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THE EFFECT OF ARGON PLASMA ON REDUCTION OF VARIABLE-VALENCE OXIDES IN SYNTHESIS OF MINERALS

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The results of studying plasma treatment of chromium, titanium, and iron oxides are discussed. It is demonstrated that variable-valence oxides become partly reduced in argon plasma.

The use of alternative energy sources in glass and glass-ceramic technologies is a promising line of development for contemporary science and engineering [1]. Plasma processes have some substantial advantages compared to traditional technologies. The most significant are the possibility of developing materials with unique sets of properties, environmental safety of technological processes, shortening of production cycles, and intensification of production. However, argon plasma contributes to partial reduction of oxides under high-temperature treatment, for instance nickel oxide is reduced to metallic nickel [2].

The present paper describes the results of studying technological parameters of plasma treatment of variable-valence oxides, which act as colorant components in synthesized spinels, rubies, and sapphires.

High-temperatures treatment of oxides was performed using a GN-5r plasma burner of a UPU-8M arc plasma gun. The operating parameters of the plasma gun were as follows: voltage 30 – 32 V, strength of current 200 – 500 A. The plasma-forming gas was argon with a flow rate of 2.0 –

3.0 m³/h under pressure of 0.24 – 0.26 MPa. The water consumption for cooling of the plasma burner was 10 kg/min.

The initial materials selected were chromium, titanium, and iron oxides (Table 1). This is due to the fact that the color of ruby is caused by chromium oxide and the color in blue sapphire depends on titanium and iron oxides. These oxides also serve as colorants for spinels. All oxides listed above have variable valence.

The scheme of plasma treatment of oxides is indicated in Fig. 1. Finely dispersed powders of chromium, titanium, and iron oxides were fed via a powder feeder to a pipeline, in which they were mixed with the plasma-forming gas and directed toward the plasma burner. After plasma treatment, the powders were collected in corundum crucibles and subjected to x-ray quantitative analysis [3].

The experiments demonstrated that rutile TiO₂ after plasma treatment is partly reduced to anasovite Ti₃O₅. The quantity of anasovite in the end product depends on the flow rate of the plasma-forming gas and on the plasma gun power.

As the plasma gun power grows, the temperature of plasma increases. This increases the weight content of anaso-

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TABLE 1

Oxide	Mass content, %			
	Cr ₂ O ₃	TiO ₂	Fe ₂ O ₃	calcination loss
Chromium	96.4	–	–	1.4
Titanium	–	98.36	0.04	1.6
Iron	–	–	98.5	1.5

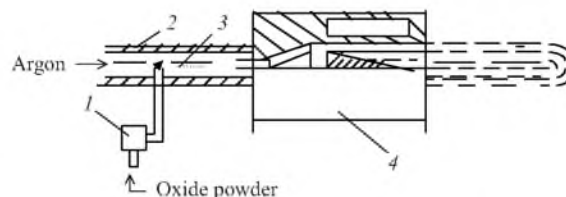


Fig. 1. Scheme of plasma treatment of chromium, titanium, and iron oxides: 1) powder feeder; 2) pipeline; 3) oxide powder dispersed in argon; 4) plasma burner.

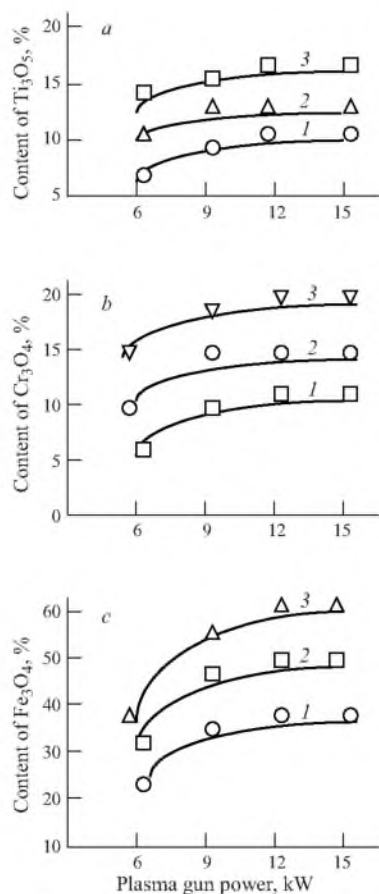


Fig. 2. Dependence of the quantity of Ti_3O_5 (a), Cr_3O_4 (b), and Fe_3O_4 (c) on plasma gun power: 1, 2, and 3) argon flow rate of 3.0, 2.5, and 2.0 m^3/h , respectively.

vite in the end product to 11.5 – 16.5% (plasma gun power 15 kW, argon flow rate 2 m^3/h).

As the flow rate of the plasma-forming gas increases to 3 m^3/h with plasma gun power of 15 kW, the temperature of plasma decreases and, accordingly, the content of anasovite decreases to 6.2% (Fig. 2a).

Escolite Cr_2O_3 after treatment in plasma flame is partly reduced to Cr_3O_4 (Fig. 2b). As the power of the plasma gun increases from 6 to 15 kW with argon flow rate 2.0 m^3/h , the content of Cr_3O_4 grows from 13.5 to 19.0%. Increasing the flow rate of argon up to 3.0 m^3/h with the plasma gun power of 15 kW decreases the formation of Cr_3O_4 in the end product to 8.8%.

Iron oxide after plasma treatment, in addition to the initial phase of hematite $\alpha\text{-Fe}_2\text{O}_3$, contained magnetite Fe_3O_4 and maghemite $\gamma\text{-Fe}_2\text{O}_3$. Consequently, hematite was partly transformed into maghemite and partly became reduced to magnetite. The content of these components to a large extent depends as well on the plasma gun parameters and the flow rate of the plasma-forming gas. As the plasma gun power grows, the number of the end phases increases, and with in-

creasing flow rate of the plasma-forming gas the number of the end phase decreases (Fig. 2c). Thus, the content of magnetite for plasma gun power of 15 kW and argon flow rate of 2.0 m^3/h reaches 61.5%.

X-ray phase analysis of initial TiO_2 identified the presence of only one phase, namely rutile $\alpha\text{-Ti}_2\text{O}$. After plasma pretreatment, apart from the main phase of rutile, peaks indicating the presence of anasovite were registered ($d = 1.512$, 1.597, 1.734, 2.073, 2.374, and 2.536 Å).

Only one phase, that is, escolite was registered in initial Cr_2O_3 . Chromium oxide after plasma treatment was partly reduced to Cr_3O_4 ($d = 1.484$, 1.618, 1.724, 2.099, 2.171, and 2.343 Å).

The diffraction patterns of iron oxide subjected to plasma treatment, apart from the main initial phase $\alpha\text{-Fe}_2\text{O}_3$, exhibited peaks typical of Fe_3O_4 ($d = 1.477$, 1.610, and 2.522 Å) and $\gamma\text{-Fe}_2\text{O}_3$ ($d = 2.085$ and 2.940 Å).

A mixture of iron and titanium oxides in a ratio of 1 : 9, which corresponds to the ratio of these oxides in sapphire, was subjected to treatment in argon plasma flame. The initial components were rutile and escolite.

X-ray phase analysis of the mixture of titanium and chromium oxides after plasma treatment indicated the presence of the following phases: hematite ($d = 1.698$ Å), magnetite ($d = 1.610$ and 2.201 Å), anatase ($d = 1.484$, 1.838, 2.508, and 3.663 Å), and anasovite ($d = 2.704$ Å). Thus, in the case of the joint presence of variable-valence oxides (TiO_2 and Fe_2O_3), their partial reduction is registered as well.

Since there are no reference data for superhigh temperatures, and considering that at temperatures above 5000 K absolutely all reaction mechanisms change and cannot be uniquely determined, the following conclusions can be made. A high-energy plasma flow imparts energy to oxygen anions in the oxides considered, which is sufficient for overcoming the potential barrier in order to leave the crystalline lattice. The absence of partial oxygen pressure in the zone of high-temperature treatment as well contributes to partial removal of oxygen anions from the crystal lattice. Accordingly, when synthesizing minerals in argon plasma, one should take into account the processes of partial reduction of variable-valence oxides.

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