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Abstract

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On Structural Indications of the Decomposition of Lower Oxides in Slags

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In the production of certain ferroalloys by the off-furnace metallothermic method, in order to obtain low contents of the reducing element in the alloys, the process is usually conducted with a deficiency of reductant. This predetermines in advance the incompleteness of the reduction reactions, as a result of which a considerable amount of oxides of the reduced metal remains in the slags obtained.

Recently, increasing evidence has appeared that, in slag melts, the incompletely reduced metal is present in the form of ions of lower valences, for example, Cr^{2+}, Ti^{2+}, Ti^{3+}, Si^{2+}, V^{2+}, Nb^{2+}, Mo^{2+}, etc.

Owing to their low stability at low temperatures, lower oxides are observed only very rarely in cooled (crystallized) slags. With respect to industrial slags of ferroalloy production, the presence of lower oxides of titanium ([1], [2]) and silicon ([3], [4]) has been reliably proved. Establishing the fact that lower oxides exist in slag melts is of very great importance for metallurgists, enabling them correctly to interpret the processes of reduction and slag formation.

Methods of microscopic study can be of great assistance in investigating lower oxides in slags. The investigations carried out on slags from ferroalloy production have convinced the authors of this.

In the microscopic study of industrial slags from the smelting of metallic chromium by the off-furnace aluminothermic method, it was found that the majority of metallic inclusions in the slags have a strictly regular arrangement. In the slag-forming minerals—corundum (α—Al_2O_3) and alkaline β-alumina ($Na_2O \cdot 11Al_2O_3$)—the metallic inclusions are arranged in the form of globular and needle-like formations, strictly oriented along definite crystallographic directions of the host minerals. In addition, in some slag samples, especially those taken from the lower horizons of slag ingots, individual areas densely saturated with globular and globule-like inclusions of metallic chromium were observed in the intervals between crystals of corundum and β-alumina. The latter also have a quite regular orientation. The origin of metallic inclusions of this kind could not be explained by a simple "entanglement" of metallic particles in the slag. On the contrary, their form and oriented arrangement indicate that they were formed during crystallization of the slag melt.

The supposition arose that lower oxides of chromium existed in the liquid slag, which, upon decomposition, could yield a metallic phase. In order to verify this supposition, laboratory smelts were carried out on a charge consisting of chromium oxide (99% Cr_2O_3), saltpeter (99% $NaNO_3$), and aluminum (99% Al). The amount of reductant (aluminum) was taken in a quantity from 80 to 102.5% of that theoretically required for reducing chromium oxide to chromium and saltpeter to Na_2O and N_2. The slags obtained consisted of corundum (20-40 vol.%), alkaline β-alumina (75–55 vol.%), and a considerable quantity of metallic inclusions. As in

as expected, in heats characterized by the greatest deficiency of reducing agent in the charge, the slags contained the largest amount of metal inclusions. In their character, the metallic inclusions in these slags fully correspond to those in ordinary industrial slags, but the picture obtained is more graphic.

The scheme of slag crystallization is as follows. Corundum crystallizes first, followed by alkaline β-alumina. Judging from their color and refractive index, both corundum and β-alumina contain considerable amounts of chromium oxide. The optical properties of these minerals are found to be variable even within one and the same grain. As a rule, the central parts of the grains have a less intense color and lower refractive indices than the peripheral parts of the grains. Not infrequently the peripheral parts of the crystals prove to be more enriched in metallic inclusions than the central parts. The process of slag crystallization is completed by the formation, in the interstices between the previously separated minerals, of grains of corundum and alkaline β-alumina of the second generation. It is in these latter grains that the largest number of metallic inclusions is observed (Fig. 1). At high magnifications (Fig. 2) it is clearly seen that these inclusions have a shape elongated in one direction, sometimes resembling dendrites (Figs. 2a, 2b). In cross sections they have rounded or oval outlines (Fig. 2c). The amount of such inclusions (as observed in polished sections) in the crystals of corundum and β-alumina is 10–15% (by volume). The dense accumulation of inclusions did not allow the orientation of the inclusions relative to the crystallographic directions of the host minerals to be determined accurately, since the latter prove to be almost opaque.

Very often the inclusions have the form of pins, with their points facing in the direction of growth. Sometimes the stems of such pins have an intermittent-dotted structure (Fig. 2e), gradually disappearing. A common feature in the morphology of the inclusions is their strict parallelism. Such a character of the metallic inclusions undoubtedly testifies to their joint growth with the host minerals. As for the metallic inclusions in crystals of corundum and β-alumina of the first generation, they are represented mainly by pin-shaped inclusions oriented strictly perpendicular to the pinacoid face (0001).

Usually the sharp end of the pins is directed toward the outer edge of the crystal; however, the reverse picture may often be observed—the pin grows and widens from the center of the crystal toward the periphery. The character of pin-type inclusions in a β-alumina crystal is shown in Fig. 3. It should be noted that, in contrast to corundum, one more type of inclusions is observed in β-alumina—metal inclusions confined to cleavage cracks (0001). In sections perpendicular to the cleavage plane, these inclusions have the appearance of narrow intermittent lines. In sections parallel to the cleavage, the inclusions acquire a sinuous-rounded form. As a rule, in places where such inclusions are accumulated, the color of β-alumina becomes more intense. All the listed varieties of metallic inclusions undoubtedly formed during the crystallization of the slag. The appearance of the metallic phase during slag crystallization can be explained only by the presence of lower chromium oxides in the slag melt.

The process of slag crystallization and the formation of metallic inclusions appears to us as follows. In the slag melt there is an equilibrium $Cr^{3+} \rightleftarrows Cr^{2+} \rightleftarrows Cr^{0}$. With the onset of crystallization, part of the Cr^{3+} ions enters the corundum lattice, causing decomposition of Cr^{2+}. The resulting metal nuclei grow on the (0001) face of corundum, which has the lowest growth rate. The formation of pin-shaped inclusions also proceeds analogously in β-alumina crystals, which can likewise dissolve chromium oxide.

Fig. 1. Microstructure of slag from the smelting of metallic chromium. 300×

Fig. 2. Character of inclusions of metallic chromium in crystals of β-alumina. 1300×

Fig. 3. Pin-shaped inclusions of metallic chromium in crystals of first-generation β-alumina. 100×

Fig. 4. a—Inclusions of titanium oxide in a crystal of alkali β-alumina. 300×; b—Inclusions of metallic molybdenum in crystals of molybdenum dioxide. 600×

In the case where the amount of lower oxides in the slag is sufficiently large, the residual melt (after crystallization of corundum and β-alumina) proves to be enriched in lower oxides. Calculations show that in the residual melt, if it is assumed that the chromium in it is in the divalent form, the ratio of CrO to Al_2O_3 is 3 : 1. This melt, in the stability region of divalent chromium, remains in the liquid state. As the temperature decreases, the decomposition of CrO into Cr and Cr_2O_3 begins; the system is in a supercooled state, and simultaneous or almost simultaneous crystallization begins of metallic chromium and alkali β-alumina or corundum, depending on the alkali content in the residual melt.

It should be noted that the formation of pins of metallic chromium in slags from the smelting of refined ferrochrome had previously been explained in approximately the same way ([5]).

Much in common with the structures described above was observed by us in slags from ferrotitanium smelting. These slags consist of corundum, alkali β-alumina, lime β-alumina, inclusions of lower titanium oxides (TiO, Ti_2O_3), and also a small number of metallic globules. We drew attention to the following.

In crystals of alkali β-alumina, which crystallizes last, inclusions of titanium monoxide (TiO) are observed; in their form and character they are quite analogous to those just considered in slags from metallic chromium smelting (Fig. 4a). Apparently, during crystallization of the slag here, because of the limited solubility of titanium oxides in crystals of corundum and β-alumina, the lower titanium oxides remained in the melt, enriching it. Since the lower titanium oxides are fairly stable at low temperatures, they did not decompose; rather, the melt separated into two phases–TiO and $Na_2O \cdot 11Al_2O_3$–which again began to crystallize simultaneously or almost simultaneously.

In conclusion, we point out that analogous decomposition structures, caused by the decomposition of lower molybdenum oxides, were obtained by us in slags from molybdenum smelting on a charge consisting of pure molybdenum trioxide and metallic silicon, introduced in an amount of 90% of that theoretically required for complete reduction of molybdenum oxide to metal. The smelting was carried out in a small laboratory alundum crucible. In the resulting slag, represented by almost pure quartz glass, small (up to 5 mm in diameter) droplet-like segregations were observed, consisting of metallic molybdenum and molybdenum dioxide. At the same time the metallic molybdenum occurred in the form of regular intergrowths in crystals of molybdenum dioxide (Fig. 4b). The character of the intergrowths is completely analogous to those shown in Figs. 1; 2, 4a. Conversion of the calculated volume amounts into molecular amounts shows that the ratio of molybdenum to molybdenum dioxide is close to the stoichiometric ratio for the reaction: $2MoO \rightarrow Mo + MoO_2$.

In the cases cited, during the decomposition of lower oxides or of the melt, the phases formed were in a sharply supercooled state. Geld and Esin ([3],[4]) give examples in which the decomposition of a lower oxide (silicon monoxide) occurs at a temperature exceeding the crystallization temperature of the decomposition products–metallic silicon and silicon dioxide. In this case a completely different type of decomposition structure is obtained–of the type of an emulsion suspension of one phase in another.

In all the examples considered above, a general regularity is revealed in the crystallization of slag melts enriched in lower oxides.

With decreasing temperature, either decomposition of the lower oxide into more stable compounds occurs, or its separation from the melt as an independent phase. In both cases characteristic structures are obtained, consisting of intergrowths of particles of metal or lower oxides with the enclosing ···

mineral as the host. Such structures may be regarded as signs of the decomposition (or separation) of lower oxides.

The detection of such structures in slags may serve as evidence for the presence of lower oxides in slag melts.

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