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A study on the carbonization and alloying process of MnO_2 by methane-hydrogen gas mixture in the presence of Fe_2O_3

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ABSTRACT

Carbonization of pure MnO_2 by CH_4-H_2 gas mixture with various $CH_4/(CH_4 + H_2)$ molar ratios in the temperature range of 900–1250 °C had been performed in our previous work. This study further investigated the carbonization and alloying process of MnO_2 by CH_4-H_2 gas mixture in the presence of Fe_2O_3 at 900–1300 °C using XRD, optical microstructure, SEM-EDS and phase diagram analyses. Carbonization test of pure Fe_2O_3 was also conducted to understand the effect of Fe_2O_3 on the carbonization of MnO_2 more explicitly. It was found that Fe_2O_3 could be carbonized to Fe_3C at 900–1150 °C. The Fe_2O_3 briquettes began to melt at 1100 °C and a large amount of Fe-C melts appeared as the temperature went up to 1150 °C. When the MnO_2 + 25 wt%Fe_2O_3 briquettes were reduced at 900–1000 °C in CH_4-H_2 gas mixture, the Fe_2O_3 was preferentially carbonized to Fe-C phase while the MnO_2 was only reduced to MnO. The formation of Fe-C phase was beneficial to the carbonization of MnO since the carbonization temperature of MnO can decrease from 1100 °C to 1000 °C. The carbonization degree of MnO was dramatically accelerated over 1100 °C due to the transformation of Fe-C phase from solid state to melts. Morphology analysis indicated that the MnO core was wrapped by the shell of Fe-C melts. The alloying process of Mn-Fe-C was conducted through the elements migration of Fe and Mn between the core and shell. At 1300 °C, the Mn-Fe-C alloy turned to melt and aggregated since the highest melting temperature of the Mn-C-25 wt% Fe system was only 1274 °C. Finally, a ferromanganese crude alloy with 68–72 wt% Mn, 20–25 wt% Fe and 6.0–8.0 wt% C was obtained when the MnO_2 + 25 wt% Fe_2O_3 briquettes were carbonized by CH_4-H_2 gas mixture at 1300 °C for 60 min.

1. Introduction

Minimizing carbon dioxide emissions is considered to be an important subject in the Iron & Steel industry from the viewpoint of green-house gas problem due to the present large consumption of solid carbonaceous materials [1–4]. Hydrogen and methane are two kinds of clean energy resources, which are used widely as reductants for the reduction of oxides [5–13], such as iron ores, SnO_2, NiO, SiO_2, and so on. These studies demonstrate the reduction of oxides by H_2, CH_4 or gas mixture is clean and efficient process.

Currently, ferromanganese alloys are predominantly produced from the manganese oxide ores reduced by solid carbonaceous materials [14–16]. Some attempts were also made to investigate the reduction feasibility of manganese oxide ores by CH_4-H_2 gas mixture [17–19]. The pre-reduction behavior of Groote Eylandt (Australia) and Wessels (South Africa) manganese ores were conducted in a fixed bed laboratory reactor in the temperature range 1000–1200 °C [18,19]. The results demonstrated that the manganese oxide ores can be reduced to Mn-Fe carbides by CH_4-H_2 gas mixture. However, the previous researches were mainly concentrated on the pre-reduction degree of the manganese ores and the reduced products were not characterized in detail. If ferromanganese alloy can be achieved during the reduction of manganese oxide ores by CH_4-H_2 gas mixture directly, it will be a new and promising gas-based reduction technique which is an alternative process for the reduction of manganese ores by solid carbonaceous materials.

In China, the main valuable oxides in the manganese oxide ores are MnO_2 and Fe_2O_3 [20,21]. Determination of carbonization of Fe_2O_3 and MnO_2 by CH_4-H_2 gas mixture, and the interactive effect between them are key scientific problems during the carbonization of manganese oxide ores. Although some investigations have been carried out on the reduction of Fe_2O_3 to Fe_3C by CH_4 or CH_4-H_2 gas mixture, the reduction temperature ranges are generally below 1000 °C. Zhang and Ostrovski [7] researched the Fe_3C formation through reducing the iron ores by CH_4-H_2 gas mixture in the temperature range of 600–925 °C, and also determined the stable existing temperature range of cementite. The kinetics of hematite reduction and formation of cementite in a CH_4-H_2 gas mixture at 700–800 °C were studied by Nasiri et al. [8]. Ghosh et al. [9] reported the reduction of porous and dense pellets of ferric oxide with CH_4 in the temperature range of 800–1025 °C. Because the carbonization of

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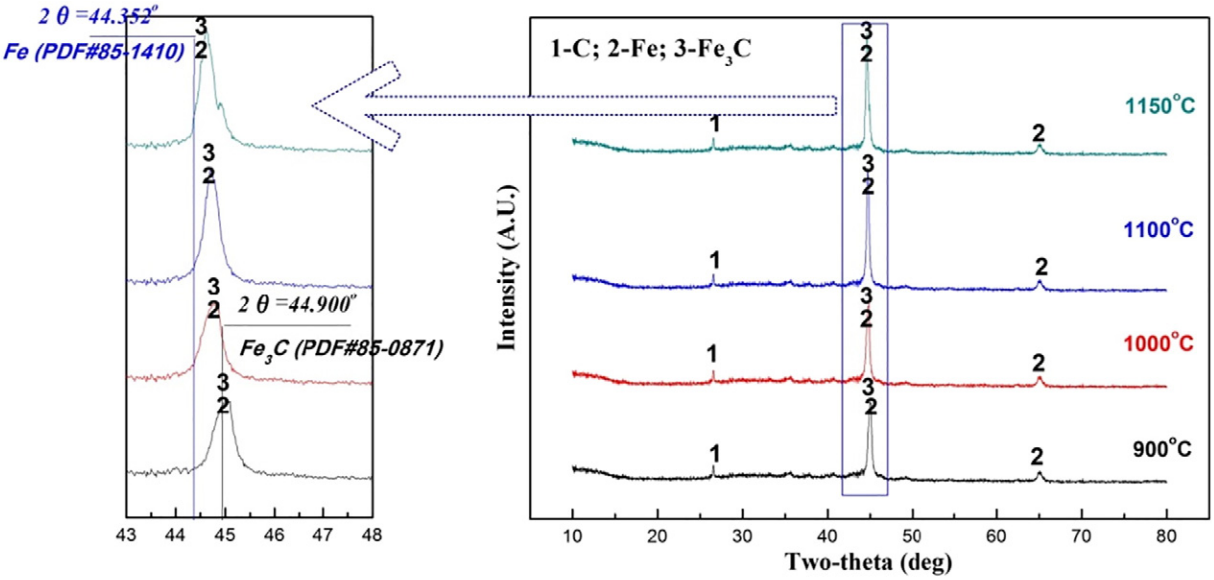

Fig. 1. XRD patterns of Fe_2O_3 briquettes carbonized at different temperatures.

manganese oxide ores to carbides by CH_4-H_2 gas mixture requires higher temperatures higher than 1000 °C, it's essential to know the carbonization behavior of pure Fe_2O_3 and MnO_2 at elevated temperatures and the interactive effect of Fe_2O_3 and MnO_2 in order to understand distinctly the carbonization and alloying process of manganese oxide ores.

Investigation on the carbonization of pure MnO_2 under various molar ratios of CH_4-H_2 atmosphere at temperature range of 900–1250 °C has been clarified in our previous work [22]. The results indicated that MnO_2 could be carbonized to Mn_7C_3 by CH_4-H_2 gas mixture above 1100 °C under 10 vol% CH_4 + 40 vol% H_2 + 50 vol% N_2. With regard to the interactive effect between Fe_2O_3 and MnO_2, some works have been carried out to determine the effect of MnO_2 on the reduction of iron ore pellets by CO gas during the ironmaking process. El-Geassy et al. [23,24] reported the influence of 2.0–6.0 wt% MnO_2 on the reduction behavior and structural changes of Fe_2O_3 briquettes with CO at 800–1100 °C, and also investigated the effect of MnO_2 on the reduction kinetics and catastrophic swelling of Fe_2O_3 briquettes. Kim and Jung [25] investigated the effect of chemically pure iron powder on the carbothermal reduction of MnO by graphite in the temperature range of 1100–1300 °C. It was demonstrated that the addition of iron affected

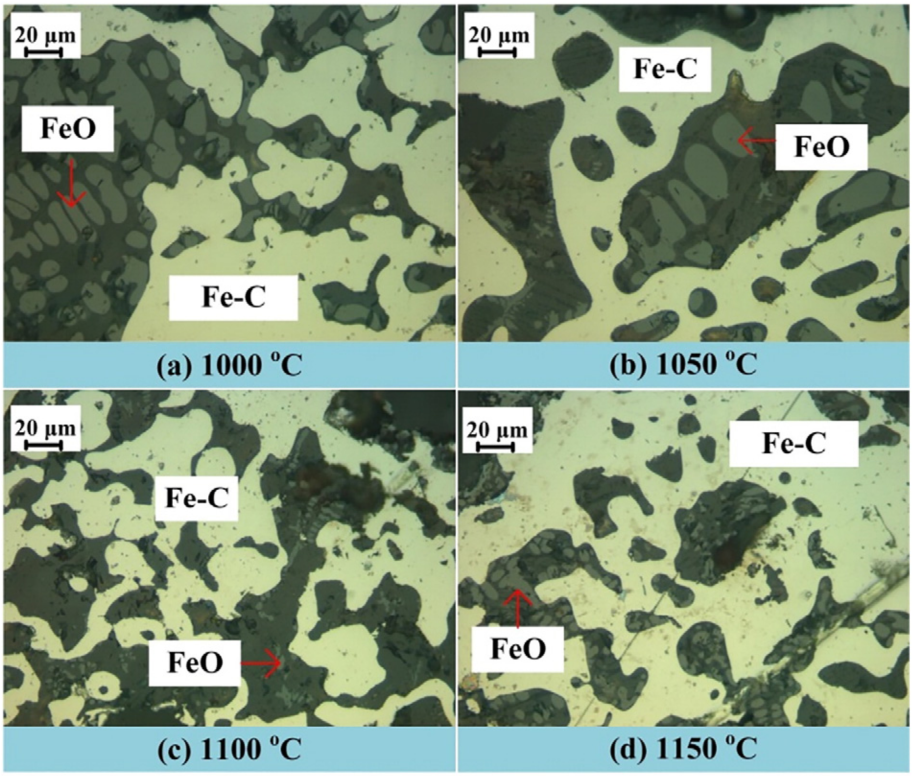

Fig. 2. Optical microstructures of Fe_2O_3 briquettes carbonized at different temperatures.