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VISCOSITY AND CRYSTALLIZATION TEMPERATURE OF FERROALLOY SLAGS FROM KAZAKHSTAN ORE

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Preliminary Note – Prethodno priopćenje

Experimental research with synthetic mixtures imitating typical ferroalloy slags is described in the paper. Samples imitating slags of high-carbon ferrochrome, ferrotitanium and high-carbon ferromanganese were made of analytical grade reagents by mixing and melting in a resistance furnace. Slag viscosity was measured with electric vibratory viscometer in the temperature range of 0 – 1 800 °C. Based on research results it is recommended to use higher basicity slags together with specific additions (fluxes) reducing slag's viscosity and melting point.

Key words: ferro/chrome/titanium/manganese, crystallization, temperature, slag, viscosity

INTRODUCTION

Physical properties of ferroalloy slag are of great importance to ferroalloy smelting efficiency, as the recovery of oxides in liquid state is limited by their diffusion into slag [1]. The slags chemistry can be generally described by the system CaO-SiO_2-Al_2O_3-MgO.

It is evident that the slag plays an important technological role in ferroalloy smelting, having direct impact on metal quality. Viscosity and crystallization point are among critically important slag characteristics.

Dynamic viscosity of a homogeneous liquid h defines a viscous friction between its separate layers of infinitesimal thickness travelling at various speeds [2]. Viscosity (t_{Cr}) at temperatures below solidification point – is apparent as it does not reflect the true internal friction force. Still, it is necessary to know it to characterize the mobility of heterogeneous systems [2-4].

The objective of the work was to determine viscosity characteristics of typical domestic ferroalloy slags in the temperature range of the smelting process.

A series of high-temperature experiments with synthetic slags was conducted in a resistance furnace. Considering the fact that presence of metal and foreign inclusions complicates the study of real slag, we used synthetic mixes imitating industrial slags chemistry.

RESEARCH METHODOLOGY

Slag viscosity was measured by electric vibratory viscometer in the resistance furnace with coal heater. Preliminary milled slag mixture (15 - 20 gram) was placed into molybdenum crucible with 17 mm inner and 30 mm outer diameter and 60 mm height. Crucible was located in isothermal zone of coal heater. Upon complete melting of the slag mixture (1 550-1 650 ºC), crucible content was thoroughly mixed with molybdenum rod. Using screw hoist, molybdenum viscometer spindle 2 mm in diameter and 40 mm long was immersed into the crucible center to a depth of 10 - 12 mm. Measurements were taken from homogeneous liquid state to complete crystallization of slag at cooling speed of 3 - 5 °C per minute. Solid slag was further remelted to extract the viscometer spindle. Furnace temperature was measured with W/Rh 5/20 tungsten-rhenium thermocouple. Hot junction of the thermocouple protected by corundum shell was applied to the crucible bottom. Viscosity value was measured by e.m.f. (mV) value on digital millivoltmeter. Viscometer was calibrated by the liquid with the density close to molten metallurgical slags. We used castor oil, measuring its viscosity at each given temperature within the range of 0,2 - 40 poise (P). The curve reflecting dependence of viscometer e.m.f. on liquid density has a smooth inclination which creates a wide measurement range for slag viscosity gauging.

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RESULTS RESEARCH

Low-carbon ferrochrome slag

Experimental research of slags properties started with low-carbon ferrochrome slag (chemical composition in Table 1). 15 slag samples were prepared and divided into five groups, each having different CaO/SiO_2 ratio: 1,3; 1,4; 1,5; 1,6 and 1,7.

Within each group the CaO and SiO_2 levels were maintained practically the same. MgO/Al_2O_3 within each group was gradually altered from high to low alumina. Controlled composition variation allowed to trace how the substitution of MgO for Al_2O_3 influenced slag viscosity and crystallization temperature.

Table 1 **Chemical composition of synthetic slags of low-carbon ferrochrome / wt. %**

Sample No.	Composition, %					C/S
	C	S	M	A	Cr	
1	2	3	4	5	6	7
1	37,89	29,15	20,56	6,86	5,51	1,3
2	38,02	29,21	13,80	14,11	4,78	1,3
3	38,11	29,33	6,92	20,71	4,85	1,3
4	39,44	28,13	20,36	6,78	5,22	1,4
5	39,61	28,33	13,51	13,71	4,75	1,4
6	39,83	28,38	6,46	19,41	5,81	1,4
7	40,70	27,11	20,70	6,90	4,45	1,5
8	41,02	27,31	13,25	13,53	4,82	1,5
9	41,13	27,44	6,52	19,64	5,18	1,5
10	42,51	26,49	19,17	6,32	5,37	1,6
11	42,61	26,65	12,64	12,47	5,53	1,6
12	42,04	26,22	6,58	19,68	5,36	1,6
1	2	3	4	5	6	7
13	42,81	25,18	20,66	6,92	4,33	1,7
14	42,97	25,17	13,73	13,48	4,54	1,7
15	43,47	25,57	6,44	19,25	5,11	1,7

*Note. The following abbreviations are used in the table: C-CaO; S-SiO_2;A-Al_2O_3;Cr-Cr_2O_3

Data on slag viscosity temperature relations are represented in the Fig.1. Curve numbers correspond to slag numbers from Table 1. The results show that above the solidification point the viscosity of slags is low, e.g. 0,06-0,33Pa/sec at 1600 ºC and 0,09-0,51Pa/sec at 1550 ºC except for the slag No.14. Based on this, the slags may be rated as so called "short slags" with viscosity raising abruptly with temperature decrease. From the Fig.1 we can clearly see that increase of Al_2O_3 content leads to contraction of viscosity range.

According to the J. Frenkel's theory of viscous flow, under unchanging structure of homogenous melt, the breaking point on viscosity curve built in "ln η – 1/T" coordinates defines the change of viscous flow activation energy (E) at liquidus temperatures (solidification onset) [2]. Figure2 reflects the dependence of viscosity logarithm (ln η) on reciprocal absolute temperature (1/T). As you can see the increase of CaO/SiO_2 ratio in slag results in higher solidification temperature. Solidification temperature was calculated by joint solving of two line equations of upper and lower branches. It was determined that, at higher slag basicity or higher MgO content, the slag solidification temperature, viscosity and, in most cases, viscous flow activation energy, increase accordingly.

Research results bring us to the conclusion that at constant basicity, altering the MgO/Al_2O_3 ratio, we can distinctly influence the mentioned properties of slag. Higher MgO content reduces the temperature range of crystallization onset. According to [3], increased MgO content complicates the sedimentation of metal drops resulting in higher Cr_2O_3 content in slag (up to 7% or more), which corresponds to the research [5]. As the tests showed, higher Al_2O_3 content increases the crystallization onset temperature range for the slags. As follows from Figure 1 the obtained data correlate with re-

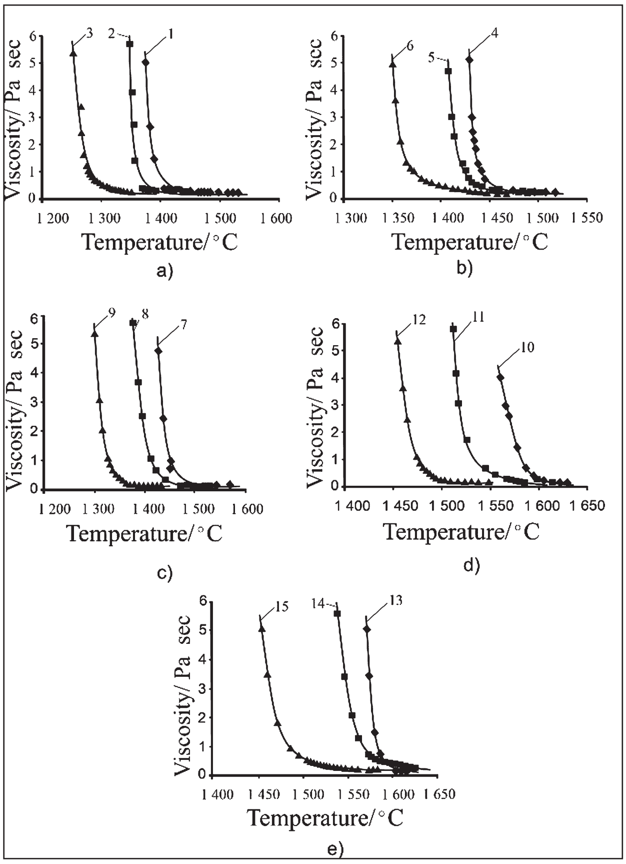

Figure 1 Temperature dependence of slag viscosity with basicity of 1,3(a); 1,4(b); 1,5(c); 1,6(d) and 1,7(e).

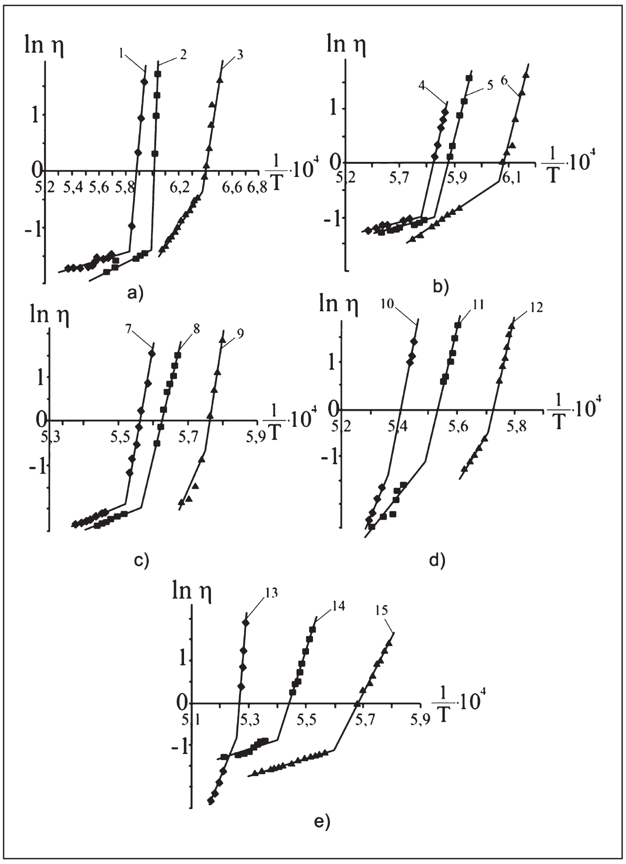

Figure 2 Dependence of viscosity logarithm (ln η) on reciprocal of absolute temperature (1/T)

sults of the research work [6]: to improve physical and chemical properties of refined FeCr slags from magnesian chromium ore it would be feasible to reduce CaO or to increase Al_2O_3 level in the slag.

Ferrotitanium slag

In ferrotitanium smelting, slag viscosity has a great impact on recovery speed and completeness of reduction process as well as on the speed of metal drops sedimentation through the slag layer [7]. Known data on ferrotitanium slag viscosity cover narrow temperature range, available information is insufficient to work out recommendations for deeper extraction of titanium.

Three slag compositions used in our experiments are represented in the Table 2.

Table 2 **Chemical composition of slags / wt. %**

Slag No.	Chemical composition, wt. %				
	Al_2O_3	TiO_2	CaO	MgO	SiO_2
1	64,2	21,8	5,1	2,0	6,9
2	60,7	21,5	10,3	1,7	6,8
3	56,0	21,1	14,8	1,6	6,7

Experimental data on FeTi slag viscosity are shown in the Figure 3.

Increase of CaO concentration from 5,1 to 14,8 % leads to significant reduction of slag viscosity with distinctive drop between 5,1 and 10,3 % CaO level and smoother decrease to 14,8 % concentration. Such behavior is apparently caused by transformation of stiff groups of β-alumina [8] into mobile combinations of calcium monoaluminate $CaO·Al_2O_3$.

Positive impact of CaO additions (up to 50%) into blast-furnace slags resulting in lower viscosity was noted earlier [9,10]. Author [10] states that increase of CaO level above 50 % leads to higher viscosity and melting temperatures of blast-furnace slags. Thus, blast-furnace slags with CaO below 50 % are similar to alumina-titanium slags in the way CaO impact their viscosity.

Experimental data were processed by least-squares method. Equations and calculation results on solidification temperatures (t_{sl} ºC) and viscous flow activation energy values (E) are given in the Table 3.

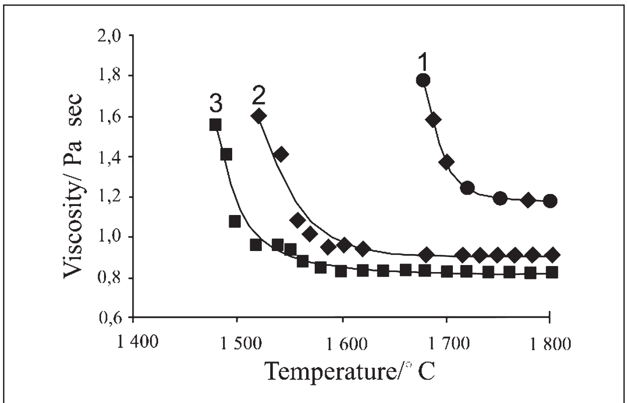

Figure 3 Changes of slag viscosity degree depending on temperature (curve numbers correspond to slag number from Table 1)

Table 3 **Solidification temperature and viscous flow activation energy of slags**

Slag No.	Equations	t_{Cr} ºC	E kJ/mol
1	ln_a = 2,3007/T-0,9513 ln_b = 51,386/T-25,731	1 707	191 4 272
2	ln_a = 1,0689/T-0,6233 ln_b = 31,606/T-17,136	1 576	89 2 628
3	ln_a = 0,5272/T-0,4568 ln_b = 23,223/T-12,823	1 562	44 1 931

Ferromanganese slag

Slag condition plays significant role in high-carbon FeMn process. Aside from mechanical aspects of metal separation, slag viscosity behavior has direct connection to physical-chemical interactions of manganese recovery process. Manganese oxide activity is directly proportional to slag basicity. However, higher slag basicity, though improving thermodynamic conditions for Mn recovery, means higher melting temperature and viscosity of slag, which greatly impairs its processability.

Numerous researchers studied viscosity and conductivity of FeMn slags, but the impact of B_2O_3 on slag properties is less investigated [10-12]. In our experiments with typical FeMn slags of varying basicity we used boron additives to investigate boric oxide impact on slags viscosity. Initial slag compositions and basicity ratios are shown in the Table 4.

Table 4 **Chemical composition of slags / wt.%**

Slag No.	Chemical composition %					C/ S
	M	C	M	S	Al	
1	18,91	38,03	1,89	29,37	11,80	1,3
2	17,83	41,54	1,78	27,70	11,15	1,5
3	17,35	43,12	1,73	26,95	10,85	1,6
4	16,46	46,03	1,64	25,57	10,30	1,8
5	15,29	49,87	1,52	23,75	9,57	2,0

*Note. The following abbreviations are used in the table: M-MnO; C-CaO; S-SiO_2;A-Al_2O_3

The Figure 4 shows viscosity curves of slag samples with boric oxide addition. Additions of B_2O_3 evidently reduce viscosity (η) and solidification temperature of manganese slags but the nature and degree of this influence differ depending on slag basicity, which is mainly explained by the formation of new phases in the system.

Thus, experimental results show that the presence of B_2O_3 in FeMn slag improves its tapping and handling conditions and helps to maintain required viscosity and solidification temperature despite high basicity. This allows to improve thermodynamic conditions of manganese recovery and reduce its losses with dump slag.

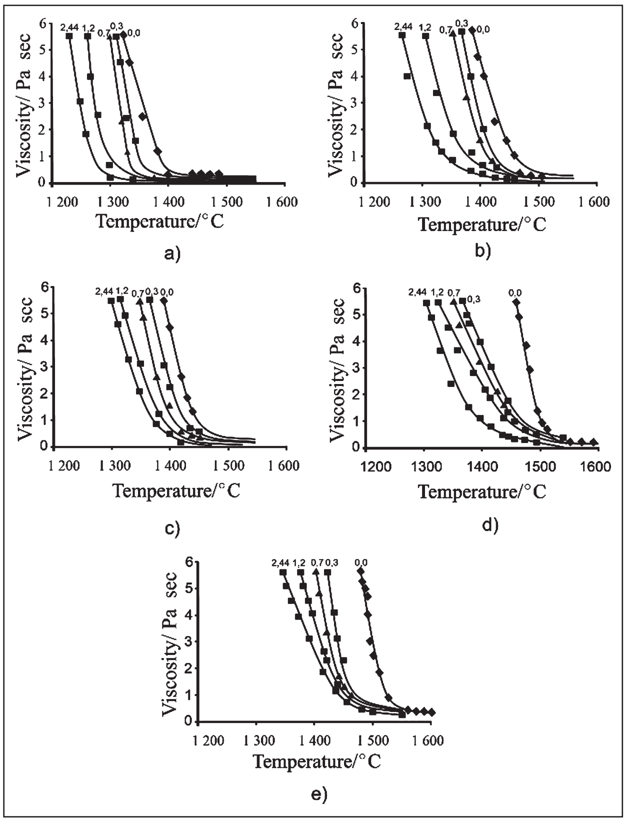

Figure 4 Viscosity polytherms of slags with 1,3(a); 1,4(b); 1,5(c); 1,6(d) and 1,7(e) basicity ratio under different B_2O_3 content (curve numbers - B_2O_3 content in slag / %)

CONCLUSION

Results of described experimental research show that typical ferroalloy slags have relatively high viscosity and melting point. It is feasible to conduct smelting under slags with higher basicity using specific additions to improve slag's properties and processability.

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