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Synthesis and magnetic properties of Fe_5C_2 by reaction of iron oxide and carbon monoxide

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The formation behaviour and magnetic properties of Fe_5C_2 were investigated. Iron oxides, as starting material, were carburetted with carbon monoxide gas by heat treatment. Fe_5C_2 was formed as a single phase in the reaction temperature range 350 to 375° C. The amount of carbon monoxide gas was controlled by mixing with nitrogen gas to prevent free carbon deposition by the disproportionation of carbon monoxide. Synthesized Fe_5C_2 particles were identified as a single phase by XRD and the weight change measurement of reactants. The saturation magnetization of Fe_5C_2 was about 100 e.m.u. g^{-1}, regardless of the reaction temperature. The coercive force decreased from 800 to 400 Oe with increasing reaction temperature.

1. Introduction

Recently, magnetic particles with high saturation magnetization have been expected to be synthesized as high quality video and cassette tapes. At present, maghaematite (γ-Fe_2O_3) is mainly used as a magnetic recording medium, because of the easy mass production of γ-Fe_2O_3 with an appropriate value of the saturation magnetization and the coercive force. Oxide magnetic materials, however, have a relatively low saturation magnetization, below 90 e.m.u. g^{-1}.

Thus, metallic iron particles have attracted attention for use as a new magnetic recording medium, which has a very high saturation magnetization ($\sim$200 e.m.u. g^{-1}). The inferior chemical stability of the metallic iron particles is known to be a serious disadvantage in use. The surface of the iron particles is gradually oxidized in air to form iron oxides of lower saturation magnetization for stabilization. The commercially available iron particles have a saturation magnetization of 130 to 150 e.m.u. g^{-1}. On the other hand, the coercive force of iron powder is very high value (> 1000 Oe).

Iron nitrides such as Fe_4N, $Fe_{16}N$, etc., also have higher saturation magnetization than γ-Fe_2O_3 and higher chemical resistances than metallic iron particles, and are expected to be used for new magnetic recording materials [1, 2]. Among these nitrides, Fe_4N has a very high saturation magnetization ($\sim$190 e.m.u. g^{-1}) [3]. There is a wide stable region of Fe_4N in the Fe–N system phase diagram [1], which enables synthesis of Fe_4N as a single phase from iron metal and ammonia gas [4, 5]. The coercive force of the Fe_4N formed is $\sim$800 Oe which is appropriate for utilization as a magnetic tape [4, 5]. However, Fe_4N also exhibits a low chemical stability causing a decrease in the high saturation magnetization ($\sim$100 e.m.u. g^{-1}) due to surface oxidation [4, 5].

Some iron carbides are candidates for magnetic materials, especially Fe_3C, Fe_5C_2 and Fe_7C_3 [6–9]. These iron carbides have acceptably high saturation magnetization ($\sim$130 e.m.u. g^{-1}) [10], although the value is lower than those of metallic iron and Fe_4N. They also have the great advantages of higher resistance to oxidation than metals and nitrides, and of suitable hardness. Therefore, iron carbides are expected to be promising as new magnetic recording media. However, it is difficult to synthesize a desired iron carbide as a single phase, because most iron carbides are metastable under 1 atm pressure [11]. Iron carbides prepared so far are also contaminated with metallic iron, iron oxides, free carbon and other iron carbides. Few papers have reported the formation behaviour and properties of iron carbides except for the saturation magnetization and the Curie points of Fe_3C, Fe_5C_2 and Fe_7C_3 [9, 10, 12].

Among these carbides, Fe_5C_2 has a relatively high saturation magnetization and is well known as the Hägg carbide [6]. However a study of the synthesis of pure Fe_5C_2 is required. This work focuses on the formation behaviour and magnetic properties of pure Fe_5C_2 for possible use as a magnetic recording medium.

2. Experimental procedure

α-Fe_2O_3 and Fe_3O_4 powders were used as starting iron sources. Table I shows the characteristics of the starting iron oxides. The particle size and shape of iron oxides were observed using a transmission electron microscope (TEM). The BET method was used to examine the specific surface area. α-Fe_2O_3(1) listed in Table I was a chemical reagent.

α-Fe_2O_3(2) particles were prepared by the thermal decomposition of α-FeOOH as follows: $Fe(NO_3)_2 \cdot 9H_2O$ was dissolved in deionized water to the concentration of about 0.1 mol l^{-1}. A small excess of KOH aqueous solution was added to the aqueous solution and then stirred for 3 d to yield a yellow

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TABLE I Specific surface area (BET method), particle size and particle shape of starting iron oxides

	Particle size (μm)	Surface area ($m^2 g^{-1}$)	Particle shape
α-Fe_2O_3(1)	0.2–0.6	7.6	Granular
α-Fe_2O_3(2)	~1	117	Acicular
Fe_3O_4	~0.02	120	Granular

precipitate (α-FeOOH). α-FeOOH thus formed was filtered and dried by thermal decomposition at 300° C for 1 h in air.

Fe_3O_4 particles were prepared by dissolving $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ (molar ratio 1 : 2) in deionized water to a concentration of about 0.1 mol l^{-1}. A small excess of aqueous NaOH was added to the aqueous solution to yield a black precipitate (Fe_3O_4). The precipitated Fe_3O_4 was dried at 100° C for 1 d.

Fig. 1 shows the experimental apparatus used in this work. About 500 mg of the starting iron oxide particles were placed in an alumina boat and put in an electric furnace with a quartz inner tube. After the iron oxide particles were heated to a prescribed temperature in a flow of nitrogen gas, carbon monoxide gas was passed into the quartz tube. Nitrogen gas was used to dilute the carbon monoxide gas. After heat treatment, the specimens were cooled in the furnace in a flow of nitrogen gas. The weight change of the specimens was measured before and after the heat treatment under the following experimental conditions: reaction temperature 250 to 600° C; holding time 1 to 4 h; carbon monoxide gas flow rate 50 ml min^{-1}; nitrogen gas flow rate 0 to 350 ml min^{-1}. The weight change of the specimens was determined from the equation

$$\text{weight change (\%)} = \frac{\text{weight of treated specimen} - \text{weight of starting iron oxide}}{\text{weight of starting iron oxide}} \quad (1)$$

The crystalline phases of the products were identified by X-ray diffractometry (XRD). The intensity ratio of Fe_5C_2(5 1 0) and Fe_3O_4(3 1 1) X-ray profiles was measured to calculate the formation of Fe_5C_2 in the specimens from the equation

$$Fe_5C_2 \text{ content (wt \%)} = \frac{I_{Fe_5C_2 510}}{I_{Fe_5C_2 510} + 0.33 I_{Fe_3O_4 311}} \quad (2)$$

The magnetic properties of the products were measured by a vibrating sample magnetometer (VSM) at room temperature in a magnetic field up to 17.5 kOe.

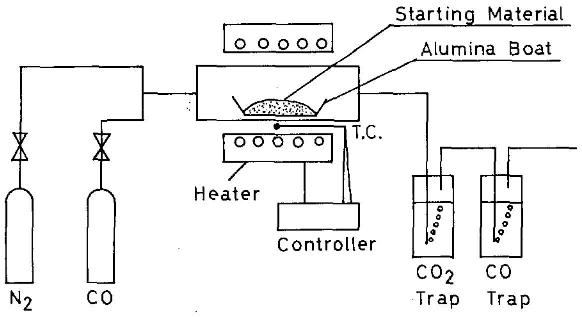

Figure 1 Experimental apparatus. TC = thermocouple.

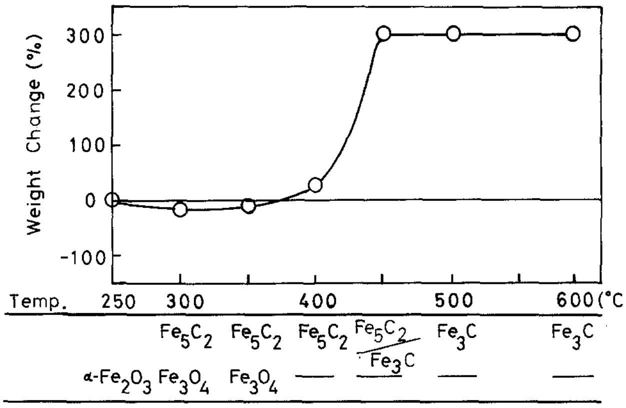

Figure 2 Effect of reaction temperature on phases formed and weight change of specimens; holding time 4 h, carbon monoxide gas flow rate 50 ml min^{-1}, starting iron oxide α-Fe_2O_3. Weight gain: carbon formation by disproportionation of carbon monoxide gas. Weight loss: reduction from iron oxide to iron carbide.

3. Results and discussion

3.1. Effect of reaction temperature on the phase formed and the weight change of specimens

Fig. 2 shows the dependence of the weight change of the specimens on the reaction temperature and of the crystalline phases on the reaction temperature. The experimental conditions were: reaction temperature 250 to 600° C; holding time 4 h; carbon monoxide gas flow rate 50 ml min^{-1}; starting iron oxide α-Fe_2O_3.

Carburization did not occur on heating in carbon monoxide gas below 250° C. The desired carbide of Fe_5C_2 was formed in the reaction temperature range 300 to 450° C. Fe_3O_4 particles formed from α-Fe_2O_3 coexisted in the specimens at temperatures between 300 and 350° C, while Fe_3C formed in the reaction temperature range 450 to 600° C. Fe_5C_2 was not formed above 450° C. No other iron compounds, except Fe_3O_4, Fe_5C_2 and Fe_3C, were detected by XRD under these conditions. These results indicate that Fe_5C_2 does form at temperatures between 250 and 450° C and Fe_3C becomes the main product above 450° C. Hofer and Cohn [10] also reported that Fe_5C_2 decomposed to Fe_3C and carbon above 550° C.

The total weight of the specimens decreases by about 20% if the reduction from α-Fe_2O_3 to iron carbide occurs. The weight change of the specimens was not observed at 250° C, because the starting iron oxide could not react to form the carbide. In the reaction temperature range 300 to 350° C, the weight change was less than 20%, because Fe_3O_4 was co-precipitated with carbide by reduction with α-Fe_2O_3. Free carbon was deposited in the specimens at temperatures from 400 to 600° C by the disproportionation of carbon monoxide gas to form carbon dioxide and free carbon. Above 450° C, a large amount of free carbon was deposited, which reflects the large weight change of the specimens to above 300%. The formation of free carbon and residual

Fe_3O_4 must be avoided in order to synthesize Fe_5C_2 as a single phase.

The above results indicate that the reaction temperature of 375° C was suitable to synthesize Fe_5C_2 particles as a single phase to avoid the deposition of free carbon. The formation behaviour of Fe_5C_2 at this temperature was investigated in detail.

3.2. Effect of iron oxides on the formation of Fe_5C_2

Table II shows the effect of starting iron oxides on the reaction of the specimens and the phases formed at 375° C under the following experimental conditions: holding time 4 h; carbon monoxide gas flow rate 50 ml min^{-1}; nitrogen gas flow rate 350 ml min^{-1}.

When α-Fe_2O_3(1) was used as a starting iron oxide, the amount of Fe_5C_2 formed was about 80 wt %. On the other hand, the amount of Fe_5C_2 formed from α-Fe_2O_3(2) and Fe_3O_4 was 100 wt %. It was found that the particle size of the starting iron oxide strongly affected the formation of Fe_5C_2. α-Fe_2O_3(1) particles have a smaller surface area than α-Fe_2O_3(2) and Fe_3O_4 (as seen in Table I). The result suggests that such a solid state reaction requires that the starting materials, have a small size and high surface area. Therefore, a longer holding time was required in order to carburet perfectly α-Fe_2O_3(1) under these conditions. When α-Fe_2O_3 was used as starting iron oxide, no iron compounds except Fe_3O_4 and Fe_5C_2 were detected in the treated specimens. These results reveal that α-Fe_2O_3 was reduced to Fe_3O_4, which was subsequently carburetted to Fe_5C_2 under the above conditions.

As shown in Table II, the weight change of α-Fe_2O_3(2) on carburization was larger than that of Fe_3O_4. Only Fe_5C_2 was detected as a crystalline phase in the specimens formed from both the starting iron oxides. The result indicates that the amount of free carbon deposited with Fe_5C_2 formed from α-Fe_2O_3(2) was larger than that from Fe_3O_4.

The particle size of Fe_5C_2 formed from α-Fe_2O_3(1) was about 1 μm and larger than that of the starting α-Fe_2O_3(1). The particle size of Fe_5C_2 formed from α-Fe_2O_3(2) was about 0.1 μm. The acicular shape of α-Fe_2O_3(2) particles as starting iron oxide could not be maintained in the Fe_5C_2 particles formed. The particle size of Fe_5C_2 formed from Fe_3O_4 was about 0.1 μm and larger than that of original Fe_3O_4 particles.

From the viewpoint of the reactivity and particle size of the Fe_5C_2 formed, Fe_3O_4 particles were selected as the most appropriate starting iron oxide for the preparation of Fe_5C_2 particles.

TABLE II Effect of starting iron oxides on formation behaviour of Fe_5C_2 at 375° C for 4 h; carbon monoxide gas flow rate 50 ml min^{-1}, nitrogen gas flow rate 350 ml min^{-1}

Starting iron oxide	Weight change (%)	Fe_5C_2 content (wt %)
α-Fe_2O_3(1)	−14	83
α-Fe_2O_3(2)	−9	100
Fe_3O_4	−20	100

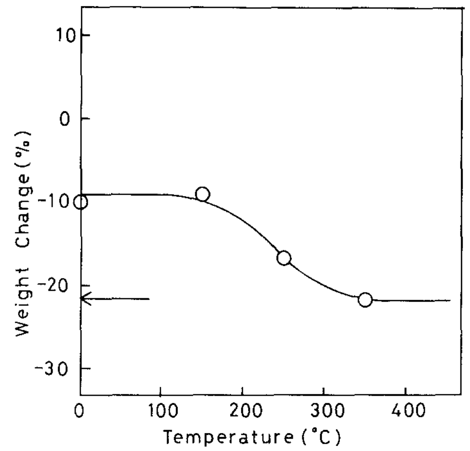

Figure 3 Relationship between weight change of specimens and nitrogen gas flow rate; reaction temperature 375° C, holding time 4 h, carbon monoxide gas flow rate 50 ml min^{-1}, starting iron oxide Fe_3O_4.

3.3. Effect of nitrogen flow rate and holding time on the reaction to form Fe_5C_2

In order to decrease the amount of free carbon deposited by the disproportionation of carbon monoxide gas, the gas had to be diluted with nitrogen gas. At temperatures around 400° C, iron oxide does not react with nitrogen to form nitrides. Fig. 3 shows the relationship between the weight change of the specimens and the nitrogen gas flow rate under the following experimental conditions: treatment temperature 375° C; holding time 4 h; carbon monoxide gas flow rate 50 ml min^{-1}; starting iron oxide Fe_3O_4.

The total weight change on the formation of Fe_5C_2 from Fe_3O_4 can be theoretically calculated to be about −20%, which is shown by an arrow in Fig. 3. The weight change of the specimens was close to −20 wt % with increasing nitrogen gas flow rate. When the nitrogen gas flow rate was adjusted to 350 ml min^{-1}, the weight change reached about −20 wt %, in which only Fe_5C_2 phase formed in the specimens. These results indicate that the amount of deposited free carbon decreased with increasing nitrogen gas flow rate and Fe_5C_2 formed as a single phase under these conditions. A representative X-ray diffraction profile of the Fe_5C_2 formed is shown in Fig. 4. The intensity and the lattice parameters agreed with those of Fe_5C_2 [13].

Fig. 5 shows the relationship between the content of Fe_5C_2 formed and the holding time. The experimental conditions were controlled as follows, according to the above results, to avoid the deposition of free carbon: reaction temperature 375° C; carbon monoxide gas flow rate 50 ml min^{-1}; nitrogen gas flow rate 350 ml min^{-1}; starting iron oxide Fe_3O_4.

The content of Fe_5C_2 formed increased with increasing holding time and reached 100 wt % when the holding time was longer than 2 h. No crystalline phases except Fe_5C_2 and Fe_3O_4 were detected regardless of the change in holding time under these conditions.

3.4. Effect of reaction temperature on magnetic properties of Fe_5C_2 particles formed

The conditions necessary for the preparation of Fe_5C_2

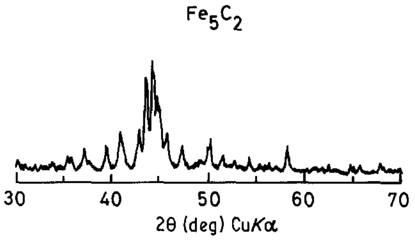

Figure 4 Representative X-ray diffraction profile of Fe_5C_2 formed as a single phase from Fe_3O_4 at 375° C for 4 h; carbon monoxide gas flow rate $50\,ml\,min^{-1}$, nitrogen gas flow rate $350\,ml\,min^{-1}$.

particles as a single phase were determined to be as follows: reaction temperature 350 to 375° C; holding time 2 to 4 h; carbon monoxide gas flow rate $50\,ml\,min^{-1}$; nitrogen gas flow rate $350\,ml\,min^{-1}$; starting iron oxide Fe_3O_4. The size of the granular Fe_5C_2 particles formed under these conditions was about 0.1 μm. Fig. 6 shows the relationship between the magnetic properties of Fe_5C_2 particles formed and the reaction temperature. The saturation magnetization of the products was found to be about $100\,e.m.u.\,g^{-1}$ regardless of the reaction temperature. However, Fe_5C_2 particles were contaminated with 10 wt % free carbon particles which were deposited by the disproportionation of carbon monoxide gas at 400° C. Thus, the saturation magnetization of pure Fe_5C_2 can be suggested by taking the coexistence of 10 wt % free carbon into account according to the following equation

$$\text{corrected } \sigma_s(\text{e.m.u. g}^{-1}) = 1.1 \times \text{measured } \sigma_s(\text{e.m.u. g}^{-1})$$

The value is corrected to about $100\,e.m.u.\,g^{-1}$. Hofer and Cohn [10] reported that the saturation magnetization of Fe_5C_2 was about $130\,e.m.u.\,g^{-1}$. The difference in the saturation magnetization may be attributable to the difference in the state of the crystal perfection of Fe_5C_2.

The coercive force of Fe_5C_2 particles formed decreased from 800 to 400 Oe with increase in the reaction temperature, because the particle size of the Fe_5C_2 particles formed increased with increasing reaction temperature and reached the multi-magnetic-domain size. The coercive force of the commercially available magnetic recording powder is controlled to 300 to 1000 Oe, therefore this coercive force of 400 to 800 Oe may be an appropriate value for use as a magnetic recording medium. A representative hysteresis loop of Fe_5C_2 particles formed as a single phase is shown in Fig. 7.

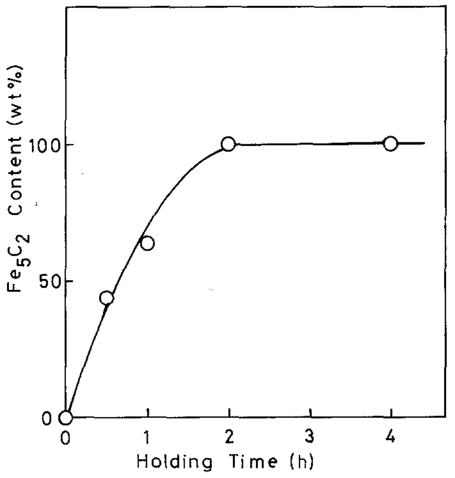

Figure 5 Relationship between the amount of Fe_5C_2 formed in treated specimens and holding time; reaction temperature 375° C, carbon monoxide gas flow rate $50\,ml\,min^{-1}$, nitrogen gas flow rate $350\,ml\,min^{-1}$, starting iron oxide Fe_3O_4.

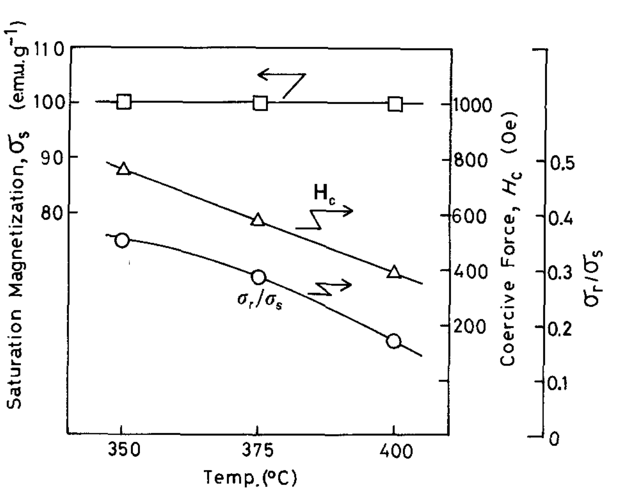

Figure 6 Effect of reaction temperature on magnetic properties of Fe_5C_2 formed from Fe_3O_4; holding time 4 h, carbon monoxide gas flow rate $50\,ml\,min^{-1}$, nitrogen gas flow rate $350\,ml\,min^{-1}$.

The ratio of the residual magnetization to the saturation magnetization $(=\sigma_r/\sigma_s)$ also decreased from 0.35 to 0.17 with increase in the reaction temperature, the same behaviour as the decrease in the coercive force. The σ_r/σ_s ratio of the commercially available magnetic recording powders is normally >0.5. The value of σ_r/σ_s ratio must be improved in Fe_5C_2 particles formed in this work by adjustment of the crystallinity and particle shape.

There are uncertainties in the magnetocrystalline anisotropy constant, the magnetostrictive constant and the single domain size of Fe_5C_2, which must be determined for pure Fe_5C_2 particles. The coercive force and σ_r/σ_s ratio of Fe_5C_2 formed in this work can be improved if well-crystallized fine and acicular particles of Fe_5C_2 can be formed by control of the reaction conditions.

The saturation magnetization and the coercive force of Fe_5C_2 particles formed did not change after the

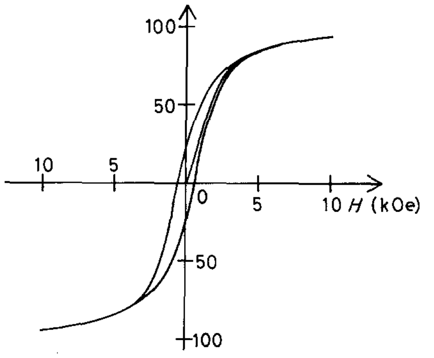

Figure 7 Representative hysteresis loop of Fe_5C_2 formed as a single phase from Fe_3O_4 at 375° C for 4 h; carbon monoxide gas flow rate $50\,ml\,min^{-1}$, nitrogen gas flow rate $350\,ml\,min^{-1}$.

particles formed were stored in ambient air for 1 month. This result reveals that the Fe_5C_2 particles formed are chemically stable in an ambient atmosphere.

4. Conclusions

Iron oxides and carbon monoxide gas were used as starting materials to synthesize Fe_5C_2 particles. The formation behaviour of iron carbides and the magnetic properties of the iron carbides formed were investigated. The following results were obtained.

1. When the reaction temperature was 250° C or below, iron carbides did not form on carburization with carbon monoxide. In the reaction temperature range 300 to 400° C, Fe_5C_2 was formed as a major phase. Fe_3C was predominantly formed above 450° C.

2. Fe_5C_2 can be synthesized as a single phase under the following conditions: reaction temperature 350 to 375° C; holding time 2 to 4 h; starting iron oxide Fe_3O_4; nitrogen gas flow rate $350\,\mathrm{ml\,min^{-1}}$; carbon monoxide gas flow rate $50\,\mathrm{ml\,min^{-1}}$.

3. The saturation magnetization of Fe_5C_2 particles was about $100\,\mathrm{e.m.u.\,g^{-1}}$ regardless of the reaction temperature. The coercive force of Fe_5C_2 decreased with increasing reaction temperature from 800 to 400 Oe, depending upon the increase in particle size.

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