Phase equilibria in the system $MgFe_2O_4$—Mg_2SiO_4

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The system $MgFe_2O_4$—Mg_2SiO_4 has been investigated in the temperature range 1550—1770°C in air. On the basis of the obtained results, the phase diagram of the pseudobinary system has been constructed showing that the initial melting occurs at 1665 ± 10°C. In addition to forsterite and magnesioferrite, the presence of magnesiowüstite in the system has been proved. The proportion of the latter phase has been found to grow with increasing temperature.

Система $MgFe_2O_4$—Mg_2SiO_4 была изучена в атмосфере воздуха в диапазоне температур 1550—1770°C. На основании полученных значений была построена фазовая диаграмма псевдобинарной системы, в которой появляется жидкая фаза при температуре 1665 ± 10°C. Помимо форстерита и магнезиоферрита было доказано присутствие магнезиовюстита, количество которого возрастает с повышением температуры.

The development of steel industry demands ever more detailed information about physicochemical properties of the refractory materials. In this connection, the effect of their chemical, phase, and mineralogical composition on the course of the high-temperature reactions during production and service needs to be studied. With respect to the Czechoslovak raw materials base it is useful to extend the knowledge of the system CaO—MgO—Fe_2O_3—SiO_2. From the view-point of refractory materials steel plant applications, the phase equilibria of the following binary systems, consisting of magnesioferrite and silicates with various CaO/MgO ratio are of interest: magnesioferrite—dicalcium silicate ($MgFe_2O_4$—Ca_2SiO_4), magnesioferrite—merwinite ($MgFe_2O_4$—$Ca_3MgSi_2O_8$), magnesioferrite——monticellite ($MgFe_2O_4$—$CaMgSiO_4$), and magnesioferrite—forsterite ($MgFe_2O_4$—Mg_2SiO_4). *El-Shahat* and *White* [1] studied the phase equilibria along the joins $MgFe_2O_4$—Ca_2SiO_4 and $MgFe_2O_4$—$CaMgSiO_4$ in air atmosphere and confirmed that above 1200°C, partial reduction of magnesioferrite resulting in the formation of magnesiowüstite occurs in such mode, as had been reported earlier [2]. After *Berezhnoi* [3] an initial liquid phase is formed in the system magnesioferrite—forsterite at about 1670°C and, in the composition of eutectic there is 75 wt % of $MgFe_2O_4$. On the basis of the results reported in [1] and [2], the occurrence of

magnesiowüstite over temperature 1200°C in the presently studied system can be anticipated.

The aim of this paper is the investigation of the phase equilibria in the system $MgFe_2O_4$—Mg_2SiO_4 in air.

Experimental

The study of the phase equilibria was accomplished by static method with quenching of the samples. Starting materials for the preparation of forsterite and magnesioferrite were powdered MgO, SiO_2, and Fe_2O_3 (A.R. grade, BDH-Chemicals Ltd., Great Britain), all with grain size $\leqq 40$ μm. After several firings with intermediate grindings, an X-ray analysis was carried out which confirmed the purity of prepared minerals.

Samples were obtained by mixing $MgFe_2O_4$ and Mg_2SiO_4 in appropriate ratios and subsequent pressing under a pressure of about 80 MPa into pellets 2 mm in diameter. The pellets were heated in air at selected temperatures from 1550 to 1770°C for 3 h. This time of heating was indicated by preliminary experiments as necessary for the attainment of the equilibrium. The temperature was measured by PtRh30—PtRh6 thermocouple which was calibrated at melting temperature of diopside and palladium.

The results of the X-ray diffraction analysis of the quenched samples are summarized in Table 1.

Discussion

As the results indicate, a partial reduction of magnesioferrite to magnesiowüstite takes place in the investigated system in air atmosphere. Thus, both the number of components and number of possible coexisting phases in the system are extended. The relations in the system $MgFe_2O_4$—Mg_2SiO_4—$(Mg,Fe)O$ are represented in a pseudobinary diagram (Fig. 1). For the construction of this diagram we used the melting temperature of forsterite — 1890°C [4] as well as the temperature of incongruent melting and of liquidus for magnesioferrite — 1713 and about 1900°C [2], respectively.

From the diagram it follows that the initial melting occurs at 1665 ± 10°C. In the subsolidus region, magnesiowüstite was observed microscopically to be present in little amounts in addition to dominant phases: spinel and forsterite. At contents of magnesioferrite under 74 wt % within 1665—1720°C occurs a three-phase coexistence region of forsterite, magnesiowüstite, and liquid. At higher magnesioferrite concentrations a three-phase field extends in the diagram in agreement with [2] up to 1713°C. Over this field up to approx. 1900°C [2] a region of magnesiowüstite—liquid coexistence is observed. In the temperature range 1720—1890°C and at concentrations lower than 67 wt % a two-phase field of forsterite and melt exists.

By comparing these results with the data in [1] it was confirmed that in connection with growing MgO content in a sequence dicalcium silicate — monticellite — forsterite the temperature of the initial melt formation increases from 1350 to 1665°C.

Table 1

Results of experiments

No.	Content of $MgFe_2O_4$ c_{MF}/wt %	Temperature of heating $t/°C$	Phases present*
1	30	1650	MF, M_2S
2		1700	M_2S, MW, melt
3		1725	M_2S, melt
4	50	1550	MF, M_2S, MW
5		1600	MF, M_2S, MW
6		1650	MF, M_2S, MW
7		1700	M_2S, MW, melt
8		1710	M_2S, MW, melt
9		1725	M_2S, melt
10	60	1650	MF, M_2S, MW
11		1710	M_2S, MW, melt
12		1725	M_2S, melt
13		1750	M_2S, melt
14		1770	melt
15	70	1600	M_2S, MF
16		1650	M_2S, MF
17		1680	M_2S, MW, melt
18		1690	M_2S, MW, melt
19		1700	MW, melt
20		1750	melt
21	73	1680	MW, melt
22		1700	MW, melt
23	73	1750	MW, melt
24	75	1650	M_2S, MF
25		1680	MW, melt
26		1720	MW, melt
27		1750	MW, melt
28	77	1750	MW, melt
29	80	1680	MF, melt, MW
30		1720	MW, melt
31	90	1600	MF, M_2S
32		1650	MF, M_2S
33		1700	MF, MW, melt
34		1720	MW, melt

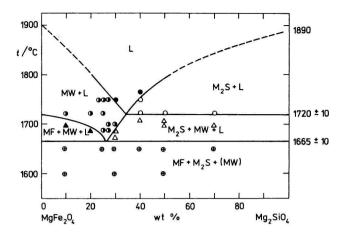*MF — magnesioferrite, M_2S — forsterite, MW — magnesiowüstite.

Fig. 1. Pseudobinary phase diagram of the system $MgFe_2O_4$—Mg_2SiO_4.
$\oplus$ $MgFe_2O_4$, Mg_2SiO_4, $(Mg,Fe)O$; $\blacktriangle$ $MgFe_2O_4$, $(Mg,Fe)O$, melt; $\triangle$ Mg_2SiO_4, $(Mg,Fe)O$, melt; $\mathbb{O}$ $(Mg,Fe)O$, melt; $\bigcirc$ Mg_2SiO_4, melt; $\bullet$ melt.

The temperature of initial melting in the system $MgFe_2O_4$—Mg_2SiO_4 obtained in this study is in agreement with the results reported in [3].

In the system Mg—Fe—Si—O a formation of solid solutions $(Mg,Fe)Fe_2O_4$ and $(Mg,Fe)_2SiO_4$ can be assumed, in which divalent Fe ions, formed by the reduction of Fe^{3+}, substitute ions of magnesia in a spinel and olivine structure, respéctively. Excessive Mg^{2+} ions are incorporated in a magnesiowüstite phase and, in consequence the ratio Mg : Fe in a solid solution $(Mg,Fe)O$ is increased. An examination of the samples by means of an X-ray microanalyzer JXA-5A did not prove the presence of Fe^{2+} in the olivine phase.

In the steel plants, the refractory linings are exposed to atmosphere with the oxygen partial pressure of about 10^{-5} Pa. In these surroundings, higher amount of magnesiowüstite will be obviously formed in the investigated system, already at lower temperatures.

Conclusion

The present phase equilibrium study provided information about behaviour of the system magnesioferrite—forsterite in the air atmosphere. From the view-point of refractory materials application, the investigation of this system at lower oxygen partial pressures will be necessary.

The lowest temperature at which the presence of liquid phase was determined in the system — 1665 $\pm 10°C$ — is in agreement with the results reported in [3].

References

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