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Preparation and Characterization of Iron Manganese Carbide by Reaction of the Oxides and Carbon in Nitrogen

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Fe_2O_3, Mn_2O_3, and their mixtures are reduced by carbon in nitrogen. The product depends on manganese loading. A cohenite Fe_3C type phase is stabilized by substituting manganese into the lattice. A single phase cohenite phase solid solution $Fe_{3-x}Mn_xC$ is prepared for 20–50% manganese loading, and a Fe_7C_3 type phase can be obtained with manganese loading of 65–80%. The nitrogen participates in the reduction of the manganese-rich oxide mixtures. A manganese carbonitride is obtained by heating the mixture of Mn_2O_3 and carbon in nitrogen. The composition of the new compound is analyzed as $Mn_2C_{0.60}N_{0.21}$ and it has a hexagonal structure with $a_0 = 4.778$ Å and $c_0 = 4.486$ Å.

INTRODUCTION

Iron carbides can be prepared in the laboratory by reducing iron oxide with carbon monoxide (1–3). However, this process is relatively hard to control and too expensive for industrial applications. It would be much easier to control and less expensive if iron carbide could be prepared by reducing iron oxide directly with carbon.

The binary phase diagram of iron and carbon indicates that the cohenite phase iron carbide Fe_3C is stable over a wide range of temperatures (4). However, this phase is only kinetically stable and is actually thermodynamically metastable. When being annealed at high temperature, fine powder Fe_3C decomposes to α-Fe (2).

It has been reported that Fe_3C can be prepared by reducing iron oxide with CO at temperatures ranging from 360 to 650°C (1, 2). At temperatures higher than 650°C, only α-Fe and carbon can be obtained (2). Direct reaction of iron and carbon can only partially convert iron to Fe_3C. When a mixture of sugar, carbon, and iron is heated at 900°C for 62 hr, the yield of Fe_3C in the product is only 13% (5). The low Fe_3C yield is probably due to the low stability of Fe_3C at the preparation temperature.

It is well known that the austenite phase Fe–C can be stabilized by manganese and chromium (6). Manganese carbides have also been reported forming various solid solutions with iron carbides (2, 7). It has also been reported that $(Fe,Mn)_7C_3$ can be obtained by direct reaction of $MnFe_2O_4$ and carbon at 1150°C (8). Therefore, it is possible that iron carbide can be stabilized by manganese and thus can be prepared by direct reaction of iron oxide and carbon in the presence of manganese oxide.

EXPERIMENTAL METHOD

Fe_2O_3 was prepared by decomposing iron oxalate ($FeC_2O_4 \cdot 2H_2O$) at 400°C. Mn_2O_3 was prepared by decomposing manganese nitrate ($Mn(NO_3)_2 \cdot 6H_2O$) at 700°C. Mixtures of Fe_2O_3 and Mn_2O_3 were prepared by decomposing $Mn(NO_3)_2 \cdot 6H_2O$ and $FeC_2O_4 \cdot 2H_2O$ together. In order to have a uniform mixture, a calculated quantity of iron oxalate was added to a 2 *M* manganese nitrate solution to make a slurry. The slurry was dried and predecomposed at 150°C for 12 hr. The partially decomposed mixture was then ground and heated at 700°C for 6 hr.

The oxides and activated carbon powder were mixed on a ball milling machine. The carbon was predried at 140°C for 2 hr before weighing. Each mixture was 20% carbon and 80% oxides or oxide mixtures by weight.

Each oxide and carbon mixture was put into an alumina boat, and the boat was set in a mullite process tube with flowing nitrogen. Since manganese is volatile and corrosive to silica at high temperatures, a quartz boat or tube could not be used. The sample was heated at 150°C for 1 hr and 300°C for 1 hr to drive off adsorbed moisture. The temperature was then brought up to the required temperature range, from 900 to 1150°C. At the end of

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heating, the sample was either quenched or slow cooled down to room temperature. In the quenching process, the sample boat was pulled out from the heating zone and cooled in a nitrogen or argon stream. The slow cooling was carried out using a temperature controller at a fixed cooling rate.

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity Cu$K\alpha_1$ radiation ($\lambda = 1.5405$ Å). The diffraction patterns were taken in the range $10° \leq 2\theta \leq 80°$ using step scan. The step size was $0.01° 2\theta$ and the scan rate was $2° 2\theta$/min.

RESULTS AND DISCUSSION

The iron oxide and manganese oxide prepared are hematite phase Fe_2O_3 and bixbyite phase Mn_2O_3, respectively. The products of the mixed oxides containing 5, 10, 20, 50, 65, 80, and 90 mole% Mn_2O_3 are all mixtures of the Fe_2O_3 and Mn_2O_3.

All the reduction products are sintered with metallic luster. No carbon can be visually observed. It is reported that carbon can be oxidized by iron oxide to both CO_2 and CO (5, 9). By weight, 18.4% Carbon is needed if the products are pure iron and CO; 21.6% carbon is needed if the products are Fe_3C and CO; and 14.0% carbon is needed if the products are CO_2 and Fe_3C. Since 20 wt% carbon is consumed, it is likely that most of the carbon is oxidized to CO. The reaction of Mn_2O_3 and carbon proceeds through a similar process.

The reaction product of Fe_2O_3 and carbon prepared at 900°C and quenched is a mixture of α-Fe and the austenite phase, which is a solid solution of carbon in γ-Fe, as indicated by X-ray diffraction analysis (Fig. 1). When cooled at a rate of 25°C/min, only α-Fe is obtained. The austenite phase formed at 900°C has decomposed completely during the slow cooling.

In either quenched or slow cooled product, no cohenite Fe_3C is detected by X-ray diffraction analysis. It appears impossible to prepare Fe_3C by direct reaction of iron oxide and carbon. Therefore, manganese has to be used to stabilize the cohenite Fe_3C phase.

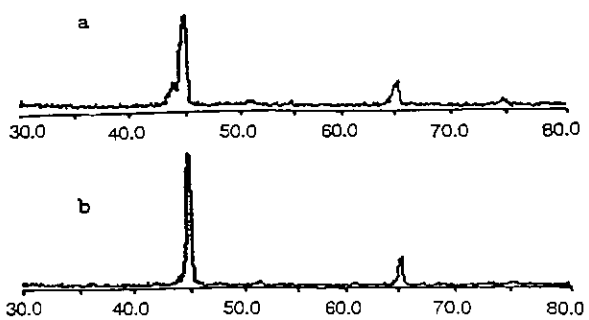

FIG. 1. X-ray diffraction patterns of the reaction products of Fe_2O_3 and carbon: (a) quenched and (b) cooled down at 25°C/min.

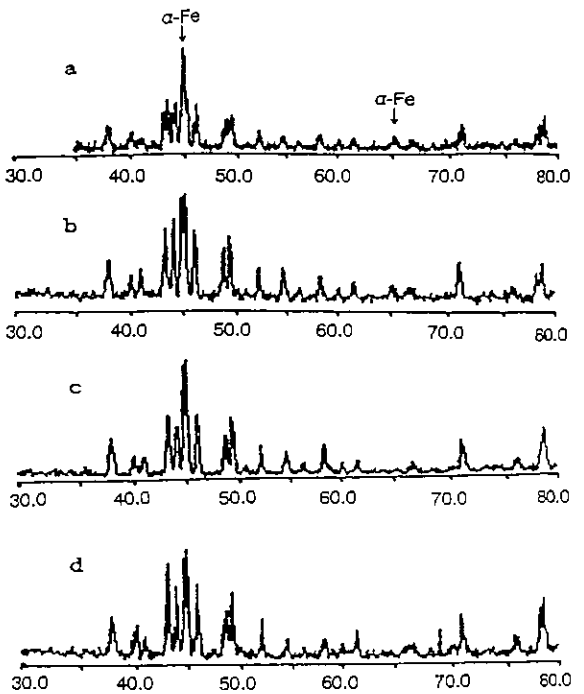

FIG. 2. X-ray diffraction patterns of the reaction products of Fe_2O_3 and Mn_2O_3 mixtures and carbon: (a) 5% Mn_2O_3, (b) 10% Mn_2O_3, (c) 20% Mn_2O_3, and (d) 50% Mn_2O_3.

The reduction temperature for the mixtures of Fe_2O_3 and Mn_2O_3 increases with increasing Mn_2O_3 loading. The oxide mixture containing 10% mole Mn_2O_3 is reduced completely at 925°C in 2 hr. However, the mixture containing 50% Mn_2O_3 cannot be completely reduced even at 950°C for 48 hr. Therefore, samples with 50% or less manganese were heated at 1000°C for 24 hr and those with more than 50% manganese were heated at 1150°C for 36 hr. In both cases, the product was cooled at 25°C/min. Under these reaction conditions, all Fe_2O_3 and Mn_2O_3 in the mixtures are completely reduced.

Reduction products depend on Mn_2O_3 loading. X-ray diffraction patterns of the product with 5, 10, 20, and 50% Mn_2O_3 are given in Fig. 2. When as little as 5% Mn_2O_3 is loaded, cohenite Fe_3C phase becomes the major phase in the product and only a small amount of α-Fe exists compared to pure α-Fe in the product when no manganese is loaded, as shown in Fig. 1.

While the reduction products containing 5 and 10% manganese are both composed of the cohenite phase and a small amount of the α-Fe phase, the only phase that can be detected by X-ray diffraction in the products containing 20 and 50% manganese is the cohenite phase. Therefore, reduction products for 20 and 50% manganese samples can be written as $Fe_{2.4}Mn_{0.6}C$ and $Fe_{1.5}Mn_{1.5}C$,

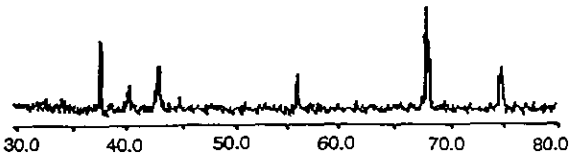

FIG. 3. X-ray diffraction pattern of the reaction product of Mn_2O_3 and carbon in nitrogen.

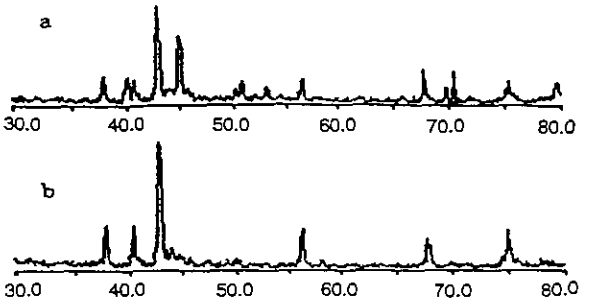

FIG. 4. X-ray diffraction pattern of the reaction products of Mn_2O_3-rich samples: (a) 80% Mn_2O_3 and (b) 90% Mn_2O_3.

respectively. The loaded manganese has substituted into the Fe_3C lattice and thus stabilized this phase.

Mn_2O_3 is reduced completely after heating at 1150°C for 36 hr in nitrogen. The product is a slightly sintered gray powder with metallic luster. The X-ray powder diffraction pattern of the product is given in Fig. 3. There appears to be no manganese or manganese oxide present. The pattern looks very close to the X-ray diffraction pattern of $(Cr,Fe)_2N_{1-x}$ reported by Robitsch (10).

The atomic radius of manganese is 1.17 Å, compared to the radii of 1.18 and 1.17 Å for chromium and iron. Therefore, a manganese atom has approximately the same size as a chromium or an iron atom. Therefore, we believe that a similar phase has been prepared.

Chemical analysis of the compound was conducted in Galbraith Laboratories, which provides commercial chemical analysis services. Two parallel samples were analyzed and the relative error is ±5%. The chemical analysis indicates that the compound contains 5.98% carbon and 2.40% nitrogen by weight. Hence, the formula can be written as $Mn_2C_{0.60}N_{0.21}$. It is very interesting to see that the inert gas nitrogen participates in the reduction of Mn_2O_3. The X-ray pattern of the manganese carbonitride $Mn_2C_{0.60}N_{0.21}$ can be indexed based on the hexagonal cell of $(Cr,Fe)_2N_{1-x}$ as shown in Table 1. The cell dimensions of this compound are determined using the least-square fitting as $a_0 = 4.788$ Å and $c_0 = 4.486$ Å, compared to 4.800 Å and 4.462 Å for $(Cr,Fe)_2N_{1-x}$ as reported (10).

The formula of the manganese carbonitride is given to indicate that nitrogen has entered into the structure rather than to show the exact stoichiometry. The chemical analysis gives the total carbon content, which includes both free carbon and carbon in the structure. It is possible that some of the carbon may be present in the free form.

In an attempt to make a similar phase Mn_2C_{1-x}, the manganese oxide and carbon mixture is heated in argon instead of nitrogen at 1150°C for 36 hr. Only a small amount of Mn_2O_3 is reduced and converted to manganese carbide $Mn_{23}C_6$. The major phase of the product is MnO. This indicates that the presence of nitrogen is essential to obtain the phase isomorphous to $(Cr,Fe)_2N_{1-x}$, and the presence of nitrogen facilitates the reduction of Mn_2O_3.

Samples containing 80 and 90% manganese are also reduced at 1150°C for 36 hr in nitrogen. X-ray patterns of the two products are given in Fig. 4. Both of the products are composed of the manganese carbonitride phase and Fe_7C_3. However, the intensity of the Fe_7C_3 lines diminishes when manganese loading increases from 80 to 90%.

In order to see at what composition the cohenite phase in the product changes to Fe_7C_3, a sample with 65% Mn_2O_3 loading is also reduced at 1150°C for 36 hr in nitrogen. The product is sintered and difficult to grind into powder. The X-ray pattern is too poor for phase identification. Therefore, the sample is heated at 1050°C for 18 hr and slow cooled. The 1050°C product has the cohenite phase

TABLE 1
Crystallographic Data of $Mn_2C_{0.60}N_{0.21}$

d space	*d* space (*)	I/I_{max}	I/I_{max}[a]	*hkl*
2.400	2.399	29	16	110
2.242	2.233	94	40	002
2.112	2.114	100	100	111
1.638	1.634	51	35	112
1.382	1.387	14	25	300
1.269	1.266	57	30	113

[a] Data reported by Robitsch for $(Cr,Fe)_2N_{1-x}$ (10).

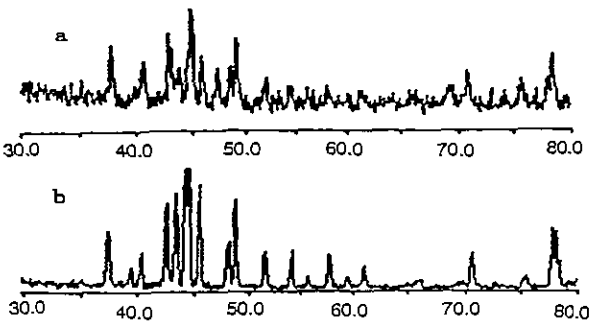

FIG. 5. Effects of Mn_2O_3 loading on the product phases: (a) 50% Mn_2O_3 and (b) 65% Mn_2O_3.

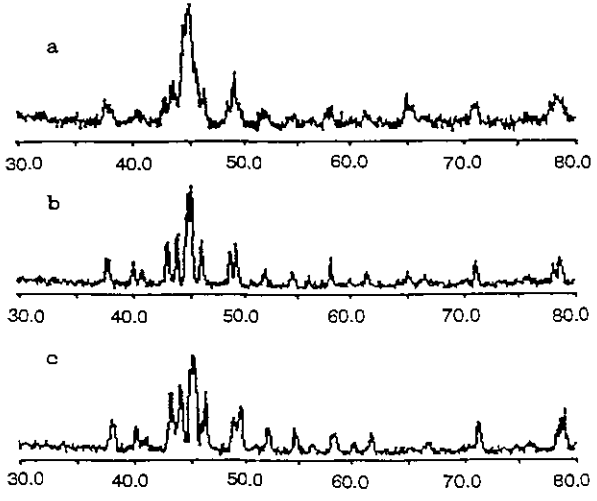

FIG. 6. Effect of manganese loading on the thermal stability of the cohenite phase: (a) Fe_3C, cooled at 5°C/min, (b) $Fe_{2.7}Mn_{0.3}C$, cooled at 5°C/min, and (c) $Fe_{2.7}Mn_{0.3}C$, cooled at 1°C/min.

as a major phase. However, Fe_7C_3 lines are readily visible (Fig. 5a). As a comparison, a 50% manganese sample is also heated at 1050°C in nitrogen. The product remains as a pure cohenite phase (Fig. 5b). This indicates that the change of the product from the cohenite phase to the Fe_7C_3 phase is due to the increased manganese loading rather than preparation temperature change.

The X-ray pattern shown in Fig. 6 indicates that substitution of manganese has stabilized the cohenite phase during annealing. When Fe_3C is heated at 900°C for 1 hr and cooled at a rate of 5°C/min, a substantial portion of the original cohenite phase decomposes to the α-Fe phase. The cohenite phase containing 10% manganese does not decompose when annealed at 900°C and cooled at 5°C/min or even at 1°C/min. This is another indication that manganese substitution stabilizes the cohenite Fe_3C phase.

It may be possible that nitrogen also takes part in the reaction during the synthesis of $Fe_{3-x}Mn_xC$ and $Fe_{7-x}Mn_xC_3$, and a small quantity of nitrogen may also enter the structure of these two compounds. It would be worth doing further study to find out in the future.

CONCLUSIONS

Fe_2O_3, Mn_2O_3, and their mixtures can be reduced by carbon in nitrogen atmosphere. The reduction products depend on manganese loading. Iron carbide Fe_3C and Fe_7C_3 can be stabilized by substituting manganese into their lattices. The cohenite phase is obtained with 5 to 50% manganese loading and the manganese substituted cohenite phase $Fe_{3-x}Mn_xC$ is stable during annealing. The Fe_7C_3 type phase is obtained for samples with 65 to 80% manganese loading. A new compound is obtained for samples with 80% or higher manganese loading. Nitrogen plays a critical role in the reduction of manganese-rich samples.

When Mn_2O_3 is reduced by carbon at 1150°C in a nitrogen atmosphere, a single phase manganese carbonitride is obtained. X-ray diffraction patterns of this new compound can be indexed on the basis of $(Cr,Fe)_2N_{1-x}$ cell and has a hexagonal structure with $a_0 = 4.778$ Å and $c_0 = 4.486$ Å. Its chemical formula is $Mn_2C_{0.60}N_{0.21}$, as determined by chemical analysis. This formula indicates that the nitrogen has participated in the reduction process and entered into the structure of the product.

REFERENCES

1. S. Yoshiyoki and D. Shigeo, European Patent 0,123,318 (1984).
2. J. P. Senateur, *Ann. Chim.* **2,** 103 (1967).
3. D. M. Schleich and Y. Zhang, U.S. Patent 5,040,552 (1991).
4. T. B. Massalski, "Binary Alloy Phase Diagrams." William and Scott, 1986.
5. T. Ya. Kosolapova, "Carbides." Plenum, New York, 1971.
6. Y. T. Qian, "Crystal Chemistry," p. 377. University of Science and Technology of China Press, Hefei, 1988.
7. K. Kuo and L. E. Persson, *J. Iron Steel Inst.* (9), 39 (1954).
8. K. Terayama and M. Ikeda, *Trans. Jpn. Inst. Met.* **25(5),** 356 (1984).
9. C. H. Bamford and C. F. H. Tipper (Eds.), "Comprehensive Chemical Kinetics," Vol. 22, p. 277. Elsevier, Amsterdam, 1980.
10. J. Robitsch, *Mitteilungsbl. Abt. Mineral. Landesmus. Joanneum.* **1–2,** 86 (1967).