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GEOCHEMISTRY

Formation of Anosovite during Carbothermal Reduction of Leucoxene

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Titanium oxides occupy a special place in the production of composite materials. The most promising way to obtain these materials is the reworking of natural titanium raw material. In this work, we attempted to synthesize the high-temperature Ti_3O_5 modification by carbothermal reduction of leucoxene from the unique Yareg titanium deposit, Komi Republic. The Yareg deposit is composed of metamorphic rocks including predominant schists and quartzitelike sandstones. The subordinate limestones, marls, tuffites, and dolerites occur as stratal bodies or are confined to the fault zones. The placer in the lower unit contains more than 40 various minerals. The major mineral of the heavy fraction is leucoxene (45–49%) of the quartz–rutile nature—rutile grains embedded in a quartz matrix, thus forming a natural composite. The abundance of minerals of titanium dioxides in the productive bed of the Yareg deposit is not correlated with their stability (the rutile-type leucoxene significantly dominates over the anatase-type leucoxene). This disagreement between the stability and the abundance of TiO_2 modifications is presumably related to the physicochemical specifics of the deposit, in particular, to the presence of oil in the bed [1–3].

The leucoxene-bearing sandstone is located in the outer contact zone of the dolerite dike, where the temperature can reach approximately 1300–1500°C. The magmatic–metamorphic transformations during the ascent of magma to a higher crustal level and the consequent pressure decrease provoke the loss of volatiles and increase of viscosity. Subsequent growth of the cooling rate leads to the formation of numerous tiny crystals or even aggregates of crystals and glass. Thus, depending on the *PT* conditions of solidification, the same magma can produce different quantitative-sequential homological series dominated by anosovite Ti_3O_5:

TiO_2 (4/*mmm*, tetragonal symmetry) → $[(Mg,Mn,Fe)TiO_3$ (3*m*, trigonal)] → $[(Ti,Al,Fe,Mg)]Ti_2O_5]$ → Ti_3O_5 (*mmm*, orthorhombic) → Ti_2O_3 (32, trigonal) → TiO (*m*3*m*, cubic).

The dressing product of the oil–titanium ore of the Yareg deposit is a 50% leucoxene concentrate (LC) with titanium and silicon oxides as the major components (~90%). The leucoxene concentrate is the basis for the production of valuable Ti-bearing materials. The major Ti-bearing phases of LC in the natural pseudobinary (SiO_2–TiO_2) system contain isomorphic admixtures of oxides of Fe (2.5%), Al (2.5–5%), and Mg (<1%).

In addition to acid leaching with H_2SO_4 and HCl, the method of carbothermal reduction of rock-forming oxides can also be applied for the extraction of pigment titanium dioxide from leucoxene concentrates. According to [4], carbothermal reduction of leucoxene in vacuum leads to the simultaneous reduction of titanium and silicon oxides with gradual removal of Si in the form of volatile monoxide (Fig. 1). The process of reduction involves the sequential formation of oxic and carbide compounds of titanium and silicon and their subsequent fractionation. The degree of fractionation depends on the amount of carbon introduced into the charge and experimental conditions (temperature, pressure, and time). The maximum fractionation was achieved at a carbon content of 10–16 wt % (the Ti/Si ratio is 98%). The dressing product is mainly composed of the anosovite-type pseudobrookite-structured phase (Ti_3O_5), which can be used for obtaining ceramics based on titanium oxide. The high-temperature modifi-

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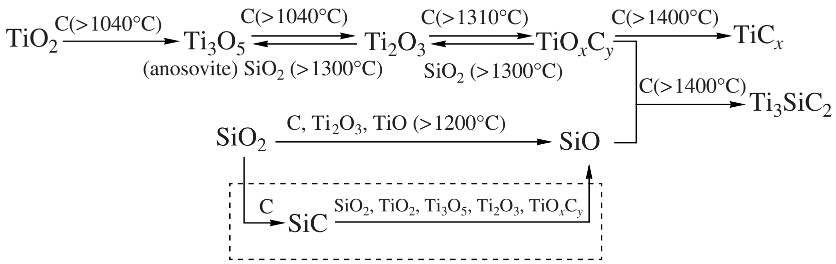

Fig. 1. Scheme of carbothermal reduction of LC in a vacuum.

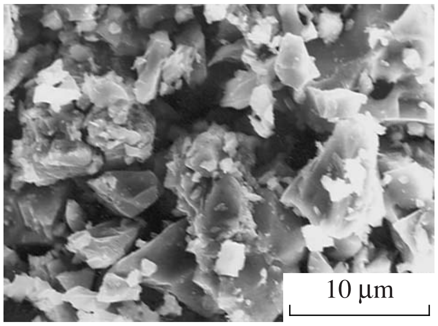

Fig. 2. Electron microscopic image of the anosovite phase.

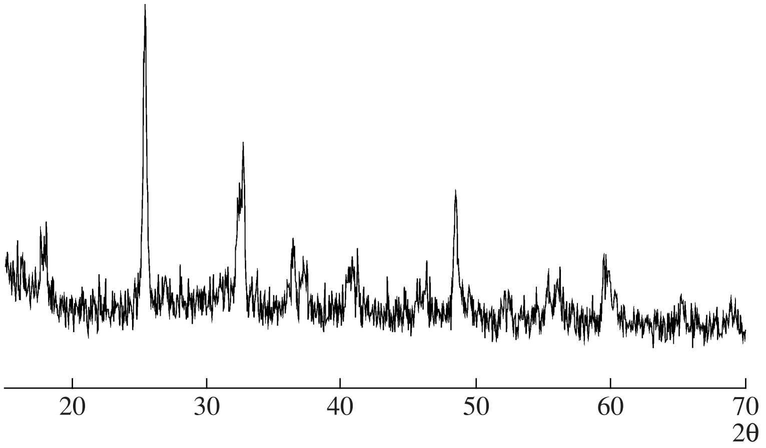

Fig. 3. XRD pattern of the anosovite phase.

cation of Ti_3O_5 stabilized at room temperature can possess both orthorhombic [5] and monoclinic [6] forms of symmetry.

We studied three samples obtained at different conditions and characterized by the highest contents of the anosovite phase (table).

The third sample is most interesting. The anosovite phase in this sample is mainly represented by equant grains 3–15 µm in size (Fig. 2). Data on the XRF analysis indicate its monophase composition, while all lines in the XRD pattern are ascribed to the pseudobrookite-structured phase (Fig. 3). Microprobe analysis indicates that the sample consists of only Ti and Al. Hence, it represents the solid solution based on Ti_3O_5, which has an orthorhombic pseudobrookite structure stabilized by the admixture of Al incorporated in the leucoxene concentrate.

Thus, the carbothermal reduction of the leucoxene concentrate in vacuum can produce, under certain conditions, solid solutions based on high-temperature modification Ti_3O_5, which was stabilized to a variable degree by admixtures in the leucoxene concentrate.

Crystallochemical characteristics of the anosovite phase

Sample no.	Initial composition	Conditions of thermal treatment	Chemical analysis	Microprobe spectral analysis	X-ray phase analysis, unit cell parameters
1	96 wt % LC, 4 wt % G	1800°C, 1 h	81.8 wt % TiO_2, 15.9 wt % SiO_2, ~2.3 wt % Fe_2O_3, Al_2O_3, MgO and others	58.24% TiO_2, 18.34% SiO_2, 15.04% Al_2O_3, ~8% MgO, Fe_2O_3, CaO	high-temperature monoclinic modification Ti_3O_5 (‹ 23-606 ICDD–JCPDS) $a = 0.979 \pm 0.001$ nm, $b = 0.990 \pm 0.001$ nm, $c = 0.375 \pm 0.001$ nm, $\gamma = 90.46 \pm 0.05°$
2	89.5 wt % LC, 10.5 wt % G	1450°ë, 41 h (multiple calcination)	95.2 wt % TiO_2, 0.96 wt % SiO_2, ~3.84 wt % Fe_2O_3, Al_2O_3, MgO and others	~91% Ti, ~9% Al	Ti_3O_5 (‹ 23-606 ICDD–JCPDS) TiC SiO_2
3	89 wt % LC, 11 wt % G	The same	The same	The same	Orthorhombic pseudobrookite-structured Ti_3O_5 (‹ 9-309 ICDD–JCPDS) $a = 0.979 \pm 0.001$ nm, $b = 0.994 \pm 0.002$ nm, $c = 0.375 \pm 0.001$ nm

This fact opens a new scope in the complex development of the Yareg deposit because the Ti_3O_5-bearing products can be used as raw material in the titanium oxide ceramics.

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