OBTAINING OF FERROSILICACHROMIUM ALLOY BY SILICOTHERMIC REDUCTION OF THE TAPASAR CHROMITES AND SLAGS OF COPPER CASTING FACTORIES

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1. INTRODUCTION

Armenia has a powerful main base for organizing from raw material the production of ferroalloys containing chrome and silicium [1]. As a chromitecontaining raw material the local chromites can serve. In recent years a great interest aroused caused by finding new chromite mine in Tapasar of the Sevan region with 43-46% Cr_2O_3 content [2, 3]. But this deposit has not yet found industrial uses because of the absence of processing technology. These ores after enrichment san serve as a chromite containing raw material. On the other hand, metallurgical waste products from Alaverdi copper smeltery in which the content of Fe reaches 38.35 % and the content of Si reaches 30.11 % can serve as iron and silicium containing raw material. Taking into consideration the fact that there is a large quantity of this waste which is connected with the development of metallurgy of non-ferrous metals and the high content of iron and silicium in these wastes, it becomes quite urgent to obtain ferrosilicachromium from these wastes and local chromites by new, advanced and efficient technology. The obtained ferrosilicachromium can serve as alloying additives for obtaining ferrous chrome, as well as chrome and silicium containing valuable steels [4-5]. To obtain ferrosilicachromium by traditional technology from appropriate metals is expensive, since metallic chrome is obtained by multiphase, complicated and labour-consuming technology[4-8]. The process of obtaining ferrosilicachromium combined with local chromites and waste products is studied by the out-of-furnace siliciumothermic reduction method. Now the economically effective and advanced method is silicothermal method for alloys obtaining. Which does not require energetic consumption as it takes place owing to exothermic reaction of reduction. It allows to provide the process out-of furnace which is the prevailing factor for the given technology [4-**6**,9,10]. Obtaining of valuable ferrosilica-chromium alloying additives from local chromites and secondary raw material by advanced and efficient technology characterizes the importance of the presented work.

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%; FeO_{total} – 13.64%; Al_2O_3 – 5.88%; MgO – 20.38%; SiO_2 – 5.06%; CaO – 2.36%; and Cr_2O_3/FeO_{total} = 3.86; MgO/Al_2O_3 = 3.47.

Mineralogically Tapasar's composition is as follows: chromspinellide ($FeO.Cr_2O_3$) – 60%; magniochromite ($FeO.Cr_2O_3$) –18%; magnetite (Fe_3O_4) – 5%; serpentine ($mSiO_2$ nAl_2O_3) –17%. Magnetite occurs in free form.

As airon and silicium containing material gives the metallurgical waste products from Alaverdi copper smeltery in which the content of Fe reaches 38.35 % and the content of Si reaches 30.11 % .

X-ray diffraction (XRD) examination with monochromatic λCuKα 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.

3. RESULTS AND DISCUSSION

The main purpose of the work is the investigation of the ferrosilicachromium obtaining process by joint silicathermic reduction of the Tapasar (Armenia) chromites (48% Cr_2O_3) and tail slags of the Alaverdi's copper factory.

Great amount of heat released at the silicathermic reduction of chromium, iron and silicon oxides that are contained in chromites and tail slags is the reason for self-propagatind high-temperature synthesis (SHS), which is realized as a combustion wave propagating through the sample of initial mixture rising the temperature in the system up to 2500-3000K[4-5,10]. As a result of chromium, iron and silicon oxides reduction a metallic phase is formed, and a mixture of oxides forms a slag containing mainly silicates and aluminosilicates.

The work is devoted to obtaining Fe-Si-Cr alloy of the following composition: 36-38 % Fe; 28-30 % Cr; 35-40 % Si. This ferrosilica-chromium alloy is applied in the industry as an acidifying and alloying additive to the chromium and silicon containing stainless steels.

For obtaining the alloy a charge was prepared containing chromite, tail slags, reducers (Fe-Si and aluminum powder), as well as CaO and $NaNO_3$. $NaNO_3$ is added to the initial mixture as an agent for increasing the reduction temperature, and CaO is used as an additive which forms a melt and integrates oxides in the charge.

The experiments were performed as follows. A green mixture prepared from initial reactants of certain proportions was homogenized and placed in a container filled with sand. Ti+C mixture was used as an igniter. Combustion was initiated by means of an incandescent wire. Duration of experiment was 12-15 min. Under these conditions a metallic alloy and slag phase were formed, which were easily separated after cooling. Both the phases were weighted. The metallic phase was examined by chemical, X-ray and microscopic analyses.

In the work firstly the yield of metal depending on the chromite to tail slag ratio was studied. The results obtained testify that the chromite/slag molar ratio of 1:1 is more convenient (Fig.1).

Increasing in this ratio led to decrease in Cr and Si amounts and obtaining a low-quality alloy. It was established that total yield of the metallic

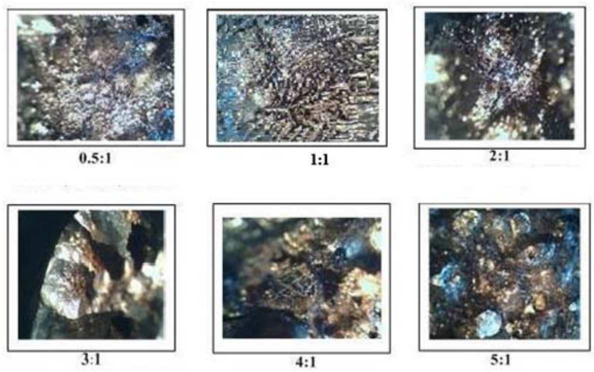


Figure 1. Microstructructure of the metallic phase with different chromite/tail slag molar ratio.

phase is also dependant on chromite/tail slag ratio. Therefore, further experiments were conducted in this optimal ratio 1:1.

In the next part of experiments the tail slag was replaced by Fe_2O_3, which led to increasing in the yield of metallic phase. Particularly, at the 1:1 molar ratio this yield increases from 62 to 80%. However larger amounts of Fe negatively influenced on the alloy quality (a porous and ductile alloy is formed).

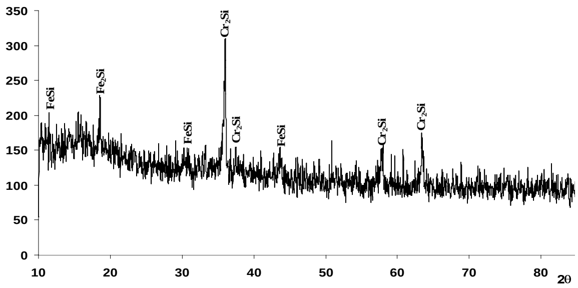
Experiments were also performed to rise Si amount (in the form of SiO_2). The best result was obtained at 6,85% content of SiO_2 in the charge. In this case 36,5% content of Si was registered in the metallic phase. Further increase in SiO_2 amount in the initial mixture leads to impairment of the quality of the metallic phase.

The yield of metallic phase depending on the amounts of CaO, Fe-Si and $NaNO_3$ was also studied. Optimal conditions for obtaining ferrosilicachromium were found to be: chromite/tail slag ratio of 1:1; contents of Fe-Si - 25%; Al - 5%, CaO - 30%, and 30% excess of

$NaNO_3$ in the charge mass. Under these conditions the composition of the obtained alloy was as follows: 35.1 % Fe, 36.35% Si and 28.53 % Cr, and extraction level of metal was 98.4%. Fig.2 illustrates XRD pattern and microstructure of the final product.

As silicon is equally well dissolved both in iron and chromium forming (Fe,Cr)Si and $(Fe,Cr)Si_2$, which are charachterized by similar

a



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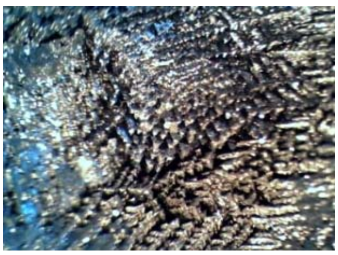


Figure 2. XRD pattern (a) and microstructure (b) of the combustion product

diffraction peaks, one can assert with confidence that ferrosilicachromium alloy is exactly obtained.

It were developed the aspects of mechanism of FeSiCr alloy obtaining process (Fig 3).

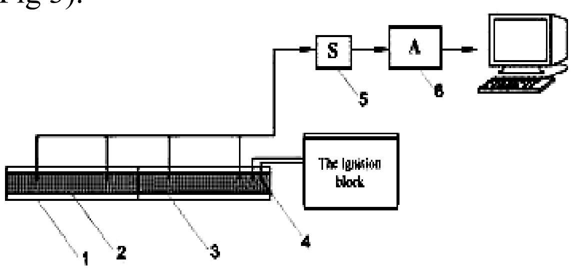


Figure 3. *Laboratory SHS reactor*

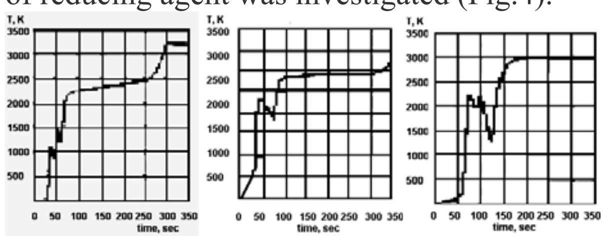
1 – Quartz boat, 2 – Thermocouples , 3 – Initial mix, 4 – Heat thread, 5 – The signal accelarator 6 - Analogue

By analog-to-digital converter Ni-USB-610M and LabView software package some theoretical problems concerning silicathermical reduction of chromite concentrate and waste by SHS method.

Experiments were carried out as follows: a certain amount of the charge was placed in a quartz boat-type crucible in a compressed or a free state, in which in a certain distance from each other (20 *mm*) 4 W-Re thermocouple (2) were recessed. The temperature was determined by the thermoelectric principle. Thermocouples were placed in the charge so that the heat loss of the environment would be minimal, which is important for accurate temperature measurement.

For registration and processing of signals obtained by means of thermocouples, they are connected to the signals amplifiers (5), after which the amplified signals are connected to the input of the Ni-USB-610M analog-digital converter, the signals obtained at the output of the latter, entered into a computer (7) and processed using the Lab View software.

Experiments were carried out as follows: to the beginning of the charge placed in quartz boat-type crucible the (Fe+C) initiator is added and with hot wire made of W the self-propagating high-temperature synthesis was initiated and the wave dispersion at a constant rate was spread, passing successively through the four thermocouples along the entire length of charge. At the end of the process the boat-type crucible was cooled, and metallic phase was allocated out of the charge. The occurrence of temperature profiles depending on the amount of reducing agent was investigated (Fig.4).



a) b) c)

Figure 4. *Temperature profiles of Fe-Si-Cr obtaining depending on the amount of reducing agent:*

a) theoretically necessary amount; b) 20% and c) 60% excess amount

By the type of temperature profiles it is evidently that the alloys synthesis is carried out in a fixed rate. However, multiple endothermic and exothermic effects associated with the synthesis of the alloy with gradual recovery and destruction of chromites in the range of 50 .... 150 sec. are observed after the reaction's starting. The thermal effects are especially amplified with increasing of reducing agent amounts. In the latter case, at the maximum amount of reducing agent and a duration of 100 .... 150 sec. on the curve the strong endothermic effect is likely associated with entire recovery of iron oxide and with final destruction of the chrom-spinelide crystal lattice. In all cases, firstly the iron is recovering, thus not violated the integrity of the crystal lattice of the chrome-spinelide. After full recovery the chromium recovery begins, thus, the reduced iron contributes to the extraction of chromium oxide. Extraction of silicon derived from the free SiO_2, contained in the charge - along with the chromium oxide extraction. Then the final recovery of chromium and silicon oxides and the synthesis of Fe-Cr-Si take place, after which the temperature of the mixture increases, reaching a maximum - up to 3000K.

Based on temperature profiles of the reduction process the values of quantities will be defined, some problems connected with SHS mechanism of the process for obtaining ferrous-silicium-chrome will be elucidated. The maximum combustion temperature (T_b) and linear combustion velocity (U_b) were defined graphically.

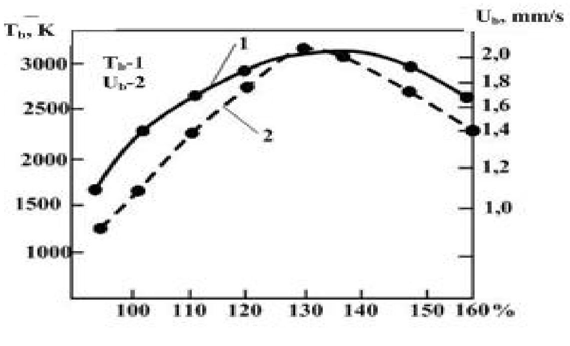


Figure 5. *Dependence of combustion temperature (T_b) and the velocity of propagation of the combustion front (U_b) from the amount of reducing agent contained in the charge*

As can be seen from the curves (Fig.5), the increase in the reducing agent leads to higher combustion temperature from 2500 to 3000K. The velocity of the combustion front (U_b) propagation increases also. This phenomenon is explained by the fact that the emission heat in the process is increasing and thermal conductivity of the synthesized alloy increases also. Studies have shown that the synthesis parameters have a significant impact on the dispersion degree of the initial feedstock. As shown in Figure 6 the dispersion increasing from 100 to 10 microns significantly increases the value both T_b and U_b.

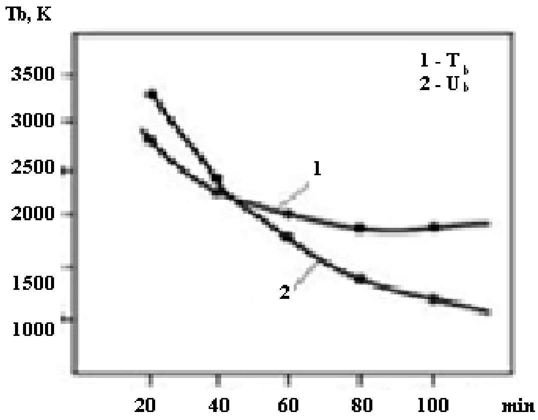


Figure 6. *Dependence of combustion temperature (Tc) and the velocity of propagation of the combustion front (Uv) the degree of dispersion of the charge*

Thus, the obtaining of temperature profiles allows to determine the dependence of combustion temperature (T_b) and the velocity of combustion front propagation (U_b) from the amount of reducing agent contained in the charge and the degree of dispersion. Simultaneously, the resulting form of profiles allowed clarifying some issues of the recovery mechanisms for ferrosilicochrome recovery applying the method of chromites recovery by ferrosilicone.

Comments to these issues may help to solve a number of technological problems of the getting ferrosilicochrome obtaining. By controlling the synthesis process it is possible to obtain the substances of a given composition, structure and characteristics. Thus, experimental investigations have demonstrated the possibility of producing valuable ferrosilicachromium alloy by joint silicathermic reduction of Tapasar's chromites and tail slags of Alaverdi's copper factory with the metal yield of 98.4%.

4. CONCLUSION

It is foreseen to perform experimental investigations in Tapasar chromite concentrate and copper-smeltery the waste products by the simultaneous silicathermic reduction method for obtaining ferrous-silicium-chrome. The dependence of metal's total output on waste product-chromite relation, on batch mixture reducing agent, the quantity of $NaNO_3$ and CaO was studied. The structure forming problems of obtained results was studied by the microscopic method in the conditions of various ratios of waste products - chromites.

The investigation of ferrous-silicium-chrome microstructure was performed by the scanning microscopic and X-ray-phase analysis method.

In terms of theoretical and experimental results of investigation performed the Tapasar chromite concentrate and waste products from copper-smeltery together with the siliciathermy reduction process by the out-of-furnace aluminothermic reduction method, the productive technology of obtaining ferrous-silicium-chrome additives will be developed and technological-economic substantiation will be performed.

The developed technology will not require huge expenses and it can be easily implemented in "Armenian Molybdenum Production" works functioning in Yerevan. Simultaneously the results obtained will create necessary prerequisites for foundation in Armenia non-traditional productions by energy and ore saving technologies which will enable to solve simultaneously the ecological problems.

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