Structure and strength characteristics of rutile ceramics obtained with the approach of oxidative constructing

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Abstract. As a result of applying the oxidative constructing approach, compact samples of rutile ceramics were obtained at 875°C for 160 days. An analysis of the distribution of microhardness over the thickness of a rutile sample obtained at 875°C at different times of synthesis indicates an inhomogeneous structure of rutile ceramics, which indicates that the material is defective due to its porosity. The regularities of changes in the nature of the layering of the structure of ceramics are established depending on the portion of the kinetic curve of the direct oxidation of titanium. It is shown that the presence of a defect in the form of a gap between the layers formed during the oxidation of titanium blanks at the stage of completion of the exponential growth of the kinetic curve is due to a natural barrier – a massive rutile ceramic layer, which limits the free access of oxygen to the TiO$_2$/Ti interface.

1. Introduction
Rutile ceramics with unique properties: chemical inertness, high dielectric constant, photocatalytic properties, is used in radio electronics, as well as a carrier of catalysts, including those working in aggressive media. The authors have implemented a new approach to the production of compact ceramic products – oxidative constructing, based on a controlled one-stage oxidation process of metal blanks of any given shape and allowing to obtain ceramic materials for structural and functional purposes [1, 2]. The application of the oxidative constructing approach makes it possible to obtain thin-walled (wall thickness of the order of 100 μm or less) honeycomb ceramic blocks, monolithic fibrous ceramic filters, gas-permeable plates and other structured ceramic products that have a developed physical surface and high gas-dynamic characteristics. Previously, the changes in the titanium workpiece during its oxidation were studied in detail, the features of the structure of the formed rutile were investigated depending on the prehistory of the initial titanium, a mathematical model was developed and verified, which describes the physicochemical processes of titanium oxidation [3], the kinetic regularities of the oxidation process of massive titanium samples were established [4], and also developed methods for producing honeycomb and fibrous ceramic products of various designs and shapes [5].

Investigation of the structure and strength characteristics of rutile ceramics obtained using the oxidative design approach is of interest and is the goal of this work.

2. Experimental
The object of research is rutile samples obtained as a result of the oxidation of VT1-0 titanium at 875°C for 160 days in a furnace with free air access. The kinetics of the process was monitored using the thermogravimetric method [6].
SEM images of ceramic specimen chips parallel to the oxide growth axis were obtained with a LEO 1420 microscope, Carl Zeiss. The studies were carried out in the secondary electron mode; application method - cathode sputtering, coating material - gold (SC 7640 Polaron unit). Using the program ImageJ, National Institutes of Health for the analysis and processing of images, the pore area of the selected areas was estimated [7].

Microhardness measurement was carried out according to GOST 9450-76 on a Wolpert 402MVD hardness tester. The indenter was a regular tetrahedral diamond pyramid with an apex angle of 136 °. The load on the indenter varied from 0.01 kg to 0.02 kg, depending on the thickness and brittleness of the ceramic samples under study.

### 3. Results and discussion

Figure 1 shows the kinetics of titanium oxidation at 875° C.

![Figure 1. Kinetics of titanium oxidation at 875°C.](image)

**I** - exponential growth; **II** - completion of exponential growth; **III** - linear section

A schematic diagram of the formation of rutile ceramics on the surface of a titanium workpiece within the framework of the oxidative design approach is shown in Figure 2.

![Figure 2. Schematic diagram of the formation of rutile ceramics on the surface of a titanium workpiece in the framework of the oxidative design approach.](image)

**C** – central region of the sample; **M** - sample area adjacent to the metal; **K** - sample area adjacent to oxygen

The result of evaluating the porosity of the synthesized material according to SEM images is shown in Figure 3.
The percentage of pores in the considered regions of SEM images of ceramic specimen chips parallel to the oxide growth axis is indicated.

As was shown by the authors earlier [8], when titanium is oxidized for 38 – 40 days (exponential portion of the kinetic curve), the growth of ceramics occurs both at the interface with oxygen (region K) and at the interface with metal (region M). Based on the evaluation of the SEM images of the synthesized samples, the porosity of the ceramics for all considered areas increases.

Upon reaching the oxidation time equal to 40 days, the kinetics of the titanium oxidation process is characterized by a linear dependence, in connection with which the growth of ceramics proceeds mainly at the interface with the metal (region M); the number of pores, as well as their average size, decreases.

According to the analysis of SEM images, the obtained ceramics has a clearly pronounced layered structure; however, the nature of the structure changes depending on the synthesis time. The formation of rutile ceramics includes the formation of porous layers that undergo coarsening during further oxidation (Figure 4).

Microhardness analysis showed the heterogeneity of the ceramic structure over the sample thickness, which can be associated with the defectiveness of the material due to increased porosity.

Figure 5, I shows the distribution of microhardness over the thickness of a rutile sample obtained for 7 days at 875°C. The distribution is generally uniform over the entire thickness of the sample. The behavior of the dependence under consideration correlates with the conclusion about the multi-layer ceramic. Region M is characterized by low values of microhardness.

Figure 5, II shows the distribution of microhardness over the thickness of a rutile sample obtained for 25 days at 875 °C. The considered distribution is typical for ceramics obtained on the exponential part of the kinetic curve.

For ceramics synthesized within 7 days, the length of the region of low microhardness values is 150 μm, while for ceramics synthesized within 25 days it is 1 400 μm, which can be explained by the fact that at the stage of oxidation, which is described by an exponential regularity, with the flow Over time, a massive ceramic layer forms, which restricts the free access of oxygen to the TiO₂/Ti interface.
As a result of the lack of oxygen in the reaction zone in the M region, a layered ceramic with defects in the form of slits is formed (Figure 4, II), which affects the strength characteristics. The phenomenon under consideration occurs due to the predominance of titanium diffusion to the sample surface over oxygen diffusion into its bulk.

Figure 5, III shows the distribution of microhardness over the thickness of a rutile sample obtained for 105 days at 875 °C, which corresponds to the linear portion of the kinetic curve. The growth of ceramics is mainly in the M area; dense low-porosity ceramics was installed (Figure 4, III). Mechanical properties in the considered area are distinguished by high values of microhardness 900 – 1000 MPa.

![Figure 5](image_url)

**Figure 5.** Distribution of microhardness over the thickness of a rutile sample obtained at 875°C for I – 7 days; II – 25 days; III – 105 days.
The center of area C is taken as "zero"; left - area M; right - area K
4. Conclusion
An analysis of the distribution of microhardness over the thickness of a rutile sample obtained at 875°C at different times of synthesis indicates an inhomogeneous structure of rutile ceramics, which indicates that the material is defective due to its porosity.

The regularities of changes in the nature of the layering of the structure of ceramics are established depending on the portion of the kinetic curve of the direct oxidation of titanium.

It is shown that the presence of a defect in the form of a gap between the layers formed during the oxidation of titanium blanks at the stage of completion of the exponential growth of the kinetic curve is due to a natural barrier - a massive rutile ceramic layer, which limits the free access of oxygen to the TiO₂/Ti interface.

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