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REM-containing silicate concentrates

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Abstract. A new method of advanced complex processing of ores containing rare-earth elements (REE) is proposed to obtain porous X-ray amorphous aluminosilicate material with a stable chemical composition which concentrates oxides of rare-earth metals (REM). The ferromanganese oxide ores of Chuktukon deposit (Krasnoyarsk Region, RF) were used for the experiment. The obtained aluminosilicate material is appropriate for treatment with 5 – 15% solutions of mineral acids to leach REM.

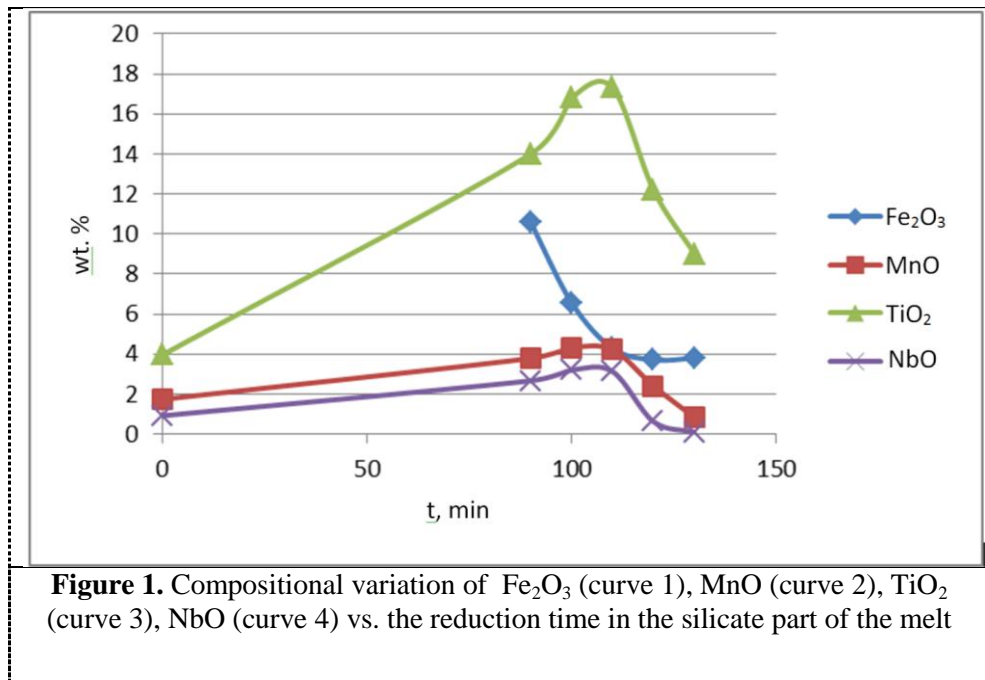
1. Introduction

For the experiment the ore samples were taken from the Chuktukon deposit. They mostly have iron-manganese oxide composition (40.0-70% Fe₂O₃ and 1-20% MnO), and contain the phases of monazite (Ce, Ln, Y, Th)HO₄, sodium-cerium bisulfate (NaCe(SO₄)₂*H₂O), calcite (CaCO₃), manganese sulfate, Ca, Ce-phosphate Ca_{0.5}Ce₂(PO₄)₃. The instability of the chemical and phase composition of the ore significantly influences physico-mechanical properties of the materials obtained on its basis. The ores under study are complex, and can hardly be enriched due to the high dispersivity of mineral constituents and mutual coalescence [1-4]. Processing of such ores requires new approaches and technology solutions.

2. Experimental

To stabilize and concentrate the rare metal ore in the silicate part of the melt, a pyrometallurgical method was chosen for deep reduction smelting with the melt separating into silicate and metallic portions. This method is also applicable for complex processing of REM-containing technogenic materials, e.g. red muds of aluminum production [5]. Brown coal was used as a reducing agent. The smelting was performed in the induction furnace KIT-25, as is done in [6, 7]. Charging material was loaded into a graphite crucible, heated during 1 hour to 1500-1550°C and kept for another hour, with the samples being taken every 10 min for chemical analysis.

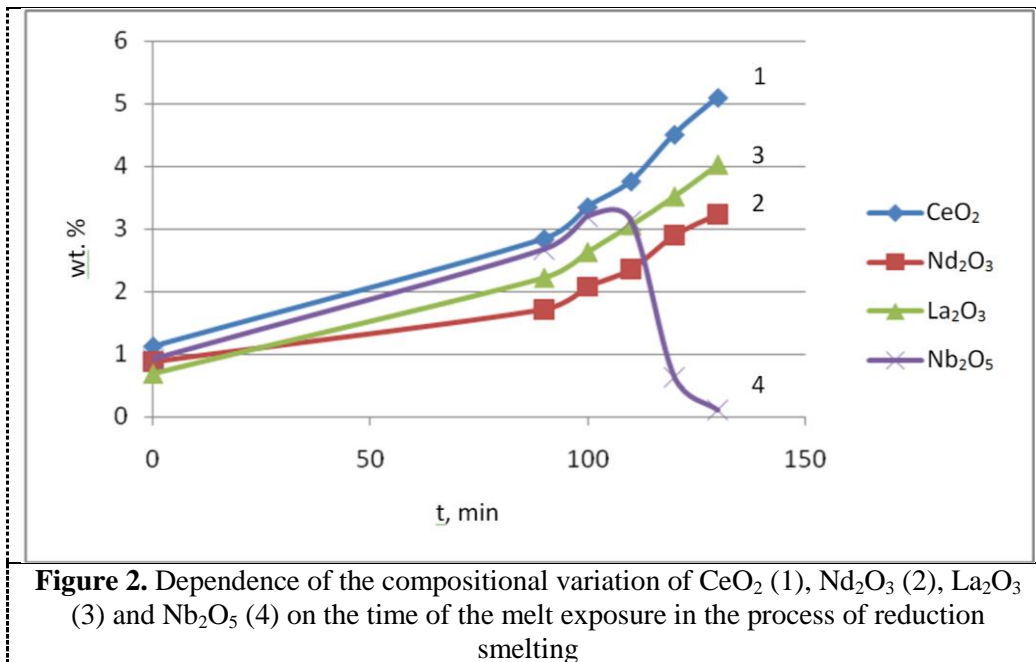




The figure 1 shows that upon reducing the ore using brown coal it is mostly iron which is transformed into metallic phase during the first 90 min from switching on the melting furnace. Some part of phosphorus is carried away with the gas phase, the other part is redistributed between the metallic and silicate part of the melt. The composition of the metal sample taken under these conditions is the following, in wt.%: Mg – 0.15; Al – 0.49; Si – 1.02; P – 3.73; S – 0.47; Ca– 0.17; V – 0.17; Mn – 2.13; Fe – 90.5; Nb – 0.26; Cr – 0.21; W – 0.11; Ti – 0.16.

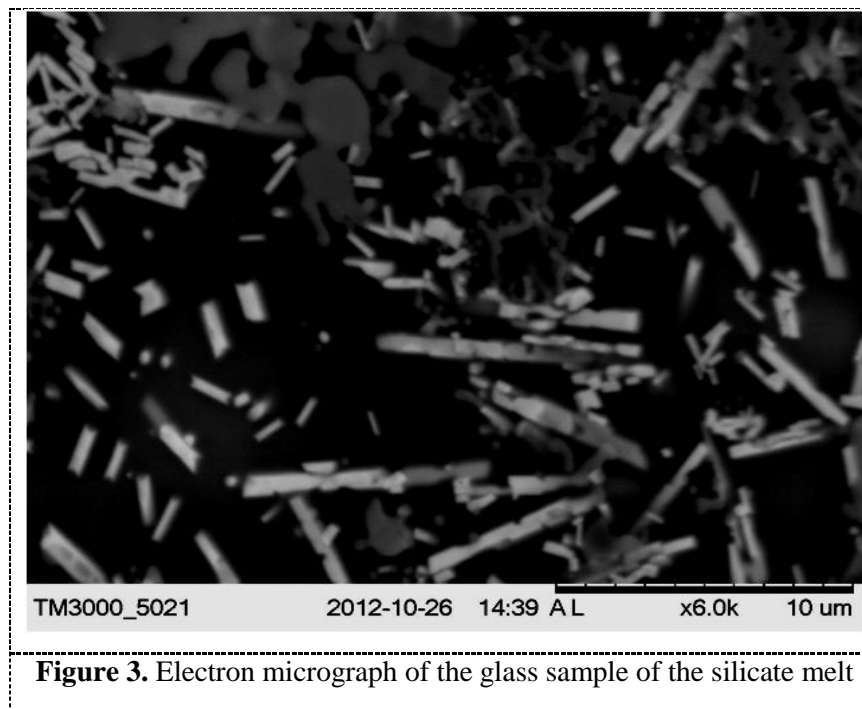
At this stage the main part of titanium, manganese and niobium is left in the slag. The reduction process intensively and deeply proceeds at 1550 - 1600° C, with the time of the melt exposure to this temperature being longer than 110 min (figure 1.). An abrupt decrease in the content of iron, manganese niobium and titanium, which can be seen in the curves in figure 1, evidences their transition into the metallic phase. A synchronous decrease of the content of these elements in the melt evidences their association [8].

The performed preliminary studies of the reduction smelting allow one to assume a possible, almost complete transition of iron, phosphorus, manganese, niobium and titanium into the metallic state. In the silicate part of the melt, the concentration of REM, alkali-earth metals, aluminum and thorium increases.



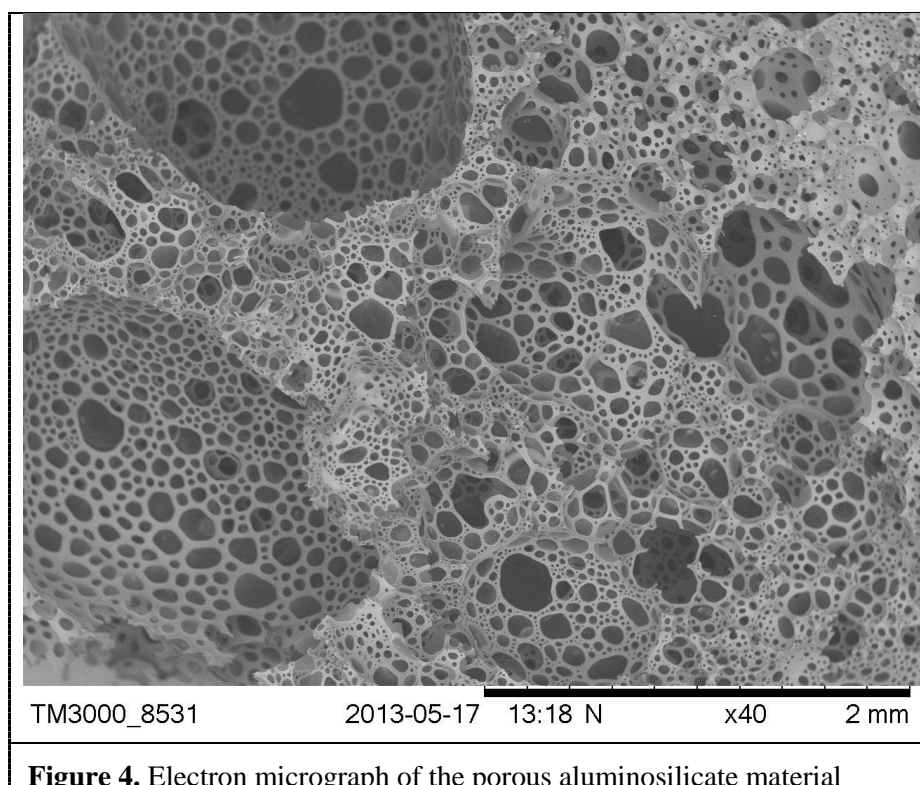
The abrupt decrease of the content of niobium oxide in the melt is due to its interaction with silicon carbide and its extraction into the metallic phase.

The silicon carbide formed in the melt by the reaction $\text{SiO}_2 + 2\text{C} = \text{SiC} + 2\text{C}$ participates in the reactions of deep reduction of niobium, iron, manganese and titanium. Here, it plays the role of a transporter-agent, resulting in these elements being extracted into the metallic phase, while the silicate part of the melt becomes enriched with rare-earth metals (figure 2, curves 1, 2, 3, figure 3).



In the figure 3 one can see an aggregation of white bars with the size ranging from 1 to 10 μm . The Rare metal imaging shows that lanthanum is associated with cerium. The detected lanthanum-cerium seeds are in the form of impurity phases in the glass structure [8]. The absence of strong bonds with the glass structure will facilitate their leaching.

The rate of REM leaching is also affected by the specific surface of the glass which increases upon its foaming. It is shown that pouring the melt into water results in the formation of a foamed aluminosilicate material which is presented in figure 4.



The maximum pore size amounts to 150-200 μm . The material represents a sponge composed of numerous porous layers, with the spacing between the layers being approximately equal to the pore diameter. The destruction of the foam layers is due to an abrupt cooling of the melt.

3. Results and discussion

As in the glass, in the foamed material one can observe the REE oxide seeds where lanthanum is associated with cerium and neodymium. The obtained material is appropriate for treatment with 5 – 15% solutions of mineral acids.

The aluminosilicate foam was used to leach REM. The composition of this material in wt. % is the following: Na_2O – 0.29, MgO – 1.98, Al_2O_3 – 9.14, SiO_2 – 26.4, SO_3 – 1.42, Cl – 0.45, K_2O – 0.91, CaO – 45.2, TiO_2 – 3.67, Cr_2O_3 – 1.06, MnO – 0.27, Fe_2O_3 – 0.53, SnO – 0.15, REM oxides – 8.53.

The unground material was treated with sulfuric acid (its concentration being 10%), the insoluble precipitate – mostly gypsum and silica – was filtered and oxalic acid was added to the filtrate for REM to precipitate (figure 5).

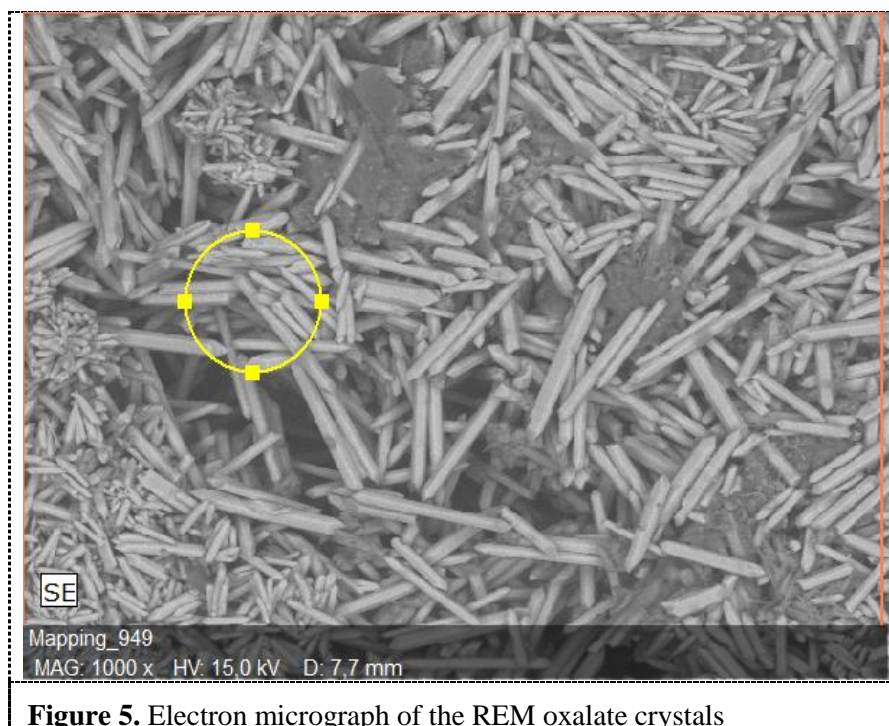


Figure 5. Electron micrograph of the REM oxalate crystals

The composition of the precipitated REM concentrate in wt.% is the following: La_2O_3 – 13.8; CeO_2 – 11.7; Nd_2O_3 – 8.7; Y_2O – 2.5; Sm_2O_5 – 2.0; ZrO_2 – 0.5; Nb_2O_5 – 0.2; Cr_2O_3 – 5.3 and others (mostly silica and aluminum oxide) – 55.3. The extraction degree was approximately equal to 60%.

The initial materials and the obtained products were analyzed in the Joint Use Center of The Krasnoyarsk Scientific Center, Siberian Branch of the Russian Academy of Sciences.

4. Conclusion

The present paper considers the peculiarities of the process of pyrometallurgical processing of ores from Chuktukon deposit, i.e. the reduction of iron, manganese, niobium, and titanium oxides. It is shown that the rate of the manganese, titanium and niobium transition into the metallic phase increases only after the formation of silicon carbide in the slag melt. The silicon carbide participates in the transport reactions of the metal reduction. Moreover, the silicon carbide formation is necessary for the pore formation in the slag melt. It has been found that it is possible to obtain a concentrate containing about 40% of oxides of rare earth metals from the silicate part of the melt.

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