and other Co-rich alloys [20]. The maximum as well as the remanent magnetizations are increased with the milling time. These results, consistent with the literature [13], are due to the reduction in magnetocrytalline anisotropy by Co grain refinement without significant silicide and oxide formations.

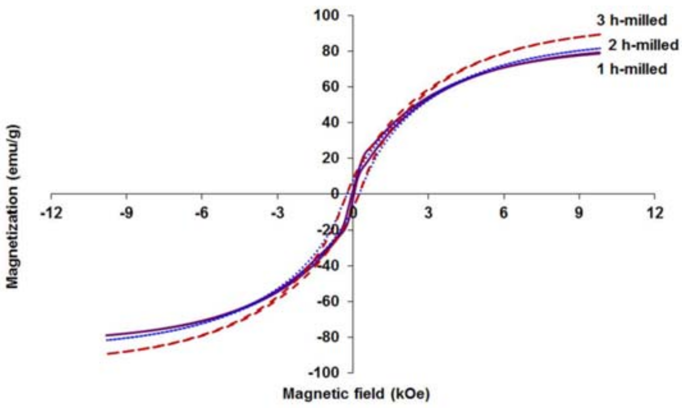

Figure 2. Hysteresis loops of Co - 60 at.% Si powders after milling for 1, 2 and 3 h.

Table 1. Remanent magnetization (M_r), magnetization in the maximum field (M_{10kOe}) and coercive field (H_c) of the ball-milled Co - 60 at.% Si powders.

Milling time (h)	M_r (emu/g)	M_{10kOe} (emu/g)	H_r (Oe)
1	2.49	78.75	41.04
2	7.56	81.67	485.38
3	8.23	89.27	242.88

Table 1 and Figure 2 also indicate that the 1 h-milled powder is magnetically soft with the lowest coercive field because of its lowest internal strain and defects. Strains and defects, increased as the milling is progressed, impede the domain wall movement as previously suggested in ball-milled Fe-Si [4, 6], Co-Si [10] and Fe-Co-Si [13] systems. Enhanced coercive fields were also reported in Co-Cu alloys by virtue of severe plastic deformation [17-18, 20]. However, the coercive field is not monotonically increased with the milling time because it is also dependent on the magnetocrytalline anisotropy. The coercive field of magnetic powders can be decreased by the longer milling time due to the reduction in anisotropy and the enlargement of particles in the cold welding process [5, 13]. It is noticed that these coercive field values are comparable to those of Co - 60 at.% Si milled for up to 8 h [10] and those of Fe powders with a high fraction of Si which could be further reduced by heat treatments [5, 6] .

Room temperature MR curves of the pressed powders are shown in Figure 3. The decrease in electrical resistance under the applied magnetic field is attributable to the GMR effect arising from the spin dependent scattering in Co clusters and Co/Si interfaces. The GMR ratio from the 3 h-milled sample is about -0.4 % whereas the 1 and 2 h-milled samples exhibit smaller changes in the resistance. It can be explained that the grain refinement by high energy ball-milling increases Co/Si interfaces and, hence, the GMR ratio. The effect of Co/Si interfaces on GMR was further examined in the thin film structure [21]. Compared with all metallic alloys [17-19], the MR ratio from the GMR effect in these ball-millled ferromagnetic-semiconductor powders is lower because the Si matrix is more electrically resistive and the milling time is relatively short. It is also noted that the electrical resistance of ball-milled Co-Si is sensitive to the temperature drift reflecting the characteristics of Si.

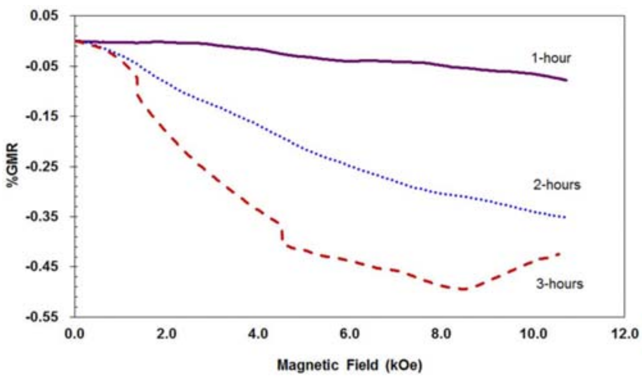

Figure 3. Room temperature MR curves of Co - 60 at.% Si powders after milling for 1, 2 and 3 h.

4. Conclusions

In the early stage of Co - 60 at.% Si milling up to 3 h, Co remains in both hcp and fcc phase and dispersed in the fcc Si matrix. The oxide, silicide or amorphous phases were not significantly induced. The magnetization is increased with increasing milling time. The coercive field was minimal in the case of the shortest milling and was modified by strains and defects. Furthermore, the milling time had a considerable effect on the MR ratio of the pressed Co - 60 at.% Si powders because the GMR effect at Co/Si interfaces was enhanced by the milling. Compared with all metallic alloys, the lower GMR ratio in the pressed Co-Si powders is due to a shorter milling time and a lower electrical conductivity of the non-magnetic Si matrix. Nevertheless, the Co-Si alloys combining magnetic response with storage properties can be obtained from the facile ball-milling technique.

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References

[1] Suryanarayana C., *Prog. Mater. Sci.*, 2004; **46**: 1-184.

[2] Aminikia B., *Chiang Mai J. Sci.*, 2013; **40**: 274-280.

[3] Tosangthum N., Meesa-Ard P. and Tongsri R., *Chiang Mai Univ. J. Nat. Sci.*, 2017; **16**: 239-253.

[4] Zuo B., Saraswati N., Sritharan T. and Hng H.H., *Mater. Sci. Eng. A*, 2004; **371**: 210-216.

[5] Kim S.H., Lee Y.J., Lee B.H., Lee K.H., Narasimhan K. and Kim Y.D., *J. Alloys Compd.*, 2006; **424**: 204-208.

[6] Ding J., Lee Y., Chen L.F., Deng C.R., Shi Y., Chow Y.S. and Gang T.B., *J. Alloys Compd.*, 2001; **314**: 262-267.

[7] He G., Jiao L.F., Yuan H.T., Zhang Y.Y. and Wang Y.J., *Electrochem. Commun.*, 2006; **8**: 1633-1638.

[8] Zhang Y., Jiao L., Wang Y., Wang Q., Zhang Y., Liu L. and Yuan H., *Int. J. Hydrog. Energy*, 2008; **33**: 4819-4823.

[9] Wang Y., Lee J.M. and Wang X.X., *Int. J. Hydrog. Energy*, 2010; **35**: 1669-1673.

[10] Rattanasakulthong W., Sirisathitkul C. and Rogl P.F., *Mater. Technol.*, 2015; **49**: 989-992.

[11] Huang J.Y., Wu Y.K., Ye H.Q. and Lu K., *Nanostruct. Mater.*, 1995; **6**: 723-726.

[12] Sort J., Nogues J., Surinach S. and Baro M.D., *Philos. Mag.*, 2003; **83**: 439-455.

[13] Yousefi M., Sharafi S. and Mehrolhosseiny A., *Adv. Powder Technol.*, 2014; **25**: 752-760.

[14] Boukherroub N., Guittoum A., Laggoun A., Hemmous M., Martinez-Blanco D., Blanco J.A., Souami N., Gorria P., Bourzami A. and Lenoble O., *J. Magn. Magn. Mater.*, 2015; **385**: 151-159.

[15] Hou X., Zhang M., Wang J., Hu S., Liu X. and Shao Z., *J. Alloys Compd.*, 2015; **639**: 27-35.

[16] Raihanuzzaman R.M., Song J.W., Lee I., Hong S.J. and Koo J.M., *Curr. Nanosci.*, 2014; **10**: 441-444.

[17] Valiev R.Z., Estrin Y., Horita Z., Langdon T.G., Zehetbauer M.J. and Zhu Y.T., *Mater. Res. Lett.*, 2016; **4**: 1-21.

[18] Nishihata S., Suehiro K., Arita M., Masuda M. and Horita Z., *Adv. Eng. Mater.*, 2010; **12**: 793-797.

[19] Rattanasakulthong W. and Sirisathitkul C., *Appl. Phys. A*, 2006; **83**: 77-81.

[20] Straumal B.B., Protasova S.G., Mazilkin A.A., Kogtenkova O.A., Kurmanaeva L., Baretzky B., Schutz G., Korneva A. and Zieba P., *Mater. Lett.*, 2013; **98**: 217-221.

[21] Kumar A. and Srivastava P.C., *J. Exp. Nanosci.*, 2015; **10**: 803-818.