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# Effect of Temperature on Chromite-Based Moulding Sands Bonded with Sodium Silicate

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## Abstract

In the paper, a research on effects of baking temperature on chromite sand base of moulding sands bonded with sodium silicate is presented. Pure chromite sand and its chromite-based moulding sand prepared with use of sodium silicate were subjected to heating within 100 to 1200 °C. After cooling-down, changes of base grains under thermal action were determined. Chromite moulding sand was prepared with use of 0.5 wt% of domestic made, unmodified sodium silicate (water-glass) grade 145. After baking at elevated temperatures, creation of rough layer was observed on grain surfaces, of both pure chromite sand and that used as base of a moulding sand. Changes of sand grains were evaluated by scanning microscopy and EDS analyses. It was found that changes on grain surfaces are of laminar nature. The observed layer is composed of iron oxide (II) that is one of main structural components of chromite sand. In order to identify changes in internal structure of chromite sand grains, polished sections were prepared of moulding sand hardened with microwaves and baked at elevated temperatures. Microscopic observations revealed changes in grains structure in form of characteristically crystallised acicular particles with limited magnesium content, intersecting at various angles. EDS analysis showed that these particles are composed mostly of chromium oxide (III) and iron oxide (II). The temperature above that the a.m. changes are observed in both chromite-based moulding sand and in pure chromite sand. The observed phenomena were linked with hardness values and mass of this sand.

**Keywords:** Foundry engineering, Chromite sand, Moulding sand, Baking temperature, Sodium silicate

## 1. Introduction

Chromite sand acquired from chromite ore, one of the most expensive materials used for base of moulding and core sands, is characterised by very good properties. Its favourable properties like resistance to heat and chemical agents result from spinel bonding with general formula  $A^{2+}B_2^{3+}O_4$  [1,2,3]. The main compounds in its composition are  $Cr_2O_3$  and FeO [2]. Chromite ores contain 31 to 58%  $Cr_2O_3$  and 13 to 21.6% FeO. Content of  $Cr_2O_3$  in chromite sand used in foundry practice should be at least 36% [2,3,4]. Melting point of chromite sand, ranging between

1700 and 1900 °C, depends on its included impurities [2]. Contamination with high-silica sand, increasing  $SiO_2$  content, results in creating a fusible compound and, in consequence, in burnings [2,5,6,7]. This compound has very high thermal conductivity [3] and linear thermal expansion of chromite grains at 1400 °C is ca. 1.4% [2]. Density of chromite sand ranges between 4.5 and 4.8 g/cm<sup>3</sup>. In comparison to high-silica sand, its bulk density is twice as big and thus binder content during manufacture of sandmixes must be adequately smaller [3]. So, moulding sands based on chromite sand should be prepared with use of high-quality binders with high bonding power [2,8]. The most often used binders are sodium silicate (water-glass) [9] and

synthetic resins [10]. In manufacture of small steel castings, chromite moulding sands are applied as unit sands. For solid steel and iron castings, they are applied as facing sands [2,3]. They do very well at making castings of manganese, carbon, high-manganese and chromium-nickel cast steels [1,2]. Moreover, chromite sand very well absorbs 2.45 GHz microwave radiation [11,12]. As the research showed, this is one of the most favourable types of base from those examined, intended for moulding sands containing water-glass, hardened by microwaves [13]. During preliminary examinations of microwave hardened and used-up chromite moulding sands containing sodium silicate, a change of colouration of base grains in touch with the cooling-down casting was observed, see Fig. 1.



Fig. 1. Discolouration of chromite sand base (bonded with sodium silicate) in the layers adjacent to iron casting

Colour of base sand in water-glass containing sandmix changed from black-oily to silver-glossy. An example of improving properties of moulding sands by baking the base at 950 °C for 10 h is mentioned in literature [2,3].

Considering the above-mentioned recommendations for baking, changes in used chromite moulding sand and high fraction of its absorbed microwave power, as well as the possibility of applying inorganic binders like water-glass, a research on the effect of temperature of poured alloy on chromite base of sandmixes was taken-up. The results should be helpful at determining directions of further research works on microwave heating of chromite-based moulding sands, with particular consideration of running the activation process similarly as for quartz-based sandmixes with water-glass [14].

## 2. Purpose and scope of the research

In order to determine changes occurring in chromite sand grains resulting from elevated temperature, a standard moulding sand was prepared. That sandmix was prepared using chromite sand produced by Magnesite Works "Ropczyce" S.A. and a selected grade of sodium silicate from Chemical Plant "Rudniki" S.A., with properties given in Table 1. For comparative purposes

and to determine influence of binder present during heating, parallel examinations were carried-out on pure chromite sand.

Table 1.

Basic parameters of moulding materials used in the research

Chromite sand base:				
Main fraction:		0.20/0.315/0.4		
Concentration of FeO [%]:		29.0		
Concentration of Cr <sub>2</sub> O <sub>3</sub> [%]:		46.5		
Concentration of MgO [%]:		9.8		
Concentration of SiO <sub>2</sub> [%]:		0.8		
Sodium silicate grade 145:				
Molar module	Oxide content (SiO <sub>2</sub> +Na <sub>2</sub> O) %	Density (20 °C) g/cm <sup>3</sup>	Fe <sub>2</sub> O <sub>3</sub> % max.	Dynamic viscosity min. (P)
SiO <sub>2</sub> /Na <sub>2</sub> O	%			
2.4÷2.6	39.0	1.45÷1.48	0.01	1

The reference moulding sand (6-kg portion) was prepared in a laboratory ribbon mixer by adding 0.5 parts by mass of binder grade 145 and stirring for 4 minutes.

The next stage was vibration thickening using an apparatus LUZ-2e and hardening with microwaves (P = 1 kW) for 4 minutes. This way prepared bricks were used for observations of the phenomena occurring on surfaces of base grains as a result of thermal action. The bricks cooled first to ambient temperature were then baked for 60 min in the range from 100 to 1200 °C in steps of 50 °C ± 5 °C, and finally cooled-down in free air. For reference reasons, the same way of heating was applied to pure chromite sand.

## 3. Results

In order to determine changes occurring on grain surfaces, a series of photographs was taken on a scanning microscope Hitachi TM-3000. The SEM imaging made it possible to identify the changes in both pure sand and the prepared moulding sand. In addition, EDS analysis was applied to identify elements on grain surfaces changing as a result of heating.

Effects of heating temperature on grain surfaces of pure sand and chromite-based moulding sand are shown in Fig. 2 and 3. It can be seen in the pictures that the change on surfaces of sandmix base grain begins at temperatures close to 700 °C, see Fig. 2a. Near to 800 °C, the changes are clearly visible (Fig. 2b) and this is similar above 900 °C (Figs. 2c and 2d).

Figure 3 shows grain surfaces of chromite sand. Like in the case of sandmix base grains, creation of a surface layer was observed with increasing temperature at ca. 800 °C. It was also found that, with increasing temperature (Figs. 3c and 3d), this layer is locally weaker and weaker joined with grains and shows a tendency for spalling and uncovering deeper layers with different structure and composition (dark grey areas in Fig. 3d).

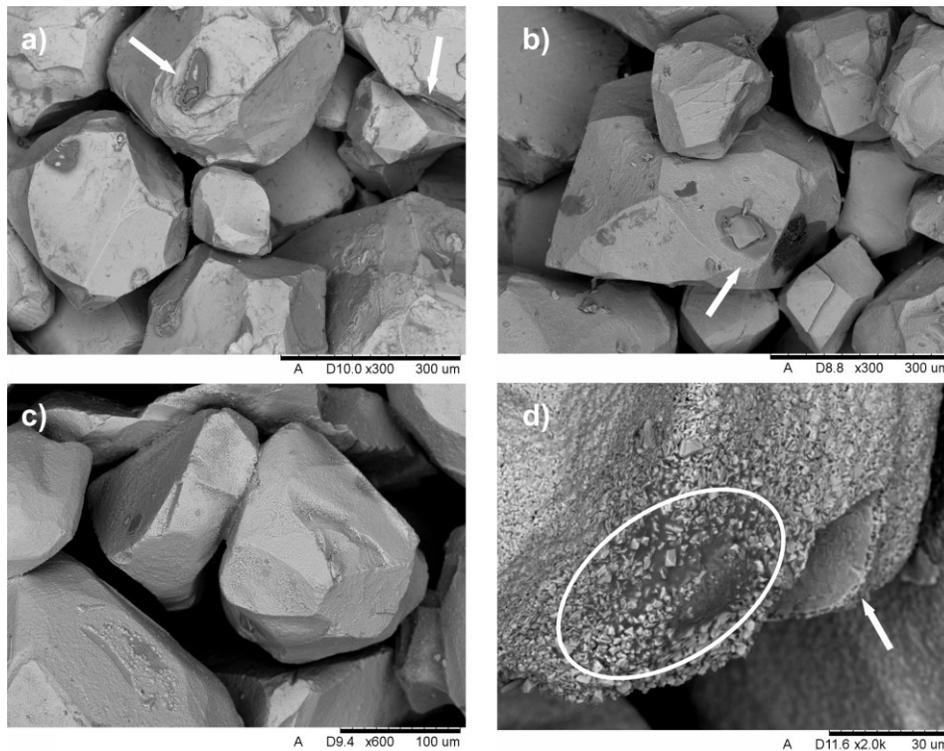


Fig. 2. Effect of heating temperature on grain surfaces of chromite moulding sand: a) 700 °C, b) 800 °C, c) 950 °C, d) 1200 °C. Visible are linking bridges and residues of binder in surface layer.

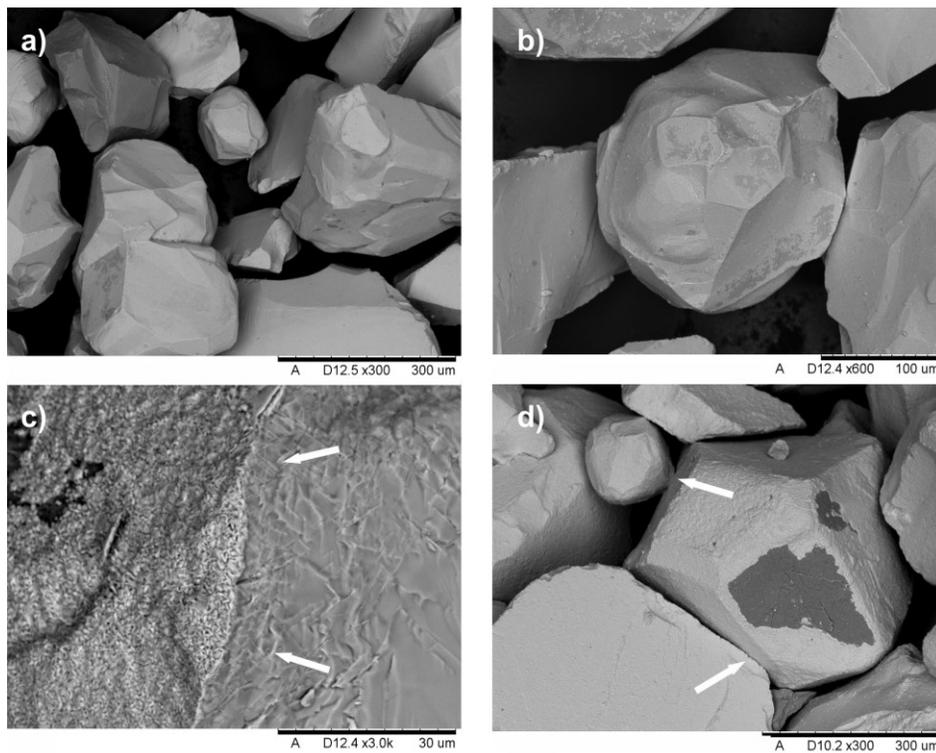


Fig. 3. Effect of heating temperature on grain surfaces of pure chromite sand: a) 700 °C, b) 800 °C, c) 1050 °C, d) 1100 °C. Linking bridges created after baking are visible in Fig. 3d.

At temperatures close to 1000 °C, the changes on grain surfaces become very clear and structure of the surface layer accepts the form of fine plates 2 to 3 μm long, see Fig. 3c. At 1050 °C and above, appearance of the layer does not change, but lighter precipitates can be seen in the uncovered internal grain structure, see Fig. 3d. In the areas from that the surface layer was detached (Figs. 3c and 3d), characteristic acicular structures intersecting at various angles were found, not observed at temperatures below 700 °C. Their appearance is best visible in Fig. 4b that shows polished section of base grain in moulding

sand. As observed, these particles were first created in the moulding sand at 1050 °C, like in pure sand, see Fig. 4c. Their appearance is clearly similar to acicular Widmanstätten structures.

Along with heating temperature increasing above 900 °C, the characteristic tendency for superficial sintering of loose sand is more and more visible, see Figs. 3d and 4d. However, the observed acicular forms in the base material of moulding sand and in the pure sand itself differ from each other in thickness of the layer in that they occur, as shown in Fig. 5.

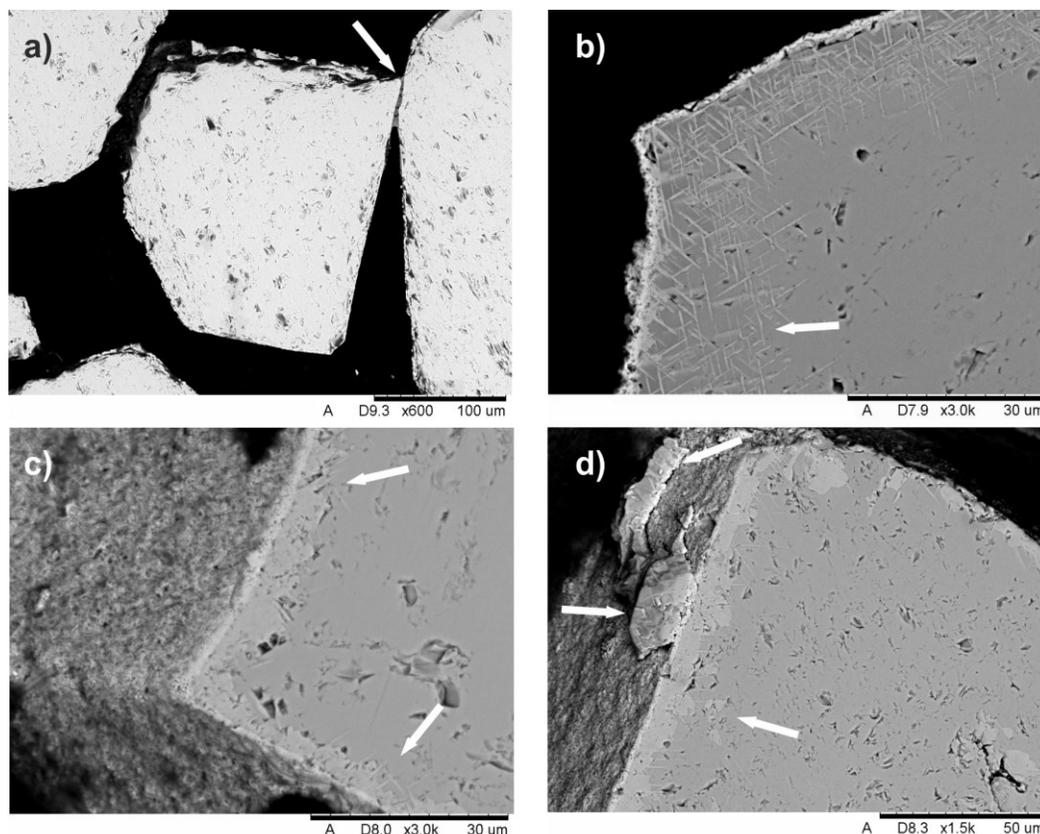


Fig. 4. Effect of heating temperature on chromite grain surfaces of moulding sand: a) 1000 °C, b) 1100 °C, and of pure sand: c) 1050 °C, d) 1100 °C. Sintered plates on grain surface are visible in Fig. 4d.

Figure 5 shows EDS analyses of base grains in the moulding sand. The results indicate that rectilinear precipitates in the grains of moulding sand are characterised by reduced concentration of magnesium (Fig. 5d), which is uniform in the whole grain volume at lower temperatures [15,16]. For the considered structures, no changes of chromium and oxygen concentrations are observed in the acicular precipitates. Iron compounds, uniformly visible on the entire observed area, are concentrated in the created surface layer. Arrangement of the acicular precipitates at grain surfaces can reflect positions of planes that create spatial structure of the material. Along with increase of heating temperature, the areas with these precipitates extend deep into the grains.

Figure 6 shows EDS analyses of pure sand grains. As can be seen in Fig. 6d, spaces between acicular precipitates show low concentration of magnesium. Images of polished sections of the grains subjected to temperature above 1050 °C (up to 1200 °C) show that the low-magnesium precipitates are created in the areas close to grain surfaces and do not occur in their centres, see Fig. 4b. It can be seen in Figs. 5c and 6c that chemical composition of plates in the created surface layer is similar in both cases (moulding sand base and pure sand), composed mostly of iron oxides. This may indicate diffusion of iron and creation of iron oxides.

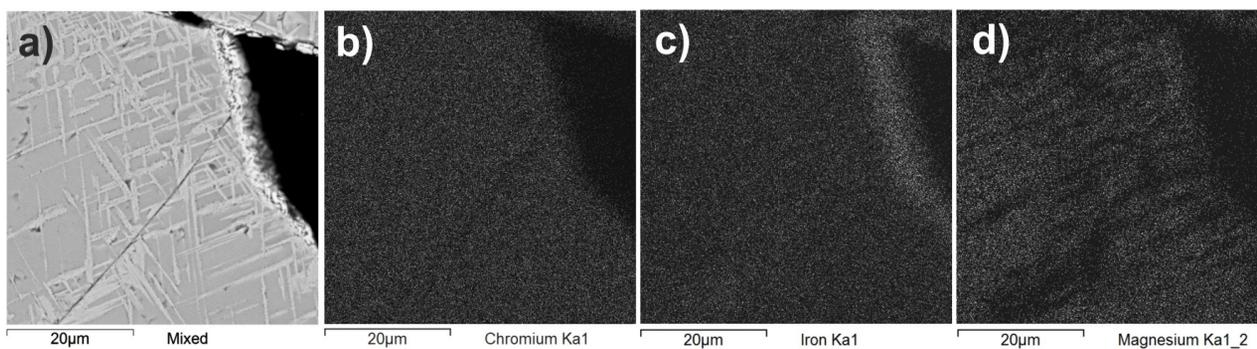


Fig. 5. Effect of heating at 1150 °C on distribution of elements in a moulding sand base grain: a) SEM view; b) Cr, c) Fe, d) Mg

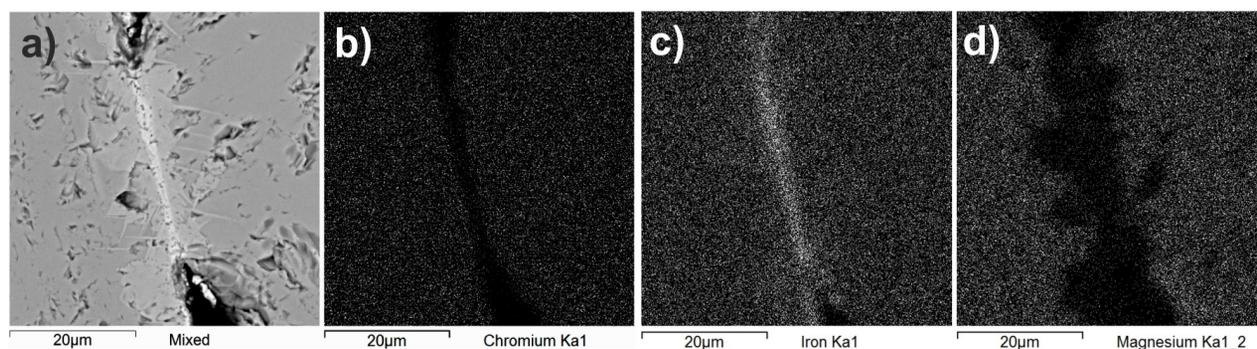


Fig. 6. Effect of heating at 1100 °C on distribution of elements in a pure sand grain: a) SEM view; b) Cr, c) Fe, d) Mg

SEM observations of surfaces and polished sections of base grains of a moulding sand with sodium silicate and of pure sand grains were complemented with Vickers hardness measurements (10 measurements per point) after baking at 800 °C, 950 °C and 1100 °C. Measurements were taken on an Innovatest 412D tester at 1.962 N for 10 s. Results are given in Table 2.

Table 2.

Vickers hardness of chromite sand grains in moulding sand and in pure sand

Baking temp. (60 min)	Average hardness [HV]		Standard deviation [HV]		Baking loss [%]
	Pure sand	Moulding sand	Pure sand	Moulding sand	Pure sand
800 °C	1588.5	2198.3	204.94	476.52	-0.14
950 °C	1360.1	1483.0	366.72	307.62	-0.40
1100 °C	1101.3	1389.3	232.08	247.10	-1.50

Hardness measurements of pure sand grains baked at 800 °C were within 1240.8 to 1962.8 HV, with average value 1588.5 HV and the smallest spread of 722 HV. For the same baking temperature, hardness of moulding sand base grains was almost 40% higher with average value 2198.3 HV and the largest spread within 1555.2 to 2969.0 HV. Average hardness of sand grains baked at 950 °C was 1360.1 HV, and average hardness of moulding sand grains baked at this temperature was 1483.0 HV, with the spread of 932 HV. Hardness at this measurement was closer to hardness of pure sand. Average hardness of sand grains baked at 1100 °C was 1101.3 HV, and average hardness of sandmix grains baked at this temperature was 1389.3 HV.

As the presented results indicate, hardness of base grains of a moulding sand with sodium silicate is higher than that of pure sand grains baked in the same conditions. This is caused by SiO<sub>2</sub> and Na<sub>2</sub>O present on grain surfaces of sandmix base, coming from the binder hardened by microwaves. General decrease of hardness of sand grains with increasing baking temperature can be also related to decreasing concentration of iron as a result of destroying spinel bonds that give the sand its properties.

In the considered temperature range, baking losses were determined from three tests with pure chromite sand, see Table 2. Negative values of the results indicate mass growth of the examined material, which can explain creation of thicker and thicker layer of iron oxides with increasing baking temperature. A result of this phenomenon is sintering of surfaces of chromite sand grains.

## 4. Results

The phenomenon of segregation of elements in grains of chromite sand begins at temperatures above 700 °C. With increasing temperature, the created layer of iron oxides becomes less and less joined with the grain, which results in easier spalling of these areas during processing of moulding sands. The phenomenon of brittleness of the surface layer and of uncovering the grain material can be favourable for reclamation of waste base of moulding sands containing sodium silicate. Structure of the iron-oxide layer also changes with increasing temperature, assuming clear lamellar form at ca. 1000 °C. At a temperature close to 1050 °C, clear segregation of magnesium starts inside the

grain, near its surface. The kind of segregation depends on the way how chromite sand is applied: as base of water-glass containing moulding sand to be hardened with microwaves or as pure sand.

The presented results give a ground for continuing research works to evaluate chromite sand as base of moulding sands to be hardened by microwave heating.

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