

Effect of basicity and chromium oxide on the viscosity of boron-containing slags

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Abstract. The main diluent for chromium-containing slags is CaF₂. However, fluorspar disadvantages make it necessary to search for a replacement. As a substitute, boron oxide allows to improve slag physical properties and environmental situation. The paper presents the experimental study results of the chemical composition and temperature influence on viscosity of slags of CaO–SiO₂–Cr₂O₃ system containing 8% MgO, 3% Al₂O₃ and 6% B₂O₃. It was found that a slag free of chromium oxide with basicity of 1.0 has a sufficiently high fluidity of 0.2–0.6 Pa·s in a wide temperature range of 1200–1350°C, due to high concentration of low-melting phases, reaching 22%, and only 11 % high-melting. A slag with 18% Cr₂O₃ and the same basicity retains a low viscosity of 0.1–1.0 Pa·s but at higher temperature of 1450–1570 °C due to increase in high-melting compound content to 27%. The viscosity of a slag with basicity of 2.5 without chromium oxide is 0.07–1.0 Pa·s in a narrow temperature range of 1650–1700°C and 0.14–1.0 Pa·s for a ‘shorter’ slag with 18% Cr₂O₃ and same basicity in even narrower range of 1650–1670°C. These slags have the highest high-melting phase content of about 50%.

1. Introduction

Currently the main method for the production of low-carbon stainless steel in the world is argon oxygen decarburization (AOD), which consists of 2 periods: oxidation and reduction. The purpose of the reduction period of smelting at AOD units is both the reduction of chromium from slag to metal and desulfurization of steel, but due to the fact that during the oxidation period a significant part of chromium is oxidized and passes into slag in the form of Cr₂O₃, the slag viscosity increases significantly [1] and the refining ability decreases [2]. The authors [2–4] note that low viscosity slags are in a narrow range of compositions, therefore the possibility of reducing the viscosity of these slags with the addition of fluorspar was studied [5, 6]. However fluorspar has many disadvantages. Aggressive effect on the lining, inconstancy of influence on the properties of slag due to the formation of volatile fluorides, which are environmentally harmful [7–10]. Boron oxide may become an alternative. B₂O₃ has a low melting point and also forms low-melting eutectics with the main components of the slag, for example, MgO·B₂O₃ (melting point 988°C), CaO·B₂O₃ (melting point 1100 °C) and others. This oxide is actively used in blast furnace production, ladle metallurgy and in continuous casting of steel [11–16]. Nevertheless the number of studies studying the effect of B₂O₃ on the physicochemical properties of chromium-containing slag [17] is extremely limited.



Slags of this process are a complex multicomponent system, the physicochemical characteristics of which determine the course of smelting, separation of metal and slag, etc. [2,18], ultimately determining the quality of steel. Therefore, the aim of the work is to study the viscosity of slags of the CaO–SiO₂–Cr₂O₃–MgO–Al₂O₃–B₂O₃ system with a basicity of 1.0–2.5, containing 0–18% Cr₂O₃, 8% MgO, 3% Al₂O₃ and 6% B₂O₃ (in this expression and hereinafter indicated by mass %).

2. Materials and methods

Synthetic slags, the compositions of which are shown in Table 1, were smelted in a resistance furnace in molybdenum crucibles from reagent grade oxides, previously calcined for 2–3 hours at a temperature of 800°C (B₂O₃ at a temperature of 100°C). The viscosity of the slag test samples was measured on an electrovibration viscometer in molybdenum crucibles in a stream of purified argon. The temperature of the slag was measured using a tungsten-rhenium thermocouple.

Thermodynamic modeling of the phase composition of the prototypes was carried out using the HSC Chemistry 8.03 software package, which allows one to calculate the equilibrium compositions and quantities of the products formed according to the Gibbs energy minimization algorithm based on the concepts of metallurgical melts as ideal associated solutions [19].

The obtained temperature dependences of slag viscosity are presented graphically in Figure 1. Table 2 contains the results of the calculation of the phase composition.

Table 1. The chemical composition of the experimental slag.

| No | Slag composition, % | | | | | | |
|----|---------------------|------------------|--------------------------------|-----|--------------------------------|-------------------------------|---------------------------------|
| | CaO | SiO ₂ | Cr ₂ O ₃ | MgO | Al ₂ O ₃ | B ₂ O ₃ | $B = (\text{CaO})/\text{SiO}_2$ |
| 1 | 41.50 | 41.50 | 0 | 8 | 3 | 6 | 1.0 |
| 2 | 59.29 | 23.71 | 0 | 8 | 3 | 6 | 2.5 |
| 3 | 46.43 | 18.57 | 18 | 8 | 3 | 6 | 2.5 |
| 4 | 32.50 | 32.50 | 18 | 8 | 3 | 6 | 1.0 |

3. Results and discussion

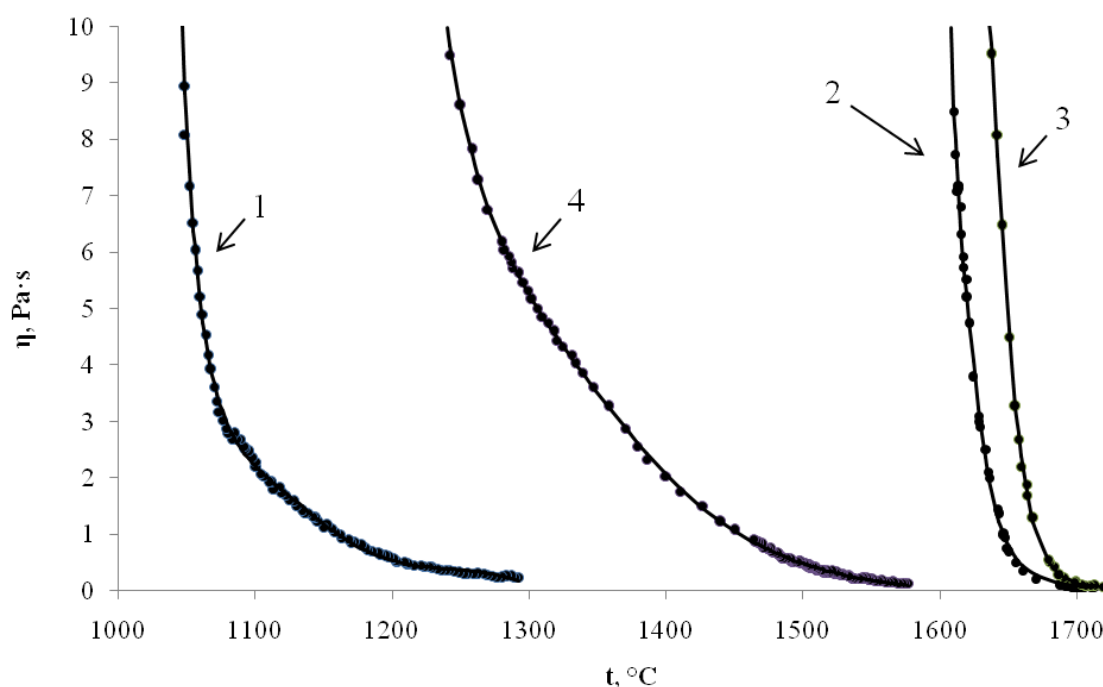
As it can be seen from Figure 1, most of the studied slags (No. 1, 2, 3) are the so-called ‘short’ slags with a pronounced inflection point. This is explained by the phase composition of the studied oxide system, namely, the content of a large number of such high-temperature compounds as 2CaO·SiO₂ and CaO·Cr₂O₃ (Table 2).

The first slag (slag No. 1), not containing Cr₂O₃, having a basicity of 1.0 and containing 6.0 % B₂O₃, is characterized by a significant concentration of low-melting phases CaO·B₂O₃, 2CaO·B₂O₃ and CaO·MgO·2SiO₂ (up to 22% in total) with only 11% of high-melting phases 2CaO·SiO₂, CaO, MgO, and has a viscosity of 0.2–0.6 Pa·s in the range of 1200–1350°C. Moreover, the overwhelming number of phases CaO·SiO₂, CaO·MgO·SiO₂, etc. accounts for the second interval (62%), which ensures a rapid speed of crystallization despite the low basicity.

An increase in the basicity of slag without Cr₂O₃ (slag No. 2), containing 6.0% boron oxide, to 2.5 is accompanied by a decrease to 5% in the fraction of low-melting phases (2CaO·B₂O₃) and an increase in the fraction of medium- and high-melting compounds to 43 and 50 % respectively, which

Table 2. Slag phase composition.

| Phases, % | $t_{\text{melting}}, ^\circ\text{C}$ | Slags | | | |
|------------------------------------|--------------------------------------|-------|------|-------|-------|
| | | 1 | 2 | 3 | 4 |
| Low-melting phases | | | | | |
| CaO·B ₂ O ₃ | 1130 | 4 | 0.1 | 0.4 | 4.5 |
| 2CaO·B ₂ O ₃ | 1280 | 9 | 5 | 9 | 8 |
| CaO·MgO·2SiO ₂ | 1391 | 9 | 0.03 | 0.2 | 8 |
| Medium-melting phases | | | | | |
| 2CaO·MgO·2SiO ₂ | 1454 | 4 | 0.4 | 1 | 3 |
| 3CaO·B ₂ O ₃ | 1460 | 1 | 14 | 9 | 1 |
| 3CaO·2SiO ₂ | 1460 | 13 | 8 | 7 | 6 |
| CaO·MgO·SiO ₂ | 1503 | 8 | 5 | 8 | 7 |
| CaO·SiO ₂ | 1540 | 23 | 3 | 5 | 22 |
| MgO·SiO ₂ | 1557 | 5 | 0.1 | 0.5 | 5 |
| 3CaO·MgO·2SiO ₂ | 1575 | 2 | 6 | 5 | 1 |
| SiO ₂ | 1710 | 6 | 0.03 | 0.1 | 5 |
| High-melting phases | | | | | |
| 2CaO·SiO ₂ | 2130 | 10 | 40 | 21 | 6 |
| CaO·Cr ₂ O ₃ | 2170 | 0 | 0 | 20.5 | 7 |
| MgO·Cr ₂ O ₃ | 2350 | 0 | 0 | 0.004 | 0.005 |
| Cr ₂ O ₃ | 2435 | 0 | 0 | 3 | 13 |
| CaO | 2570 | 0.2 | 6 | 2 | 0.2 |
| MgO | 2852 | 1 | 4 | 4 | 1 |

**Figure 1.** Temperature dependence of slag viscosity. 1–4 – slag numbers.

Causes a shorter crystallization at higher temperature (slag No. 2). Despite the increase in the fraction of the low-melting phase 2CaO·B₂O₃ to 9% in slag No. 3, which has the same basicity but contains 18% Cr₂O₃, an increase in the fraction of high-melting phases 2CaO·SiO₂, CaO, CaO·Cr₂O₃, Cr₂O₃ and MgO to 53% provides it similar nature of the dependence of viscosity curve on temperature. In this case slag No. 2 and No. 3 have a viscosity of 0.07–1.0 Pa·s in the range of 1650–1700°C and

up to 1.0 Pa·s at a temperature of 1670°C, respectively.

An increase in the basicity of slag without Cr₂O₃ (slag No. 2), containing 6.0% boron oxide, to 2.5 is accompanied by a decrease to 5% in the fraction of low-melting phases (2CaO·B₂O₃) and an increase in the fraction of medium- and high-melting compounds to 43 and 50 % respectively, which causes a shorter crystallization at higher temperature (slag No. 2). Despite the increase in the fraction of the low-melting phase 2CaO·B₂O₃ to 9% in slag No. 3, which has the same basicity but contains 18 % Cr₂O₃, an increase in the fraction of high-melting phases 2CaO·SiO₂, CaO, CaO·Cr₂O₃, Cr₂O₃ and MgO to 53% provides it similar nature of the dependence of viscosity curve on temperature. In this case slag No. 2 and No. 3 have a viscosity of 0.07–1.0 Pa·s in the range of 1650–1700°C and up to 1.0 Pa·s at a temperature of 1670°C, respectively.

Slag No. 4 is 'long' and doesn't have a pronounced inflection point due to low basicity and a large number of glass-forming oxides SiO₂, B₂O₃. The presence in the slag of the studied oxide system of 18 % chromium oxide, acting at a basicity of 1.0 or more as a network-former, increases the degree of slag polymerization [17]. With a slight decrease relative to slag No. 1, of the content of low-melting phases CaO·B₂O₃, 2CaO·B₂O₃, CaO·MgO·2SiO₂ up to 21%, the fraction of high-melting 2CaO·SiO₂, CaO, CaO·Cr₂O₃, Cr₂O₃ and MgO increases up to 27% at the expense of compounds with an medium melting point. That leads to heterogenization of the oxide system and viscosity up to 0.1–1.0 Pa·s at increased temperature of 1450–1570°C.

4. Conclusions

As a result of a study of the physical properties of the slags of the studied oxide system it was found that boron oxide provides the formation of low-melting phases and a sufficiently high fluidity of the slags of the CaO – SiO₂ – Al₂O₃ – MgO – B₂O₃ system even at a high content of chromium oxide. The addition of 18% chromium oxide, acting at a basicity of 1.0 or more as a complexing agent, increases the degree of slag polymerization and the fraction of high-temperature phases in the slags of the studied oxide system, accompanied by their heterogenization and viscosity increase.

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