Scientific basis for creation of construction materials based on titanium and alumina minerals

O Kotova, A Shmakova and A Ponaryadov
Laboratory of Mineral Raw Technology, Institute of Geology Komi SC UB RAS, 167982 Syktyvkar, Russia
E-mail: kotova@geo.komisc.ru

Abstract. Currently there is a need in affordable and accessible materials with specific physical and chemical properties. Al- and Ti-minerals are excellent test objects for correlation between structure and physical properties of mineral. For example, corundum and ilmenite are related to the same structural type (rhombohedral lattice R3) and possess various physical properties. With the help of modern equipment we studied titanium- and aluminum-containing concentrates of natural raw and also products of various kinds of influences on them, which showed signs of nanostructuring. We observed methods of directional change of physical and chemical characteristics of Al- and Ti- minerals and creation of new commercial products.

1. Introduction
Al- and Ti-minerals (products of natural and technogenic processes) are considered in the applied mineralogy as geomaterials for specific technological tasks.

Aluminum and titanium, among other non-ferrous metals (copper, magnesium, lead, zinc, tin), have a great industrial importance. The cost of non-ferrous metals, as compared with black metals, is high; besides the world market has greatly increased demand for technological and environmental parameters of commercial products. All this stipulates the necessity, firstly, to obtain a deeper knowledge about Al and Ti minerals as carriers of chemical elements and useful properties, about their actual crystal structure; secondly, to understand the mechanisms of changes of the parameters of the minerals under the influence of natural and anthropogenic impacts; thirdly, to obtain new products competitive in the world market [1–4].

The main purpose of this work is the development of scientific base for the creation of construction materials based on titanium and aluminum minerals.

2. Objects and Experimental procedure
The objects of study are Al- and Ti-minerals of natural raw (bauxites, ilmenite-leucoxene ores) and their products (including those with signs of nanostructuring).

The main method of monitoring of the composition and properties of titanium ores and associated minerals, as well as the products of technological processes is a quantitative phase analysis.

The shape and size of mineral were obtained by TEM JSM-6400. Other modern methods were also used, for example, X-ray fluorescence techniques (XRF), optical-mineralogical methods (stereomicroscope MBS-10, polarizing microscope POLAM L-311), etc.

Applying X-ray small-angle scattering method to bauxites we show that the rocks include fine particles with linear size equal to 40 nm. To prove the data of small-angle scattering we tested the
samples of hematite-boehmite bauxites from the Vezhayu-Vorykvinskoe deposit with the help of electron microscopy. The results of small-angle scattering comply with electron microscopy results (Figure 1).

Figure 1. Dependence intensity from angle and SEM secondary electron image of aggregated particles in hematite-boehmite bauxites.

3. Results and Discussion

The development of geomaterial industry should be supported by appropriate resource base. Aluminum ores (bauxites especially) are deficit Russian mineral resource. The main reserves of bauxites in Russia are related to Iksinskoe and Kalinskoe deposits of the Northern Urals, which cannot meet the needs of the domestic industry. Vezhayu-Vorykvinskoe deposit in Timan province (Komi Republic) is promising. Russian aluminum plants operate mainly from imported and tolling raw [4, 5].

The mineral resources of titanium ores are concentrated mainly in the primary deposits of the Northwest (Kola Peninsula, Murmansk region) and Ural (Chelyabinsk region) federal districts and complex (with zirconium) placers from Northern (Komi Republic), Central, Volga and Ural federal districts. According to the content of titanium and technological properties these deposits are inferior to foreign ones.

The changeability of the ores and their further behavior at processing and enrichment is directly connected with their composition and genesis. The stages of ore transformation are often hard to determine. It is possible to get information from the study of such objects but with more pronounced transformations. We studied titanium minerals and stages of their transformation in exogenous conditions of modern coastal-marine placers (on the example of Australia) due to problems of study of buried paleoplacers (e.g. Pizhma, Russia). The complex of mineralogical and analytical methods was used to study the mineral composition, morphostructural characteristics and alteration degree of minerals from the modern coastal-marine placer Stradbroke (Eastern Australia) and Pizhemskoe paleoplacer from Middle Timan (Russia) [1].

It was established that the ore sands of Stradbroke ilmenite are predominated by ilmenite, and Pizhemskoe titanium deposit – by leucoxene (Figure 2). Paleoplacers of Pizhma represent more rebellious ores due to predominant titanium (and not only) structures, alongside with the main ore components there are other metals, which occurrence form can be different (isomorphic impurity, independent mineral phases).

The physical and chemical characteristics of Ti- and Al-minerals often do not meet the demands of consumers. The methods of directional change of these characteristics under various types of energy impacts are widely used and developed. For example, the most important obstacle for technological processes is the enrichment of bauxites by nonmagnetic ferrous oxides - goethite-hydrogoethite and hematite-hydrohematite. There is an assumption that if goethite and hematite are transformed to the ferromagnetic phases in the bauxites, then it could provide separation and selective recovery of aluminum and ferrous components, which in turn will improve the quality of aluminum concentrate and give the possibility to obtain additional - ferrous – industrial product. This is confirmed by the
experience of transformation of nonmagnetic oxyhydroxides and ferrous oxides into magnetite to improve the washability of the iron ores. At present we have convincing evidences of the efficiency of irradiation of ferrous nonmagnetic materials by high-energy electrons, which results in transformation of non-magnetic and low magnetic minerals into ferromagnetic minerals [6].

**Figure 2.** Titanium minerals of modern coastal-marine placer in Stradbroke Island, Eastern Australia (A) and Pizhma pale placer in Middle Timan (B).

Using a modern instrument base for mineralogical studies, we at the first time examined the effect of thermal and radiation-thermal influence on Middle Timan ferriferous bauxites (Figure 3) to improve their technological properties.

**Figure 3.** Image of thin sections of bauxites in plane polarized light (a) Clastic structure of boehmite-diaspore-chamosite-anatase-rutile aggregates. (b) Hematite-goethite structures in the form of concretions

We showed that after heating up to 600°C and 60 minutes-soaking a complete decomposition of goethite and boehmite occurred with formation of hematite and γ-Al₂O₃ spinelide accordingly. The magnetic properties of the bauxites reduced and the yield of magnetic fraction was lower. The radiation-thermal exposure results in forming ferromagnetic phases (Figure 4), which facilitates the separation of alumina and ferriferous components of the bauxites, and also allows solving the problem of selective extraction of phases of rare and rare earth elements. To realize this scenario it is necessary to disintegrate bauxite substance more finely.

It should be noted that titanium and aluminum ores are raw for compositional materials. In the article [3] were studied the dependence of physical properties on the structure of composite materials prepared from natural ilmenite, and alumina ceramics (Figure 5) with different content of impurities. X-ray analysis showed that in both cases the corundum structural type was predominant. The observed effect of the strong influence of impurities on the radiophysical characteristics allows synthesizing both radiotransparent and radioabsorbing materials (Figure 6) with the same crystal structure.
Figure 4. XRD pattern of radiation-thermal modified bauxite and thermal dependence of volumetric magnetic susceptibility revealed in different experiments: 1 — heating without irradiation, 2 — heating with irradiation, 3 — magnetic susceptibility values in the irradiation experiments after 20 min exposure at 200 and 300 °C.

Figure 5. The unit cell of corundum (trigonal rhombohedral crystal system, space group R3c to (1 - oxygen atom, 2 - Al atom in corundum and Fe atom in ilmenite, 3 - Al (Cr, Fe) atom in corundum or Ti in ilmenite [3].

Figure 6. Reflectance and transmission spectra of ceramics with corundum structure [3].
RF properties of ceramic and composite materials based on corundum and ilmenite are characterized by the simultaneous expression of both scattering and absorption. The fine structure of reflectance spectra is characteristic for solid solutions with a complex chemical composition. Therefore to obtain radiotransparent materials it is necessary to minimize the amount of impurities. During the synthesis of radioabsorbing materials, on the other hand, it is necessary to add magnetically active impurities forming a dielectric ferrite-like structure. The materials, synthesized from natural ilmenite, can be used as EMR (electromagnetic radiation) absorbers, and on the basis of corundum ceramics containing active impurities it is possible to produce SHF (super high frequency) filters, which are EMI transmissive in the narrow frequency range.

New applications of titanium ore based on its mineralogical and processing characteristics have a real commercial interest: the list of commodity products is expanding (and consequently the prospects for production), energy costs are reducing, environmental risks are decreasing, efficiency of sustainable development of region is increasing. One of the promising directions of solution of this problem can be the synthesis of titanium dioxide nanotubes from mineral raw materials (for example from titanium ore of Pizhemske deposit) [7].

In recent decades one-dimensional nanostructure materials, derived from titanium dioxide, have been widely used in photocatalysis, as a base for catalysts, implants, reagents enhancing blood coagulability, batteries etc. [2, 8].

Due to a high cost of commercially available TiO$_2$ nanoparticles their synthesis from cheap natural raw materials by hydrothermal method becomes very important.

The TiO$_2$ nanotubes (figure 7) were obtained using simple hydrothermal method in Laboratory of mineral raw in Institute of Geology Komi SC UB RAS. An inexpensive natural raw material – non-magnetic fraction of gravity concentrate of titanium ore of Pizhemske deposit – was used as a starting material. The synthesized titanium dioxide nanotubes have outer diameter 70–100 nm and length up to 4500 nm. The synthesized TiO$_2$ nanotubes have a large surface area that results in a good sorbent material.

**Figure 7. SEM image and XRD patterns for TiO$_2$ nanotubes obtained from natural leucoxene ore (Pizhemske deposit)**

The main (strategic) task of mineralogical geomaterial science is to combine the efforts of specialists in related scientific areas (geologists, mineralogists, crystallographists, chemists, physicists, engineers and others) with the aim of

- development of theoretical and experimental bases of the development of mineral resources,
• determination of fundamental laws of formation and properties of natural and technogenic structures (including nanoscale phases), their kinetic and dynamic features in technological processes,
• development of methods for directed change and decomposition of geomaterials in the process of technical functioning
• synthesis of new materials and creation of science-based technologies.

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