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INVESTIGATION OF THE PHYSICAL PROPERTIES OF EXISTING SLAGS OF HIGH-CARBON AND REFINED FERROCHROME OF THE AKTOBE FERROALLOY PLANT

Abstract. The article discusses waste from ferroalloy production and a review of the chemical analysis of ferrochrome slags. The authors analyze the composition of slags, their physical and chemical properties, as well as their impact on the environment. The article examines the physical properties of existing high-carbon and refined ferrochrome slags. The authors also analyze in detail the composition of high-carbon ferrochrome slags, their physical and chemical properties, as well as their difference from refined ferrochrome slags, and their impact on the environment. The article also discusses the physical properties of existing slags used in the production of the mentioned types of ferrochrome. This article provides an overview of the composition and physicochemical properties of high-carbon and refined ferrochrome slags, identifies the main components and determines their potential practical value.

Key words: *slags, high-carbon ferrochrome, refined ferrochrome, phase composition, crystallization, expanded clay, viscosity.*

Ақтөбе ферроқорытпа зауытының жоғары көміртекті және тазартылған феррохром қождарының физикалық қасиеттерін зерттеу

Андатпа. Мақала жоғары көміртекті және тазартылған феррохром өндірісі кезінде түзілетін шлактарды зерттеуге арналған. Бұл мақалада жоғары көміртекті және тазартылған феррохром өндірісі кезінде түзілетін шлактардың құрамын зерттеу де берілген. Авторлар шлактардың құрамын, олардың физикалық және химиялық қасиеттерін, сонымен қатар олардың қоршаған ортаға әсерін талдайды. Мақалада қолданыстағы жоғары көміртекті және тазартылған феррохромды шлактардың физикалық қасиеттері қарастырылады. Сондай-ақ авторлар жоғары көміртекті феррохромды шлактардың құрамын, олардың физикалық және химиялық қасиеттерін, сонымен қатар олардың тазартылған феррохромды қождардан айырмашылығын және олардың қоршаған ортаға әсерін егжей-тегжейлі талдайды. Мақалада феррохромның аталған түрлерін өндіруде қолданылатын бар шлактардың физикалық қасиеттері де қарастырылады. Мақалада жоғары көміртекті және тазартылған феррохромды шлактардың температураға тәуелділігі графиктер мен кестелер түрінде берілген.

Түінді сөздер: *қож, жоғары көміртекті феррохром, тазартылған феррохром, фазалық құрамы, кристалдану, керамзит, тұтқырлық.*

Исследование физических свойств существующих шлаков высокоуглеродного и рафинированного феррохрома Актюбинского завода ферросплавов

Аннотация. Статья посвящена исследованию шлаков, образующихся при производстве высокоуглеродистого и рафинированного феррохрома. Данная статья также представляет собой исследование состава шлаков, образующихся в процессе производства высокоуглеродистого и рафинированного феррохрома. Авторы анализируют состав шлаков, их физико-химические свойства, а также влияние на окружающую среду. В статье рассмотрены физические свойства существующих шлаков высокоуглеродистого и рафинированного феррохрома. Авторы также подробно анализируют состав шлаков высокоуглеродистого феррохрома, их физико-химические свойства, а также их отличие от шлаков рафинированного феррохрома, и воздействие на окружающую среду. В статье также рассматриваются физические свойства уже существующих шлаков, используемых в производстве упомянутых видов феррохрома. В процессе исследования были получены ожидаемые результаты, которые представлены в виде таблиц и графиков.

Ключевые слова: *шлаки, высокоуглеродистый феррохром, рафинированный феррохром, фазовый состав, кристаллизация, керамзит, вязкость.*

Introduction

The production of high-carbon and refined ferrochrome is an important part of the metallurgical industry. These alloys are used in the production of stainless steel, alloys with high chromium content, as well as in other industrial fields such as the aluminum industry, high-speed steel production and other industries. The process of producing ferrochrome involves the use of ore, chromium oxides and coal. However, the formation of slags is an integral part of this process.

Slags formed during the production of ferrochrome are a by-product formed as a result of the interaction of raw materials with a piece of iron, which is used as a reaction medium for the chromium enrichment process. Slags, as a rule, contain a significant amount of chromium, aluminum, silicon oxides and other elements that are present in the ores and additives used.

Slags from the production of high-carbon and refined ferrochrome play an important role in the alloy production process. They have a variety of properties that can affect the processes of alloy production, such as viscosity, density, thermal conductivity and heat capacity. In addition, during the formation of slags, metallic and non-metallic impurities are removed from the alloy, which affects its chemical composition and properties.

The purpose of this work is to study the properties, composition and influence of slags from the production of high-carbon and refined ferro-chromium on the process of obtaining alloys. We will also look at possible ways to use slags as secondary raw materials or additives for other production processes. This aspect is of interest both from an environmental point of view and from the point of view of optimizing production processes.

Research methods

In accordance with the schedule, the physical properties of 22 slag ferroalloys presented by the Aktobe plant were experimentally studied. Their chemical analyses are shown in Table 1.

They were synthesized at the Aktobe Ferroalloy Plant by adding various fluxes to natural slags. Samples 1-6 (Table 1) were obtained by adding high-carbon ferrochrome ceramic clay to the smelting slags, samples 7-11 by adding calcium borate to the same slags, and 12-16 by adding refined ferrochrome smelting slags. Refined ferrochrome smelting slags, where from 0 to 25% of expanded clay was introduced, are also presented for research. Chemical analyses of all slags were performed at the Aktobe Ferroalloy Plant.

Additives are introduced into the slags in small increments (2%). Often, in this case, the physical properties change slight-

Table 1

Chemical analyses of natural slags

Кесте 1

Табиғи токсиндердің химиялық талдаулары

Таблица 1

Химические анализы натуральных шлаков

№ sample	Material	Flux	Chemical composition of the slag, %							
			Cr_2O_3	SiO_2	CaO	MgO	Al_2O_3	FeO	B_2O_3	$Cr_{мет}$
1	HCFC slag*	without additive	9,4	26,0	1,7	42,0	16,8	2,3	-	4,9
2	HCFC slag	2% expanded clay	4,2	28,8	3,6	42,1	19,6	1,0	-	1,3
3	HCFC slag	4% expanded clay	2,6	30,9	2,5	43,8	18,5	0,8	-	1,1
4	HCFC slag	6% expanded clay	3,0	31,5	2,4	43,3	18,4	0,8	-	1,0
5	HCFC slag	8% expanded clay	3,5	31,4	2,2	43,2	18,4	0,8	-	1,1
6	HCFC slag	10% expanded clay	3,2	32,1	2,1	43,0	18,5	0,8	-	0,9
7	HCFC slag	2% calcium borate	3,2	28,5	2,5	45,7	18,5	0,6	0,5	1,0
8	HCFC slag	4% calcium borate	3,5	27,8	3,7	44,0	17,9	0,8	1,7	0,8
9	HCFC slag	6% calcium borate	3,2	28,7	3,5	45,1	17,9	0,4	1,2	0,8
10	HCFC slag	8% calcium borate	5,0	27,2	4,3	43,0	17,2	1,0	2,3	1,4
11	HCFC slag	10% calcium borate	5,0	26,7	4,9	41,9	17,2	0,9	2,6	1,4
12	HCFC slag	2% RFC slag**	2,3	28,7	3,0	46,1	18,5	0,5	0,05	1,0
13	HCFC slag	4% RFC slag	1,7	28,8	4,0	45,8	18,2	0,5	0,05	0,7
14	HCFC slag	6% RFC slag	3,6	27,8	4,5	45,0	18,1	0,5	0,05	1,1
15	HCFC slag	8% RFC slag	2,3	29,4	5,7	44,5	17,1	0,6	0,01	0,9
16	HCFC slag	10% RFC slag	2,7	28,5	6,5	43,8	17,0	0,5	0,01	1,0
17	RFC slag	without additive	7,8	25,2	47,1	12,4	5,5	1,1	-	-
18	RFC slag	5% expanded clay	8,1	27,0	44,1	12,0	5,6	3,0	-	4,0
19	RFC slag	10% expanded clay	4,3	31,0	44,2	12,3	6,7	1,2	-	1,3
20	RFC slag	15% expanded clay a	4,1	31,0	43,1	12,7	6,9	1,1	-	1,3
21	RFC slag	20% expanded clay a	4,0	33,0	41,0	12,2	7,5	1,0	-	1,3
22	RFC slag	25% expanded clay	4,9	35,2	38,2	11,9	7,5	1,0	-	1,2

1 * – HCFC slag-high carbon ferrochrome slag;
2 ** – RFC slag-refined ferrochrome slag.

ly and to fix this, a regular change in the chemical composition of the slag with the additive is important, i.e. it is important to accurately enter the specified composition. This can be estimated by comparing the compositions of natural slags with calculated ones (Table 2).

There can be no complete coincidence of real and calculated compositions due to unavoidable errors:

- *averaging of initial samples;*
- *weighing of individual components;*
- *fusion of slag and flux at high temperatures;*
- *chemical analysis of finished samples.*

These errors are strictly regulated, determined by the accuracy class of the devices and techniques used and, subject to the technical specifications for performing this type of work, do not exceed plus or minus 10%.

Let's compare the compositions of natural and calculated slags. When 2% expanded clay is added to slag No. 1 HCFC, the Cr_2O_3 content in it drops from 9.4 to 4.2% (Table 1), i.e. by 2.2 times, and the ***FeO*** content by 2.3 times. This contradicts calculations, because expanded clay has a high ***FeO*** content (7.7%) and an increase in the amount of this additive should lead to an increase in the ***FeO*** content in the slag, and not to a drop. This is confirmed by the calculation. When 2% expanded clay was added to this slag, the ***FeO*** content naturally increased and amounted to 2.41% (Table 2). The two-fold distribution does not fit into the permissible TU 10%.

The conditions of sample preparation are unknown to us, but it can be assumed that the melting was carried out in a graphite crucible, the carbon of which recovered chromium and iron, causing a drop in the content of their oxides in the slag. The latter in the slag are in the form of high-temperature spinel $FeO*Cr_2O_3$, a decrease in the amount of which will lead to a drop in the refractory slag, and it will be incorrect to attribute the effect of changing its physical properties to the introduced flux. The role of carbon, which led to a decrease in the content of chromium and iron oxides in the slag, may be decisive. This also applies to the content of Sgmet metal chromium in the slag.

Table 2

Calculated slag compositions

Кесте 2

Қождардың есептік құрамы

Таблица 2

Расчетные составы шлаков

№ sample	Material	Flux	Chemical composition of the slag, %							
			Cr_2O_3	SiO_2	CaO	MgO	Al_2O_3	FeO	B_2O_3	$Cr_{мет}$
1	HCFC slag	without additive	9,4	26,0	1,7	42,0	16,8	2,3	-	4,9
2	HCFC slag	2% expanded clay	9,24	26,62	1,7	41,22	16,78	2,41	-	4,8
3	HCFC slag	4% expanded clay	9,09	27,21	1,69	40,48	16,77	2,51	-	4,7
4	HCFC slag	6% expanded clay	8,94	27,78	1,69	39,76	16,75	2,61	-	4,6
5	HCFC slag	8% expanded clay	8,8	28,33	1,69	39,07	16,74	2,7	-	4,54
6	HCFC slag	10% expanded clay	8,66	28,86	1,68	38,4	16,73	2,79	-	4,45
7	HCFC slag	2% calcium borate	9,21	25,49	2,69	41,17	16,47	2,25	0,84	4,8
8	HCFC slag	4% calcium borate	9,04	25,0	3,63	40,38	16,15	2,21	1,65	4,7
9	HCFC slag	6% calcium borate	8,87	24,53	4,55	39,62	15,85	2,17	2,43	4,6
10	HCFC slag	8% calcium borate	8,7	24,07	5,43	38,89	15,55	2,13	3,19	4,54
11	HCFC slag	10% calcium borate	8,54	23,64	6,27	38,18	15,27	2,09	3,91	4,45
12	HCFC slag	2% RFC slag *	9,368	25,98	2,59	41,42	16,58	2,28	-	4,8
13	HCFC slag	4% RFC slag	9,34	25,96	3,45	40,86	16,37	2,25	-	4,7
14	HCFC slag	6% RFC slag	9,31	25,94	4,27	40,32	16,16	2,23	-	4,6
15	HCFC slag	8% RFC slag	9,28	25,93	5,06	39,81	15,96	2,21	-	4,54
16	HCFC slag	10% RFC slag	9,25	25,91	5,83	39,31	15,77	2,19	-	4,45
17	RFC slag	without additive	7,8	25,2	47,1	12,4	5,5	1,1	-	-
18	RFC slag	5% expanded clay	7,49	26,74	44,93	11,92	6,0	1,6	-	-
19	RFC slag	10% expanded clay	7,21	28,14	42,96	11,49	6,45	2,06	-	-
20	RFC slag	15% expanded clay	6,95	29,41	41,15	11,09	6,87	2,48	-	-
21	RFC slag	20% expanded clay	6,72	30,58	39,5	10,73	7,25	2,87	-	-
22	RFC slag	25% expanded clay	6,5	31,66	37,98	10,40	7,6	3,22	-	-

HCFC slags with the addition of calcium borate (No. 7-11) also differ from the calculated ones for the reasons stated above. In addition, there is a large deficiency in the slag of boric anhydride B_2O_3 against the calculated content. The calcium borate supplied to the plant contains about 12% hydrated moisture and, when charging, it is necessary to take into account the reduced content of boric anhydride in it against its amount in the calcined substance.

A distinctive feature of RFC slags with the addition of RFC slags (No. 12-16) is the presence of B_2O_3, although it is not present in the original RFC slag (No. 17), which is added. RFX slags with the addition of expanded clay (No. 17-22) also differ from the calculated ones, especially for chromium and iron oxides.

The physical properties of the slags and their phase composition are investigated. The viscosity is determined using an electrovibration viscometer, the temperature of the beginning of crystallization is determined by the dependence of viscosity on the inverse absolute temperature, the temperature of the end of crystallization is determined by stopping the spindle of the viscometer with complete crystallization of the tested slag, and the phase composition is determined by thermodynamic-diagram analysis.

Results

The results of viscosity studies of all 22 slags are shown in figures 1-4. They are divided into groups. The numbers of the viscosity curves correspond to the numbers of the slags according to Table 1. The first group (No.1-6) shows the temperature dependence of the viscosity of slags with the addition of expanded clay (Figure 1). All of them have a low viscosity upon melting, since they are composed mainly of forsterite, which has a simple phase structure of isolated tetrahedra $(SiO_4)^{4-}$ (Table 3). The addition of expanded clay does not have a noticeable effect on the viscosity in the melted state, as can be seen from the course of the curves in Figure 1. This is due to the practical immutability of the initial slag structure (No. 1) of the simplest form of isolated tetrahedra, due to the dominance of forsterite and magnesian spinel (Table 3). Only at high clay consumption do triple compounds appear in the slags, for example, anorthite (CAS_2) with a skeleton-type anion structure, which makes the course of the temperature dependence of viscosity smoother.

According to experimental data, the addition of expanded clay slightly reduces the temperature of the beginning of crystallization of the slag of the HCFC (Table 4). Theoretically, a strong decline could not be expected. Silica (57.5%) and alumina (16%) contained in clay in large quantities contribute not to a decrease, but to the growth of high-temperature forsterite **(M_2S)** in the slag and the retention of refractory magnesium spinel (MA) at a high level (Table 3).

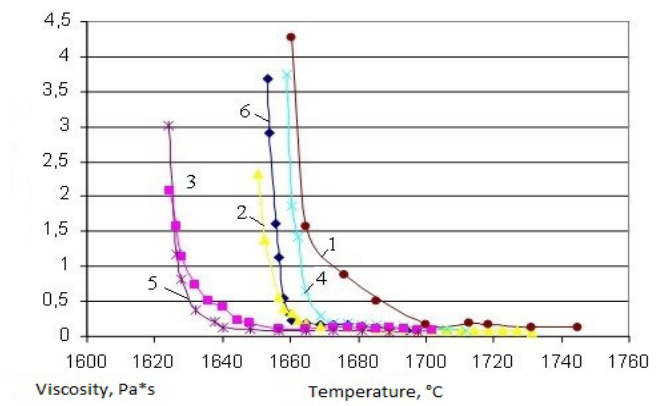

Figure 1. Temperature dependence of slag №1-6 viscosity.
Сурет 1. №1-6 қождардың тұтқырлығының температураға тәуелділігі.
Рис. 1. Температурная зависимость вязкости шлаков №1-6.

It should also be taken into account that the loss of refractoriness was facilitated by the removal of a part of the spinel **$FeO*Cr_2O_3$** from the slag due to its reduction to metal during slag preparation in a graphite crucible.

It can also be noted that all the studied slags of this group are «short», i.e. crystallizing in a narrow temperature range. This can be seen both in the course of the viscosity curves (Figure 1) and in the ratio of the temperatures of the beginning and end of crystallization, i.e., the crystallization interval (Table 4).

The addition of expanded clay does not expand, but narrows the temperature range of crystallization. If the initial (without additives) slag No. 1 had 43°C, then the introduction of only 2% clay narrowed this interval to 17°C (slag No. 2). This is typical for all the slags of this group.

Figure 2 shows the dependences of the viscosity of the slags of HCFC with the addition of calcium borate. As in the previous case, they have a low viscosity upon melting, not exceeding 0.25-0.50 Pa*s. The dominant phase components of the initial slag also play a major role here.

The temperature of both the beginning and the end of crystallization of slags decreases here more intensively than in the case of expanded clay additives. Thus, when 10% calcium borate is injected into the slag, the temperature of the beginning of crystallization decreases from 1698 to 1610°C, i.e. by 88°C. The temperature range also expands, reaching 54-86°C with the first additives (Table 4). The phenomenon of calcium and monticellite (CMS) borates, which are more fusible than forsterite and magnesian spinel, is the reason for this. But the potential capabilities of **B_2O_3** to reduce the refractoriness of slag are not fully realized. Firstly, for reasons unknown to us, the content of **B_2O_3** in the final slag is almost 2 times less than in the calculated one.

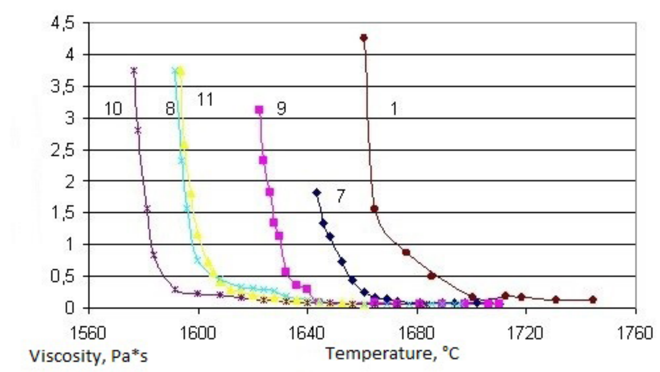

Figure 2. Temperature dependences of slag №7-11 viscosity.
Сурет 2. №7-11 қождардың тұтқырлығының температуралық тәуелділігі.
Рис. 2. Температурные зависимости вязкости шлаков №7-11.

Secondly, the excess of **CaO** present in calcium borate, reacting with forsterite, lowers the amount of the latter (Table 3):

$$CaO + 2MgO{\cdot}SiO_2 = (CaO{\cdot}MgO{\cdot}SiO_2) + MgO$$

But the **MgO** released in this case, crystallizing in the form of more than forsterite refractory periclase (M – in Table 3), reduces the effect of **B_2O_3**. In this regard, pure boric anhydride having a melting temperature of 450°C or borate ore with a fusibility of 1050°C are more effective than relatively refractory (tcr. = 1230°C) and contributing a lot of **CaO** calcium borate. With a calcium borate consumption of 10%, the crystallization temperature drops from 1698 to 1610°C, i.e. by 880°C. If the same amount of **B_2O_3** is added with pure boric anhydride or borate ore, then the temperature of the beginning of crystallization decreases by 150°C, i.e. almost twice as much as was shown by us in previous studies.

Figure 3 shows the effect of slag additives produced by refined ferrochrome on the physical properties of the HCFC slag. These compounds are also highly mobile (less than 0.5 Pa *s) at high temperatures, since the initial structure is mostly preserved, and the added slag is almost entirely composed of isolated **SiO_4** tetrahedra of bicalcium silicate, the content of which in the RFC slag reaches 72.8% (Table 3). With the addition of RFC slags, the temperature of the beginning of crystallization of HCFC slags decreases (Table 4). This is due to the appearance of a relatively low-temperature triple compound **$CaO*MgO*SiO_2$** (CMS in Table 3) as a result of the interaction of the main components of these slags:

$$2\,MgO{\cdot}SiO_2 + 2CaO{\cdot}SiO_2 = 2(CaO{\cdot}MgO{\cdot}SiO_2)$$

The temperature range of crystallization of slags is small and does not exceed 50°C (Table 4).

Figure 4 shows the effect of expanded clay additives on the viscosity of refined ferrochrome production slags. Both the initial and the slags with the addition of melting are very mobile (0.25-0.50 Pa*s).

Table 3

Phase composition of industrial slags

Кесте 3

Өндірістік қождардың фазалық құрамы

Таблица 3

Фазовый состав производственных шлаков

№ slag	Phase composition, %													
	M	*CMS*	*M_2S*	*MA*	*MCr*	*FCr*	*C_2MS_2*	*CMS_2*	*CAS_2*	*$M_2A_2S_5$*	*C_2S*	*CCr*	*C_3MS_2*	*C_2AS*
1	0.50	4.83	57,66	23,86	5,84	7,29								
2			56,61	27,51	2,64	3,14	6,71	3,35						
3			60,80	26,03	1,14	2,52	0,42	9,06						
4			62,13	23,30	1,67	2,49		5,44	4,94					
5			62,56	22,53	2,31	2,49		3,66	6,43					
6			64,42	20,37	1,91	2,49			10,44	0,34				
7	1,44	7,06	61,06	26,06	2,45	1,90								
8	1,86	10,58	57,10	25,55	2,33	2,55								
9	1,42	9,88	59,14	25,27	3,02	1,24								
10	2,09	12,29	54,14	24,54	3,74	3,17								
11	2,04	14,16	51,99	24,84	4,06	2,89								
12	2,11	8,46	60,23	26,03	1,59	1,55								
13	2,70	11,28	57,97	25,63	0,81	1,58								
14	3,12	12,62	54,07	25,37	3,23									
15	2,12	15,97	54,76	23,94	1,31	1,86								
16	3,09	18,32	50,94	23,96	2,11	1,55								
17	8,92			7,74	6,65	3,45					72,86	0,35		
18	4,77			7,82	2,21	9,37					38,68		37,11	
19				6,80	2,24	3,73					1,33		80,93	4,94
20		19,33			2,27	3,17	2,70						53,46	18,76
21		16,45			2,39	3,17	21,49						36,05	20,43
22		6,517			3,58	3,14	58,88						7,44	20,43

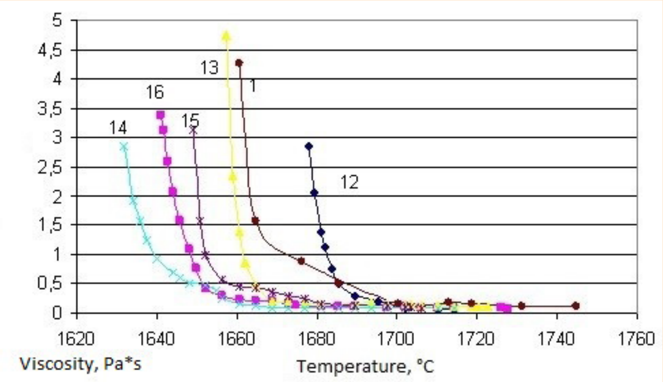

Figure 3. Temperature dependence of slag №12-16 viscosity.
Сурет 3. №12-16 қождардың тұтқырлылығының температураға тәуелділігі.
Рис. 3. Температурная зависимость вязкости шлаков №12-16.

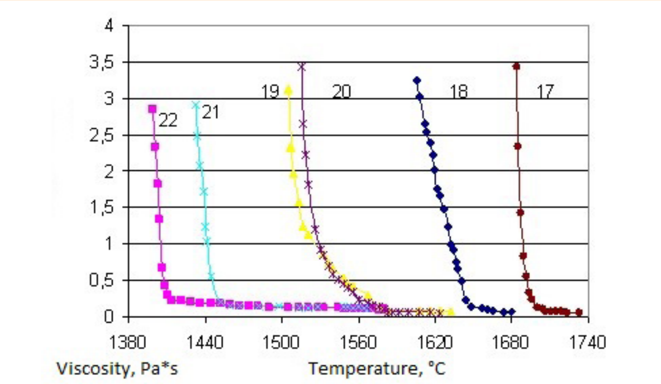

Figure 4. Temperature dependence of slag №17-22 viscosity.
Сурет 4. №17-22 қождардың тұтқырлылығының температураға тәуелділігі.
Рис.4. Температурная зависимость вязкости шлаков №17-22.

The introduction of expanded clay reduces the temperature of the beginning of crystallization of slags and extends the crystallization interval. But all of them are «short», i.e. they crystallize quickly. Expanded clay is not one of the classic fluxes such as fluorides, borates, chlorides, sodium compounds, which intensively reduce the refractory properties of charges and slags. And therefore, only at high clay consumption can a noticeable (more than 100°C) decrease in the crystallization temperature be achieved (Table 4). This is due to a decrease in the content of the highest temperature phase in it – bicalcium silicate (tcr. = 2130°C). But the assimilation of a large amount of clay in a ladle is difficult, preferably in a heated container.

With the addition of 15% expanded clay, the slag completely leaves the field of bicalcium silicate (Table 3) and for this reason should not disintegrate. This consumption (15%) it can be reduced due to the presence of passive stabilizers (**Cr_2O_3,** etc.) in the initial slag, which must be verified experimentally.

In the case of loading the studied additives into the furnace, it is necessary to assess their impact on the technical and economic indicators of melting, in the bucket variant – the sufficiency of heat for their assimilation.

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