JOURNAL OF MATERIALS SCIENCE **36** (2001) 1735–1740

Formation of ternary carbide Fe_3Mo_3C by mechanical activation and subsequent heat treatment

T. TSUCHIDA
Division of Materials Science and Engineering, Graduate School of Engineering,
Hokkaido University, North 13 West 8, Kita-ku, Sapporo, 060-8628 Japan
E-mail: tsuchida@eng.hokudai.ac.jp

Ternary carbide, Fe_3Mo_3C was prepared from the powder mixture of Fe/Mo/C = 1/1/1 which was ground for 3 h in a planetary ball mill and subsequently heated at a temperature as low as 700°C, its amount increased with heating temperature. In contrast, when the 1 h-ground and unground samples were heated at 700–1000°C, Mo_2C formed. From the results obtained about the effect of mixing ratio, grinding time and heating temperature of Fe/Mo/C samples on the formation of Fe_3Mo_3C, it was found that the formation of Fe_3Mo_3C strongly depends on the mixing homogeneity and the activated state of the particles of Fe, Mo and C components induced by mechanical grinding. Fe_3Mo_3C obtained belongs to a hard magnet, having saturation magnetization of 0.4 emu g^{-1}, remanence of 0.13 emu g^{-1} and coercivity of 200 Oe. © *2001 Kluwer Academic Publishers*

1. Introduction

Mechanical activation or mechanosynthesis induced by ball-milling is an attractive, promising process for the production of new materials [1], particularly for advanced materials such as metal carbides and nitrides. We have recently developed a technique of mechanical activation assisted self-propagating high-temperature synthesis (SHS) in air. This technique is based on SHS induced by exposing metal-graphite powder mixtures mechanically activated to air and has been successfully applied to the synthesis of carbides and nitrides of Al, Zr, Nb, Ta and Hf [2–9], and of ternary borocarbide of Al_3BC [9]. On the other hand, a process that combined mechanical activation and subsequent heat treatment, which is sometimes called the mechanical activation assisted solid-state reaction, is a traditional, but still important process to synthesize useful materials at lower temperatures.

Recently, the study on the formation and properties of carbides involving two or more metals has been noted, because these carbides are expected to have novel properties compared with individual monometal carbides [10]. In general, however, it is very difficult to produce ternary or more carbides at the temperatures below the melting points of starting materials, mainly because of the difficulty in mixing the constituent powder particles homogeneously. It is well known that the mechanical activation enhances the reactivity of solids as well as their mixing homogeneity and lowers remarkably the reaction temperature. Therefore, the application of a mechanical activation assisted solid-state reaction technique for preparation of ternary carbides is very interesting. However, we can not find only one paper reported by Di *et al.* [11] on the formation of ternary carbide Fe_3Mo_3C, where the stoichiometric powder of Fe/Mo/C = 3/3/1 was milled using a home-built planar-type milling device in vacuum for 194 h and subsequently heated up to 1000°C.

In the present study, in order to discuss the optimal conditions and reaction mechanism for the formation of Fe_3Mo_3C by this technique, the powder mixtures with different mixing ratios of Fe/Mo/C = 6/6/1 ~ 1/1/6 were mechanically activated by grinding and subsequently heated at 600–900°C. The magnetic property of Fe_3Mo_3C obtained was also measured.

2. Experimental procedures

The procedures of mechanical activation of metal-graphite powder mixtures have been in detail described in the previous papers [2–9]. Fe and Mo metals (particle size below 150 μm, 99.9% purity, Kojundo Chemical Laboratory) and natural graphite (mean flake size 5 μm, 97% carbon, 2% ash and 1% volatile component, Nippon Kokuen Industry) were used as starting materials. These powders were mixed in various molar ratios of Fe/Mo/C = 6/6/1, 3/3/1, 3/3/2, 1/1/1, 2/2/3, 1/1/3 and 1/1/6 in an agate mortar, loaded in air in a p-7 planetary ball mill (Fritsch, Idar-Oberstein, Germany), and then ground for 1–3 h. The grinding was interrupted every 30 min and sample was scraped from the balls and the side walls of the jar and then reloaded to continue grinding. A 25 ml jar and seven balls of tungsten carbide (12 mm diameter) were used for grinding. The ground sample was taken out of the jar after different times of grinding, and then heated up to 500–1100°C at a heating rate of 10°C min^{-1} in a flowing argon of 30 ml min^{-1} in a TG-DTA-2000 apparatus (Mac Science). Powder X-ray diffraction (XRD) patterns were obtained with a RINT-2000 (Rigaku Denki) using Ni-filtered Cu K_α radiation, if necessary, with a RINT-1.300 (Rigaku Denki) using Fe-filtered Co $K\alpha$ radiation as well. Optical microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were carried out with a SZH-ILLB microscope (Olympus), and a JXA-8900M-WD/ED combined microanalyzer (JEOL) at an accelerating voltage of 15 kV and an emission current of 30 μA. The powder sample dispersed in ethanol by ultrasonication was placed as a drop on a glass plate or a brass stub and then dried. The magnetization curve was measured using a vibrating sample magnetometer (VSM-3, TOEI) at a maximum field of 5 kOe. The sample (ca. 30 mg) was compacted into an aluminum pan (diameter of 5 mm and depth of 2.5 mm) using PMC adhesive wax.

3. Results and discussion

The Fe/Mo/C samples with various molar ratios, 6/6/1, 3/3/1, 3/3/2, 1/1/1, 2/2/3, 1/1/3 and 1/1/6, were ground for 1–3 h in a planetary ball mill. When all samples ground for 2 h were transferred into a graphite crucible (inner diameter of 30 mm and depth of 40 mm) and exposed to air, they self-ignited instantly and an exothermic reaction evolving red heat was sustained for a few minutes. The reaction temperature measured by an optical pyrometer attained to 600–700°C. Such an exothermic reaction occured no longer for the samples ground for further lengthened time.

Fig. 1 shows the XRD patterns of Fe/Mo/C = 1/1/1 samples ground for 0 (unground), 1, 2 and 3 h, respectively. Mo peaks, compared with Fe peaks, apparently decreased in intensity and broadened with increasing grinding time, and the 002 peak of graphite almost disappeared after 1 h of grinding. These results indicate the size diminution and the increase in lattice strain of Mo metal particles, and the disappearance of the stacking order of the graphite layers and the formation of disordered carbon with fine particle size [2]. A trace of α-Fe_2O_3 can be seen in the samples ground for 2 and 3 h, which was formed by the exothermic reaction evolving red heat described above. Even after the grinding for 8 h, the formation of Fe_3Mo_3C or other carbides could not be entirely detected. Almost similar behavior was also observed in the XRD patterns for the ground samples with other molar ratios of Fe/Mo/C, apart from the difference in relative intensity of Mo, Fe and C.

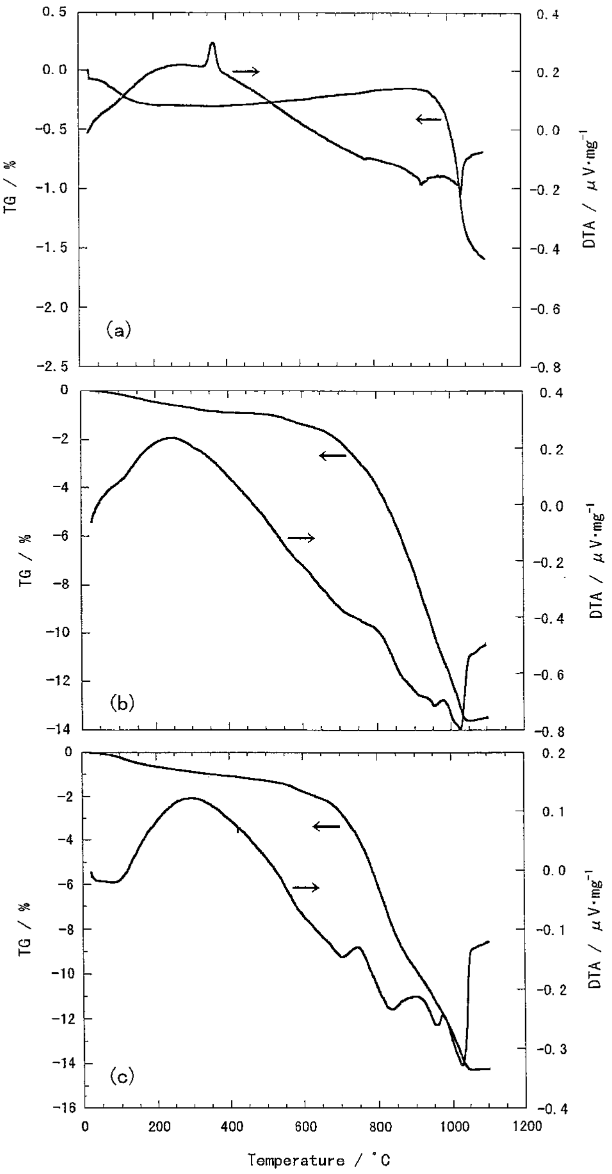

Figure 2 The TG-DTA curves of Fe/Mo/C = 1/1/1 samples which were ground for (a) 0 (unground), (b) 1 and (c) 3 h, measured at a heating rate of 10°C min^{-1} and in a flowing argon of 30 ml min^{-1}.

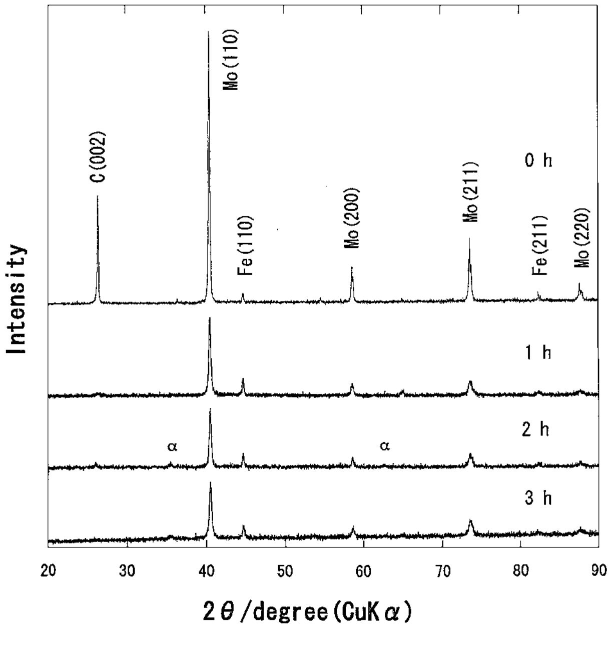

Figure 1 The XRD patterns of Fe/Mo/C = 1/1/1, samples which were ground for 0 (unground), 1, 2 and 3 h, respectively. α: α-Fe_2O_3.

Fig. 2 shows the TG-DTA curves for the unground, 1 and 3 h-ground Fe/Mo/C = 1/1/1 samples. For the comparison, the TG-DTA curves for the unground samples of Fe/C = 1/1, Mo/C = 1/1 and C were also measured, though not shown in figure. In Fig. 2a the unground sample of Fe/Mo/C = 1/1/1 showed an exothermic peak at 360°C and an endothermic peak at 1040°C, and very small endothermic peaks at 770 and 930°C,

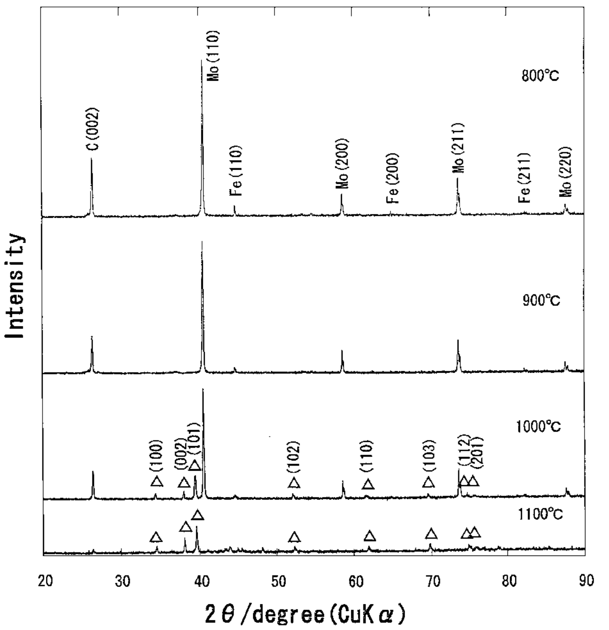

Figure 3 The X-ray diffraction patterns for the unground Fe/Mo/C = 1/1/1 samples which were heated at 800, 900, 1000 and 1100°C for 30 min, respectively, on TG-DTA runs shown in Fig. 2a. △: Mo_2C.

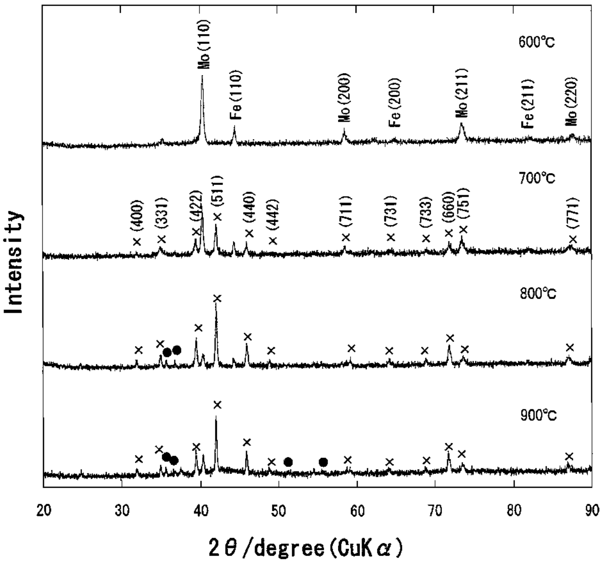

Figure 4 The X-ray diffraction patterns for the Fe/Mo/C = 1/1/1 samples which were ground for 3 h and subsequently heated at 600, 700, 800 and 900°C for 30 min, respectively, on TG-DTA runs shown in Fig. 2c. ×: Fe_3Mo_3C, ●: $FeMoO_3$.

TABLE I X-ray diffraction results of Fe/Mo/C samples with various molar ratios which were ground for 1 and 3 h and subsequently heated at 800°C for 30 min

Fe/Mo/C	After heating of 1 h-ground samples	After heating of 3 h-ground samples
6/6/1	Mo > Fe ≫ Fe_3Mo_3C	Mo > Fe, Fe_3Mo_3C, $FeMoO_3$
3/3/1	Mo > Fe > Fe_3Mo_3C ≫ Mo_2C	Mo, Fe_3Mo_3C > Fe > $FeMoO_3$
3/3/2	Mo_2C > Fe ≫ Mo, Fe_3Mo_3C	Fe_3Mo_3C, Fe > $FeMoO_3$ > Mo
1/1/1	Mo_2C ≫ Fe	Fe_3Mo_3C, Fe > $FeMoO_3$ > Mo
2/2/3	Mo_2C > Fe	Fe_3Mo_3C ≫ Mo, Fe ≫ $FeMoO_3$
1/1/3	Mo_2C > Fe	Mo_2C ≫ Mo, Fe
1/1/6	Mo_2C ≫ Fe	Mo_2C ≫ Fe

respectively. The former two peaks were also observed in the unground Mo/C = 1/1 sample, and the latter two peaks in the unground Fe/C = 1/1 sample as well. In TG curve the weight losses of ca. 0.3 and 1.5 wt% were observed at around 100 and 1000°C. These losses are considered to be due to the release of the water or gases adsorbed on the graphite and to the oxidation reaction of graphite itself with a trace amount of oxygen, which might have remained in TG-DTA apparatus even by purging with argon before and during heating [4]. Fig. 3 shows the XRD patterns for the unground Fe/Mo/C = 1/1/1 samples, which were heated up to 800, 900, 1000 and 1100°C, and then held for 30 min, respectively, on TG-DTA runs. No reaction product was detected in the samples heated at 800 and 900°C, whereas Mo_2C was detected at 1000°C, its amount increased at 1100°C.

On the other hand, the TG-DTA curve for the 1 h-ground Fe/Mo/C = 1/1/1 sample in Fig. 2b is apparently different from that of the unground sample in Fig. 2a. In particular, in TG a big weight decrease of ca.12 wt% occurred at the temperature between 600 and 1000°C, corresponding to the oxidation of carbon disordered by mechanical activation, as shown in Fig. 1. The TG-DTA curve for the 3 h-ground sample in Fig. 2c is very similar to that of the 1 h-ground sample. From the XRD patterns obtained for the 1 h-ground samples heated at 500–900°C, Mo_2C began to form at 600°C, increased with increasing reaction temperature and formed as almost a single phase at 900°C. In contrast, as can be seen from Fig. 4 the formation of Fe_3Mo_3C, instead of Mo_2C, occurred at 700°C and remarkably developed at 800–900°C, though accompanied with a trace amount of $FeMoO_3$. It seems to be found for the first time that ternary carbide Fe_3Mo_3C could be formed at temperature as low as 700°C by a process combined mechanical activation and subsequent heat treatment. The present conditions for Fe_3Mo_3C formation are much milder than those reported by Di *et al.* [11], where the stoichiometric powder of Fe/Mo/C = 3/3/1 was milled in a vacuum for 194 h and subsequently heated up to 1000°C. Such difference in the formation conditions may depend on the different grinding equipment, in which the energy transfers to the powders are not the same orders.

Furthermore, the XRD results for the Fe/Mo/C samples with various mixing ratios, which were ground for 1 and 3 h and then heated at 800°C for 30 min are summarized in Table I. In general, it can be seen from Table I that in the 1 h-ground samples Mo_2C mainly formed, though a small amount of Fe_3Mo_3C also formed for the samples with less amount of C, i.e., Fe/Mo/C = 6/6/1 ∼ 3/3/2. In contrast, in the 3 h-ground samples Fe_3Mo_3C formed preferentially, and Mo_2C formed in only the samples with much amounts of C, i.e., Fe/Mo/C = 1/1/3 and 1/1/6. Such a dependence of the product phase on the mixing ratio of Fe/Mo/C is considered to be due to the difference in the mixing homogeneity and the mechanically activated state of the particles of starting materials (Fe, Mo and C) induced after the grinding for 1 and 3 h, which is further discussed below. The

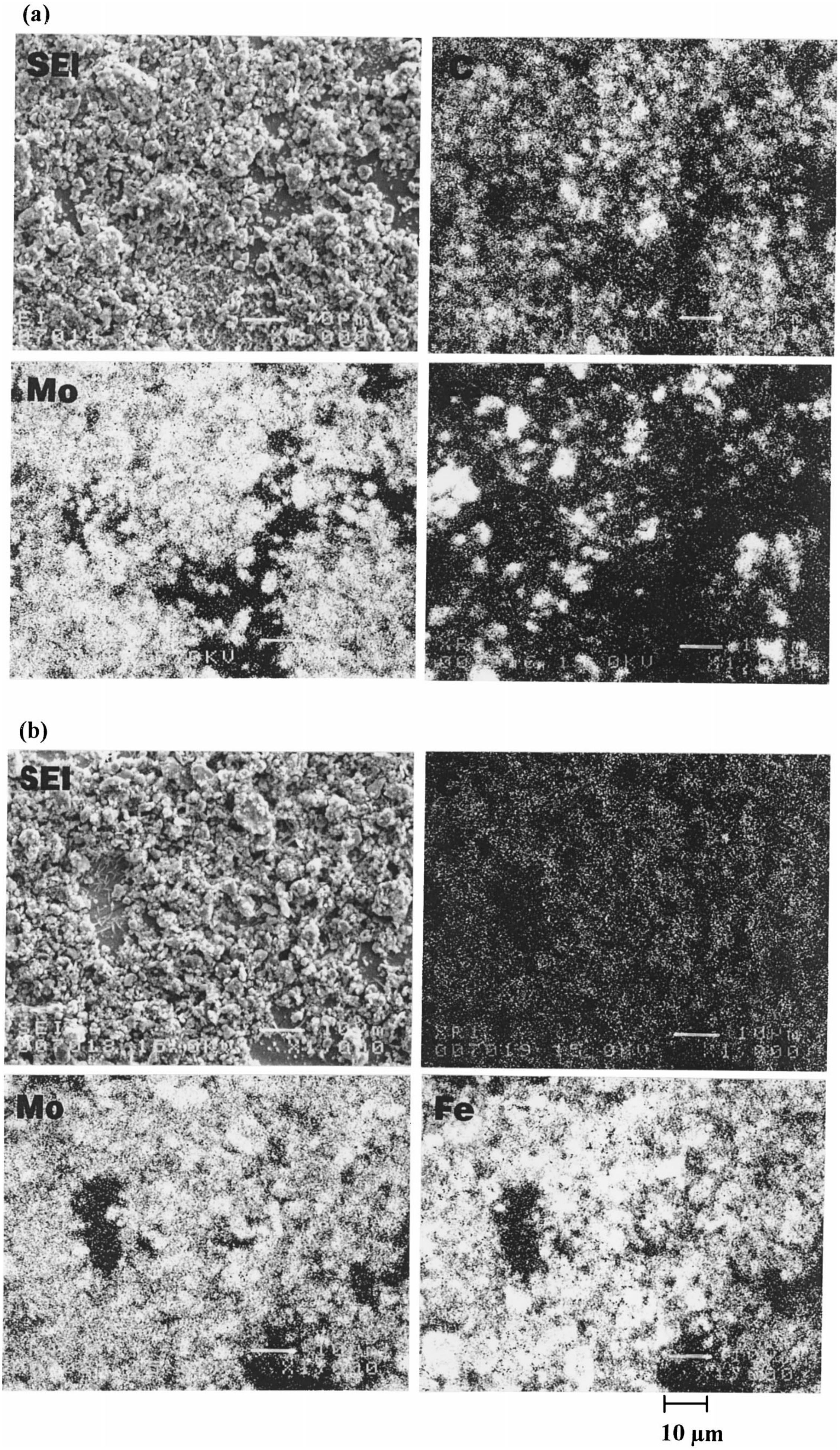

Figure 5 The secondary electron images and associated elemental maps of the (a) 1 and (b) 3 h-ground Fe/Mo/C = 1/1/1 samples before heating.

formation of $FeMoO_3$ in the 3 h-ground samples seems to be attributable to the reaction of Fe and Mo metals mechanically activated with a trace amount of oxygen remained in TG-DTA apparatus or of activated Mo metal particles with α-Fe_2O_3 formed after grinding for 2 h, as shown in Fig. 1.

From the optical micrographs for the unground sample of Fe/Mo/C = 1/1/1, it was found that there is entirely neither a homogeneous distribution between the component particles of Fe, Mo and graphite nor an intimate contact between them. However, after grinding for 1 and 3 h the particle size of the three components decreased remarkably and their mixing homogeneity was much improved, but the fine structure could not be distinguished between them. Therefore, SEM-EPMA observation was utilized to investigate effectively the fine structure of the 1 and 3 h-ground samples. In the 1 h-ground sample in Fig. 5a, the homogeneous distribution between the particles of Mo and C components, except for the Fe metal particles, can be seen, which would provide favorable circumstances for the formation of Mo_2C. In contrast, in the 3 h-ground sample in Fig. 5b the excellent homogeneous distribution between the particles of Mo, Fe and C components was observed. Therefore, such a creation of homogeneous distribution and intimate contact between these component particles finely divided and disordered by mechanical activation is considered to be essential to the formation of the ternary carbide, Fe_3Mo_3C. Furthermore, in general, it is well known that the mechanical activation creates numerous structural defects which enhance the solid-state reaction between the components of the initial powder mixture and lead to the formation of metastable or amorphous compounds. If the amorphous Fe_3Mo_3C, though could not be detected to X-ray, was formed during mechanical grinding for 3 h, they might act as a preferred nucleation site during recrystallization by heat treatment. This assumption can be verified by transmission electron microscopy (TEM).

On the other hand, the free energy of formation is also an important factor in oder to determine which is the more stable form in the temperature range under consideration, Mo_2C or Fe_3Mo_3C. The free energy of formation of Mo_2C (in unit per one mole of Mo, according to the reaction $Mo + 1/2C = 1/2Mo_2C$) was calculated to be ca. -30 kJ mol^{-1} in the temperature range of 25 to 850°C [12]. The free energy of formation of Fe_3Mo_3C has not been reported yet, but can be estimated to be a comparable value to that for Mo_2C.

Figure 6 shows the room temperature hysteresis loop in the magnetization curve of Fe_3Mo_3C obtained from the Fe/Mo/C = 1/1/1 sample which was ground for 3 h and subsequently heated at 800°C for 30 min, from which the unreacted Fe was removed out by treatment with HCl solutions. Since this sample still contained a small amount of C, Mo and $FeMoO_3$, the measurements of magnetization curves for the latter two were also carried out. These magnetization properties were insignificant, however. Thus, the magnetization curve shown in Fig. 6 was decided to correspond to Fe_3Mo_3C itself. Saturation magnetization of 0.4 emu g^{-1}, remanence of 0.13 emu g^{-1} and coercivity of 200 Oe can be read from the figure. These values indicate that Fe_3Mo_3C belongs to a hard magnet.

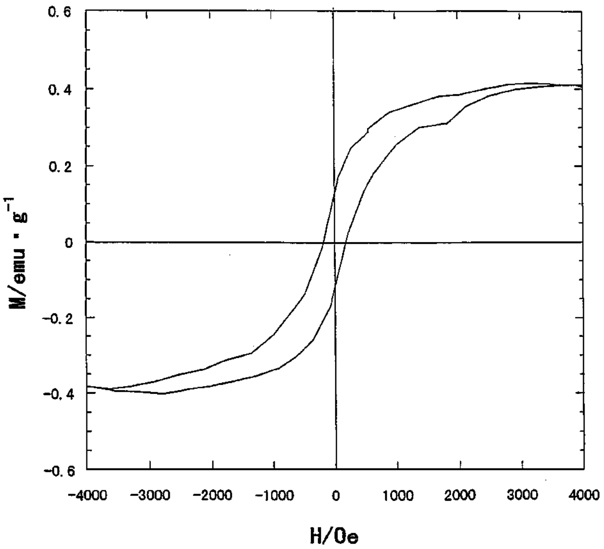

Figure 6 The room temperature hysteresis loop of the magnetization curve of Fe_3Mo_3C obtained from the Fe/Mo/C = 1/1/1 samples which was ground for 3 h and subsequently heated at 800°C for 30 min.

4. Summary

In order to discuss the optimal conditions and reaction mechanism for the formation of ternary carbide Fe_3Mo_3C by mechanical activation assisted solid-state reaction, the powder mixtures with different mixing ratios of Fe/Mo/C = 6/6/1–1/1/6 were ground for 1–3 h in a planetary ball mill and subsequently heated at 600–900°C. Fe_3Mo_3C formed mainly from the powder mixtures which were ground for 3 h and subsequently heated, whereas Mo_2C formed from the powder mixtures which were ground for 0 and 1 h and then heated. From the results obtained about the effect of mixing ratio, grinding time and heating temperature of Fe/Mo/C samples on the formation of Fe_3Mo_3C, it was found that the formation of Fe_3Mo_3C strongly depends on the mixing homogeneity and the activated state of the particles of Fe, Mo and C components induced by mechanical grinding. Fe_3Mo_3C obtained belongs to a hard magnet, having saturation magnetization of 0.4 emu g^{-1}, remanence of 0.13 emu g^{-1} and coercivity of 200 Oe.

Acknowledgment

The author is grateful to Mr. K. Suzuki for carrying out some of the experiments and to Dr. K. Hamada for his help in useful discussion and measurments the magnetic property.

References

1. E. GAFFET, F. BERNARD, J.-C. NIEPCE, F. CHARLOT, C. GRAS, G. L. CAER, J.-L. GUICHARD, P. DELCROIX, A. MOCELLIN and O. TILLEMENT, *J. Mater. Chem.* **9** (1999) 305.
2. T. TSUCHIDA, T. HASEGAWA and M. INAGAKI, *J. Amer. Ceram. Soc.* **77** (1994) 3227.
3. T. TSUCHIDA, T. KITAGAWA and M. INAGAKI, *Eur. J. Solid State Inorg. Chem.* **32** (1995) 629.

4. T. TSUCHIDA and T. HASEGAWA, *Thermochim. Acta*. **276** (1996) 123.
5. T. TSUCHIDA, T. HASEGAWA, T. KITAGAWA and M. INAGAKI, *J. Eur. Ceram. Soc*. **17** (1997) 1793.
6. T. TSUCHIDA, T. KITAGAWA and M. INAGAKI, *J. Mater. Sci*. **32** (1997) 5123.
7. T. TSUCHIDA, M. KAWAGUCHI and K. KODAIRA, *Solid State Ionics* **101–103** (1997) 149.
8. T. TSUCHIDA and Y. AZUMA, *J. Mater. Chem*. **7** (1997) 2265.
9. T. TSUCHIDA and T. KAN, *J. Eur. Ceram. Soc*. **19** (1999) 1795.
10. S. T. OYAMA, "The Chemistry of Transition Metal Carbides and Nitrides" (Blackie Academic & Professional, London, 1996) p. 1.
11. L. M. DI, A. CALKA, Z. L. LI and J. S. WILLIAMS, *J. Appl. Phys*. **78** (1995) 4118.
12. I. BARIN, "Thermochemical Data of Pure Substances" (VCH, Weinheim, Federal Republic of Germany, 1989) p. 544.

Received 8 December 1999
and accepted 3 August 2000