Effect of Additions of Aluminosilicate and Silicate Materials on the Softening Temperature of Chromite Ore

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Abstract—The temperatures of the beginning and end of softening and the temperature range of softening of the fines of the rich chromite ore of the Donskoy Ore Mining & Processing Plant in Kazakhstan are experimentally determined. The following natural and technical silica-containing materials, which are considered as fluxing additions to decrease the melting temperature of the chromite ore, are investigated: aluminosilicate clays, microsilica, and quartzite of various fractions. The effect of additions of the natural and technical silica-containing materials on the temperatures of the beginning and end of softening and the temperature range of softening of the chromite ore of DODPE is analyzed. The influences of various materials and their fraction compositions on the temperature of softening of the chromite ores are compared.

INTRODUCTION

The Kempirsai deposit in Kazakhstan is the largest chromite ore deposit in the CIS space (confirmed resource of 300 mln t, which accounts for 95% of the total CIS resource). The annual extraction of the Donskoi Ore-Dressing and Processing Enterprise (DODPE) is 4.0 mln t, and about 50% of them are represented by fines and the wastes of mining and beneficiation, which are accumulated at piles [1]. The reserves of these types are ~1.9 mln t poor ores with an average Cr_2O_3 content of ~35.3%, ~13.4 mln t off-grade ores with an average Cr_2O_3 content of ~21.2%, and 5 mln t beneficiation tails with an average Cr_2O_3 content of ~30.6% [2].

Because of deficient lump ore, enterprises have to consider the possibility of sintering of the fines of rich chromite ores (>45% Cr_2O_3) and the use of off-grade (in Cr_2O_3 content) ores (29−35%) in production. Agglomeration has the maximum output among the sintering methods. As compared to pelletizing, this technology does not require additional fragmentation of ore raw materials.

The main problem of the agglomeration of chromite ores is related to their high melting temperature, which influences the sintering temperature and the resistance of equipment and determines the necessity of choosing fluxing additions. The softening mechanism is rather complex, since chromium spinelide $(Fe,Mg)O_n \cdot (Cr,Fe,Al)_2O_3$ has a high melting temperature ($T_m > 1800°C$) and sintering is accompanied by a decrease in the pores size in the material, closer contact between particles, solid-phase mineral formation, and redox processes. The quantity and composition of gangue, which has a relatively low melting temperature, and fluxing materials play an important role in the case of chromium ores.

A decrease in the melting temperature during the agglomeration of chromite ores is most often achieved by additions of small fractions of quartzite. Magnesite and quartzite are used as fluxing additions in the agglomeration practice in Japan [3]; sodium silicate, quartzite, quartz sand, silicate glass breakage are used in the Russian Federation [4]; and carbon−silicon shale, boron-containing additions [5], schungite ores [6], microsilica, and quartzite [7] are used for these purposes in Kazakhstan. When choosing an addition among these materials, it is necessary to take into account possible minimization of the transport and material costs apart from a decrease in the sintering temperature of chromite ores.

The temperature of the onset ($T_{s.s}$) and end ($T_{f.s}$) of softening and the temperature range of material softening (ΔT) depend on the mineralogical composition of the material, the degree of contacting of particles of different minerals, the particle size, and the physical state of particles. To a first approximation, these parameters determine the lower temperature boundary of the melting zone [8], i.e., the beginning of formation of a liquid phase that is necessary to form a strong agglomerated cake, and make it possible to estimate the reducibility of ores (for shaft furnace conditions, it is desirable to have a high temperature of the onset of softening and a short softening range [9]). Aluminosilicate clays are sufficiently universal silica-containing materials according to their abundance in nature and cost. The purpose of this work is to estimate

Table 1. Chemical composition, temperature, and softening range of samples 1'−8'

Sam-ple	Material	Component content, wt %								Temperature, °C		
		Cr_2O_3	SiO_2	Al_2O_3	MgO	CaO	FeO	S	P	$T_{s.s}$	$T_{f.s}$	ΔT
1'	Ekibastuz clay	−	58.24	15.88	2.95	1.30	7.10	<0.03	<0.03	769	1128	369
2'	Buskul' clay	−	51.8	29.6	3.07	0.3	11.63	<0.03	<0.03	927	1545	618
3'	Karasorsk clay	−	59.9	18.3	0.93	0.83	15.42	<0.03	<0.03	944	1214	270
4'	Microsilica (0.1−0.5 μm)	−	95.5	0.53	1.04	0.42	0.74	0.15	0.03	915	1467	552
5'	Pervoural'sk quartzite (fines −2 mm in size)	−	97.6	1.2	Unavailable	0.1	0.27	<0.03	0.014	1620	1700	80
6'	The same (2−3 mm in size)	−	97.6	1.2	"	0.1	0.27	<0.03	0.014	1660	1710	50
7'	DODPE ore (3−5 mm in size)	47.7	9.7	5.0	22.2	0.5	11.5	0.022	0.010	1410	1820	410
8'	The same (−3 mm in size)	48.2	8.58	7.08	20.6	1.04	11.9	0.023	0.015	1221	1664	443

their fluxing ability to decrease the softening temperature of chromium ores.

EXPERIMENTAL

Table 1 gives the chemical compositions of the chromite ore of DODPE to be studied and a number of fluxing additions. Medium specimens were taken from samples by quartering according to State Standard GOST 26136−84.

The temperatures of the onset, end, and softening range were determined according to State Standard GOST 26517−85 [10]. The materials were preliminarily milled and screened to produce a material with a particle size of 3−5 mm (flux fraction size of 2−3 and 3 mm) and placed in a crucible. The compressed material layer height was 50 ± 1 mm. Experiments were carried out at a constant load on a material, which was transferred through a rod pressing from above, and upon heating in an argon flow at a rate of 10°C/min. The temperature of the onset of softening was taken to be the temperature at which the rod was submerged into a sample to a depth of 1% of the total layer height, and the temperature of the end of softening was taken to be the temperature at which the rod submersion depth in a material (shrinkage Δl, %) was 40% of the initial layer height. For all samples, experiments were repeated at least three times. The temperature of the onset of softening was calculated and the arithmetic mean of the temperatures of the onset of softening of three identical samples, and the softening temperature range was calculated as the difference between the temperatures of the end and onset of softening.

RESULTS AND DISCUSSION

Table 1 and Fig. 1 present the temperatures of the onset and end of softening and the temperature ranges of softening of the chromite ore fines of DODPE
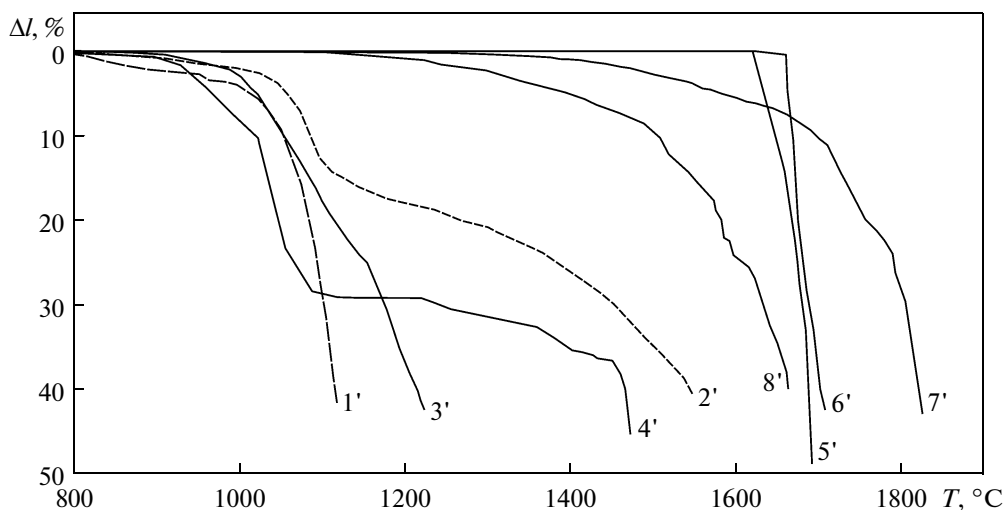

Fig. 1. Shrinkage of samples 1'−8' of the initial charge materials vs. the heating temperature (see Table 1).

Table 2. Temperatures of the onset ($T_{s.s}$) and end ($T_{f.s}$) of softening and the temperature range of softening (ΔT) of samples 1–11 of the chromite ore of DODPE (3–5 mm in size) with various fluxing additions

Sample	Addition material	Addition content*, wt %	Temperature, °C		
			$T_{s.s}$	$T_{f.s}$	ΔT
1	Quartzite (fines −2 mm in size)	5	1145	1550	405
2	The same	10	1066	1477	411
3	Quartzite (2−3 mm in size)	10	1159	1550	391
4	Microsilica (0.1−0.5 μm)	5	1107	1511	404
5	The same	10	1110	1509	399
6	Ekibastuz clay	5	1128	1497	369
7	The same	10	1103	1449	346
8	Buskul' clay	5	1104	1569	465
9	The same	10	1090	1488	398
10	Karasorsk clay	5	1140	1605	465
11	The same	10	1040	1453	413

* With respect to the ore mass.

(fractions 3−5 and −3 mm insize), quartzite (2−3 and −2 mm), microsilica (0.1−0.5 μm), and aluminosilicate clays (2−3 mm).

A series of experiments on mixtures of the chromite ore of DODPE with various fluxes (clay, microsilica, quartzite) in an amount of 5 and 10 wt % were performed to estimate the effect of these fluxes on the ore shrinkage parameters during nonisothermal heating (Table 2, Figs. 2−4).

As follows from Table 1, the softening parameters of the fines of rich chromite ore (fraction −5 + 3 mm in size) differ substantially from those of the low-fraction (−3 mm) material.

It should be noted that a change in the quartzite particle size from 2−3 mm to −2 mm weakly influences the temperature of the end of softening (1710 and 1700°C, respectively) but decreases the temperature of the onset of softening from 1660 to 1620°C. Quartzite is characterized by the highest temperatures $T_{s.s}$ and $T_{f.s}$ and the narrowest softening temperature range (50−80°C) among the fluxing additions under study. In the case of microsilica addition (whose chemical composition is close to quartzite), we have $T_{s.s}$ = 705−745°C and the ΔT range is rather wide (552°C).

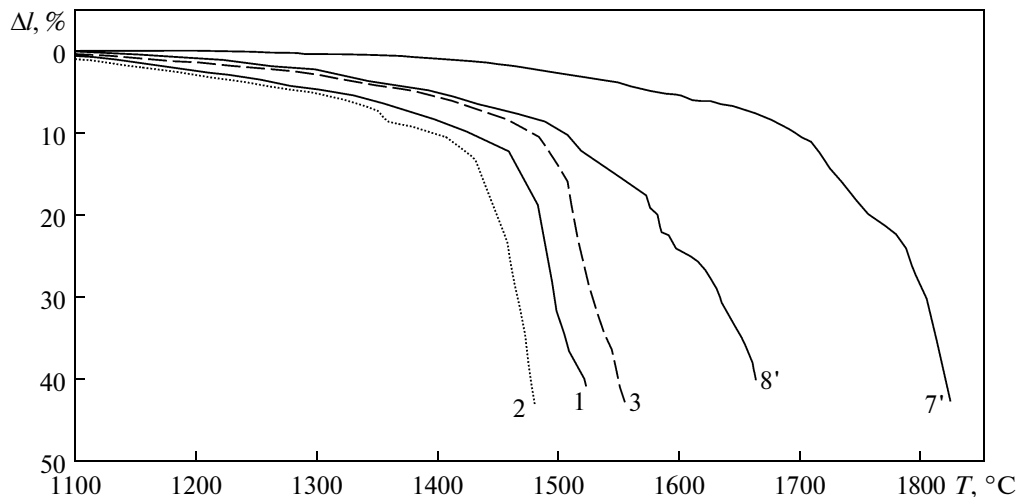The difference between the temperatures of softening of the clays under study (from Ekibastuz, Buskul',

Fig. 2. Shrinkage of samples 7' and 8' (see Table 1) of the chromite ore of DODPE with various particle sizes as compared to (1)−(3) shrinkage of mixtures of the chromite ore of DODPE with 5 and 10 wt % quartzite of various fractions at various temperatures (see Table 2).
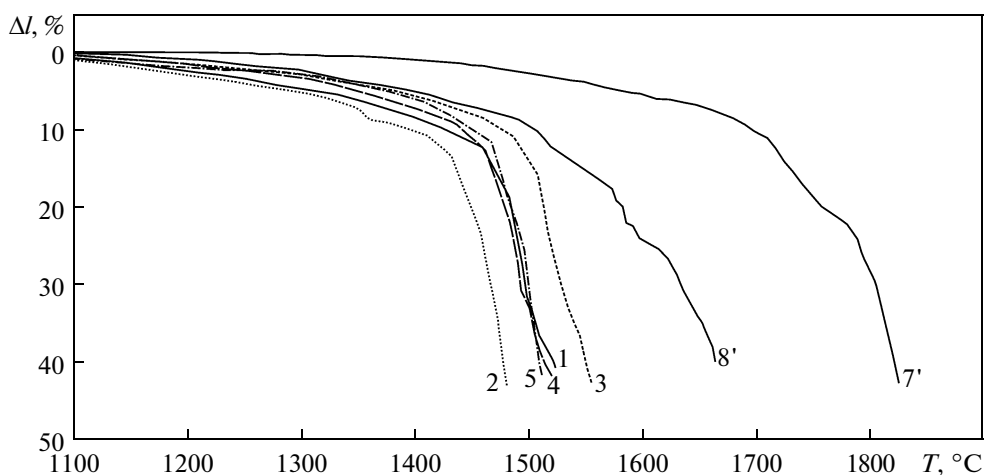
Fig. 3. Shrinkage of samples 7' and 8' (see Table 1) of the chromite ore of DODPE with various particle sizes as compared to (1)−(5) shrinkage of mixtures of the chromite ore of DODPE with 5 and 10 wt % quartzite and microsilica at various temperatures (see Table 2).
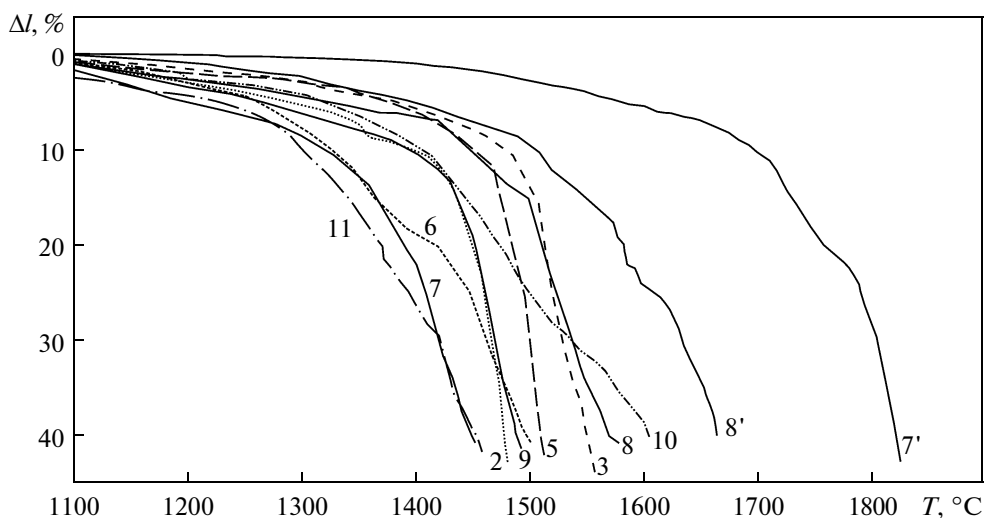

Fig. 4. Comparison of the temperature dependences of the shrinkage of sample 7' and 8' and samples 2, 3, 5−11 (see Table 2) of mixtures of the DODPE ore with the fluxes under study.

Karasorsk) is mainly related to the variations of the contents of Al_2O_3, SiO_2, and FeO, which form low-melting-point compounds (mainly fayalite $FeO \cdot SiO_2$ [11, 12]) and a liquid phase. This phase favors sintering of chromite ore particles at a lower temperature, in contrast to the interaction of the gangue of chromite ore with SiO_2 of quartzite or microsilica.

Clay sample 3' (Table 1, Fig. 1) has a relatively narrow softening range (270°C), and the temperature of the onset of its softening is higher (944°C) than that of sample 1' (759°C). The wide temperature range of softening of sample 2' (618°C) is likely to be related to a high alumina content as compared to other clay samples.

The influence of various types of fluxing additions to the softening temperature of chromite ore was studied when they were added in an amount of 5 and 10% of the ore mass (Table 2). Experiments with the addition of quartzite to chromite ore showed that its finest fraction (−2 mm) in an amount of 10 wt % led to a decrease in the temperature of the end of softening to 1477°C (Fig. 2).

Figure 3 shows the shrinkage of chromite ore with 5 and 10 wt % microsilica used as a flux (curves *4*, *5*) and compares it with a quartzite addition (curves *1−3*). The fragmentation of quartzite results in a substantial decrease in the temperature of the end of softening (to 1447 as compared to 1550°C), and the complexity of a uniform distribution of microsilica in a mixture with chromite ore in the crucible volume because of substantial differences in the fraction compositions of

the materials makes it possible to reach a larger decrease in the temperature of the end of softening when 10 wt % quartzite with a particle size of -2 mm is added (1477°C) as compared to the addition of 10 wt % microsilica (1509°C). As follows from the data in Fig. 3, the effect of quartzite fines (-2 mm) in an amount of 5 wt % and the effect of microsilica in an amount of 5 and 10 wt % on the shrinkage parameters of the chromite ore of DODPE are comparable, i.e., a decrease of $T_{f.s}$ from 1820°C to 1477 and 1509°C.

The addition of 5 wt % clay decreases the temperature of the end of softening of chromite ores from 1820 to 1497−1605°C (Fig. 4), which is comparable with the addition of 10 wt % quartzite fines (-2 mm in size; decrease to 1477°C). The addition of 10 wt % aluminosilicate clay decreases the temperature of end of softening most strongly, to 1449−1488°C.

As follows from Fig. 4, a decrease in the temperature of the end of softening is significant (down to 1497°C) upon the addition of 5 wt % Ekibastuz clay (sample 6). The decrease of $T_{f.s}$ is comparable with the addition of 10 wt % milled quartzite (sample 2, to 1477°C). The effects of 5 wt % Ekibastuz or Karasork clay (samples 6, 9) on $T_{f.s}$ differ (1497 and 1605°C, respectively), whereas the temperatures of the end of softening become close (1449 and 1453°C, respectively) when 10 wt % Ekibastuz or Karasork clay are added (samples 7, 11). This finding is likely to indicate a stronger effect of the ore particle size in this temperature range as compared to the flux content.

CONCLUSIONS

(1) We studied the temperatures of the onset ($T_{s.s}$) and end ($T_{f.s}$) of softening and the temperature range (ΔT) of softening of chromite ore and potential fluxing materials, compared them under the same conditions, and revealed substantial differences in their physicochemical properties.

(2) It was experimentally shown that fragmentation differently affects material shrinkage Δl (%) during nonisothermal heating under load and that the ratio of ore fraction size to the flux particle size is important (shown for a mixture of ore with microsilica).

(3) Aluminosilicate clays were shown to be a promising flux for the agglomeration of chromite ore fines, since they decrease the temperature of appearance of a liquid phase, which is required for sintering of chromium spinelide grains.

(4) To a first approximation, the effect of the type of flux on a decrease of the sintering temperature can be estimated from the temperatures of the onset and end of softening and the temperature range of softening.

(5) To develop technological recommendations for the agglomeration of chromite ores, it s necessary to obtain additional data on the behavior of materials upon heating due to the combustion of fuel in a layer, the required amount of coke, the rational batch moisture, and the optimal material particle sizes.

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