

## Effect of Addition of Silicate and Aluminosilicate Fluxes on Structure and Phase Composition of Chromium Sinter

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**Abstract**—The microstructure of the fluxes (aluminosilicate clays) tested during pilot sintering of the chromium ore fines of the Don ore-dressing and processing enterprise is studied. The composition of the liquid phase that forms upon softening of materials and bonds chromospinelide grains is analyzed by chemical, electron-probe, and X-ray diffraction analyses. The results demonstrate that the clays have a similar morphology and differ substantially in the phase composition of both the initial fluxes and the binder in the composition of the chromium ore sinter with clay additions. The phase composition of the binder formed upon addition of aluminosilicate clays is compared with the application of an anthropogenic silica-containing flux (microsilica). A relation between the phase composition of the initial fluxes and the aluminosilicate binder in the composition of chromium sinter is found, and the advantages of aluminosilicate clays are demonstrated.

**Keywords:** chromium ore, fluxes, clays, production wastes, sinter, strength characteristics, binder, X-ray diffraction analysis, and electron-probe microanalysis

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### INTRODUCTION

The basic problem of sintering the fines of a chromium ore is related to its high melting temperature, which affects the sintering temperature and, hence, the resistance of equipment. This problem is usually solved by choosing fluxing additions, in particular, small fractions of quartzite and its mixtures with magnesite [1]. Moreover, sodium silicate, quartzite, quartz sand, and breakage of silicate glass are applied in the Russian Federation [2, 3]. In Kazakhstan, carbon–silicon shales and boron-containing additions [4, 5], silica-containing microsilica, and quartzite [6] were used to perform sintering at different times.

In [7], we proposed to apply a number of aluminosilicate clays instead of “classic” fluxes, such as microsilica and quartzite, and studied the influence of additions of a number of silicate and aluminosilicate fluxes on the softening temperature of a chromium ore, which is a reference for estimating the lower temperature boundary of sintering [8]. It was shown that, along with the quantity of microsilica, quartzite, and aluminosilicate clays added to an ore, the softening temperature depends substantially

on the fraction compositions of both chromium ore and quartzite, which is most widely used [2, 3, 6]. As the particle sizes decrease, the temperature of the end of softening and, correspondingly, the lower temperature boundary of sintering decrease. Here, microsilica can be considered as a substitution for quartzite in the form of a maximally dispersed silicon-containing material.

The results of studying the softening temperature were used to determine the optimum quantity of flux in the pilot experiments on sintering chromium ore fines that were performed in the experimental shop of AO Aksu Ferroalloy Plant [9]. It was shown that the sintering rate was maximal and the strength characteristics of sinters were best when aluminosilicate clays were added to chromium ore. In comparison with other fluxing additions, these clays have the following advantages: lower costs of preparation for sintering as compared to the costs of disintegration and scattering of quartzite and the cost that is lower than that of microsilica, which is widely used in the production of high-quality concrete, by a factor of 2–3 [10].

For clays to be successfully applied as fluxes, it is necessary to refine the difference between the mechanisms of formation of a liquid phase and, then, the binder of chromium sinter and to study the structure of the binder in the sinters produced using classic silicate fluxes (quartzite, microsilica) and various aluminosilicate clays.

## EXPERIMENTAL

To study the influence of fluxes on the structure formation in the binder of chromium sinter, we took samples of initial clays and fresh cleavages of sintered ore raw materials with the same flux content, namely, microsilica and Ekibastuz, Karasor, and Biskul clays in an amount of 10 wt % of the ore fine mass, for an electron-microscopic investigation and X-ray diffraction (XRD) analysis (Table 1).

### *Microstructural Investigation*

Electron-microscopic studies were carried out on a Jeol JSM-7001F scanning electron microscope. X-ray fluorescence analysis was performed with an energy dispersive Oxford INCA X-max 80 spectrometer attached to the microscope. The sample surface was analyzed using secondary and backscattered electrons, and the maps of element distributions on the sample surfaces were plotted.

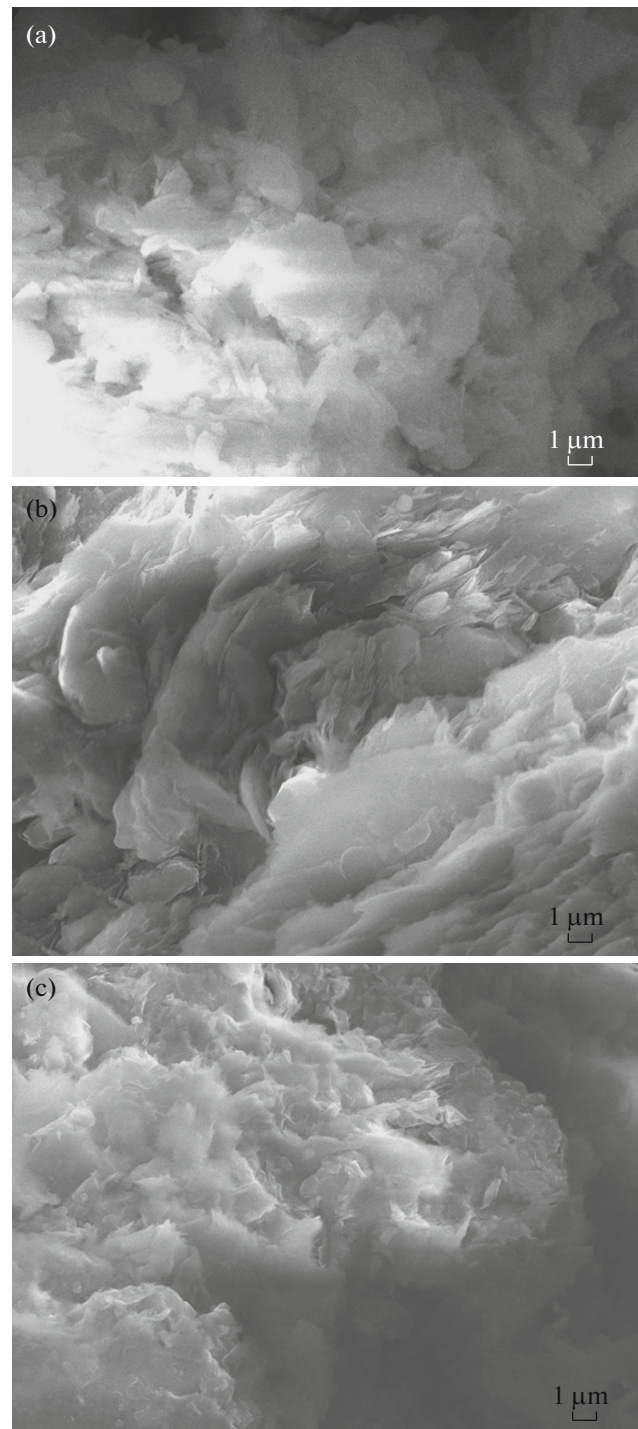
### *Phase Composition*

X-ray powder diffraction was used to determine the phase compositions of clay and ore samples. X-ray diffraction patterns were recorded at room temperature (298 K) on a D8 ADVANCE diffractometer (CuK $\alpha$  radiation, accelerating voltage of 40 kV, current of 40 mA, position-sensitive VANTEC-1 detector,  $\beta$  filter). X-ray diffraction patterns were recorded in the angular range 5°–81° at a step of 0.021° along the axis of diffraction angle 2 $\theta$  at an exposure of 493 s per point. X-ray diffraction patterns were interpreted using the DIFFRAC<sup>plus</sup> software package [11] and file PDF4 of ICDD (International Center for Diffraction Data) [12].

## RESULTS AND DISCUSSION

All three clay samples differ weakly in morphology despite their different chemical compositions. Their microstructure is represented by layered grains, which are made of individual thin flakes 0.5–10  $\mu\text{m}$  in diameter and are typical of clays (Fig. 1) This structure improves the cohesive properties of clays during subsequent moistening of a sintering charge due to the “overlapping” of neighboring flakes over a large area.

Fresh cleavages were prepared for an electron-microscopic investigation of sintered screened chromite with 10 wt % of flux. The best visualization of the morphology of grains and the binder was obtained under backscattered electron conditions (Fig. 2).



**Fig. 1.** Secondary-electron images of the microstructures of the clays of (a) Ekibastuz, (b) Buskul, and (c) Karasor deposits.

The bright regions in all images correspond to the phase that contains heavy elements (chromites), and the dark regions correspond to silicate phases. The black regions are pores in a silicate melt.

**Table 1.** Chemical compositions of the materials under study, wt %

Material	Cr <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	FeO	S	P	K <sub>2</sub> O	Na <sub>2</sub> O	Others
Ekibastuz clay	—	58.24	15.88	2.95	1.30	7.10	<0.03	<0.03	1.57	1.7	2.0
Buskul clay	—	51.80	29.60	3.07	0.30	11.63	<0.03	<0.03	1.52	2.7	0.5
Karasar clay	—	59.90	18.30	0.93	0.83	15.42	<0.03	<0.03	1.69	2.61	3.72
Microsilica (0.1–0.5 μm)	—	95.50	0.53	1.04	0.42	0.74	0.15	0.03	0.35	0.5	—
Chromium ore of Don GOK (3–5 mm)	47.7	9.70	5.00	22.20	0.50	11.50	0.022	0.01	—	—	—

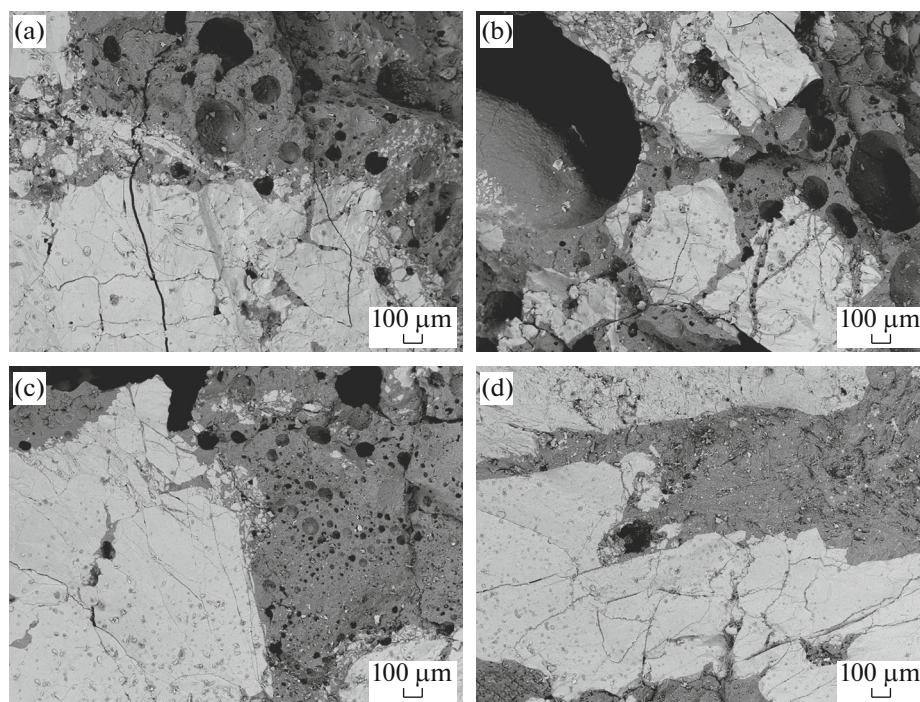
During sample preparation, cracks propagate through chromite grains rather than along the interface between chromite phases and the binder, which proves a good penetration and interaction between the chromite phases and the silicate melt.

All fluxes used to form a strong sinter of chromium ore fines are silicate and aluminosilicate materials, which have a significantly lower temperature of the end of softening than that of chromium ore (Table 2). The addition of these fluxes in an amount of 10 wt % substantially (by 310–370°C) decreases the softening

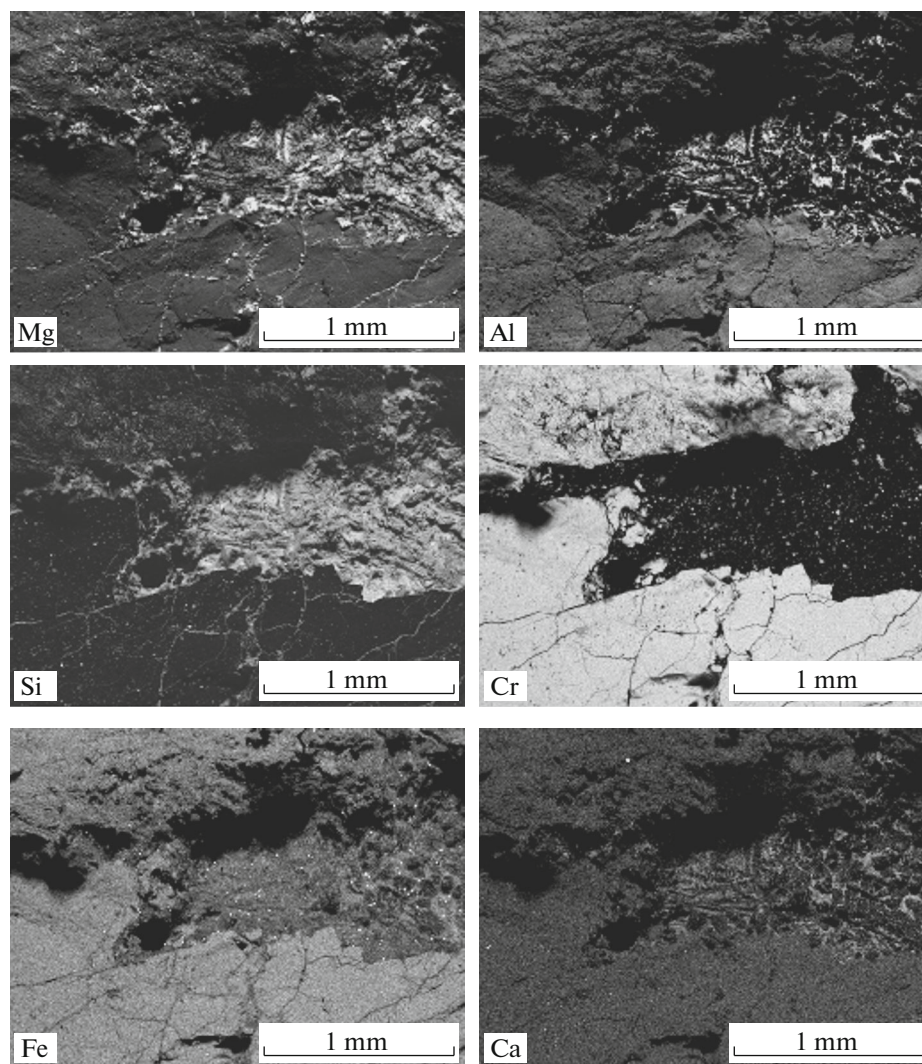
temperature (correspondingly, melting temperature) of chromium ore (see Table 2).

The use of microsilica, which is enriched in refractory silica (see Table 1), as a flux decreases the temperature of the end of softening of chromium ore by 310°C (see Table 2), and the application of low-melting-point clays additionally decreases (by ~50°C) the temperature of the end of softening.

To study the mechanism of formation of a chromium sinter binder based on some silicate and alumi-



**Fig. 2.** Backscattered-electron images of the microstructure of sintered chromium ore samples with the addition of 10% flux: (a–c) Buskul, Karasar, and Ekibastuz clays, respectively; (d) microsilica.



**Fig. 3.** Maps of element distribution over the area of a sintered chromium ore sample with 10% microsilica (Table 2, line 9).

nosilicate fluxes, we studied the microstructure and the phase composition of the sintered samples.

After sintering, the samples with all four versions of fluxes have a strong structure of the binder (Figs. 2a–2c), and the fraction of a glass phase in it does not exceed 20–40%. The number of coarse pores decreases when microsilica is added (see Fig. 2d).

To study the chemical compositions in various regions in the microstructure of sintered samples, we used micromapping to estimate the distribution of main elements over the polished section of certain area.

The composition of the binder in the samples prepared using fluxes of all types is the same: the bonding silicate phase is enriched in magnesium and iron oxides, which come from chromspinelide grains (Figs. 3–6). The softening temperatures of the clays (Table 2, lines 1–3), which are lower than that of

microsilica (Table 2, line 4), provide intensification of mineral formation, which promotes accelerated sintering of chromium ore due to a substantial decrease in the softening temperature of a mixture with the clays as compared to version 9 with the use of a silicate material (see Table 2, lines 6–8). The application of clays as fluxes, the composition of which causes their transition into a liquid state at lower temperatures, is likely to favor a more intense interaction with chromite grains, including the formation of glass-crystalline phases between them.

In all cases, the sinter phases contain aluminum and magnesium silicates irrespective of the type of applied fluxes, which makes it impossible to explain the differences in the strengths of the formed sinters and the sintering rates for different clays [9].

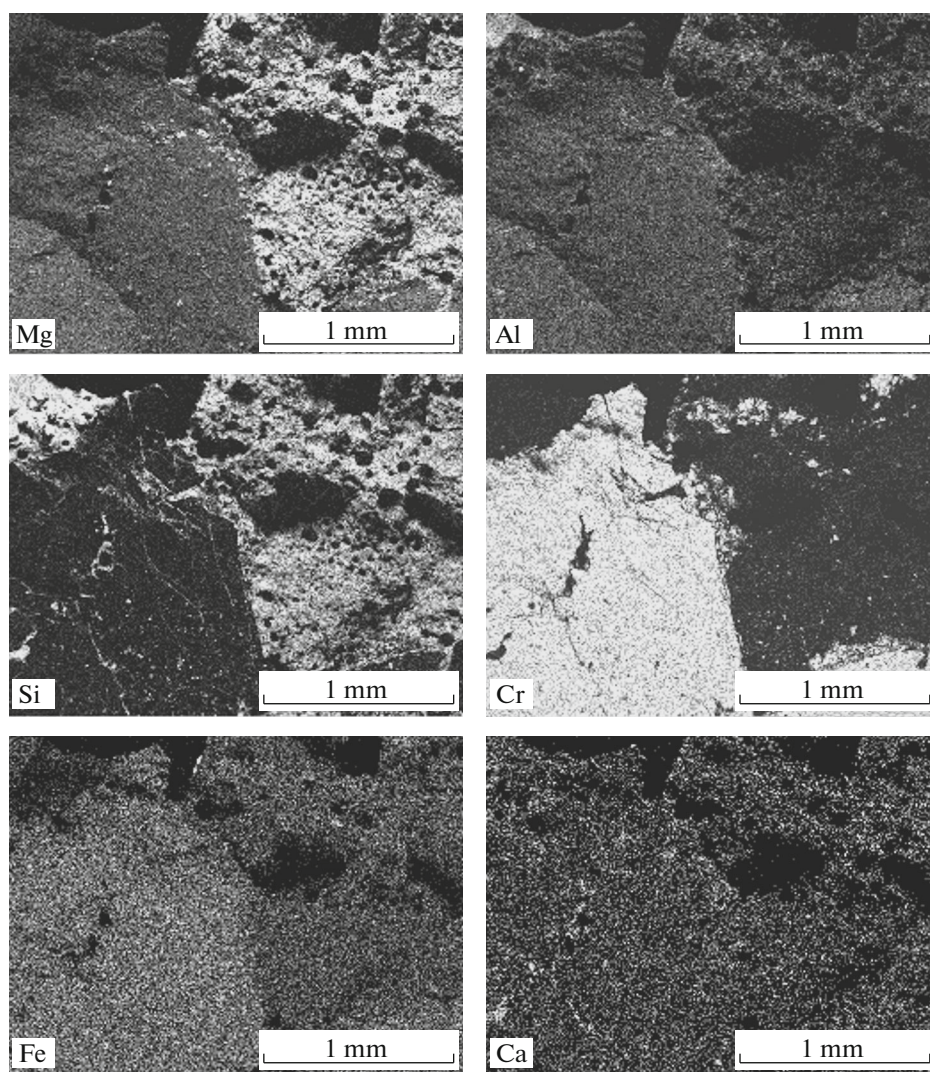


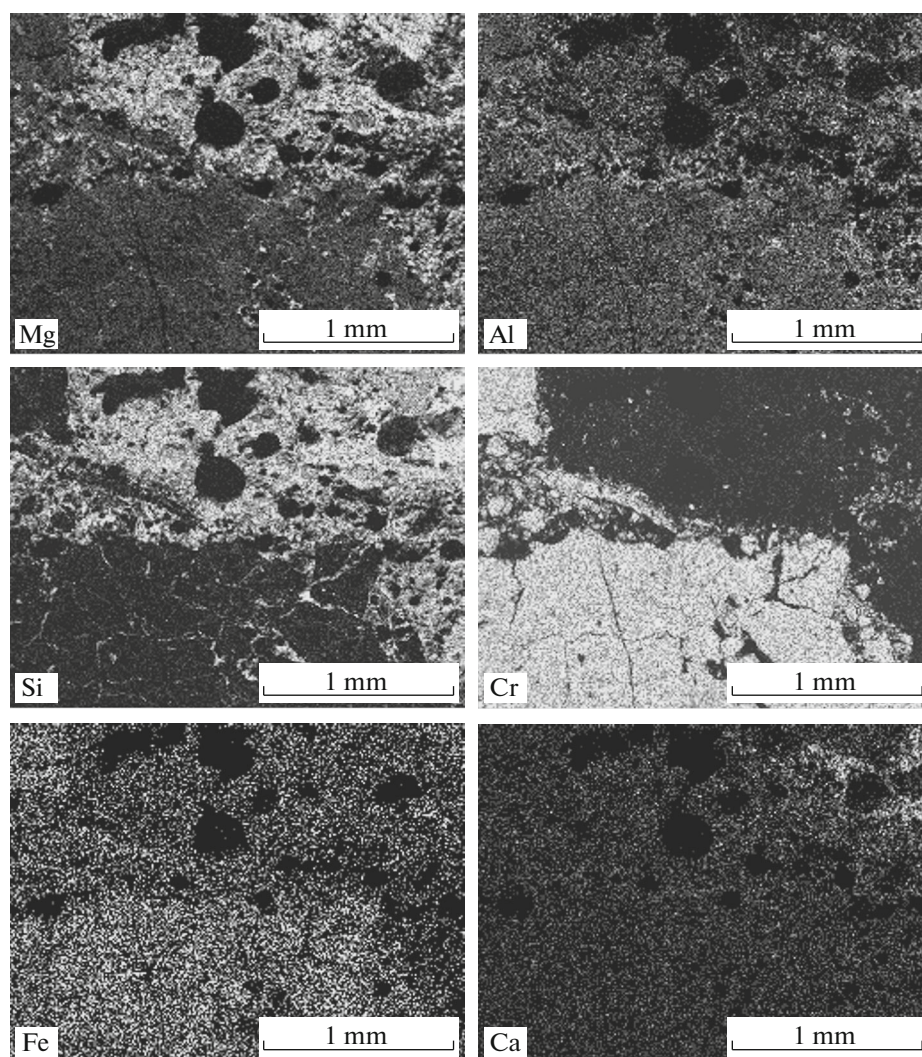
Fig. 4. Maps of element distribution over the area of a sintered chromium ore sample with 10% Ekibastuz clay (Table 2, line 6).

As follows from the results of XRD analysis of initial aluminosilicate clay samples, the kaolinite clays have close chemical compositions, belong to the same

type, and differ substantially in phase composition (Table 3). Figure 7 shows the X-ray diffraction patterns of chromium ore samples with added silicate and

Table 2. Temperatures of the onset ( $t_{o,s}$ ) and end ( $t_{e,s}$ ) of softening and the temperature range of softening ( $\Delta t$ ) of the initial materials and chromium ore samples with flux additions

No.	Material	Temperature		
		$t_{o,s}$	$t_{e,s}$	$\Delta t$
1	Ekibastuz clay	759	1128	369
2	Buskul clay	927	1545	618
3	Karador clay	944	1214	270
4	Microsilica (0.1–0.5 $\mu\text{m}$ )	915	1467	552
5	Chromium ore of Don GOK (3–5 mm)	1410	1820	410
6	The same + 10% Ekibastuz clay	1103	1449	346
7	" + 10% Buskul clay	1090	1488	398
8	" + 10% Karador clay	1040	1453	413
9	" + 10% microsilica (0.1–0.5 $\mu\text{m}$ )	1110	1509	399



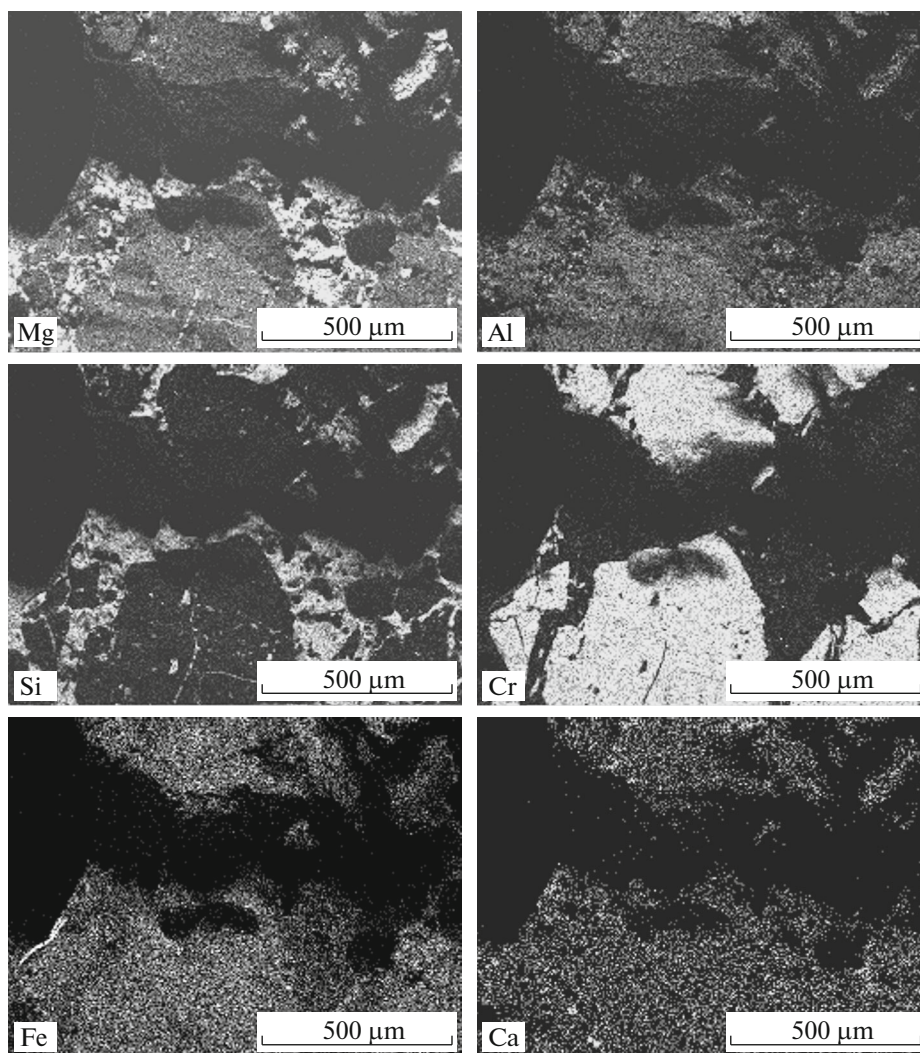
**Fig. 5.** Maps of element distribution over the area of a sintered chromium ore sample with 10% Buskul clay (Table 2, line 7).

aluminosilicate fluxes. Several phases are present in the chromium ore samples with flux additions after heating to the temperature of the end of softening, and

the main phase is chromium spinel. The binder contains a significant amount of magnesium olivine (forsterite)  $Mg_2SiO_4$ . Its relative fraction in the case of

**Table 3.** Phase compositions of aluminosilicate clays, wt %

Clay	Quartz	Muscovite	Kaolinite	Calcite	Albite
Ekibastuz	52.2	14.3	20.9	3.5	9.1
Buskul	15.7	12.3	72.0	—	—
Karador	29.6	30.8	39.6	—	—



**Fig. 6.** Maps of element distribution over the area of a sintered chromium ore sample with 10% Karasor clay (Table 2, line 8).

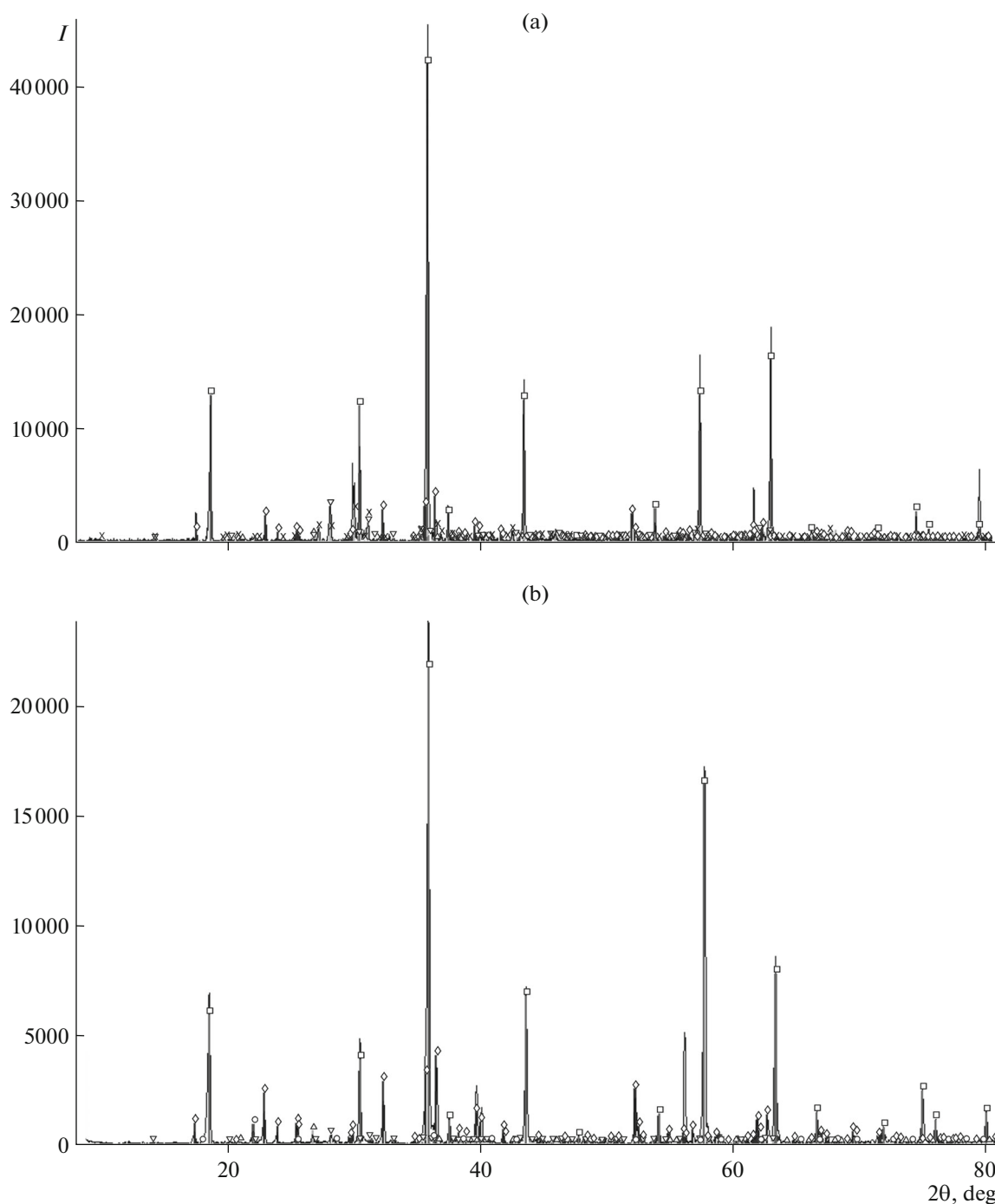
application of microsilica (Fig. 7a) or the Karasor clay (Fig. 7d) is approximately half the fraction in the case of introduction of the Ekibastuz clay (Fig. 7b) or the Buskul clay (Fig. 7c). The binder in all samples contains an insignificant amount of quartz.

The version of fluxing by a microsilica addition differs from the versions with other fluxes in the presence of significant amounts of enstatite  $Mg_2[Si_2O_6]$  and clinoenstatite  $Mg_2Si_2O_6$  (which is absent when other fluxes are added) in the composition of sinter (see Fig. 7a). This difference can be related to the influence of the dispersity of the fluxing material (0.1–0.5 μm) and its active reaction with MgO of the chromium ore and explains the higher temperature of the end of softening as compared to other samples despite a small fraction of the flux (Table 2, line 4).

The phase composition of the sample with added Ekibastuz clay is close to the version with the Buskul clay in the amount of forsterite in the binder composition, and cristobalite is present in the structure (see Fig. 7b).

The enstatite content in the sample with added Buskul clay is twice as large as that in other samples (see Fig. 7c). This sample is also characterized by the presence of mullite in the structure [13], the formation of which can be explained by a high  $Al_2O_3$  content (Table 1, 29.6 wt %) as compared to other clays.

The absence of various silicate phases, apart from forsterite and quartzite, in the amounts that are comparable with that in the microsilica-containing sample is likely to be associated with the formation of a non-crystallizing glass phase (Fig. 7d).



**Fig. 7.** X-ray diffraction patterns of chromium ore samples with the addition of 10% flux after heating to the temperatures of the end of softening: (a) microsilica; (b–d) Ekibastuz, Buskul, and Karasor clays, respectively.  $I$  is the absolute unit of reflected X-ray radiation. ( $\square$ ) Stands for chromite; ( $\diamond$ ) for forsterite; ( $\triangle$ ) quartz, ( $\nabla$ ) enstatite; ( $\times$ ) clinoenstatite; ( $\circ$ ) cristobalite; and ( $\bullet$ ) mullite.

## CONCLUSIONS

(1) The microstructure of the binder in the composition of chromium ore sinters with added silicate and aluminosilicate fluxes was studied. The main phases in the sinters are chromspinelide and forsterite.

(2) It was shown that relatively refractory chain silicates, namely, enstatite and clinoenstatite, were present in the binder composition in the case of microsilica, which is a silica-containing material.

(3) The application of aluminosilicate materials (clays) was shown to prevent the formation of enstatite,



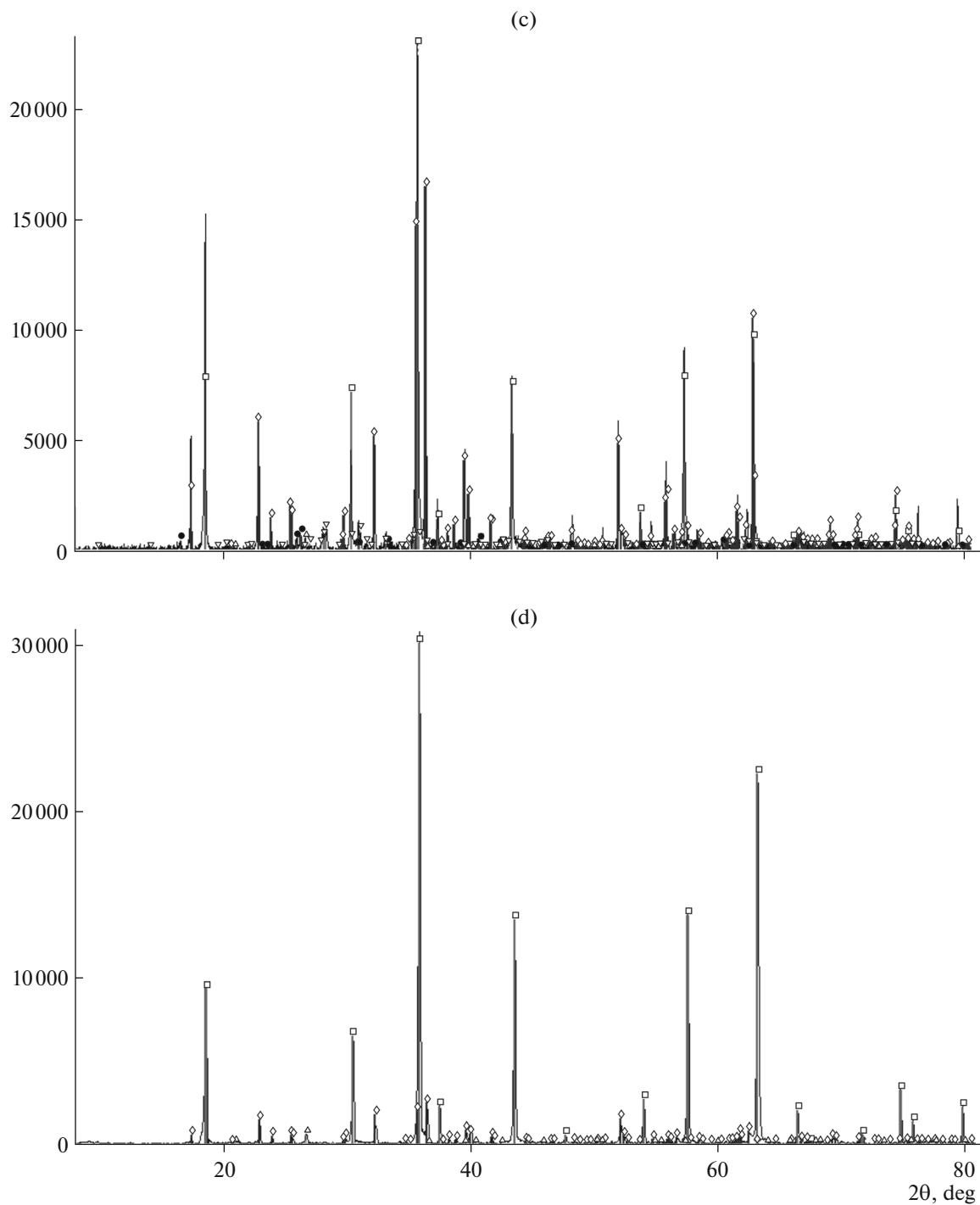


Fig. 7. (Contd.)

and a high content of kaolinite and muscovite in the clay composition improves the sintering parameters.

was performed using the equipment of the Center for Collective Use Ural-M.

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