INTERACTION OF IRON, MANGANESE, AND SILICON WITH MAGNESITE REFRACTORIES

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Manganese, silicon, and aluminum, which are added to steel as reducing or alloying agents, interact with the mineral constituents of a magnesite hearth and form solid solutions, as well as spinel, silicate, and other phases, some of which pass into the slag, while some remain in the metal in the form of intermetallic compounds and nonmetallic inclusions. The conditions for, and mechanisms of, these reactions are of great practical interest, since they are closely related to the quality of the steel smelted.

The literature gives rather detailed consideration to the interaction of iron oxides with chromite [1] and dinas [2] in open-hearth furnaces. Very few data have been published on the reaction of the metallic constituents of steel with magnesite hearths [3, 4].

In order to study the processes by which manganese, iron, and silicon interact with magnesite refractories, we melted these metals in 150 cm³ crucibles fabricated from Satkinsk magnesite and containing about 92% MgO. Hydrogen-reduced iron, 99.99999% pure semiconductor silicon, and 99.99% pure manganese were used. Heating was carried out in a Kryptol furnace at 1600°C for 1 h. The crucibles were then cooled, freed of metal, weighed, sectioned vertically, and subjected to detailed petrographic analysis in the form of polished and clear sections and immersion preparations.

The mineral phases were identified by petrographic and x-ray diffraction* analysis [5]. The mineral and intermetallic (Mg–Si) phases were locally isolated from the metal [6] and analyzed by the microcrystallographic method [7, 8].

Interaction of Iron with Magnesite Crucible. A solid, black-colored reaction zone 4–5 mm thick was formed on the bottom and walls of the crucible during melting or iron. Its microstructure was coarse-grained. The principal mineral constituent was magnesiowustite. Its composition varied within broad limits,

* The x-ray analysis was made by Z. A. Shevchenko.

Fig. 1. Microstructure of reaction zone of magnesite crucible after melting of iron (x 110, reflected light): a) penetration of metallic iron into crucible; 1) metallic iron; 2) magnesiowustite; b) dendritic crystallization of magnesiowustite (white) in periclase; c) precipitation of acicular and dendritic hematite crystals (white) in magnesiowustite.

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Fig. 2. Microstructure of reaction zone of magnesite crucible after melting of manganese ($\times$ 110, reflected light): a) superficial (tephroite) portion of reaction zone with bead-like inclusions of metallic manganese; b) lamellar deposits of manganese — magnesia spinel (white) in periclase.

as was indicated by a variation in color from light-yellow to dark-brown or almost black, a variation in refractive index from 1.750 to 2.20, and an increase in the lattice constant of the periclase crystals. The grains of this solid solution usually surrounded aggregates of metallic iron (Fig. 1a).

Magnesioferrite ($N = 2.36$, cubic system, red color) was formed in portions of the reaction zone, crystallizing in the form of large or small dendrites within the periclase crystals (Fig. 1b). In rare instances, small needles and dendrites of hematite were observed in such pseudomorphoses (Fig. 1c). The silicate phases were small and filled the interstices between the periclase and magnesiowustite crystals. Fayalite aggregates were detected in the thin slag films on the ingot surface, creating additional cavities in the crucible structure that promoted deeper penetration of the iron (see Fig. 1a).

Our experimental results showed that the mechanism by which magnesite reacts with iron takes the following form. The metallic iron, in the molten state, first penetrates the crucible through its pores and cracks. It is then oxidized to FeO or Fe$_2$O$_3$. The extent of the oxidation is governed by the amount of oxygen present in the reaction zone, i.e., the crucible pores and the molten metal.

Interaction of Manganese with Magnesite Crucible. A black reaction zone with a more compact structure appeared in the areas of the crucible in direct contact with the molten manganese. This zone was especially distinct in the bottom of the crucible, where it was 2-3 mm thick. The thickness of the reaction zone on the crucible walls was 1-2 mm. A through crack in the wall, through which metal flowed, was formed during melting. The area of the crucible near the crack turned black, became more compact, and had an appearance resembling that of the reaction zone.

The mineral composition of the crucible was substantially altered. We established that the main source of the oxygen that oxidized the metallic manganese was the air in the crucible pores and that which entered the crucible through the cracks.

The mineral composition of the reaction zone was heterogeneous over the crucible thickness. Its superficial portion (Fig. 2a) consisted principally of tephroite (biaxial, $Ng = 1.780$, $Np = 1.760$, colorless). The portion of the crucible in direct contact with the unmodified zone consisted of concretions, which were apparently of an MgO—MnO solid solution. These crystals were round in shape and had a variable refractive index, ranging from 1.780 to 1.90. Their color varied from golden to greenish. A metallic phase, which can be conditionally regarded as manganese, was infrequently encountered, taking the form of small beads embedded in the tephroite.

Large periclase crystals ($N = 1.737$) highly saturated with spinel growths along their cleavage planes predominated in the crack in the crucible; the spinel deposits were arrayed in the form of parallel or mutually perpendicular bands or dendrites (Fig. 2b). It can be assumed that the composition of these spinelide phases corresponded to the formula MgO·Mn$_2$O$_3$ [9].