

INVESTIGATION OF PHASE CHANGES IN MASSIVE TITANIUM PREFORMS IN THE PROCESSES OF OXIDATIVE CONSTRUCTING

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Abstract

The phase composition of massive titanium preforms obtained using oxidative constructing of thin walled ceramics (OCTC) selected from the exponential section of the kinetic oxidation curve is investigated. It is demonstrated with the help of X-ray phase analysis (XPA) that the phase composition of the preform at the oxidation temperature of 875°C represents a number of oxygen and nitrogen based solid solutions.

Key words: titanium oxidation, titanium dioxide, rutile, titanium nitride.

1. INTRODUCTION

Earlier [1], a new approach to obtaining ceramic items with a complex shape (namely, oxidative constructing of thin walled ceramics, OCTC) was proposed. It lies in preforming of items with practically any complex shape from single thin walled or fiber metal fragments and subsequent direct oxidation of this metal preform yielding formation of a monolith ceramic item preserving the geometry of the source metal fragments. Later, this approach was tested using massive metal preforms with a thickness greater than 1 mm.

2. MATERIALS AND METHODS

The processes taking place in the metal-oxide interface and in the bulk of the parent metal during oxidation of massive titanium preforms have not been studied in detail. To elucidate this problem, the oxidation of a number of massive 10 mm thick titanium disk shaped specimens 61.2 mm in diameter was experimentally investigated under similar conditions. Five preforms were selected to study the structural and morphological changes taking place in titanium at the exponential stage/

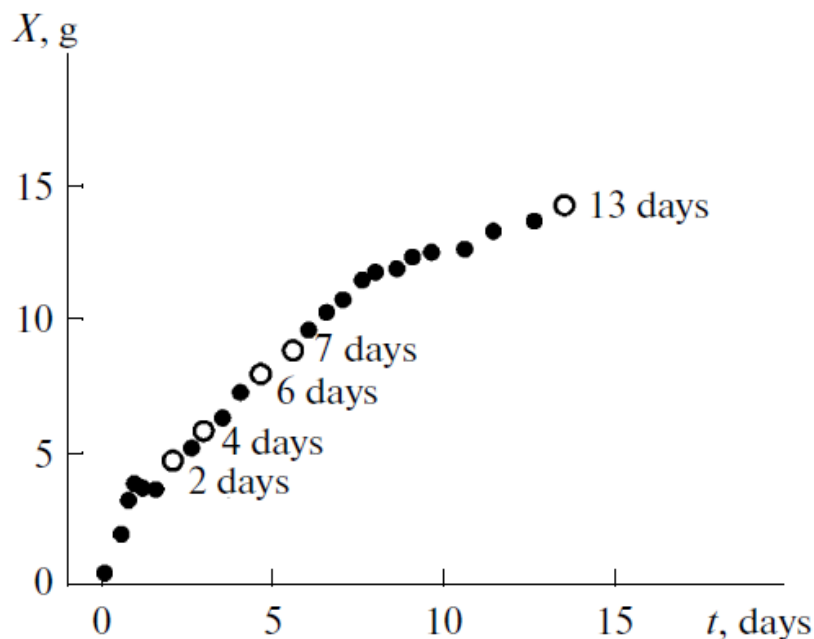


Fig. 1. Kinetics of titanium preform oxidation.

The time of specimen annealing (2 and 13 days) corresponded to the initial and final stages of the exponential oxidation stage. The preforms kept in the oven for 4, 6, and 7 days, respectively, were chosen as intermediate points. Fig. 1 shows the position of the analyzed specimens on the oxidation curve.

Titanium of VT1-0 grade was selected as a material for the source specimens. The oxidation was performed at the temperature of 875°C in an oven with a free access of atmospheric air. Cube shaped specimens with a 10 mm face were cut out for performing the XPA.

Earlier [1], it was revealed that a layer on the order of 1 μm (namely, a solid solution of oxygen in titanium) is observed at the metal-oxide interface from the side of titanium. After oxidation of this series and cutout of the specimens for the experiment, a golden layer was observed at the metal-oxide interface. The phase composition of this layer was determined with an XRD-6000 diffractometer (Shimadzu) using a tube of CuK_α radiation in the range of angles 2θ from 15° to 80°. The diffraction patterns were identified on the basis of the JCPDS data (the international databank on power diffraction standards) [2].

To exclude irrelevant peaks belonging to a standard metal holder, it was decided to perform imaging using a specially designed glass holder. With the depth of the glass holder cell taken into account, the cubes cut out for the XPA were divided into two parts. The phase composition of the specimens was studied layer by layer. For this, the specimen after each double sided shooting was polished on both sides to the depth of 100 μm with the help of a jeweller's saw with a 20 μm grain diameter and the treated surface was cleaned with alcohol. The specimens were polished until the phase composition on both surfaces of the analyzed specimens coincided.

3. RESULTS AND DISCUSSION

The results of the XPA on the VT1-0 source titanium allowed calculating the parameters of the lattice for the metal before the beginning of the oxidation process ($a = 2.9553$ and $c = 4.6814$ Å). Any deviation of the parameter a from the reference value can be related to the process of obtaining the source metal preforms, namely, with some amount of impurity atoms embedded into the lattice. After the rutile grown on the metal surface was removed, the surface of the metal was evened for performing the XPA. The first X-ray images taken in the process of the surface evening revealed the following phases on all specimens: TiO_2 (the basic phase), TiO , Ti_2O , and TiN in the subordinate state for the specimen kept in the oven for 13 days. The percentage of the above phases depended on the time of the metal oxidation in the oven. The diffraction patterns were taken until the instant when the phase composition of the surface facing the air completely coincided with the phase composition of the metal in the specimen bulk.

The parameters of the hexagonal lattice were calculated on the basis of the peaks characterized by the maximum intensity observed during imaging. The variations in the lattice parameters were plotted according to the results of the X-ray study as a function of the section depth. The plots were constructed in the direction from the metal center to the metal-oxide interface. The dependences are shown in Fig. 2 and micrographs of the analyzed samples are shown in Fig. 3

On the basis of the XPA results, for the specimen kept in the oven for 2 days and corresponding to the initial stage of exponential oxidation, the conclusion can be made that the phase composition is uniform over the entire bulk of the specimen except the near surface metal-oxide interface. The calculated lattice parameters for the body of the preform corresponded to the parent VT1-0 titanium. In the near surface zone with the width on the order of 100 μm , the basic phase was $\text{TiN}_{0.3}$ (41-1352). In addition, Ti_2O (11-0218) and TiO_2 (21-1276) were detected as "traces". A sharp jump in the hexagonal lattice parameters up to the parameters corresponding to the tetragonal lattice of TiO_2 (21-1276) was observed at the metal-oxide interface. In addition, when studying the near surface layer, the authors of [3] revealed a pronounced specificity of the coherent scattering area (CSA) that can be related to the high energy of nucleation of new crystals at the metal-oxide interface. Owing to this, an increase in the layer thickness is predominantly determined by the growth of the initially formed crystals whose competition yields the formation of a well marked texture.

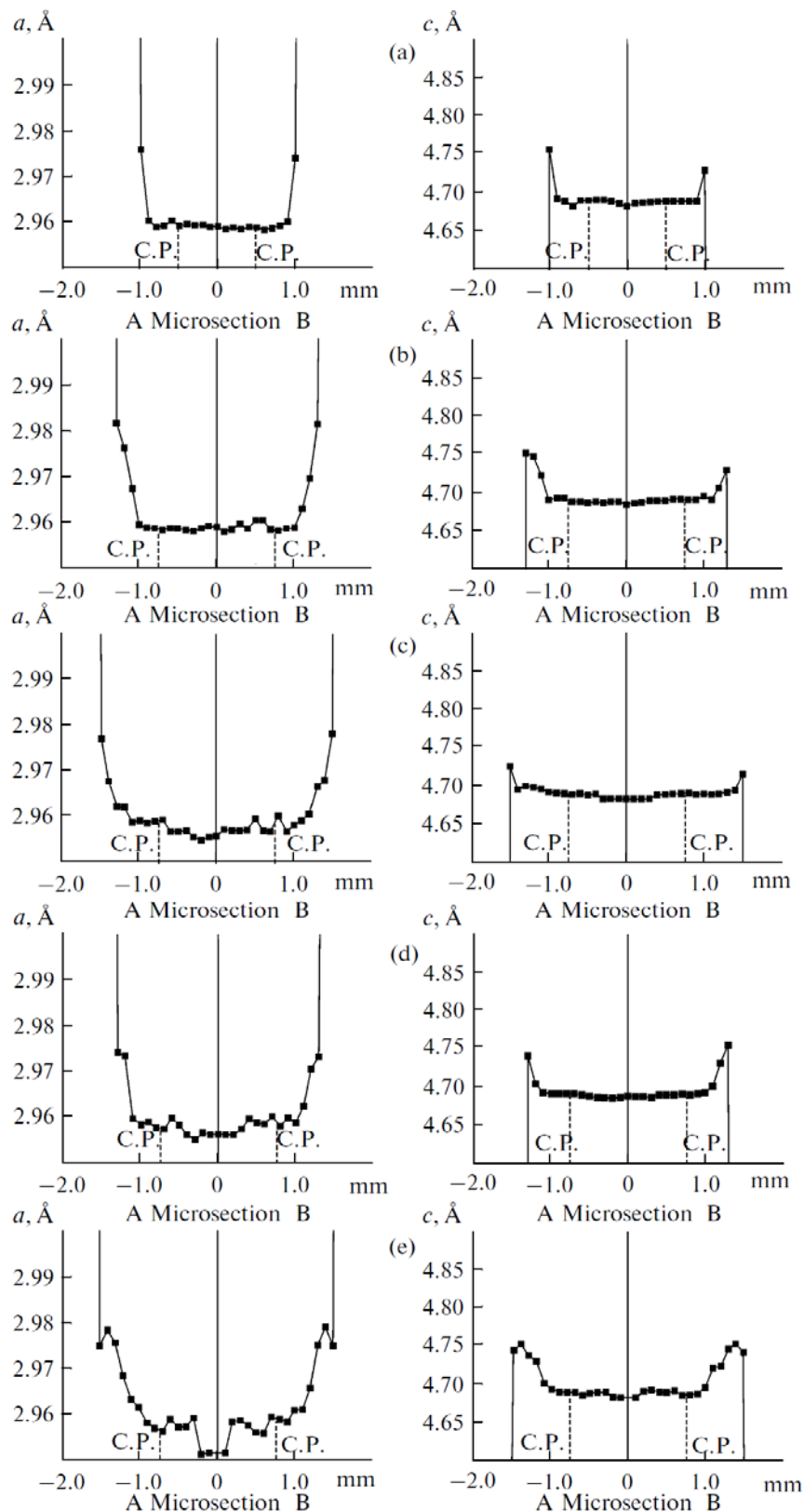
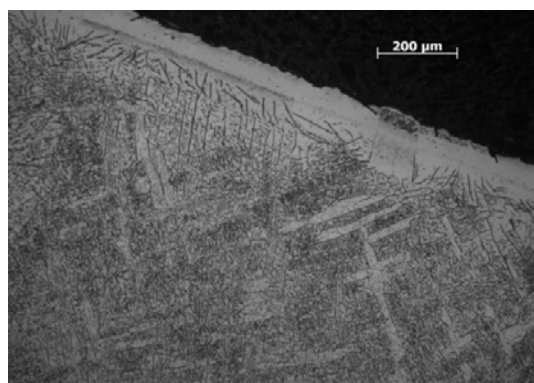
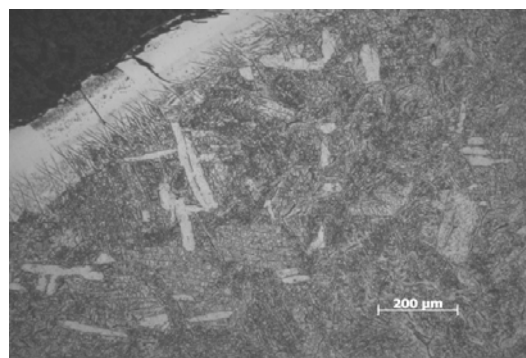


Fig. 2. Lattice parameters a and c for the specimens kept in the oven for (a) 2 days, (b) 4 days, (c) 6 days, (d) 7 days, (e) 13 days. The plot was constructed in the direction from the metal center to the surface. Zero marks the specimen center along the X axis; the reference parameter of the Ti(44-1294) [2] lattice is marked on the Y axis.

A and B are two halves of the specimen. C.P. mark the points of the phase composition coincidence on the analyzed specimens.



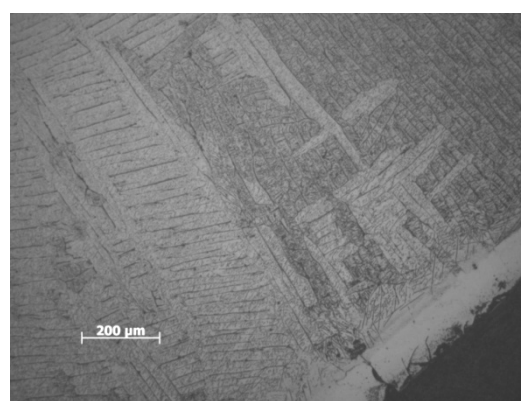
(a)



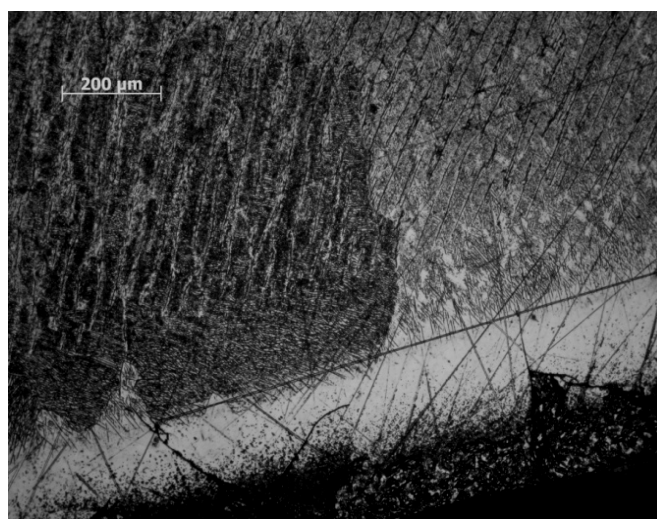
(b)



(c)



(d)



(e)

Fig. 3. Micrographs of the analyzed samples oven for (a) 2 days, (b) 4 days, (c) 6 days, (d) 7 days, (e) 13 days.

The thickness of the remaining body of the metal at the instant when the phase composition of the surfaces of the analyzed specimens coincided was on the order of 7.1 mm.

It can be seen by the example of the specimen kept in the oven for 4 days that the width of the near surface region with the $\text{TiN}_{0.3}$ (41-1352) basic phase increases to 300 μm . In this case, the content of the TiO_2 (11-0218) and TiO_2 (21-1276) phases remains minimal. In addition to the aforementioned phases, a negligible concentration of the $\text{TiN}_{0.26}$ (44-1095) phase was also detected. The lattice parameters in the metal bulk are constant and correspond to the parent titanium. Thus, it can be assumed that the formation of nitride phases at the initial exponential stage of oxidation yields screening of the metal bulk from the penetration of oxygen deep into the specimen; as a result, no changes in the lattice parameters in the center of the preform are observed.

The above dynamics on variations in the parameter c of the hexagonal titanium lattice in the process of oxidation at the exponential stage allow assuming that the octahedrons in the titanium lattice which are not filled with the oxidizer ions form columns extended along the c axis of the crystal. Such incomplete filling of the octahedra yields formation of the channels for embedding of the oxidizer ions into the hexagonal titanium lattice. Nitrogen serves as an oxidizer for the body of the metal preform; the depth of its penetration into the bulk is substantially larger than that of oxygen [3].

The thickness of the remaining body of the metal at the instant when the phase compositions on the surfaces of the analyzed specimens coincided was on the order of 6.7 mm.

On the basis of the variations in the lattice parameters of the specimen kept in the oven for 6 days, rearrangement of the body of the preform without any changes in the phase composition becomes evident. This can be explained by the redistribution of micro flaws over the bulk of the preform. Their concentration becomes maximal in the near surface region and decreases toward the center of the specimen. As a result, the parameters in the center of the specimen approach the reference values for the lattice of titanium (44-1294) in accordance with the JCPDS data. In this case, the extension of the region where $\text{TiN}_{0.3}$ (41-1352) is a basic phase remains unchanged. This fact points to the preservation of the screening properties of the nitride layer.

The thickness of the remaining body of the metal at the instant when the phase compositions on the surfaces of the analyzed specimens coincided was on the order of 6.4 mm.

The tendency toward rearrangement of the main body of the metal revealed in the specimen kept in the oven for 6 days was also observed in the specimen annealed for 7 days. The above two specimens differed in the dynamics of variations in the parameter c in the process of oxidation of the metal preform. In 7 days, the magnitude of the parameter c becomes constant for the entire bulk of the unoxidized metal. This can be related to the embedding of the oxidizer atoms into the lattice vacancies due to their rise to the metal-oxide interface and recombination of point flaws (impurity atoms, vacancies).

The penetration of nitrogen inside the preform becomes possible because of the fact that the near surface nitride layer loses its screening properties. This can be related to plastic deformation, fragmentation, and disorientation of the growing crystallites of a new phase, which yields a less pronounced texture in the near surface layers and substantial critical stresses resulting in the formation of the channels for the gas transport into the preform [4-7].

An area with the width on the order of 300-400 μm where $\text{TiN}_{0.3}$ (41-1352) is the basic phase and Ti_2O (11-0218) and $\text{TiN}_{0.26}$ (44-1095) are in the subordinate state was revealed on the surface of the analyzed specimen.

The thickness of the residual metal at the instant when the phase compositions on the surfaces of the analyzed specimens coincided was on the order of 6.2 mm. The results of the XPA of the specimen kept in the oven for 13 days made it possible to reveal a region with the width on the order of 300 μm in the center of the specimen corresponding to the parameters of the lattice of almost pure Ti(44-1294). It is followed by a titanium region with the width on the order of 8.5 mm with the lattice distorted by the atoms of the embedded oxidizer. Then there is a region with the width of 200 μm whose lattice parameters correspond to $\text{TiN}_{0.26}$ (44-1095) and a region with the width of 300 μm on the metal-oxide surface identified as $\text{TiN}_{0.3}$ (41-1352). After the final nitride region, the lattice parameters drastically increase and reach values corresponding the TiO_2 (21-1276) lattice. No regions corresponding to lower oxides such as TiO_2 (11-0218) and TiO (89-3074) were detected. They were observed only on the first microsections from the surface (100-200 μm) as "traces". Jump-like variations in the lattice parameter a were observed over the entire region where the titanium lattice is preserved, the parameter c being almost constant.

The thickness of the remaining body of the metal at the instant when the phase compositions on the surfaces of the analyzed specimens coincided was on the order of 5.5 mm.

4. CONCLUSIONS

Thus, on the basis of the experimental data, the conclusion can be made that the oxidation mechanism is divided into two processes, namely, diffusion of nitrogen and oxygen into the metal and diffusion of titanium from the bulk of the preform toward the surface. For the ion lattice of rutile to be constructed on the metal surface (with the stoichiometry and electrical neutrality being preserved), such a scheme requires simultaneous diffusion of titanium and electrons from below.

Taking into account the assumption concerning the effect of the concentration and positioning of point flaws in the lattice on the oxidation process, note that the flaws, whose concentration can vary over the length of the growing crystallites and determine the existence of a concentration gradient, play a role in the diffusion mechanism. In other words, we deal with the point flaws formed in the lattices of titanium based compounds in the case of their deviation from the stoichiometric composition.

Such analysis of the variations in the lattice parameters in the process of oxidation at the exponential stage made it possible to reveal that the octahedra in the titanium lattice that are not filled with the oxidizer ions form a column extended over the crystallite c axis and, thus, incomplete filling of the octahedra yields formation of the channels for embedding of the oxidizer ions into the hexagonal titanium lattice.

The transition from the exponential law on the kinetic oxidation curve to the linear law can be related to the onset of the time independent concentration gradient of nitrogen and oxygen atoms in the bulk of the titanium preform. This condition is observed only when the near-surface layer with $\text{TiN}_{0.3}$ (41-1352) as a basic phase loses its screening properties for the preform bulk. As a result, a concentration gradient for nitrogen and oxygen is formed over the metal bulk.

In this case, it can be assumed that, at the initial stage of oxidation when the exponential law is valid, the rate of total absorption of the oxidizer atoms decreases in time, which is confirmed by the onset of a nitrogen concentration gradient in the body of the preform.

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