IMPACT OF POWDERY OXIDE LAYER IN THE TITANIUM/RUTILE SYSTEM PREPARED BY OXIDATIVE CONSTRUCTING OF CERAMIC MATERIALS

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Abstract

The powder oxide layer is formed at the interface between the metal and monolithic oxide after several days of titanium oxidation of bulk titanium samples at 750-900°C. The produced titanium oxides were characterized by means of SEM, XRD techniques. The formation mechanism of the powder oxide layer is discussed.

Key words: oxidative constructing, titanium oxidation, powdery rutile, ceramic

1. INTRODUCTION

Modern preparation technologies of metal oxide-based ceramic materials are related to the sintering of powder oxides of metals. In this case, serious limitations take place in preparing shaped final products, in particular, having thin-wall configurations. Moreover, various extraneous substances (solvents, bonds, etc.) used during the sintering of powders result in the contamination of final products.

To eliminate the aforementioned shortcomings, a new approach was suggested and brand new process for the preparation of thin-walled oxide ceramics was developed [1], which is based on the controlled oxidation of metallic performs and called oxidative constructing (OC). The approach was found to be rather simple, efficient, and economy. The used technique almost gives no waste products and are ecological (no toxic substances are formed).

One of more interesting directions in using the OC for the preparation of rutile ceramics is the high-temperature oxidation of titanium. Rutile prepared in using such a technique can be applied as condenser ceramics, high-Q dielectric resonator (microwave technique), field-effect transistors, catalytic membranes, and selective membranes for the separation of gas-mixture.

The oxidation process was found to be rather rapid beginning from 750°C. The oxide formed on the titanium surface during oxidation of massive (bulk) samples has a dense structure. Although the ceramics is sufficiently dense, no spalling the oxide from the metal surface takes place during the whole oxidation process and, even under certain conditions (at stage of intense exponential growth), the ceramics formed has the high adhesion for the metallic core. This growth process characterized by complex kinetics, in general, exhibits an exponential-linear dependence on the oxidation time. It should be noted also that the oxidation oneself is a prolonged process and, depending on assigned tasks, can take tens and, sometimes, hundreds days. The change of oxidation mechanism occurs at the bifurcation point whose position depends substantially on the process temperature and geometry of sample used for the oxidation.

Even after several days of oxidation of bulk titanium samples at 750-900°C, along with the monolithic oxide, the powder oxide layer is formed at the interface between the metal and monolithic oxide. Moreover, its amount varies depending on the time of oxidation. This can indicate the appearance of an important factor that either affects the oxidation process or results from processes occurring inside the metal/ceramic system.

2. EXPERIMENTAL RESULTS

To clarify peculiarities of the formation of powdery layer, we studied a series of titanium samples that have the same prehistory and are similar in the preform shape. As the starting material, we used cast titanium (prepared by arc melting of VT1-00 alloy); samples were prepared in the form of disks 60 mm in diameter and 20 mm in thickness. All samples were placed into an electric resistance furnace and subjected to oxidation at 875°C. The oxidation of each perform was finished at a certain instant time corresponding to a specific point in the kinetic curve of oxidation (Fig. 1). The used times of oxidation were 5, 14, 20 and 55 days (samples 1, 2, 3, 4, respectively).
Fig. 1. Kinetics of titanium oxidation at 875°C: m is the oxide mass reduced to the unit surface; \( \tau_b \) is the bifurcation point; arrows 1, 2, 3, 4 indicate stages of kinetic curve, which correspond to number of samples withdrawn from the furnace after 5, 14, 20, and 55 days, respectively. Dashed line is the extended theoretical exponential curve.

Figure 2 shows the curve of growth of the powdery layer.

Fig. 2. Curve of growth of powdery rutile
The appearance of very small amounts of powdery oxide is observed even after first 5 days of oxidation, i.e., at the stage of intense growth of monolithic rutile. Subsequently, as the oxidation process develops, its amount increases. It follows from Fig. 3, Fig. 4 that, within the time range under consideration, the time dependence of reduced mass is linear and characterized by sufficiently high correlation coefficient ($R^2 = 0.992$).

The microstructure of the materials was studied by scanning electron microscopy (SEM) using a LEO 1420 (Zeiss) electron microscope and secondary electron image mode; the instrument resolution is 3.2 nm (at 20-30 kV). The maximum magnification is to 30000. During sampling, the structure of material was not disturbed. X-ray diffraction patterns of samples completely correspond to the powder rutile (JCPDS database).

Micrographs taken with the scanning electron microscope are shown in Fig. 3 and Fig.4. The studies were performed taking into account the fact that, during oxidation, different phases directly adjacent to the powdery oxide can affect its microstructure (areas contacting with the metal and monolithic rutile were studied individually).

The studies allowed us to find that the powder layer contacting directly with the metal differs from that adjacent to the monolithic rutile in the size of particles (crystallites) composing the layer. In particular, rutile particles in the area adjacent to titanium are smaller than those in the area adjacent to the monolithic oxide.

The particle size in the area adjacent to the metal is 0,2-0,3 µm (Figs. 3a, 3b, 4a, 4c) and remains almost unchanged during oxidation. The particle size in the area adjacent to the monolithic oxide increases from 0,3 to 3-5 µm (Figs. 3c, 4b, 4d).

Fig. 3. SEM micrographs ($\times$10000) of powder layers formed during oxidative constructing at 875°C: (a) sample 1; at the interface with the metal: (b) sample 2; at the interface with monolithic TiO$_2$: (c) sample 2
This layer is a certain indicator of the course of oxidation process of metallic preform. The presence of a great amount of crystallites (hundreds nanometers in size) near the interface with metal indicates the developed nucleation. The character of porosity, slight consolidation of particles formed the layer, and layered structure of the material are likely to be explained by continuous displacement of the reaction initiation zone (metal surface) to the sample center.

To clarify the effect of prehistory of titanium on the character of behavior of the powdery layer during oxidation, we performed experiments with preforms 15 mm in diameter (d) and 15 and 30 mm in length (l) prepared from titanium of different grades: VT1-0, VT1-00, single-crystal titanium (grown by Czochralski technique), titanium prepared by iodide process, and cast titanium. For all titanium samples, the oxidation was finishes at the stage described by a linear law; the single-crystal titanium is an exception since the stage corresponding to the linear law does not yet start (Fig. 5).
Fig. 5. Oxidation kinetics of different titanium samples: (1) titanium prepared by iodide process; (2) VT1-0; (3) VT1-00; (4) single crystal; and (5) cast

Figures 6-8 shows SEM micrographs of prepared powders.

Fig. 6. Micrographs of rutile powders formed during oxidation of different titanium samples: (a) single crystal; at the interface with the metal: (b) cast titanium; at the interface with monolithic TiO$_2$; (c) cast titanium
Fig. 7. Micrographs of rutile powders formed during oxidation of different titanium samples. At the interface with the metal: (a) VT1-0, (c) VT1-00; at the interface with monolithic TiO\textsubscript{2}: (b) VT1-0, (d) VT1-00

Fig. 8. Micrographs of rutile powders formed during oxidation of iodide titanium samples: (a) at the interface with the metal, (b) at the interface with monolithic TiO\textsubscript{2}

Studies of the phase composition of oxides formed in all samples, which were performed using a XRD-6000 diffractometer (Shimadzu), Cu K\(\alpha\) radiation, a nickel \(\beta\)-filter, and a 20 angular range of 15-75\(^\circ\), showed the presence of only rutile in the powdery layer. Table 1 shows the lattice parameters of rutile in the powdery layer.
Table 1

Lattice parameters of the powdery rutile formed on different titanium samples

<table>
<thead>
<tr>
<th>Sample / Lattice parameter</th>
<th>c, Å</th>
<th>a, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystal</td>
<td>2,9605</td>
<td>4,5962</td>
</tr>
<tr>
<td>Iodide titanium</td>
<td>2,9606</td>
<td>4,5964</td>
</tr>
<tr>
<td>VT1-0</td>
<td>2,9616</td>
<td>4,5966</td>
</tr>
<tr>
<td>VT1-00</td>
<td>2,9612</td>
<td>4,5972</td>
</tr>
<tr>
<td>Cast titanium</td>
<td>2,9616</td>
<td>4,5980</td>
</tr>
<tr>
<td>Experimental error</td>
<td>±0,0015</td>
<td>±0,0025</td>
</tr>
</tbody>
</table>

The dependence of particle size of rutile on its location within the powdery layer was observed for all samples, except single-crystal titanium. In our opinion, this results from the incomplete oxidation process at the stage described by exponential law. In terms of the study, no effect of impurity composition on the formation of powdery layer was found.

3. CONCLUSIONS

The studies performed allow us to state that the interface between the metal and monolithic rutile is a powdery rutile layer that acts as a reactor in the course of oxidation, in which the nucleation of crystallites and their growth occur. The growth kinetics of the layer is described by linear law, and the structure of the formed layer allows us to conclude the completeness of the reaction. In this case, the growth of monolithic oxide is accompanied by the increase in the particle size of powdery layer adjacent to the monolithic rutile from 0,2 to several micrometers, whereas the particle size of the powdery layer adjacent to the metal remains unchanged and equal to ~0,2 μm. The different prehistory of initial titanium performs (VT1-0, VT1-00, iodide technique, casting, and single crystal growth by Czochralski technique) gives no substantial effect on the structure of formed monolithic rutile.

REFERENCES