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Fabrication of Fe-TiO_2 nano-composite powders by mechanical alloying

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The effects of mechanical alloying on the solid state reaction of hematite, Fe_2O_3 and titanium have been investigated at room temperature. We found that the displacement reaction between a Fe_2O_3 and a more reactive Ti metal can be induced by mechanical alloying. Fe-TiO_2 nano-composites in which TiO_2 particles were dispersed in an Fe matrix with nano grain size were obtained by mechanical alloying the mixture of Fe_2O_3-Ti elemental powders for 30 hrs. The average grain sizes of iron in the Fe-TiO_2 nano-composite could be reduced to the 20 nm range as estimated by X-ray diffraction line-width measurements. We also show magnetic evidence for the solid state reduction by mechanical alloying through changes in saturation magnetization and coercivity.

Key words: nano-composite, mechanical alloying, saturation magnetization.

Introduction

Mechanical alloying (MA) has been recognized as a worthy technique for synthesizing equilibrium and non-equilibrium materials through solid-state diffusion under intense mechanical deformation [1-5]. In particular, it has been shown that the mechanical alloying through high energy ball milling may prove to be a useful and cost-effective method for the production of nano-structured materials with high performance [6, 7].

Investigations of the magnetic properties of nano-composite MA powders is of interest because of possible applications as permanent magnets, recording, and giant magnetostrictive materials [8-11]. Magnetic measurements can also be used to obtain information on magnetic phase composition, particle size distribution, and microstructures. The mechano-chemical reductions of a metal oxide by a more reactive metal have been demonstrated and usually occur through complex reactions, forming several intermediate, non-equilibrium phases [12-17]. In the present work, we studied the formation of Fe-TiO_2 nano-composites by solid state reduction during ball milling of Fe_2O_3 and Ti powders:

$$2Fe_2O_3 + 3Ti \rightarrow 4Fe + 3TiO_2$$

X-ray diffraction spectra suggest that the reduction of hematite by titanium is a relatively simple reaction, involving one intermediate phase. Magnetic measurements may supply more useful indirect information about the details of the MA process, as well as the properties of the nano-composite materials. In this way, we can point out what is unique in the solid state reduction by MA in the Fe_2O_3-Ti system.

Experimental

The mechanical alloying was carried out at room temperature with a mixture for hematite (99.9%, <0.1 μm in size) powders and pure titanium (99.9%, <150 μm in size) powders with a molar ratio 2:3 under a pure Ar (99.999%) gas atmosphere. A planetary ball mill (Fritsch Pulverisette 5) was used with its vial rotation of 200 rpm. The vial and balls are made of the hardened steel (SKD11) and tungsten carbide(WC), respectively. The total mass of powders was about 20 g and the ratio of balls to powders was 7:1. Milling was interrupted for 6 minutes in every 30 minutes to suppress the excessive temperature rise of the vial and balls.

The structural change of ball-milled powders was studied by X-ray diffraction in continuous and step scanning modes with Cu-Kα radiation. The morphology of the particles was observed using a scanning electron microscope (SEM). The magnetization at room temperature was measured with the vibrating sample magnetometer (VSM) calibrated using a pure Ni disk (99.99%). The maximum applied magnetic field was 15 kOe.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns for the Fe_2O_3-Ti powders ball-milled for various time intervals.

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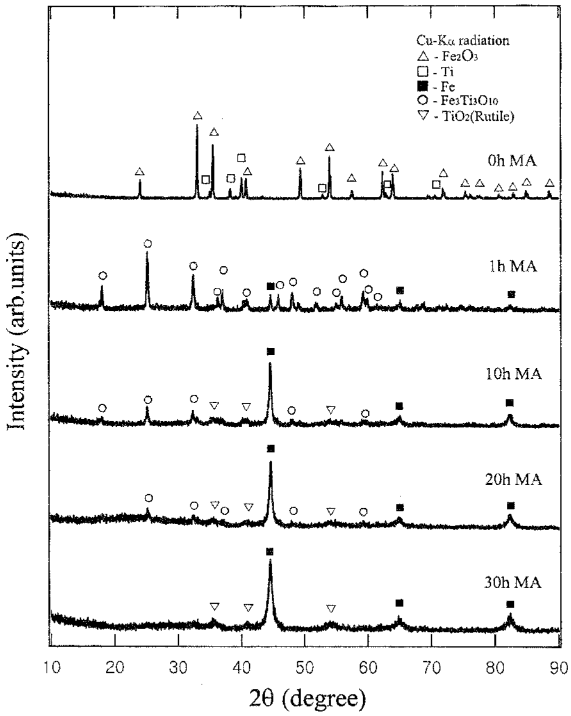

Fig. 1. X-ray diffraction patterns of Fe_2O_3-Ti powders as a function of milling time.

It can be seen that the diffraction lines associated with Fe_2O_3 and Ti completely disappear after 1 h MA treatment and, instead, the lines of Fe plus the intermediate phase $Fe_3Ti_3O_{10}$ are formed. In contrast, a two-phase mixture of α-Fe and TiO_2 was formed after 30 h MA,

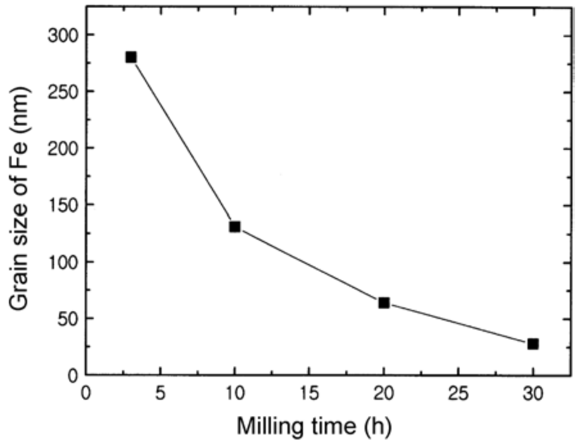

Fig. 2. Grain size of Fe in Fe-TiO_2 nanocomposite powders as a function of milling time.

indicating the solid state reduction by MA was completed. The broadening of the α-Fe diffraction lines is caused by the refinement in grains and also by the accumulation of defects and strains [18, 19].

Figure 2 shows the average grain size of Fe in MA powders as estimated by X-ray diffraction pattern line-width measurements. As is clear from Fig. 2, the Fe grain size was gradually decreased with increasing milling time and finally tended to reach 24 nm. This suggests that the Fe-TiO_2 nano-composites in which TiO_2 particles were dispersed in a ductile Fe matrix with nano grain size were obtained by mechanical alloying of the mixture of Fe_2O_3-Ti elemental powders.

The change in the morphology of MA powders was

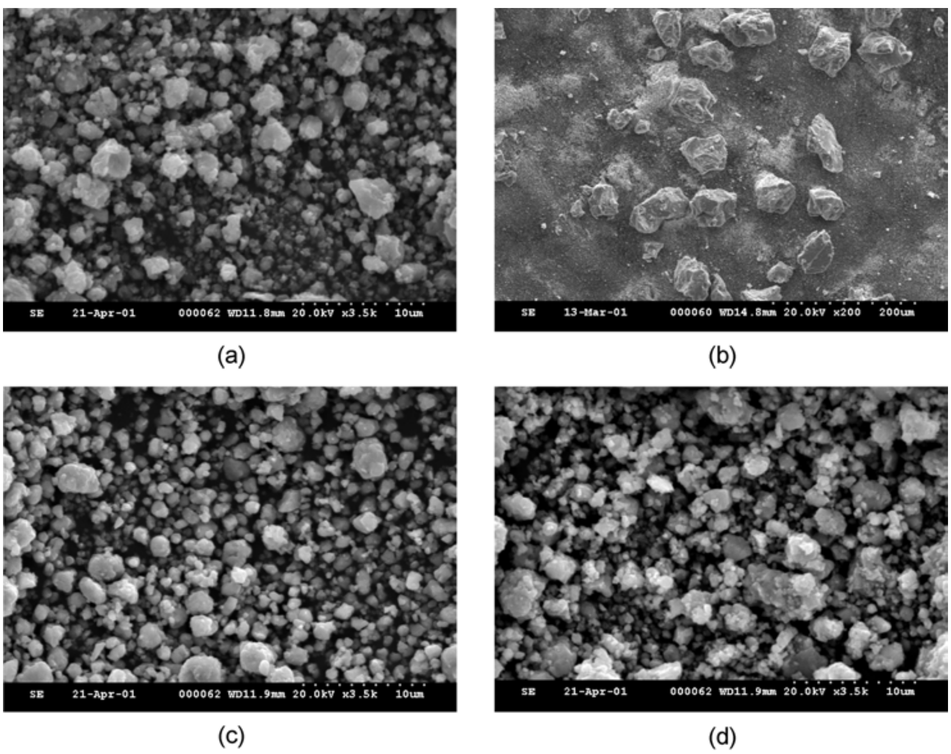

Fig. 3. SEM micrographs of Fe_2O_3-Ti powders ball-milled for (a) 0 h, (b) 2 h, (c) 4 h, (d) 30 h.

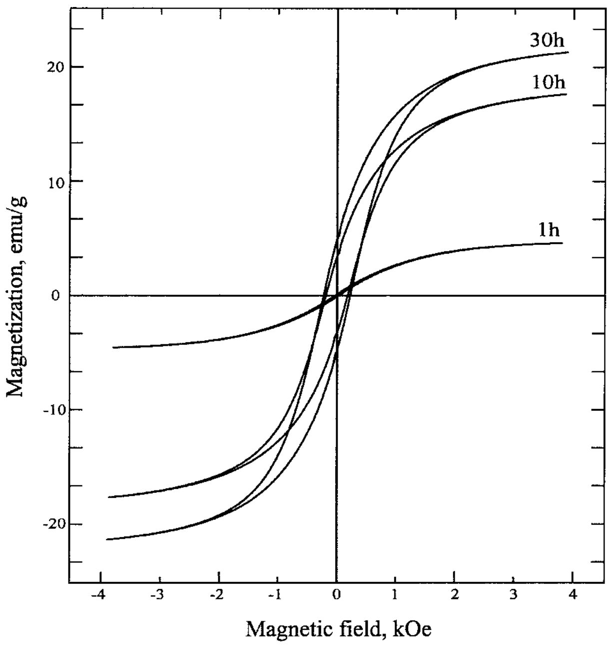

Fig. 4. Room temperature hysteresis loops of Fe_2O_3-Ti powders ball-milled for (a) 1 h, (b) 10 h, (c) 30 h.

studied as a function of milling time. Figure 3 shows scanning electron micrographs for the Fe_2O_3-Ti powders treated by MA for 0 h, 2 h, 4 h and 30 h. The powder after MA for 30 h is fairly round and its size distribution is centered at about 1.5 μm diameter. By contrast, the powders after MA for 2 h and 4 h are more irregular and agglomerated and their size distributions are much broader.

The variation of the magnetic properties with MA time has been investigated at room temperature by a vibrating sample magnetometer in magnetic fields up to 15 kOe. From these magnetic measurements, we can obtain more indirect information about the details of the MA process, as well as magnetic phase composition, particle size distribution, and microstructures. The room temperature hysteresis loops of ball-milled Fe_2O_3-Ti powders are shown in Fig. 4 as a function of MA time. Obviously, the change in saturation magnetization of the samples indicates the transformation from the initial hematite phase to iron through solid state reduction. In addition, the similar shape of the hysteresis loops for 10 h and 30 h MA samples is due to the the fact that iron particles are magnetically harder compared to the 1 h MA sample. This means that the grain size of iron in the Fe-TiO_2 nano-composites is decreased with increasing milling time.

Figure 5 shows the milling time dependence of saturation magnetization for ball-milled Fe_2O_3-Ti powders. It is seen that the saturation magnetization is increased with milling time and then gradually saturated to 20.3 emu/g after 30 h MA. As recognized from Fig. 1, the increase in Ms with milling time originates from the increasing iron phase produced by solid state reduction. In addition, it should be emphasized that the saturation of Ms after 30 h MA means an end to the displacement reaction in the Fe_2O_3-Ti system. Hence, the magnetic data can supply a better understanding of the amount of iron phase produced by ball milling.

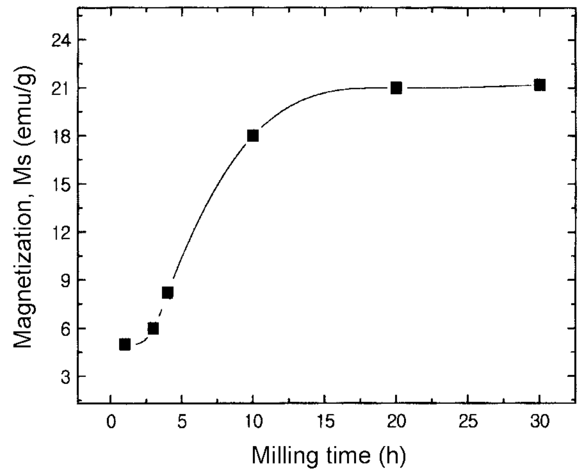

Fig. 5. The milling time dependence of saturation magnetization, Ms of ball-milled Fe_2O_3-Ti powders.

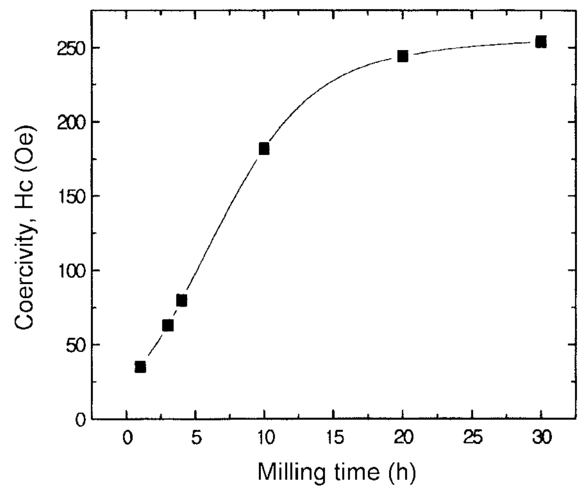

Fig. 6. The milling time dependence of coercivity, Hc of ball-milled Fe_2O_3-Ti powders.

The coercivity of Fe_2O_3-Ti powders ball-milled for various time intervals is shown in Fig. 6. At an early stage of MA, it can be seen that the coercivity is very low, suggesting that a relatively large grain size and defect-free iron particles are formed. By contrast, Hc gradually increases up to 280 Oe after 30 h of ball milling. As can be realized from Fig. 2, the decrease in grain size of iron particles in Fe-TiO_2 nano-composite powders is responsible for the high coercivity [11-13]. Studies to relate the present X-ray diffraction and vibrating sample magnetometer analyses to the microstructures of ball-milled Fe-TiO_2 nano-composite powders are in progress.

Conclusions

We have revealed that the magnetic Fe-TiO_2 nano-composite powders may be produced by mechanical alloying of a mixture of hematite and pure titanium powders in an Ar atmosphere. The X-ray diffraction and magnetic data have been discussed simultaneously in order to achieve a better understanding of the solid state reduction induced by mechanical alloying. Fe-TiO_2 nano-composites where TiO_2 particles were dispersed in a ductile iron matrix with a grain size of 20 nm were obtained after 30 h of ball milling. The saturation magnetization was increased with increasing milling time and then gradually saturated to 20.3 emu/g after 30 h MA. The magnetic hardening due to the reduction of the iron grain size by MA was also observed.

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References

1. C.C. Koch, O.B. Cavin, C.G. Mckamey and J.O. Scarbrough, Appl. Phys. Lett. 43 (1983) 1017-1019.
2. U. Mizutani and C.H. Lee, J. Mat. Sci. 25 (1990) 399-406.
3. L. Schultz, J. Less-Common Metals 145 (1988) 233-238.
4. A. Calka, Appl. Phys. Lett. 59 (1991) 1568-1570.
5. T. Fukunaga, N. Kuroda, C.H. Lee, T. Koyano and U. Mizutani, J. Non-Cryst. Solids 176 (1994) 98-103.
6. E. Hellstern, H.J. Fecht, Z. Fu and W.L. Johnson, Mater. Res. Soc. Symp. Pro. 132 (1989) p. 137.
7. S. Linder and M. Pedersen, J. Appl. Phys. 75 (1994) 5867-5870.
8. J.M.D. Coey and H. Sun, J. Magn. Magn. Mater. 87 (1990) L251-L255.
9. C.H. Lee and Y.S. Kwon, Metals and Materials 8 (2002) 151-154.
10. L. Schultz and J. Wecker, J. Appl. Phys. 64 (1988) 5711-5715.
11. B.H. Lee, B.S. Ahn, D.G. Kim and Y.D. Kim, J. Korean Powder Metallurgy Institute 9 (2002) 182-187.
12. M.P. Horvath and L. Takacs, IEEE Trans. on Magntics 28 (1992) 3186-3189.
13. J. Ding, W.F. Miao, R. Street and P.G. McCormick, Script Materialia 35 (1996) 1307-1310.
14. K. Tokumitsu, Mat. Sci. Forum 88-90 (1992) 715-719.
15. P. Matteazzi and G. Le Caer, J. Am. Ceram. Soc. 74(6) (1991) 1382-1387.
16. G.G. Schaffer and P.G. McCormick, Appl. Phys. Lett. 55 (1989) 45-47.
17. C.H. Lee, Proceeding of Korean Association of Crystal Growth (1997) p. 81.
18. T. Fukunaga, N. Kuroda, C.H. Lee, T. Koyano and U. Mizutani, J. Phase Equilibria 14 (1993) 167-171.
19. W.H. Hall, J. Inst. Met. 75 (1948) 1127-1134.