

CHROMIUM OBTAINING FROM ARMENIAN CHROMITE CONCENTRATES BY SHS IN THE PRESENCE OF CHLORIDES

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1. INTRODUCTION

Armenia is rich in chromite mines that can serve as raw materials for the chromium production. For this purpose Tapasar chromite mines recently discovered in the area of lake Sevan can be used. These mines contain Cr_2O_3 from 43 to 46%, but yet they have not found industrial use because of lack of processing technology [1]. Therefore, there is a need to create a new small-scale production with modern treatment methods and with relatively small investments, which will allow to extract metallic chromium from local chromites.

Nowadays metallic chromium is obtained from pure Cr_2O_3 and the production is considered to be to be expensive, energy-consuming, laborious and expensive equipments are required. This is why metallic chromium costs approximately 75% of the price of Cr_2O_3 [2,3]. From this point of view it is important to develop new inexpensive technologies based on the production of low-price Cr_2O_3 . Chromites contain non desirable elements apart from the main component (Cr_2O_3), such as silicon (SiO_2 -5,06%), iron (FeO -13,64%) and magnesium oxides (MgO -20,38%), which are also reduced during the Cr_2O_3 reduction process and remained in the metal as contaminations. Chromites apart from the main constituent Cr_2O_3 contain also undesirable elements in the form of oxides of silicon (SiO_2 -5,06%), iron ($\text{FeO}_{\text{total}}$ - 13,64%) and magnesium (MgO - 20,38%), which stay in metallic chromium during the reduction process, contaminating the metal. Purification of Cr_2O_3 from these mixtures is deemed as an important and urgent problem.

It is well known that enrichment of chromites may be realized by gravitation method removing mainly SiO_2 and increasing the content of Cr_2O_3 from 43-46% up to 52.89% [4,5]. However the obtained concentrate does not fit the requirements of metallurgy for production of pure metallic chromium by the ratios of $\text{Cr}_2\text{O}_3/\text{FeO}$ and $\text{MgO}/\text{Cr}_2\text{O}_3$, as well as by the content of Cr_2O_3 . Iron and magnesium oxides are chemically interconnected with the chromium oxide in the obtained chromite concentrate forming strong spinel

structure that impedes the preparation of pure chromium oxide without iron and magnesium contaminations. It is well known that in this case the chromium concentrate is subjected to selective chlorination at 873-1073K, resulting in iron chlorination and sublimation in the form of FeCl_3 , and the formed MgCl_2 doesn't sublime but remains in the liquid form in the chromite concentrate. After the chlorination process MgCl_2 is also removed by washing of the obtained residue, thus a Cr_2O_3 -rich superconcentrate is obtained [6-8]. Nevertheless, this technology is connected to the emission of chlorine containing toxic contaminations and creates numerous environmental problems polluting water and air environment. From this perspective there is a need to develop more efficient technologies for obtaining chromite superconcentrate, which further may be converted to metallic chromium by the aluminothermic reduction using the self-propagating high-temperature synthesis (SHS) method.

Thus, the main objectives of the research are: 1) to enhance the reactivity of Tapasar chromites by the mechanochemical activation in the presence and absence of chlorides with the aim to obtain a superconcentrate with high content of Cr_2O_3 ; 2) to extract metallic chromium without iron and magnesium impurities by the direct aluminothermic reduction of the Cr_2O_3 superconcentrate in the presence of chlorides

2. EXPERIMENTAL

Investigations were carried out on the chromite concentrate from Tapasar. Average chemical composition of the concentrate is as follows: Cr_2O_3 - 52,68%; $\text{FeO}_{\text{total}}$ - 13,64%; Al_2O_3 - 5,88%; MgO - 20,38%; SiO_2 - 5.06%; CaO - 2,36%; and $\text{Cr}_2\text{O}_3/\text{FeO}_{\text{total}} = 3,86$; $\text{MgO}/\text{Al}_2\text{O}_3 = 3.47$.

Mineralogically Tapasar's composition is as follows: chromspinellide ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$) - 60%; magniochromite ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$)-18%; magnetite (Fe_3O_4) - 5%; serpentine ($m\text{SiO}_2 n\text{Al}_2\text{O}_3$)-17%. As

may be seen the concentrate mainly is composed of chromspinellide and magniochromite. Magnetite occurs in free form. Vibration planetary mill (2474 rpm) of *ML-30* type was used for grinding (pretreatment) of the chromite concentrate (down to $-0,1 + 0,74$ mm in size). A sample with the mass of 50 g was vibro-treated by this procedure. Mill ball diameter is 0,8 cm, weight: 1750 gr. Milling duration was 60, 90, 120 min.

The sample obtained after the experiments was filtered for the quantitative determination of chromium, magnesium and iron in the solution, both by the atomic-adsorption and photo-calorimetric methods. X-ray diffraction (XRD) examination with monochromatic $\lambda\text{CuK}\alpha$ radiation (DRON-3 diffractometer) was performed. Scanning electron microscope (SEM) VEGA TS 5130MM, Tescan, Czech Republic, Microanalysis System INCA Energy 300, Oxford Instruments, UK7 and Energy Dispersive X-ray microanalyzer were used for metallographic investigations.

To measure the interaction temperature W-Re thermocouples were used.

3. RESULTS AND DISCUSSION

In this work the results of mechanochemical activation in the presence and absence of chlorides were compared with the data of high-temperature roasting. For this purpose prior to mechanochemical activation in the same conditions conversions of chromite concentrate were investigated under heat treatment.

The roasting of Tapasar chromite concentrates was investigated in the absence of chlorides and in the thermal activation conditions. It was shown that thermal treatment significantly changes the structure of the Tapasar chromites concentrate. Thermogravimetric analysis results of Tapasar chromites are presented in Fig. 1.

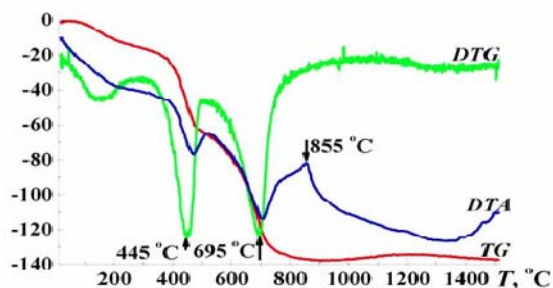


Fig.1. Thermograms of the chromite concentrate oxidation. DTG – the rate of mass change, DTA – differential thermal analysis, TG – mass change of the sample.

Thermogravimetric examinations were performed for samples of 2 grams at heating rate $10^{\circ}\text{C}/\text{min}$. During the heating mass loss of the sample, characteristic phase transformations and corresponding temperatures of these transformations were registered.

Heating at temperatures exceeding 1300°C a mass loss is observed, probably conditioned by the decomposition of Fe_2O_3 into Fe_3O_4 and O_2 by the following reaction: $3\text{Fe}_2\text{O}_3 = 2\text{Fe}_3\text{O}_4 + 1/2\text{O}_2$, as well as by the formation of solid solution $[\text{Fe}_3\text{O}_4, \text{FeCr}_2\text{O}_4]:\text{Fe}_3\text{O}_4 + \text{FeCr}_2\text{O}_4 = [\text{Fe}_3\text{O}_4\text{FeCr}_2\text{O}_4]$.

During high-temperature processing of chromites chemical transformations take place related to partial oxidation of bivalent iron and the formation of magnetite. This latter makes it possible to perform magnetic separation. However, these magnetic separation experiments appeared to be inefficient, because some amounts of iron, magnesium and chromium oxides moved to the non magnetic fraction, resulting in a significant decrease of chromium oxide content in the magnetic fraction. By this reason further investigations on high-temperature roasting of chromite concentrates were carried out in the presence of chlorides, expecting to obtain Cr_2O_3 -rich superconcentrate by removing iron and magnesium volatile compounds due to the chlorination process [7,8].

The influence of various chlorides (NaCl , CaCl_2) on high-temperature chlorination (roasting) of iron and magnesium oxides was studied. Roasting experiments were carried out in the tube furnace at temperatures 873, 973 and 1073K for durations of 60, 90, 120 minutes.

The experiments have shown that at theoretically calculated amount of the reducer the best results are obtained when chlorination of iron and magnesium oxides was performed in the presence of NaCl . Chlorination during 120 min at 1073K results in iron conversion degree of 99,1%, and that of for magnesium 91,0%. After washing and drying the concentrate has the following composition: Cr_2O_3 – 74,12%, FeO – 5,46%, Al_2O_3 – 6,08%, MgO – 8,49%, SiO_2 – 3,30%, CaO – 2,55%.

Nevertheless, to increase the reactivity of chromites by thermal activation in the presence or absence of chlorides a special furnace and high temperatures were needed. For this reason alternative ways to increase the reactivity of chromites were sought, among which mechanochemical activation by fine grinding method was selected as the most suitable [9].

Below the results of XRD analysis are presented (Fig. 2) for mechanochemically activated

chromites during 60, 90 and 120 min. As may be seen from the Fig.2, the increase of duration of mechanochemical activation from 60 to 120 min leads to significant increase in the intensity of peaks (especially for peak 3). These peaks are characteristic for iron and magnesium free oxides formed after the decomposition of crystalline structure of iron and magnesium chromites. This indicates that during mechanochemical activation deep structural and chemical conversions take place, which promote the growth in chromium spinel and magnetite amounts, consequently stimulates enrichment the chromite. At the same time this confirms that iron, containing in the chromite was intensively oxidized into magnetite.

Thus, experiments on mechanochemical activation have shown that the grinding

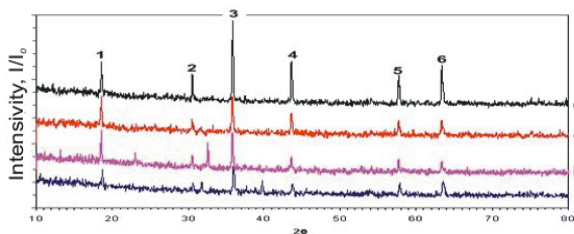


Fig. 2. XRD patterns of the chromite concentrate for the initial mixture (a) and mechanochemically activated during 60 min (b); 90 min (c); 120 min (d) with the characteristic peaks: 1-(Mg,Fe)(Cr,Fe)₂O₄ (1,2,3,4,5); 2-Fe₃O₄ (2,3,4,6).

promotes partial decomposition of chromium spinel and magnesium chromite into separate oxides and the oxidation of FeO into magnetite. Although iron and magnesium oxides stay entirely in the chromite concentrate. Taking into account this fact, further mechanochemical activation was performed using theoretically calculated amounts of chlorides (NaCl, CaCl₂) for complete chlorination of iron and magnesium oxides. The products

Also the quantities (wt.%) of elements were determined before and after activation process. According to experimental data, mechanochemical activation of chromites in the presence of chlorides was more efficient as results in significantly increase in the mass fraction of chromite in the concentrate. Grinding in the presence of NaCl leads to the mass fraction of Cr₂O₃ 77,23%, and 65.5% in the presence of CaCl₂. Simultaneously the content of iron (3,66-4,24%) and magnesium (7,39-7,78%) oxides in the concentrate decreases significantly. XRD analyses of samples mechanochemically activated for 120 min in the presence of NaCl was conducted (Fig. 3). Thus, the washed chromite concentrate obtained after 120 min. activation in the presence of NaCl had the following composition; Cr₂O₃ – 77,23%, FeO – 3,66%, Al₂O₃ – 5,64%,

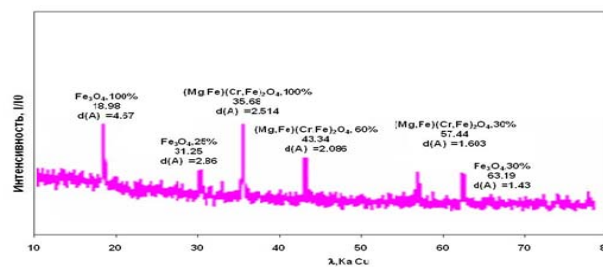


Fig. 3. XRD patterns for washed chromite samples after 120 min activation in the presence of NaCl

MgO – 7,39%, SiO₂ – 4,15%, CaO – 2,24%. This concentrate is quite suitable raw material for an industrial technology of metallic chromium production.

The comparison of thermal and mechanochemical activation of chromites has shown that according to the preliminary experiments volatile chlorides of iron and magnesium were obtained in both the cases and after the removal of these chlorides chromium content in the concentrate increased significantly. Though, there is a principal difference between these two processes: in the first case the initiation of reaction takes place due to the heat, and in the second case - due to the mechanical effect[10].

As a raw mixture for experimental investigations previously mechanochemically activated over 120 min and washed chromite superconcentrate was used. Aluminothermic reduction experiments were performed by the following way. A green mixture of the reactants containing chromite superconcentrate, aluminum powder, KClO₃, K₂Cr₂O₇ and calcium oxide was homogenized and placed into a heat-resistant capacitor filled with sand. Then combustion initiator was added and self-propagating high-temperature synthesis was initiated by means of an incandescent wire. Under these conditions the reduced chromium represents spherical metal particles, collected on the bottom, and other oxides (MgO, K₂O, CaO) contained in the chromite concentrate result in sparingly soluble silicates and aluminosilicates (as a slag) reacting with Al₂O₃ and SiO₂, which could be easily separated from the metallic spheres after cooling. Both the metallic and silicate phases were examined by chemical, microscopic and XRD analysis methods.

Extraction degree of the metallic phase depending on amounts of the reducer, KClO₃, K₂Cr₂O₇ and CaO at constant amounts of other components in the initial mixture was studied. Growth of KClO₃ amount in the initial mixture leads to increase in the quantity of KCl (a product of KClO₃ decomposition), which promotes the

formation of volatile iron chloride and decreases the iron content in the metallic phase. Under these conditions a slow increase of aluminum content (from 0.2 to 1.4%) was registered. In all cases the metallic phase was free of magnesium traces. To decrease significantly the content of iron in the metallic phase sodium chloride was also added to the initial mixture. As a result the following composition of the initial mixture: chromite superconcentrate – 53,5%, aluminum powder – 24,9%, KClO_3 – 3,5%, $\text{K}_2\text{Cr}_2\text{O}_7$ – 6,1%, NaCl – 9,4% and CaO – 2,6 % was considered as the optimal. Metallic chromium obtained from this mixture contains 0.49% of Fe and 3.49% of Al, and extraction degree for the target metal reached 91,6%.

In Table 1 the results of chemical analysis of metallic phases obtained under optimum conditions from aluminothermic reduction of the chromite concentrate, activated in the presence of NaCl and non-activated are displayed. As may be seen, the results obtained for the activated and non-activated

Table 1. Chemical analysis of metallic phases.

Metallic phase composition, %	Cr	Al	Fe	Si	Mg	O	N
Non-activated	89,71	4,47	2,59	1,96	0,02	0,555	0,0065
Activated	93,89	3,49	0,49	1,58	0,019	0,525	0,0062

samples are quite different. In the metallic phase obtained from the reduction of the activated sample mass fraction of chromium is higher (93,89%) and that of Fe (0,49%), Si (1,58%) and partly Al (3,49%) are lower. In both cases, excess of aluminum in the metallic phase was connected with the excess of the reducer. As experiments have shown, in the opposite case the yield of chromium significantly decreases. The presence of silicon in the metallic phase in both the cases apparently is related with the fact that reduction was performed in the sand and this latter partly participated in the reduction process. To avoid silicon traces in the metallic phase, MgO powder was added between the sand and the raw mixture.

Metallic phases obtained from the non-activated and activated in the presence of NaCl and washed samples were subjected to X-ray analysis. The patterns obtained are shown in the Fig. 4. According to the diffractograms presented, in either case only characteristic peaks of chromium are registered, but they are more distinct for the activated sample.

The structure of metallic phases obtained was also examined by scanning electron microscopy

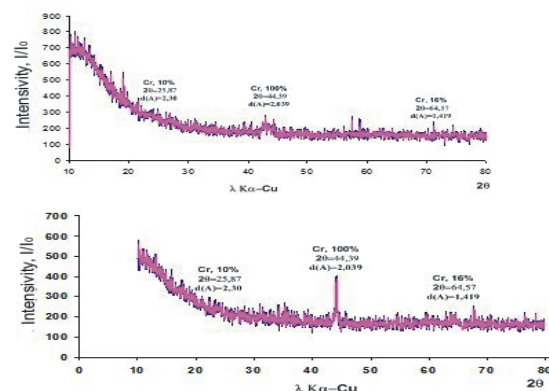


Fig. 4. XRD patterns of the metallic chromium obtained from samples: (a) non-activated and (b) mechanochemically activated during 120 min in the presence of NaCl .

(Fig. 5). As can be seen, the metallic phase obtained from the aluminothermic reduction of activated samples is more homogeneous.

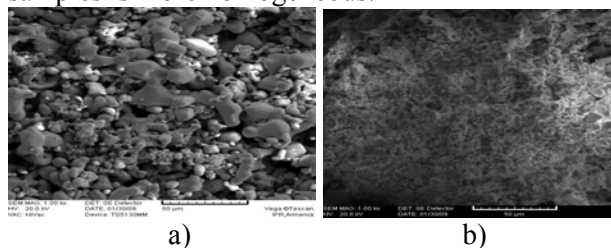


Fig. 5. SEM images of metallic phases obtained from aluminothermic reduction of the chromite concentrate: (a) non-activated and (b) mechanochemically activated during 120 min in the presence of NaCl .

Chemical and mineralogical analyses studies performed for the slags obtained result in the chemical composition of slags: Al_2O_3 – 63,64%; Cr_2O_3 – 0,51%; SiO_2 – 3,2%; $(\text{Na}, \text{K})_2\text{O}$ – 14,86%.

Some theoretical aspects concerning to the SHS aluminothermic reduction of chromites in the presence of chlorides were investigated, such as combustion front propagation, measuring the values of linear velocity and maximum temperature. These values were determined based on temperature profiles of the reduction process at various amounts of the reducer in the raw mixture.

Some questions related to the mechanism of metallic chromium production by the SHS aluminothermic reduction of chromites in the presence of chlorides were clarified. Thus, in all cases the processes of iron and magnesium chlorination, chromium oxide reduction and slag-formation of mixed oxides occur simultaneously, resulting in the formation of metallic chromium with negligible traces of iron and magnesium. Under these conditions the temperature of the raw mixture reaches the maximum level up to 3000K.

Thus, the results of theoretical and

experimental studies have shown that the combination of mechanochemical activation and SHS processes make it possible to obtain metallic chromium with fine-dispersed structure and proper physicochemical properties.

4. CONCLUSION

For the purpose of obtaining chromite superconcentrate the results of mechanochemical activation of Tapasar chromite concentrates in the presence and absence of chlorides were compared with those of high-temperature roasting processes. With this aim in view, before mechanochemical activation tests the transformations of chromite concentrate during thermal processing were studied. On the basis of thermogravimetric and microscopic analyses it was shown that thermal processing without chlorides significantly changes the structure of Tapasar chromite concentrate. Iron (II) oxide contained in the chromium-spinel converts to magnetite, that allows to enrich chromites by magnetic separation after the thermal processing and to obtain chromites with technical purity which is undesirable.

The influence of various chlorides on the chlorination process of the chromite concentrate was considered. It was shown that theoretical quantity of the reducer provides maximum level of chlorination when the chlorination of iron and magnesium takes place in the presence of NaCl. Mass fraction of Cr_2O_3 after thermal processing of superconcentrate during 120 min in the presence of NaCl and washing amounts to 77,23%, but chromium was also partly chlorinated (up to 15%) in this conditions

Transformations of Tapasar chromite concentrate during mechanical processing with and without chlorinating agents changes were investigated. It was shown that mechanochemical grinding of chromites in the presence of chlorides is more efficient and results in significant increase in the mass fraction of Cr_2O_3 in the concentrate. Chromium superconcentrate containing 77,23 wt.% of Cr_2O_3 is obtained after 120 min grinding in the presence of NaCl and washing. Appropriately, the content of iron and magnesium oxides in the concentrate decreases significantly. The comparison of thermal processing and mechanical activation of chromites points to the advantage of the latter.

Based on experimental investigations of the aluminothermic reduction of Tapasar chromite concentrates, optimum composition of the initial mixture was chosen. Metallographic analyses of metallic phases obtained from the non-activated and

activated by NaCl chromite concentrate were performed. For these two cases the following chemical compositions of metallic phases were established: Cr - 89.71%, Al - 4.47 %, Fe - 2.59%, Si - 1,96%, Mg - 0,02%, O - 0,555%, N - 0,0065% and Cr - 93,89%, Al - 2,39 %, Fe - 0,49 %, Si - 1,58 %, Mg - 0,019%, O - 0,525%, N - 0,0062%. It was shown that combination of mechanochemical activation and SHS processes enables obtaining the metallic chromium with fine structure and improved physicochemical properties.

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