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INTERPHASE PHENOMENA DURING CONTACT OF FERROCHROMIUM WITH NONMETALLIC INCLUSIONS AND SLAGS

by

R. B. Lobzhanidze, A. F. Filippov, and P. P. Yevseyev

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Interphase interaction of ferrochromium with inclusions and slags was studied. Wetting of nonmetallic inclusions by ferrodes was studied on alumina, silica, and magnesium oxide substrates. The effect of CrO on slags was examined; it was concluded that its accumulation in slags lowers their refining properties.

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П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

INTERPHASE PHENOMENA DURING CONTACT OF FERROCHROMIUM WITH NONMETALLIC INCLUSIONS AND SLAGS

R. B. Lobzhanidze, A. F. Filippov, and P. P. Yevseyev

Increasing the quality of smelted alloy steels and alloys is inseparably connected with an increase in the degree of nonmetallic inclusion contamination of the ferrous alloys (especially ferrochromium) used for the alloy [1]. The degree to which nonmetallic inclusions are removed from ferrous alloys during treatment with slag melts depends, other conditions being equal, on the composition of the metal, slag, and inclusions and on the interphase phenomena on the contact boundaries. In this work a study is made of the interphase interaction of ferrochromium with inclusions and slag.

Surface tension and density of the ferrochromium. The method of maximum pressure in a bubble was used to measure the density and surface tension. A detailed description of the installation and procedure for this research was given in work [2]. A 120-g metal sample was melted in an alundum crucible in argon; oxygen and nitrogen were removed by passing through titanium sponge heated to 900°C. Bubbles of inert gas were blown out at the end of an alundum capillary with an outer diameter of 6-7 mm. Accuracy in measuring density and surface tension was determined at ±5% and ±3%, respectively.

The chemical composition of the metal (%) and the results of the study have the following values:

Cr	Si	C	P	S	O	Al	(1) σ, эрг/см²	(2) Плотность, г/см³
71,50	0,1	0,06	0,05	0,02	0,34	0,05	1010	6,96
70,50	0,98	0,05	0,04	0,03	0,37	0,055	970	6,89
74,9*	0,1	0,026	—	—	—	—	1182	—
68,2*	1,09	0,025	—	—	—	—	960	—

*Data of O. S. Bobkova [3].

KEY: (1) σ, erg/cm²; (2) Density, g/cm³.

The measured surface tension of the ferrochromium (970-1010 erg/cm²) was found to be substantially lower than the calculated value (1370 erg/cm²) for the two-component system Fe-Cr, as obtained from the Shishkovskiy equation:

$$\sigma = \sigma_{Fe} - 2000 \lg [1 + (F_i - 1) N_i], \text{ erg/cm}^2, \qquad (1)$$

where F_i is an empirical constant equal to 1.75 for chromium;

N_i is the mole fraction of chromium in ferrochromium.

The lower values of surface tension for ferrochromium are explained by the presence in the metal of the surface-active elements C, P, and S and, especially, oxygen. Depending on the silicon content the density of the ferrochromium at 1700°C varies from 6.96 to 6.89 g/cm³.

Wetting of nonmetallic inclusions by ferrochromium. For the study of interphase phenomena on the ferrochromium/inclusion boundary substrates were prepared of alumina, silica, and magnesium oxide. The substrates were polished with diamond wheels to obtain a level surface. Studies were carried out on an installation with a horizontal tubular graphite heater in an atmosphere of purified argon.

Drops of metal weighing 5-8 g, located on a substrate which was leveled horizontally with an optical sight, were photographed 2-3 times at 1700°C through quartz glass installed in the front water-cooled cover of the furnace; photography interval was 3 min.

The stable edge angle was measured on the negative images of the drops by means of a projector. Angle measurement accuracy was ±3 degrees. The edge angles found and the surface tension were used to calculate the work of adhesion and interphase tension on the metal/inclusion boundary by the formulas

$$W_{в} = \sigma_{м}(1+\cos\theta) \text{ erg/cm}^2; \tag{2}$$

$$\sigma_{м-в} = \sigma_{в} - \sigma_{м}\cos\theta \text{ erg/cm}^2. \tag{3}$$

[в = inclusion]

The approximate results at 1700°C indicated surface tension of ferrochromium equal to 1000 erg/cm^2, while $\sigma_{в}$ was 905 erg/cm^2 for Al_2O_3 [4], 1000 erg/cm^2 for MgO [5], 307 erg/cm^2 for SiO_2 [5].

Wetting the various oxide substrates with ferrochromium at 1700°C gave the following results:

(1) Материал подложки	(2) θ, град.	(3) $W_{а}$, эрг/см²	(3) σ, эрг/см²
SiO_2	73	1293	14
Al_2O_3 . . .	90	1000	905
MgO	125	425	1575

KEY: (1) Substrate material; (2) θ, deg.; (3) erg/cm^2.

The largest edge angle θ is obtained for the magnesium oxide substrate (125 deg.). With an increase in the chemical interaction between the substrate and the metal the angle is reduced. The greatest spreading of the metallic melt over the substrate is observed with the oxide of smallest thermodynamic strength — silica. Other conditions being equal, the rate at which inclusions float up out of the metallic melt can vary in accordance with values of σ_{M-B}. Inclusions of MgO and Al_2O_3 should have a rate of removal several tens of times greater than the silicate particles.

Interphase tension on the ferrochromium/slag boundary. The separation of the slag and metallic phases in the bath depends on the magnitude of wetting of the metal by the slag. There is special interest in the influence of the chromium oxide appearing in the slag during chromium alloy production on the interphase interaction of these two phases.

Study of interphase tension on the metal/slag boundary was carried out by the "drop on drop" method on an installation for studying the wettability of oxide substrates by the metal. Slag was fed onto the surface of the molten metal over an alundum tube past upward through an opening in the furnace.

Drops of molten slag were photographed on contrast film with a "Start" camera with a "Jupiter-11" telephoto lens. The edge angle was measured from the negative images by means of a projector; measurement accuracy was ±3 degrees. The value of the edge angle was found experimentally as the average of 3-5 measurements.

Calculation of interphase tension and work of adhesion was accomplished by the following formulas:

$$\sigma_{м-ш} = \sqrt{\sigma_м^2 + \sigma_ш^2 - 2\,\sigma_м\sigma_ш\cos\theta},\ \mathrm{erg/cm^2} \qquad (4)$$

$$W_a = \sigma_м + \sigma_ш - \sigma_{м-ш}, \qquad (5)$$

[ш = slag]

The table and the figure show the results of investigation of the influence of chromium oxide on the properties of the interphase boundary of the metal with the slag.

Surface properties of slags with additions of chromium oxide at the boundary with ferrochromium at 1700°C.

(1) Номер шлака	(2) Химический состав шлака, %					(3) $\sigma^{*}_{шл}$ эрг/см²	(4) θ град.	(3) W_a эрг/см²	(5) Межфазное натяжение $\sigma_{м-ш}$ эрг/см²	(3) $W^{**}_{к.шл}$ эрг/см²	(3) S^{***}, эрг/см²
	CaF_2	CaO	Al_2O_3	BaO	Cr_2O_3						
1	97,25	0,72	—	—	—	250	24	479	771	500	—21
2	95,37	0,88	—	—	0,69	265	43	440	825	531	—91
3	94,52	1,12	—	—	3,00	272	36,5	475	797	544	—69
4	92,67	1,60	—	—	5,08	272	25	510	761	543	—33
5	90,25	1,80	—	—	7,78	278	25	523	755	557	—34
6	72,52	4,32	—	20,89	—	252	43	419	833	504	—85
7	78,38	4,22	—	21,02	1,10	255	41	431	824	510	—79
8	69,09	4,22	—	20,82	2,65	258	41	436	822	516	—80
9	67,23	3,60	—	19,71	6,90	274	27,5	508	766	548	—40
10	64,65	2,50	30,50	—	—	236	43,5	411	825	473	—62
11	60,19	7,55	30,60	—	1,29	252	41	425	826	503	—78
12	55,64	7,98	30,70	—	3,26	260	38	450	810	520	—70
13	50,96	10,30	31,54	—	5,82	265	36,5	469	796	530	—61
14	49,54	11,42	30,26	—	7,58	270	26,5	505	765	541	—36
15	4,25	41,98	53,25	—	—	485	46,5	753	731	969	—216
16	4,05	41,67	53,08	—	0,52	511	45	779	732	1022	—243
17	4,10	41,36	52,56	—	1,41	519	44	798	721	1038	—240
18	3,89	41,05	51,39	—	3,40	515	44	792	722	1029	—237
19	3,80	40,75	50,06	—	5,21	516	41	820	696	1032	—212
20	3,60	38,48	50,84	—	6,68	521	40	835	686	1042	—207

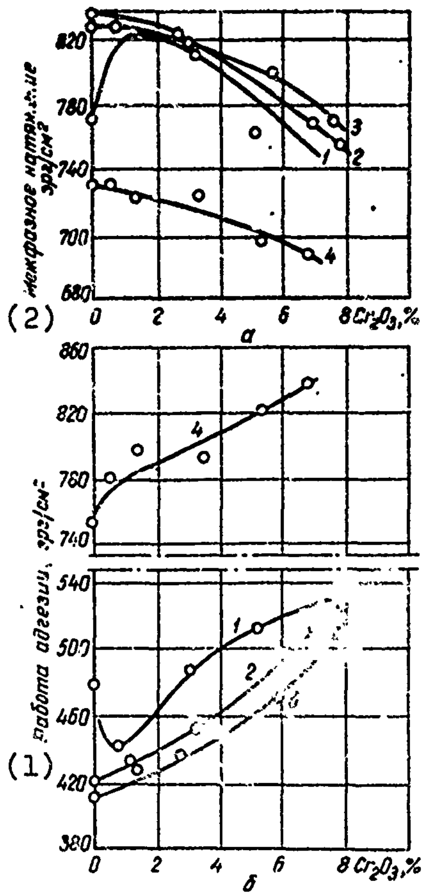
*Values of surface tension of slags were obtained in this work.

**Work of slag cohesion $W_{к.шл} = 2\sigma_{ш}$.

***Spreading coefficient $S = W_a - W_{к.ш}$.

KEY: (1) Number of slag; (2) Chemical composition of slag, %; (3) erg/cm²; (4) deg.; (5) Interphase tension $\sigma_{м-ш}$ erg/cm².

The magnitude of interphase tension on the metal/slag boundary is determined by the difference in the structure of the contacting phases. The smaller this difference the smaller the interphase tension and the better they wet one another. The introduction of chromium oxide into a calcium fluoride melt first reduces and then increases the work of adhesion between the chromium alloy and the slags (see figure). The influence of additions of chromium oxide on W_a and $\sigma_{м-ш}$ for melts of CaF_2–BaO, CaF_2–Al_2O_3, and Al_2O_3–CaO is manifested differently in the qualitative sense.



Influence of chromium oxide on interphase tension (a) and work of adhesion (b) of slags vs. ferrochromium at a temperature of 1700°C: 1 – slags 1-5; 2 – slags 6-9; 3 – slags 10-14; 4 – slags 15-20.

KEY: (1) Work of adhesion, erg/cm^2; (2) Interphase tension, erg/cm^2.

An increase in the adhesion of chromium slags to ferrochromium creates additional difficulties for separating the metallic and slag phases. In this respect the lime-alumina slags are poorest, since they have the highest work of adhesion to the chromium alloy as compared with the fluoride slags (see table). Practice in ferroalloy production indicates a similar influence of chromium oxide: slags containing a greater quantity of chromium oxides show more welding to the ingots.

S. B. Yakobashvili [6] established that interphase tension of a flux with a high content of silicon oxide (∿40%) and magnesium oxide (∿35%) was reduced from 905 erg/cm^2 for low-carbon steel to 700 erg/cm^2 when 9.16% Cr was introduced into it. This is connected with oxidation of the chromium metal and transfer of chromium oxide into the slag. Enrichment of the slag melt with chromium oxide brings the structure of the contacting phases closer together and thus reduces interphase tension.

From the point of view of removing inclusions from metal it is best to use slags which have high interphase tension with the metal. Among the investigated slags these include the high-fluoride fluxes with interphase tensions of 770-830 erg/cm^2 (see table). Lime-alumina fluxes have smaller interphase tension (730 erg/cm^2) and in this respect their application is less desirable. The introduction of chromium oxide in all cases reduces $\sigma_{\text{м-ш}}$, which lowers the conditions for removing inclusions from the metal.

Consequently, accumulation of chromium oxide in the slag lowers its refining properties.

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