REACTION MECHANISMS OF Fe_3C FORMATION FROM IRON OXIDES WITH CO AND CO-H_2 GAS MIXTURES[1]

Yasushi Sasaki [2]
Deuk-Li Kong[3]
Kotarou Satoh[4]
Mitsutaka Hino[5]

Abstract

Iron carbide (Fe_3C) is produced by reactions of Fe_2O_3 powder with CO and CO-H_2 gas mixtures at 923K. The effect of the gas composition on phases formed during the reaction of Fe_3C formation from Fe_2O_3 is examined by XRD analysis. The possibility of direct Fe_3C formation without the formation of α-Fe phase based on thermodynamical evaluation has been experimentally investigated. In the case of Fe_3C formation with CO gas, α-Fe phase has not been found during the reaction of Fe_3C formation. Conditions for Fe_3C formation in the Fe-O-C-H system are thermodynamically evaluated. From this thermodynamical evaluation, Fe_3C can be produced by α-Fe carburization in the reaction of iron oxide reaction with CO-H_2 was expected. However, α-Fe was not obsreved in the present study. Undetected α-Fe phase can be explained by the generation of Fe_3C from the development of the *micro-twinning structure* in α-Fe during the reduction reaction.

Key words: Fe_3C; Metastability; Carbon deposition; Micro twinning.

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[2] *Professor , GIFT, POSTECH, Pohang, Korea (South)*

[3] *Graduate student , GIFT, POSTECH, Pohang, Korea (South)*

[4] *Graduate student, Graduate School of Engineering, Tohoku University, Sendai Japan.*

[5] *Professor, Graduate School of Engineering, Tohoku University, Sendai Japan.*

1 INTRODUCTION

Iron carbide (Fe_3C) offers the potential for the development of new iron and steel-making technologies. Fe_3C has attracted wide attention due to the several potential benefits: (a) larger concentration of carbon of 6.7 mass% possibly used as an energy source, (b) relatively low energy consumption to produce Fe_3C due to lower operational temperature of about 550-650°C. Due to the metastability of Fe_3C, however, the details of its reaction mechanism has not yet been fully established.

The formation of Fe_3C is potentially associated with carbon deposition from gas phase since the carbon activity in the gas phase for Fe_3C formation is higher than unity. However, the formation of free carbon must be preferably suppressed to carry out the stable and efficient Fe_3C conversion process from iron oxide. As a practical process, Fe_3C formation in Fe-C-O-H system as well as Fe-C-O system can be applicable. Recently thermodynamic asesseement of the Fe-C-O-H was carried out.(1) This paper discusses the Fe_3C formation mechanism and the metastable conditions for the Fe_3C formation in Fe-C-O-H system.

2 PHASE STABILITY OF Fe_3C

Figure 1 (a) and (b) show the calculated phase stability diagrams for the system Fe-C-O system at 800K and 923K, respectively.

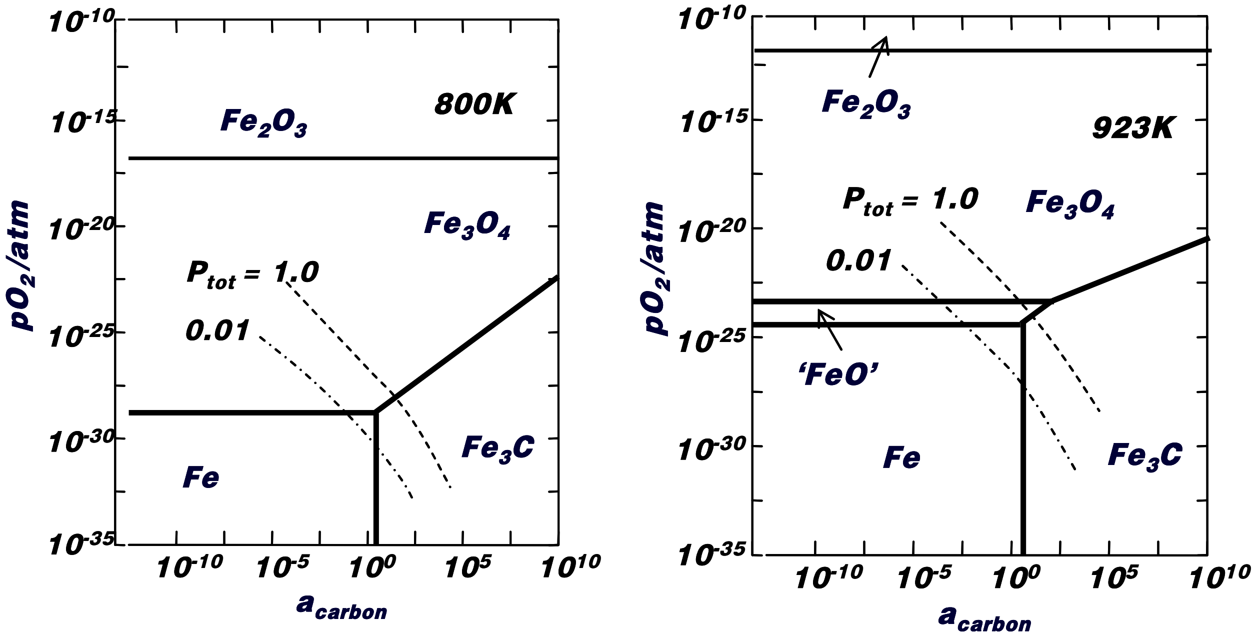

Figure 1. (a) Phase stability diagram for the system Fe-C-O at 800K. (b) Phase stability diagram for the system Fe-C-O at 923K.

In Figure 1, only Fe_3C is considered as a carbide, since Hägg carbide (Fe_5C_2) is known to be unstable above 573K. Both figures clearly show the existence of Fe_3C where the carbon activities are higher than unity. These systems possesse three degrees of of freedom. Thus, if temperature, oxygen pressure and carbon activity are specified, system's total pressure cannot be specified, rather automatically fixed. The possible reaction pathes corresponding with several total pressures are also shown in Figure 1. Intrigueingly, in the case of the total pressure of 1 atm, Fe_3C may be formed directly from Fe_3O_4 or FeO without the formation of Fe. Reduced Fe is known to be a very effective catalyst for carbon deposition, the elimination of Fe formation is favorved for the stable Fe_3C formation. For the Fe-C-O-H system, the total pressure can be specified, since the degree of freedom increases to 4. Conejo et al.calculated Fe-C-O-H phase stability diagram in various conditions.(2) The metastable Fe-C-O-H configuration in ternary presentation at 850K and 1atm is reproduced in Figure2. As clearly shown in Figure 2, Fe phase extends from H corner to C-O side. In this case, hypothetical direct conversion of magnetite or wustite into Fe_3C will be elimnated. A combination of high temperature (>850K) and low pressures (<1atm) promotes the field for metallic Fe to dominate the entire lengthe of the diagarm. The calculation method of Fe-C-O-H configuration phase stability diagram is found elsewehere.(2)

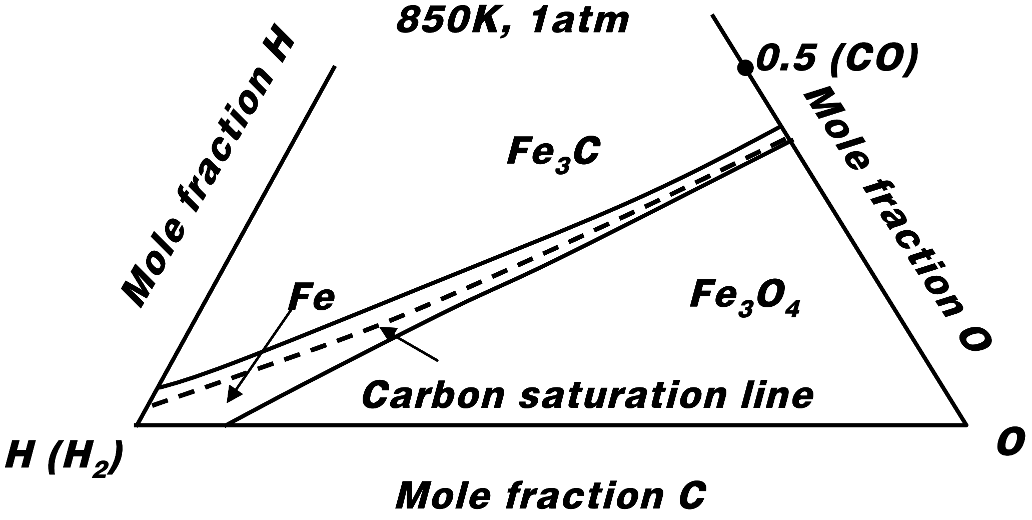

Figure 2. Phase stability diagram for the system Fe-C-O-H at 853K and 1atm.

3 EXPERIMENTAL

High purity Fe_2O_3 powder (99.99%) was used in the study. The gases CO, H_2 and Ar had initial purities of 99.9, 99.99 and 99.999%, respectively. The CO gas was further purified by passing through columns of magnesium percolate and silica gel, the other gases were passed through copper turnings at 873K, and dried. The experimental arrangement is schematically shown in Figure 3.

The flow rates of Ar, CO and H_2 gases were controlled by using Mass flow controllers. The reaction gas mixture was passed to the preweighed Fe_2O_3 sample in an alumina boat placed in an alumina reaction tube (22 mm ID) in a horizontal resistance furnace. The temperature of the furnace was controlled by means of a Pt/Pt-13%Rh thermocouple. The isothermal zone of the furnace was about 40 mm and the Fe_2O_3 sample in the alumina boat was placed in the center of the isothermal zone. The reaction tube was heated to 923K with flowing Ar gas and kept at 923K for 20min, then the reacting gas was introduced. After particular reaction time, the reacting gas was changed to Ar and reacted sample was moved to the end of the reacting tube to quench the sample. The reacted samples were analyzed by X-ray diffraction.

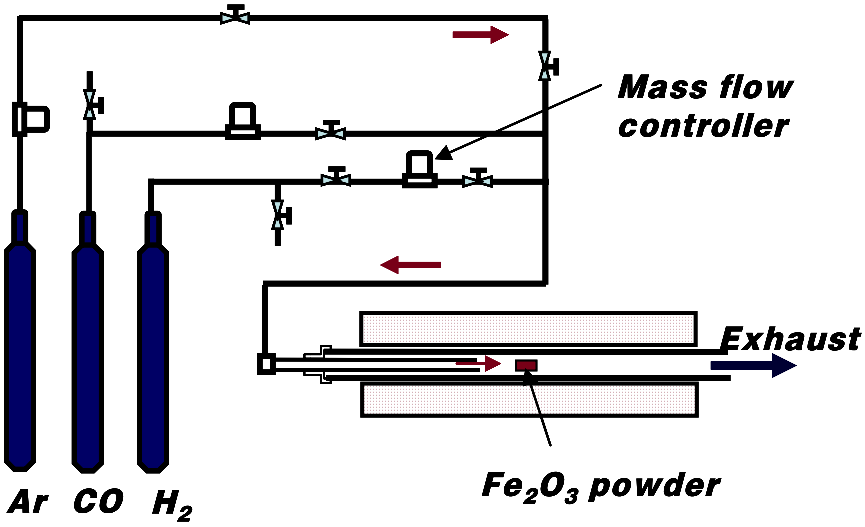

Figure 3 experimental arrangements.

4 RESULTS AND DISCUSSION

4. 1 Cementitation with CO Gas

Phases formed in the reaction of Fe_3C formation with CO at 873K as a function of reacting time are shown in Figure 4. After 15 min, the formation of Fe_3C and carbon deposition are confirmed. As shown in Figure 4, the apparent intensities of Fe_3C do not likely to change with time after 15 min, but those of carbon increases with time. It simply suggests that Fe_3C formation may be retarded by the carbon deposition. Namely, for the formation of Fe_3C, the activity of carbon in the reacting gas was adjusted to more than1 in the present experimental condition. Once carbon deposition starts, however, the carbon activity becomes to be unity so that Fe_3C cannot be formed after the carbon deposition. As already mentioned, Fe_3C is relatively unstable material so that it has a chance to decompose into C and Fe. When the decomposition of Fe_3C occurs, Fe is produced along with graphite. Fe is known to be a good catalyst for the carbon deposition reaction. Produced Fe acts as catalysts for further graphite deposition. This deposition leads to an accelerate carbon deposition reaction.(3) Once carbon deposition starts, the reacting gas hardly access to the Fe_3C surface. Consequently the formation of Fe_3C must stop. The amount of produced α-Fe particles can be very small so that they were not identified by XRD analysis. The Fe_3C decomposition can be initiated by the decrease of carbon diffusion rate due to the increase of thickness of Fe_3C phase. Namely, with decrease of carbon diffusion rate, the carbon concentration at the surface gradually increases and finally supper-saturated to start carbon deposition. Thus, for the formation of Fe_3C without carbon deposition, the fine powder of iron oxide can be favored.

It is noted that α-Fe phase was not detected from X-ray analysis in the reaction of Fe_3C formation with CO at 873K even at the very early stage reaction of 2 min and 5 mim although Fe_3C was found to formed at those time. As already mentioned, the direct formation of Fe_3C from Fe_3O_4 can be possible from thermodynamical evaluation. But it does not necessarily mean that α-Fe is not formed. If the reaction rate of Fe_3C formation from Fe is significantly large, the Fe phase may not be observed.

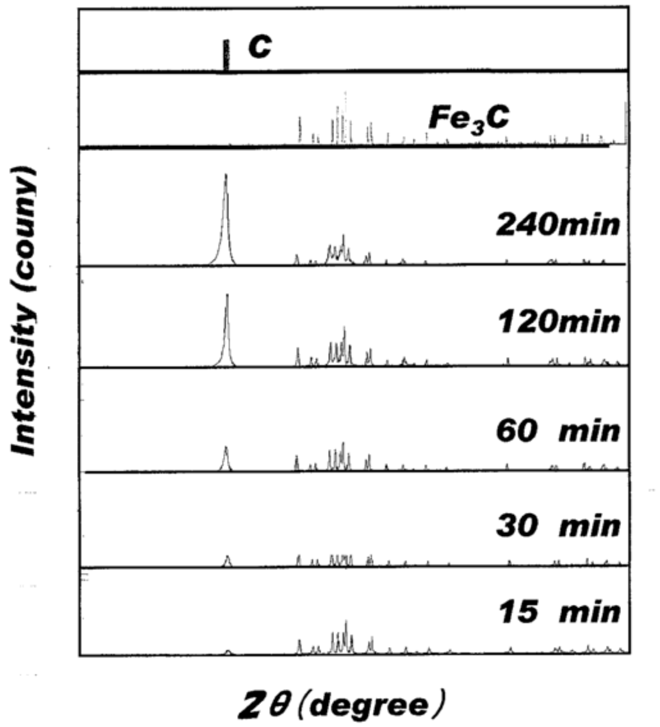

Figure 4 The change of XRD patterns of Fe_2O_3 powder reacted at 873K with CO gas as afunction of reating time.

Hyde et al.(4) have emphasized that twinning in certain system generates types of co-operation polyhedra not available within the parent phase and that such generation mechanism may provide a sufficient chemical driving force to introduce repeated twinning on a microscale such that new crystal phases are introduced. For example, the generation of Fe_3C from *hcp structure of iron* is shown in Figure 5. Fe_3C is orthorhombic, and almost perfect twinned hcp Fe with the carbon atoms in the trigonal prisms. The relevance of the twinned hcp model for its structure is strongly substantiated by the observed orientation relationships between Fe_3C and ε-iron carbide, Fe_2C (which is hcp Fe with C in about 1/3 and ½ of the octahedral interstices). (4)

In the present study, no individual particles were found which mainly consisted of pure α-Fe. Audier et al.(5) said that the existence of twin planes iron atoms in hcp structure and that at the twin composition plane carbon atoms sit at new sites as Fe_3C from their TEM and Mösbauer analysis. However, the reason why the micro-twinning must be introduced for the Fe_3C forming process from iron oxide is not established at all. Surprisingly they also reported the existence of γ-Fe. All these result means that the Fe_3C formation from iron oxide must be a quite complex process than currently considered. Further work is certainly needed to examine the existence and role of micro-twinning for the formation mechanism of Fe_3C form iron oxide.

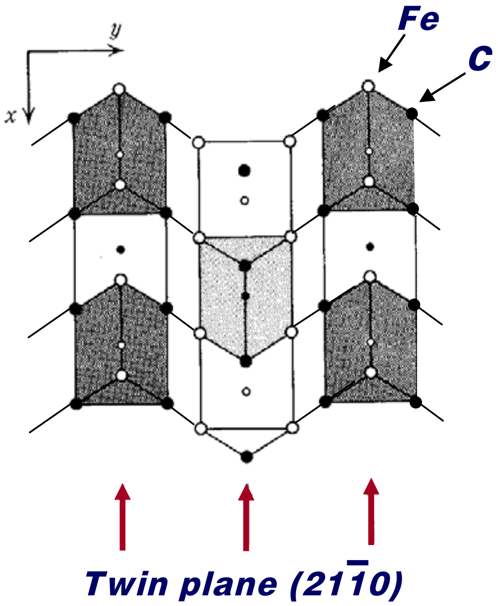

Figure 5 Fe_3C structure projected on (001). Large circles are metal atoms, smaller ones are carbons.

4. 2 Cementitation with CO-H_2 Gas Mixtures

The observed phases formed by the reaction of Fe_2O_3 powder with CO-H_2 gas mixtures as a function of gas composition at 873K is shown in Fig. 6. As already mentioned, with pure CO gas (shown in Figure 6 as point c), Fe_3C Fe_3O_4 and C were formed. At the H_2/CO ratio of 3 and 1 (shown in Figure 6 as a and b, respectively), Fe_3C and C were existed. Since the carbon saturation line is existed under the boundary line between Fe_3C and Fe, carbon deposition can be potentially occurred along with the formation of Fe_3C.

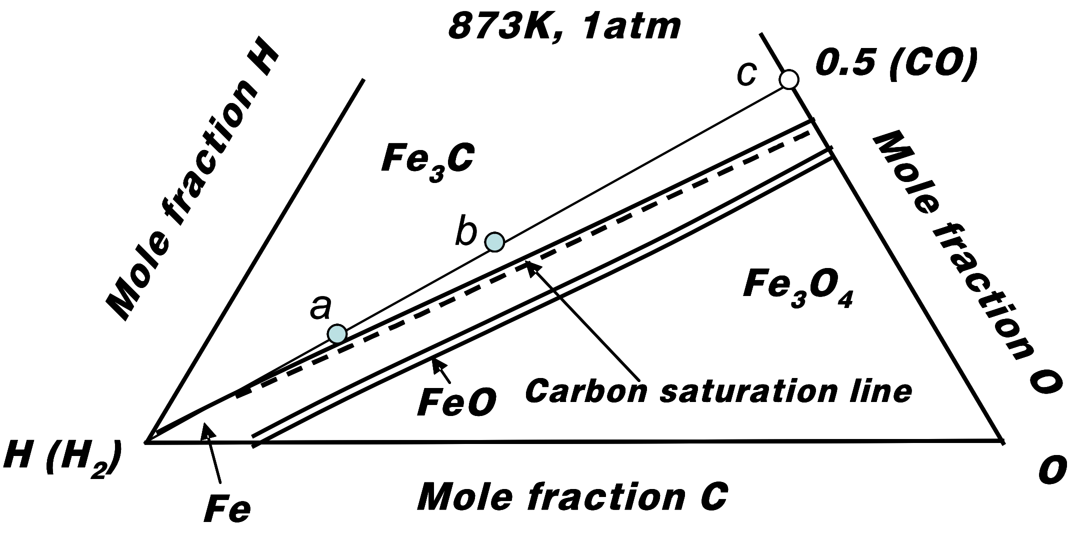

Figure 6 Observed phases formed during the reaction of Fe_2O_3 powder reacted with CO gas and H2-CO gas mixtures at 873K.

From the phase stability diagram shown in Figure 6, it is expected that α-Fe will be formed before the formation of Fe_3C if the reduction reaction starts from iron oxide. Interestingly, α-Fe phase was not detected at the points a and b. Unobserved α-Fe phase may be explained by the generation of Fe_3C from *hcp structure of iron* as already mentioned. However, the mechanism how and the reason why the micro-twinning structure in the α-Fe introduced during the Fe_3C formation from iron oxide is not yet clarified at all.

5 CONCLUSIONS

Fe_2O_3 powder samples were carburised at 873K in CO and CO-H_2 gas mixtures. By using X-ray diffraction analysis the existence of Fe_3C and graphite on the quenched samples was confirmed. Carbon deposition can be initiated by the decrease of carbon diffusion rate due to the increase of thickness of Fe_3C phase. Thus, for the formation of Fe_3C without carbon deposition, the fine powder of iron oxide as a resource can be favored to maintain the diffusion rate high. For the carburization of iron oxide with CO-H_2 gas mixtures, α-Fe is expected to form before the formation of Fe_3C if the reduction reaction starts from iron oxide. However, α-Fe phase has not been detected. The reason that α-Fe phase was not detected can be explained by the development of micro-twinning in the reduced α-Fe.

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