# INTERACTION WITH STEEL OF REFRACTORIES CONTAINING OXYGEN-FREE ADDITIONS

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Refractories containing in their composition carbon and oxygen-free compounds such as carbides, nitrides, borides, etc. are acquiring increasing practical value [1].

Present and future areas of their use include the linings of converters and electric arc furnaces, refractories for ladle gate valves and teeming of steel in continuous billet casting machines, etc.

In their interaction with molten metals these refractories exhibit specific features, some of which are discussed in this article.

As a first approximation as the result of the high surface activity of oxygen and sulfur in it (their surface activity may exceed the content by tens of times) the surface of molten steel may be represented in the form of the highly electronegative anions $O^{2-}$ and $S^{2-}$ in coordination with the cations $Fe^{2+}$, $Mn^{2+}$, etc. In interaction with the oxidizable elements of the refractories the anions form intermediate products all the way to oxides, including gaseous ones.

The corrosion of carbon-containing refractories under the action of steel under equilibrium conditions may be represented in three stages [2]:

at the steel—refractory contact under the action of surface-active oxygen, oxidation of the carbon occurs and a decarburized zone is formed;

the decarburized zone with increased porosity rapidly forms a slag and the products of the interaction have decreased refractoriness, mechanical strength, and thermal coefficient of volumetric expansion differing from the original material;

for these reasons the slagged layer of the refractory is rapidly washed away by the steel.

The increase in metal resistance of a refractory with the addition of oxygen-free additions, particularly carbon, is the result of the following facts:

frequently, the carbon addition is made by impregnation or precipitation from the gaseous or liquid phase into the finished refractory and the carbon partially replaces the porous spaces, mechanically preventing penetration of the molten metal;

the products of gasification of the carbon pneumatically prevent penetration of the molten metal into the voids;

in the microvolumes carbon deoxidizes the molten metal in contact with it and the highly active oxide forms of iron are converted into less active lower oxides all the way to the metallic state, a confirmation of which is the presence of beads of pure iron in the reaction zones of carbon-containing refractories after their wetting even by slag.

To the products of gasification of carbon are added the gases entrapped in the void space and the gaseous products of reduction by carbon of the oxides of the refractory occurring according to reactions of the type:

$$(SiO_2,\ Al_2O_3,\ ZrO_2,\ ZrO_2\cdot SiO_2,\ MgO\ \text{etc.})_{sol}+C_{sol}\rightarrow CO_{gas}+SiO_{gas}\ AlO_{gas}\ \text{etc.}$$

These reactions occur both in the contact zone and in the thickness of the refractory with diffusion of CO and gaseous suboxides into the contact zone. In addition, the decomposition of oxygen-free compounds is possible according to reactions of the form

$$Si_3N_4\rightarrow 2N_2+3Si.$$

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Under actual conditions such as in passage of the metal along metal feed lines ejection of air into the metal—refractory contact zone is also possible [3, 4].

Therefore, the gaseous layer at the steel—refractory contact creating the conditions for a reduction in the degree of wetting is partially a product of chemical interaction of the contacting phases. This was the subject of discussion of [2, 5], and in* [6, 7] the addition of graphite, carbides, borides, and nitrides to refractories for the purpose of increasing their metal resistance is recommended.

A convenient means of observation of the chemical interaction of such refractories is an instrument for determination of wetting. In [8] with the use of motion pictures the wetting by slag of the surface of refractories impregnated with resin was recorded and "incompletion" of the process of spread of the slag and the formation of a final wetting angle differing from 0 deg were observed while in spreading of the slag on refractories without carbon the process is completed by full wetting, that is, until a wetting angle approximately equal to 0 deg.

This article presents the result of investigation of the wetting of refractories with oxygen-free additions by molten 45 steel in a medium of argon.† The compositions and properties of the investigated refractories are presented in Table 1 and the experimental results in Table 2.

The samples of 45 steel were taken from a single heat and contained 0.008% oxygen and 0.037% sulfur and the oxygen content in the argon was 0.0003%.

Visually the picture of wetting was different. Sometimes visible interaction was completed 15-20 sec after fusion of the drop while in other cases it continued during the whole hold.

The experimental approach was supplemented by calculation of the equilibrium compositions for the different variations of the oxygen-free compound—$[O^{2-}, S^{2-}]$ system.‡ By the preliminary calculation it was shown that the basic component of the steel $[Fe^{2+}]$ does not influence the course of the process, which may be considered as basically an oxidation process. The data for calculation of the equilibrium compositions in the oxygen-free compound—$[O^{2-}, S^{2-}]$ system was taken from [9-17].

Calculation of the systems in which boron nitride BN, aluminium nitride AlN, silicon carbide SiC, boron carbide $B_4C$, zirconium diboride $ZrB_2$, silicon nitride $Si_3N_4$, silicon oxynitride $Si_2ON_2$, and graphite C were present as the oxygen-free compounds was done on an ES-1020 computer. For the calculations $T = 1800$ K and $p = 0.1$ MPa were used.

For the purpose of comparison of the refractories with each other, the following coefficients were calculated:

$K_d$ — the coefficient of stability, determined as the ratio of the number of moles of undissociated oxygen-free compound to the number of moles of it before interaction in %;

$K_n$ — the molar coefficient of gas formation determined as the ratio of the number of moles of gas liberated during the interaction to the number of moles of the oxygen-free compound before the interaction;

$K_m$ — the mass coefficient of gas formation, the number of moles of gas liberated as the result of the interaction occurring per unit of weight of the original oxygen-free compound in moles/kg;

$K_V$ — the volume coefficient of gas formation, the number of moles of gas liberated as the result of the interaction occurring per unit of volume of the original oxygen-free compound in moles/dm³.

It should be noted that the gaseous phase of the carbon-containing compounds consists practically completely of CO and of the nitrogen-containing refractories almost completely of $N_2$.

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*Claim No. 2724430 (Federal Republic of Germany), 1977.

†The work on determination of the wetting angle was done under the supervision of E. A. Prokof'eva.

‡The brackets designate that these components are found in the molten steel.

TABLE 1. Compositions and Properties of the Investigated Refractories

| Designation of refractory | Sample composition | Open porosity, % | Gas permeability, $10^3$ $\mu m^2$ |
|---|---|---|---|
| ShG | Chamotte–graphite with 21 wt. % C | 22,1 | 2,5 |
| 1M | Mullite with add. of 10% BN | 19,9 | 0,5 |
| 2K | Corundum with add. of 20% $Si_3N_4$ | 18,3 | 0,5 |
| N | 100% $Si_3N_4$ | 22,0 | — |
| BS | Base BN, remainder $SiO_2$ | 1,4 | <0,5 |
| 66 | Base $Si_3N_4$, remainder BN | 21,6 | 1,2 |
| 61 | Base BN, remainder $Si_3N_4$ | 30,7 | 1,8 |
| 2 | Base BN, remainder $SiO_2$ | 18,5 | <1,0 |
| 27 | Base $SiO_2$, remainder BN | 0,9 | <0,5 |

TABLE 2. Test Results

| Designation of refractory | Wetting angle θ, deg, at 1550°C in argon with a hold of, min | | | | | Character of interaction, number |
|---|---|---|---|---|---|---|
| | 0 | 2 | 5 | 10 | 15 | |
| ShG | 129 | 125 | 121 | 119 | 120 | 5 |
| 1M | 128 | 128 | 127 | 120 | 124 | 3 |
| 2K | 113 | 121 | 122 | 118 | 112 | 3 |
| N | Intense reaction (θ not recorded) | | | | | 10 |
| BS | 128 | 123 | 121 | 122 | 122 | 2 |
| 66 | 108 | 107 | 110 | 114 | 114 | 3 |
| 61 | 112 | 104 | 105 | 106 | 108 | 5 |
| 2 | 123 | 123 | 118 | 108 | 110 | 6 |
| 27 | 113 | 111 | (θ not recorded) | | 100 | 9 |

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*No. 10, a drop of molten metal jumps up on the base, corresponds to the greatest interaction and No. 1 corresponds to vibration of the surface of the drop; in all cases the cooled drop does not adhere to the base.

TABLE 3. Values of the Coefficients of Dissociation and Gas Formation of the Oxygen-Free Compounds and Graphite

| Coefficients | BN | AlN | SiC | $B_4C$ |
|---|---|---|---|---|
| $K_d$, % | 43,8 | 33,6 | 36,6 | 73,3 |
| $K_n$ | 0,315 | 0,360 | 0,824 | 0,443 |
| $K_m$, moles/kg | 12,7 | 8,8 | 20,5 | 8,0 |
| $K_V$, moles/dm³ | 27,9 | 27,4 | 65,9 | 20,1 |

| Coefficients | $ZrB_2$ | $Si_3N_4$ | $Si_2ON_2$ | C |
|---|---|---|---|---|
| $K_d$, % | 68,7 | 0 | 7,1 | 62,1 |
| $K_n$ | 0,184 | 1,206 | 0,987 | 0,442 |
| $K_m$, moles/kg | 1,6 | 8,6 | 9,9 | 36,8 |
| $K_V$, moles/dm³ | 10,1 | 27,0 | 27,0 | 82,7 |

The values of the calculated coefficients are presented in Table 3.

In resistance to failure by molten steel the investigated compounds may be arranged in the order (in order of decrease in resistance): $B_4C$ > $ZrB_2$ > C > BN > SiC > AlN > $Si_2ON_2$ > $Si_3N_4$.

Silicon oxynitride and nitride are not resistant to steel.

At the same time in gas creating capacity these compounds are arranged (in order of decrease) in the following manner: C > SiC > BN > AlN > $Si_2ON_2$ > $Si_3N_4$ > $B_4C$ > $ZrB_2$.

In the development of refractories for teeming of steel the composition of the charge must include oxygen-free compounds, and the selection of the specific compound and the necessary quantity of it depend upon the problem being solved. The results of the calculations made make it possible to select the form of addition.

For example, if necessary to obtain a quite strong gas layer on the surface of the metal feed line channel to combat clogging, additions of silicon nitride or oxynitride may be used in the refractory since gas will be liberated even in teeming of well-deoxidized metal. This principle is realized in the nozzle of the continuous billet casting machine intermediate ladle proposed in Japan, which is not subject to clogging,[*] and the same idea is used in a number of other developments.[†]

A high capacity for gas formation is possessed by graphite, which at the same time is sufficiently resistant to failure by the oxidizing components of the molten steel. These properties and also its comparatively low cost permit quite wide use of graphite and other carbon components for the production of refractories not wetted by steel, including the plates of gate valves, refractories for continuous billet casting machines, converter linings, electric furnaces, etc.

There is no doubt that, in addition to the above, a significant role in solution of the question of the desirability of use of the various oxygen-free compounds is played by the whole combination of technical and economic factors. In the use of oxygen-free compounds in fired parts it is necessary to provide protection of them during firing and to provide for the possible reactions between the components of the charge. Graphite (carbon) may react with silica, silicon, and mullite [2, 18, 19] while boron nitride, aluminum nitride, and other oxygen-free compounds are practically inert toward the components of the charge at normal temperatures.

It is also known that the oxygen-free compounds formed in parts in firing serve as an additional binder. For example, the role of secondary silicon carbide formed during firing of graphite-containing refractories with the addition of crystalline silicon [20], a nitride and an oxidizing binder,[‡] and a binder containing aluminum nitride [21] is known.

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[*] Claim No. 45-6251 (Japan), 1966.

[†] Claim No. 57-18981 (Japan), 1972; patent 3003046 (Federal Republic of Germany), 1980.

[‡] Patent 1564927 (Great Britain), 1980.

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