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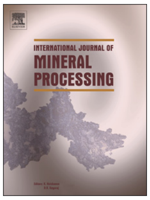

The kinetics of hematite reduction and cementite formation with CH_4-H_2-Ar gas mixture

Yousef Nasiri, Masoud Panjepour *, Mehdi Ahmadian

Department of Materials Engineering, Isfahan University of Technology, 84156-83111, Isfahan, Iran

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ABSTRACT

The kinetics of hematite reduction and formation cementite were studied by a gas mixture of 30 vol% CH_4, 60 vol% H_2 and 10 vol% Ar, inside a fixed-bed reactor at 700–800 °C and different times in this research work. The percentage of reduction was determined by thermogravimetry method with a precision of 0.001 g. The results obtained showed that the hematite pellets were first reduced to metallic iron and then cementite is formed. The kinetic modeling has shown that the reduction rate of hematite pellets is controlled by the mixed mechanism of chemical reaction-diffusion at the interface of and the rate of the formation of cementite is controlled by the chemical reaction of methane adsorption on the surface of reduced iron. On the other hand, the results showed that the temperature and time of the process are the two very important factors in the formation of cementite and its stability. In fact, by increasing the temperature (from 700 °C to 800 °C) led to increase in the rate of cementite formation. But, selection of an appropriate temperature can be very effective in the rate of the decomposition of cementite into metallic iron and graphite. The results of XRD and Feritscope demonstrated that at 750 °C over time even for 80 min, a negligible percentage of cementite is decomposed. Furthermore, the images obtained from SEM and RLM showed that an increase in time can also change the formed cementite morphology from layer state to block state.

1. Introduction

Iron carbides and specially cementite (Fe_3C) have gained special importance from several aspects in recent years; one as the supplementary material in steel making and the other in production of resistant pieces applicable at high temperatures. With regard to the high consumption of energy in electric arc furnaces (EAF) during the process of steel making, the use of cementite with 6.7 wt% C not only reduces the consumption of energy, but it also increases the lifetime of firebricks and graphite electrodes, generates foamed slag, reduces solvent gases in steel, better purifies the molten steel and improves the quality of steel (Geiger and Stephens, 1993; Garraway, 1996; Geiger, 1994). On the other hand, the suitable mechanical properties of pure cementite at high temperature (Nakashima et al., 2007; Umemoto et al., 2001) (e.g. strength, high elasticity, wear resistance) can justify the use of this material in the construction of pieces applicable at high temperature. During the last decades, Fe_3C is produced from the reduction and carburization of iron oxides by the use of different gas mixture (CH_4-H_2 (Egashira et al., 2000; Zhang and Ostrovski, 2001a, 2001b), CO-H_2 (Conejo and Martins, 1997), CO-H_2-H_2O (Iguchi et al., 2001). In other words, iron oxide is first reduced to metallic iron and then by its carburization, Fe_3C is formed in the process. Different studies have been performed on the effect of a gas composition, gas pressure, temperature, and additives on the formation of cementite (Egashira et al., 2001; Nakagawa et al., 1999; Longbottom et al., 2007; Longbottom, 2005; Weissber and Zimmels, 1983). For example, Nakagawa et al. (1996) studied the hematite reduction by the use of gas mixtures consisting of CO-H_2 or CH_4-H_2 at different temperatures and on fixed and fluidized beds. Their results demonstrated that the cementite formed at 750 °C with the gas ratio of 40/60, CH_4/H_2 can bring about the most stability. Also, Zhang et al. (2000) studied the effect of temperature on the formation and stability of cementite on a fixed bed at different times. Their results showed that temperature was one of the important parameters for the formation of cementite. On the one hand, by increasing the process temperature up to 900 °C led to an increase in the rate of cementite formation and on the other hand, it also increases the rate of carbon deposition (i.e. cementite decomposition; $Fe_3C = 3Fe + C$). In 1995, Grabke and Müller-Lorenz (1995) found out that the presence of sulfur can have a positive effect on the stability of iron carbide. In 1997, the researches performed by Hayashi and Iguchi (1997a, 1997b) on the formation of iron carbide in H_2-CO gas mixture with negligible amount of sulfur also showed that the formation of iron carbide and its decomposition were a function of sulfur content, carbon activity, temperature and time of the process. Li et al. (2006) studied the effect of TiO_2, Cr_2O_3,

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* Corresponding author.
E-mail addresses: u.nasiri@ma.iut.ac.ir (Y. Nasiri), panjepour@cc.iut.ac.ir (M. Panjepour), ahmadian@cc.iut.ac.ir (M. Ahmadian).

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MnO, and V_2O_5 additives on the formation of cementite at 750 °C. In fact, they presented that the addition of MnO and Cr_2O_3 had no significant effect on the formation of cementite, while the addition of V_2O_5 and TiO_2 increased and decreased the rate of iron carbide formation, respectively.

In general, the reduction of hematite and cementite formation with CH_4-H_2 gas mixture can be divided into three stages (Zhang and Ostrovski, 2001a; Egashira et al., 2000; Longbottom, 2005).

a) Reduction of iron oxide to metallic iron

$$3Fe_2O_{3(s)} + H_{2(g)} = 2Fe_3O_{4(s)} + H_2O_{(g)} \tag{1}$$

$$Fe_3O_{4(s)} + H_{2(g)} = 3Fe_xO_{(s)} + H_2O_{(g)} \tag{2}$$

$$Fe_xO_{(s)} + H_{2(g)} = Fe_{(s)} + H_2O_{(g)}. \tag{3}$$

b) Adsorption and decomposition of methane on the surface of the reduced iron

$$CH_{4(gas)} = CH_{4(ads)} \tag{4}$$

$$CH_{4(ads)} = CH_{3(ads)} + H_{(ads)} \tag{5}$$

$$CH_{3(ads)} = CH_{2(ads)} + H_{(ads)} \tag{6}$$

$$CH_{2(ads)} = CH_{(ads)} + H_{(ads)} \tag{7}$$

$$CH_{(ads)} = C_{(ads)} + H_{(ads)} \tag{8}$$

$$C_{(ads)} = [C]_{inFe} \tag{9}$$

$$2H_{(ads)} = H_{2(gas)}. \tag{10}$$

c) Formation of iron carbide

$$3Fe + [C]_{inFe} = Fe_3C. \tag{11}$$

However, the total reactions produced in these three stages can be summarized in the following two reactions:

$$Fe_2O_{3(s)} + 3H_{2(g)} = 2Fe_{(s)} + 3H_2O_{(g)} \tag{12}$$

$$3Fe + CH_{4(gas)} = Fe_3C_{(s)} + 2H_{2(gas)}. \tag{13}$$

In 1970, Grabke (1970) studied the kinetic of iron carburization in a gas mixture of CH_4-H_2. The results obtained from his research showed that the rate of iron carburization could be controlled by Reaction (6). The results of Zhang and Ostrovski (2002) have shown that cementite formation the overall reaction rate could be controlled by Reaction (4); its equation is presented as follows:

$$\text{rate} = K^{+} P_{CH_4} \theta_v \tag{14}$$

where K^{+} is the rate of constant; and θ_v is the fraction of the vacant sites at the surface of reduced iron. Their results also showed that the order of reaction could be between 0 and 1.

In spite of this fact that many researches have been done on the field of iron carbide formation but the researches that studied the kinetic modeling for this matter are less and remained unclear yet. However, in this research, the kinetics of hematite reduction and cementite formation with CH_4-H_2-Ar gas mixture in an isothermal process at different temperatures and time were studied. In other words, the authors are tried to present a mechanism and kinetic model to determine the rate of cementite formation.

2. Materials and experimental methods

2.1. Materials and sample preparation

In this research, iron oxide powder with a purity of more than 99.7% hematite by weight and with a particle size range of 53–150 μm and average particle size of 87 μm was used; its chemical analysis is presented in Table 1.

The above hematite powder is mixed with 10% naphtha by weight (as cold-setting resin) and for sample preparation (to form the cylindrical pellets with size of 9 mm in diameter and 5 mm in height), 500 mg of this mixture is pressed by 500 N for 60 s. The green pellets were then sintered under air atmosphere at 900 °C for 4 h and then left to cool down in the furnace to room temperature. Hence, naphtha added during the sintering process is completely evaporated.

2.2. Experimental setup

Experimental setup to carry out the reduction and carburization process is schematically presented in Fig. 1. This setup including: gas flow control system, gas dehumidification and gas mixture system, reactor system, furnace and temperature control system. The flow rate of CH_4-H_2-Ar gas mixture (with composition of 30 vol% CH_4, 60 vol% H_2 and 10 vol% Ar) was kept constant at 1000 cm^3/min. The reduction and carburization process reactor also consists of two quartz tube. The inner tube is the place for the sample consisting of the gas inlet and the outer tube is designed for the discharge of the reacted gas. The temperature control system also consists of a thermocouple of type K connected to a data logger. The sample along with the holding basket is placed inside the inner case. The holding basket made of Platinum. The samples were first heated under atmospheric argon up to different temperatures of the reduction and carburization process; 700, 750 and 800 °C, and then they went under the processes at different times and CH_4-H_2-Ar gas atmosphere. After carrying out the processes, the samples were cooled under argon atmosphere. As an example, the profile of the temperature applied to the sample during the processes and the cooling of the pellets at 750 °C are presented in Fig. 2.

The percentage change of reduction (R%) during the reduction process is calculated according to the following equation:

$$R\% = \frac{W_0 - W_t}{W_{Oxygen}} \times 100 \tag{15}$$

where W_0 is the initial weight of the sample; and W_t is the sample weight during the processes of reduction and carburization in different times, so that the expression of W_{Oxygen} shows the value of the total oxygen in the sample.

The fraction of the formed cementite is determined by the following equation:

$$\alpha_{Fe_3C} = \frac{W_C^t}{W_C^{max}} \tag{16}$$

where according to the Reaction (11), α_{Fe_3C} is the fraction of the cementite formed; W_C^t is the weight of the adsorbed carbon in time t; and W_C^{max} is the maximum weight of the carbon adsorbed for the formation of cementite in the sample.

Table 1
Chemical composition of hematite powder.

Composition	Fe	V_2O_5	Al_2O_3	Mn	P	S	TiO_2
Weight percentage	69.27	0.01	0.05	0.20	0.011	0.013	0.03

The remaining weight of the hematite powder is the oxygen combined with iron present in the raw material.