OXIDATION OF TITANIUM POWDER WITH HEATING IN AN AIR ATMOSPHERE

V. V. Tavgen', E. V. Shinkareva,
E. V. Karpinchik, and Yu. G. Zonov

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Titanium powder is introduced as a current-carrying filler into composites with inorganic binders in preparing resistive coatings [1, 2]. Property stability and operating reliability of composite current-carrying coatings depend mainly on the oxidation of titanium powder under the action of oxygen from the air. Oxidation of monolithic specimens of titanium has been studied quite well [3-6]. In particular, it is established that the phase composition of the oxide film varies from TiO_2 in the outer layer to TiO and suboxides in the inner layers.

We have studied oxidation processes for finely-dispersed (grain size less than 40 μm) titanium grade PTOM (TU 14-1-3086—80) prepared by hydride-calcium reduction. The powder contained 0.08% (wt.) N, 0.05 C, 0.4 H, 0.1 Si, 0.08 Ca and 0.004% (wt.) Cl. Apart from α-Ti in the original powder there is a small amount (judging from the intensity of diffraction maxima) of $TiH_{1.924}$, i.e., the hydrogen contained in the titanium (0.4% (wt.) or 16.2% (at.)) bonded into hydride.

Titanium powder was held in a corundum boat for 1 h in air at temperatures from 300 to 800°C. Selection of calcining conditions for specimens was based on the results of prior kinetic studies (Fig. 1). With a fixed temperature the main mass of the titanium powder manages to react during 1 h, after which the process slows down sharply, probably connected with diffusion of oxygen into the reaction zone through the layer of oxidation product.

Comprehensive thermal analysis carried out in a MOM derivatograph with a rate of temperature increase of 5 deg/min (a sample weighing 3 g was set up on the plate holders). The surface structure of specimens was studied in a JSM-35C scanning electron microscope with a 6000-fold magnification. X-ray phase analysis of powders was performed in a DRON-3 diffractometer (copper K_α-radiation, NI-filter) using a GPVT-1500 high-temperature attachment for recording x-ray diffraction patterns at temperatures differing from room temperature.

On the DTA curve for titanium in the temperature range 300-320°C an endothermic effect is observed not connected with a change in specimen weight (Fig. 2). On cooling of a specimen heated to 360°C in the temperature range 240-180°C an exothermic effect is recorded (Fig. 2b). In the range 20-360°C there are also reversible changes of specimen phase composition. Whereas with an increase in temperature to 275°C titanium hydride $TiH_{1.924}$ is retained, at 350°C it is not recorded by x-ray phase analysis (Fig. 3). With this temperature diffraction maxima are noted in x-ray diffrction patterns of a compound not identified by us with interplanar distances 2.39, 1.69, and 1.37. During subsequent specimen cooling to room temperature the titanium hydride phase is revealed again and the maxima disappear which we connect with the unidentified phase. The intensity of diffraction maxima for α-Ti in the temperature range 20-350°C are almost unchanged. Consequently, the endothermic effect at 310°C is due to transformation of titanium hydride. According to the phase diagram for the titanium-hydrogen system [7] at 319°C there is eutectoid transformation of titanium hydride (γ-phase) into α- and β-Ti.

Comprehensive thermal analysis (Fig. 2) makes it possible to separate four stages of oxidation for titanium powder in air with the temperature increasing at a rate of 5 deg/min. The increase in specimen weight as a result of combining oxygen from the air is observed after 280°C. The rate of the process increases constantly with further heating to 495°C. On reaching this temperature, slow oxidation changes into rapid reaction accompanied by release of a significant amount of heat, which is indicated not only by a clearly defined exothermic effect on the DTA curves, but also a burst on the temperature curve as a result of specimen warm-up. The specimen weight at 620°C increases by 12.7%. Then in the temperature range 620-680°C the oxidation rate falls markedly.
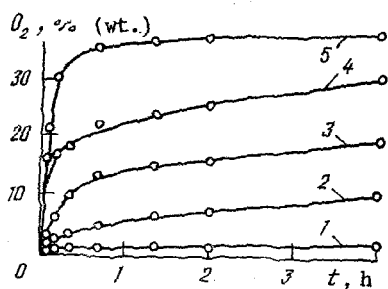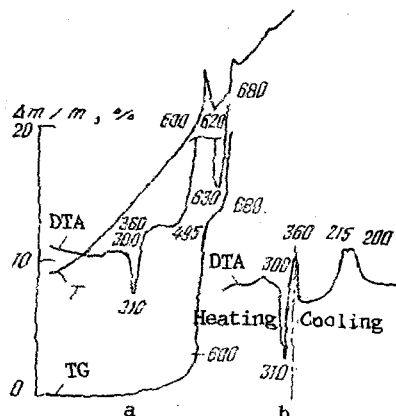
Fig. 1. Oxidation of titanium powder in air at temperatures of 500 (1), 600 (2), 650 (3), 700 (5) and 800°C (5).

Fig. 2. Results of comprehensive thermal analysis of titanium powder specimens (a) and differential heating and cooling curves of it in the temperature range 20-360°C (b).
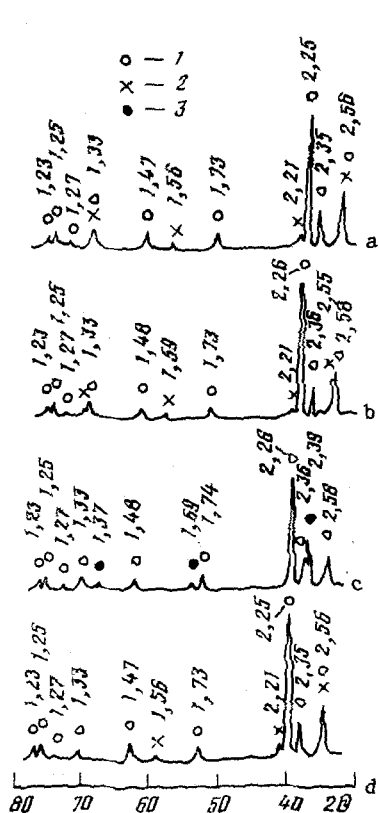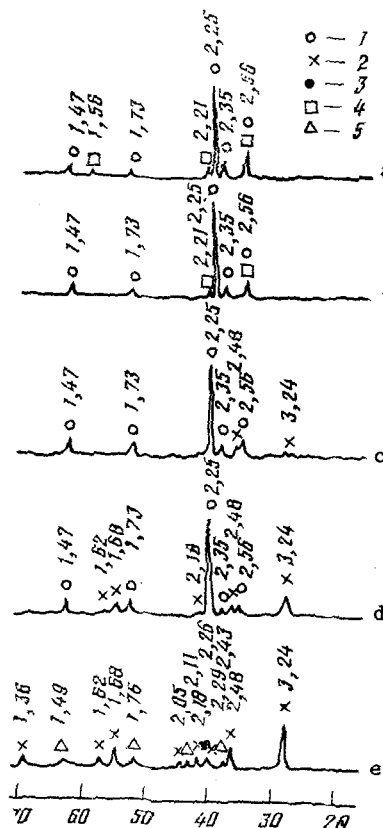

Fig. 3. X-ray diffraction patterns for specimens of titanium powder at 20 (a), 275 (b) and 350°C (c), and also at 20°C after cooling from 350°C (d). 1) Ti; 2) TiH$_{1.924}$; 3) unidentified phase.

Fig. 4. X-ray diffraction patterns of original titanium specimens (a) and those heat treated at 500 (b), 600 (c), 700 (d), 800°C (e). 1) Ti; 2) TiO$_2$; 3) Ti$_2$O; 4) TiH$_{1.924}$; 5) unidentified phase.

If we proceed from general topochemical features, then the stage of increase in oxidation rate is connected with generation of a process which then occurs in a kinetic region. The slowdown in reaction is caused, as a rule, by formation of a dense layer of oxidation product which promotes a changeover of it into a diffusion region. If the reaction product layer
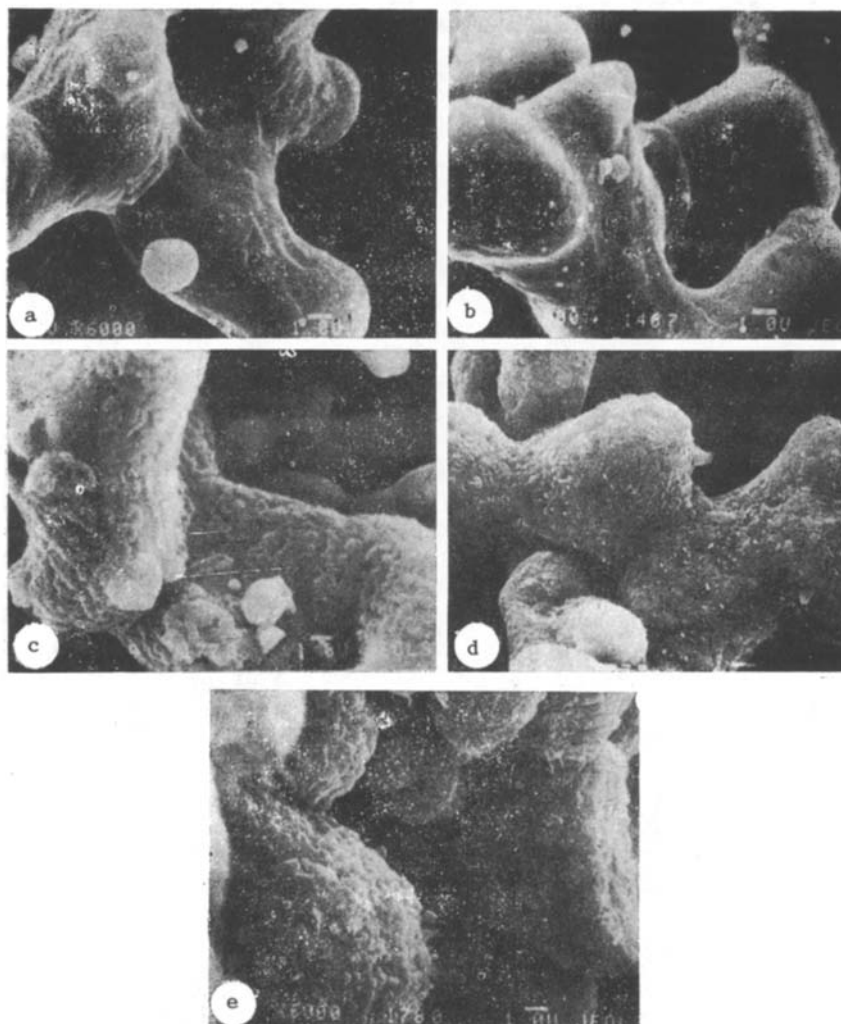
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Fig. 5. Particles of original titanium powder (a) and that heat
treated in air at 500 (b), 600 (c) 700 (d), 800°C (e).

is stable with further heating the process almost ceases. If further heating leads to break-
down of this layer, the reaction may accelerate again and proceed to the end. In fact, at
temperatures above 680°C oxidation of titanium powder occurs again at an increasing rate.
The release of heat with a simultaneous increase in specimen weight does not cease up to com-
plete metal oxidation which sets in at 940-960°C.   The final increase in specimen weight is
64.7%, which is close to the value calculated for the process of forming titanium dioxide
from metal.

The mechanism described for oxidation of titanium powder is confirmed by the results
of x-ray phase analysis. In x-ray diffraction patterns for specimens held for 1 h at 300-
500°C there are no diffraction maxima for titanium oxides (Fig. 4). The rutile phase only ap-
pears after 600°C. The intensity of diffraction maxima for TiO_2 increases as the oxidation
temperature increases, but the intensity of maxima for titanium metal decrease. In a speci-
men treated at 800°C rutile and a small amount of TiO_2 are mainly detected, and titanium me-
tal is not revealed.

One more indicator of processes which occur during oxidation of titanium powder are
electron microscope exposures. The original powder consists of individual or branched den-
dritic particles circular in shape with a size from one to several tens of microns (Fig. 5).
After heat treatment at 500°C the surafce of titanium particles is almost unchanged, but the
texture of the metal is clearly distinguishable in pictures of the original powder smoothed
due to formation of an oxide film. At 600°C a considerable part of the surface of particles
is covered by a flaky film forming a labyrinth structure. With an increase in oxidation
temperature to 700 and 800°C all of the surface of particles is covered by an oxide layer with
crystals of flaky form. The size of crystals increase with an increase in temperature. Perpen-

dicular to the surface of particles, thin acicular rutile crystals grow which cause powder sintering. It should be noted that in all stages of oxidation the original surface relief and the rounded shape of particles are retained.

Thus, slow oxidation of finely-dispersed titanium by oxygen from air commences at 280°C and it increases sharply at 600-620°C. The dense film of oxides which forms plays a passive role limiting access of oxygen to the titanium surface. In the final stage of oxidation at 700-720°C the oxide film becomes coarsely crystalline, porous, and with an increase in temperature the process is completed by total oxidation of titanium to TiO_2.

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POSSIBILITY OF REMOVING FLUORINE FROM THE SURFACE OF SILICON
NITRIDE POWDER WITH CHEMICAL REAGENTS

G. N. Komratov and Yu. M. Shul'ga

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Silicon nitride powder prepared under industrial conditions contains the so-called production impurities. The effect of them on operating properties of articles by powder metallurgy may be considerable. A comprehensive study of impurity properties will make it possibe to predict its effect on powder sinterability, and also on the properties of final articles.

We have studied the distribution and condition of fluorine ions, i.e., an impurity element in silicon nitride powder grade N-1 (from the firm Shtark). Information is obtained by the method of x-ray photoelectron spectroscopy (XPS) about the structure of the surface layer of a solid with a thickness of not more than 4 nm.

In order to determine the total content of fluorine in powders, metals which interfere in the analysis were first removed in the form of hydroxides, and then a normal spectrophotometric method was used with an alizarin complexing agent. The XP-spectra were recorded on a Varian IEE-15 instrument with a magnesium anode ($h\eta$ = 1253.6 eV). Calibration of spectra was carried out with respect to the C1 s-peak (285 eV). During exposure a vacuum of 133 mPa was maintained in the analyzer chamber. The composition of the surface layer of specimens was calculated by the equation

$$[C_i] = \frac{I_i}{\sigma_i \sum_i \frac{I_j}{\sigma_j}}, \quad \text{\% (at.)},$$

where I is integral photoelectron line intensity; σ is photoionization cross section. Summation was carried out for analytical lines of all elements detected by means of XPS: Si2p, N1s, F1s and O1s. Values of σ were taken from Scofield tables [1].