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SELECTION OF THERMO-MECHANIC MODE OF PELLET MOLDING FROM TiO_2 POWDER FOR MAGNETRON APPLICATION OF COMPOSITE COATINGS ON PARTS

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It is advisable to make film coatings based on titanium dioxide for the details of instrumentation industry to reduce their resistance from compositions with other oxides. It is desirable to prepare the compounds during coating stage by magnetron method. Comparison of the designs of magnetron installations substantiates the rationality of using an installation with a single magnetron, equipped with a pellet from a composition of powders based on titanium. The coating technology using a single magnetron equipped with a composite pellet is described using an example of the application of wear-resistant self-lubricating coatings from a Ti + WS_2 composition. To equip the magnetron with a TiO_2 powder pellet, the task was to ensure the greatest uniformity of the density distribution in the pellet volume, and to achieve the greatest value of this density. As a result of the study of the technology of hot molding of TiO_2 powder described in the article, the efficiency of combining the heating of a powder with its compaction in one operation is shown. During this operation, the dependence of the density of the produced pellet on the molding temperature, pressure, holding time under pressure and grain size was experimentally investigated. The chosen thermomechanical mode of TiO_2 pellet molding is substantiated. By using the following mode (in the studied range) of molding it is possible to produce the pellet with the highest density: temperature 1300 °C, pressure 40 MPa, holding time under pressure 20 min, and grain size 2.2 μm.

***Key words*:** titanium dioxide; film coatings of parts; deposition in magnetron; magnetron pellets composite; modes of forming pellets; study

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Introduction. Titanium dioxide is widely used in various industries. It is one of the most important strategic materials. Possessing the properties of a semiconductor with *n*-conductivity, titanium dioxide is a promising material for the formation of solid electrolytes and materials that have catalytic properties.

However, the wide use of TiO_2 as a solid electrolyte is hindered by its great resistance to ionic conductivity, in contrast to the resistances of other oxides – Co_3O_4, SnO_2, Sb_2O_5. Analysis of the properties of titanium dioxide and methods of its synthesis [1, 3] indicates the possibility of changing its ionic conductivity by adding to its composition oxides of SnO, Co_2O_3, Sb_2O_5, AgO, which have higher conductivity.

In instrumentation titanium dioxide is used as a film coating. In this case, the problem of increasing its conductivity can be solved not during TiO_2 synthesis, but at the stage of coating. Important tasks of modern machine building are solved by joining efforts of specialists from different scientific fields, as well as technologists and designers, because production process involves various physical-chemical technologies [13-15]. Currently manufacturing parts with different properties of its deep and surface layers are solved by applying coatings [2, 5]. The authors of this article have experience in applying wear-resistant self-lubricating composite coatings from titanium-based materials to machine parts and cutting tools [4, 6].

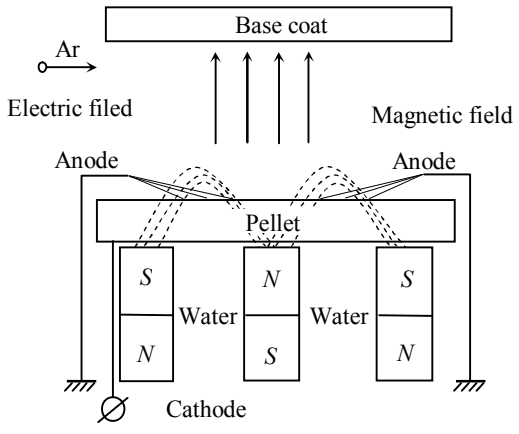

Fig.1. Layout of magnetron

Coating method. The thin-film coatings are created in vacuum installations based on magnetrons. Magnetron is a system of permanent magnets with a powerful magnetic field, cathode and anode, which attracts electrons (Fig.1). The lines of the force field between the cathode and the anode are directed perpendicular to the lines of force of the magnetic field.

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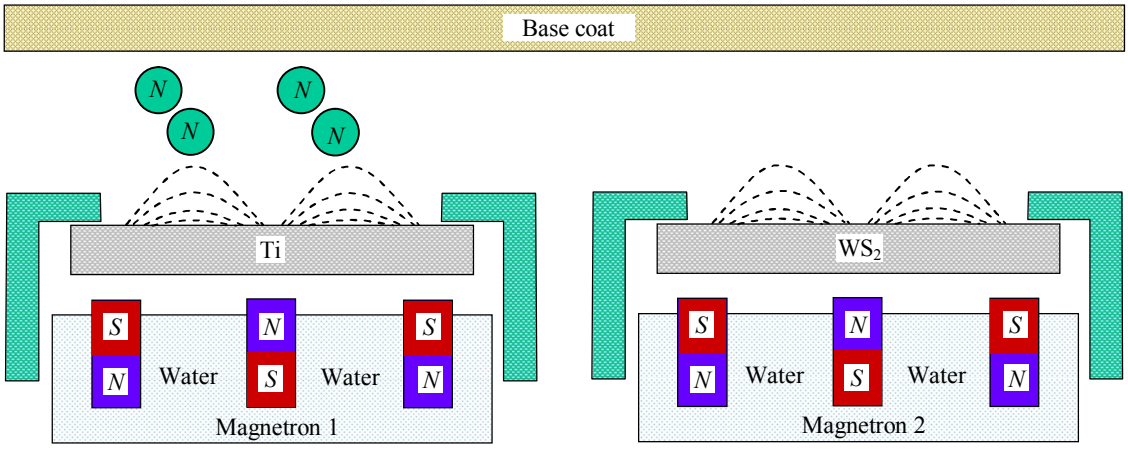

Fig.2. Two magnetrons with pellets made of Ti and WS_2

Magnetron has advantages over similar electrovacuum devices: electrons, because of enlarged flight trajectory make more collisions with working gas molecules, hence, the ionization level of the gas increases. The installation can contain one or more magnetrons (Fig.2 and 3).

To obtain composite self-lubricating coatings in installations with two magnetrons (see Fig.2) two pellets from different materials (solid and lubricating) are used. To obtain a multilayer coating, the magnetrons are turned on alternately and simultaneously for the composite coating. In a single-magnetron installation (Fig.3), the composite pellet consists of a mixture of solid and lubricating components.

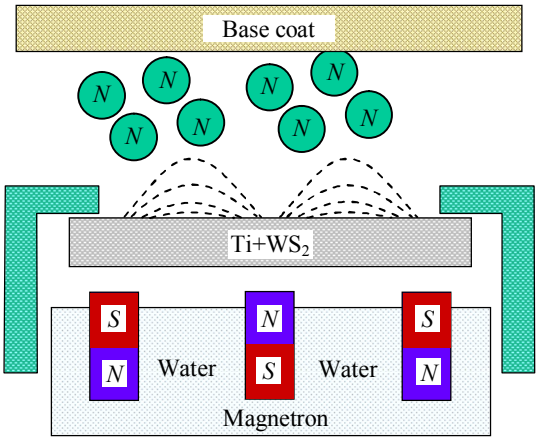

Fig.3. A single magnetron with a composite pellet

Spraying of the pellet material occurs by means of ionic bombardment. The following processes occur in the magnetron chamber. In cross magnetic and electric fields, the electron trajectories in the direction from the cathode to the anode are bent. Under the action of these fields, while moving in the direction of their flight, the electrons rotate. In the way, electrons collide with the atoms (or molecules) of the working gas and ionize it. Positively charged ions of the working gas move to the cathode and hit the pellet. When an ion collides with the pellet, it transfers its energy. It is accumulated in the outer layers of the pellet and at a certain stage the particle of the pellet material leaves the crystal lattice.

After leaving the pellet, the particle passes moves to the base coat. On the way it goes through some chemical and physical interactions with substances in the working chamber. For example, when they apply titanium nitride with a pellet made of pure and nitrogen as the reactive gas; the particle undergoes the chemical reaction during its motion, and the finished working substance is deposited on the substrate. However, since the chamber has not only necessary components, the film coating could be contaminated with impurities such as metal oxides.

When a sufficient number of particles of a working substance are accumulated on the surface of the base coat, the crystal lattice starts to build. First, the particles accumulate in the so-called «potential wells» of the base coat and form local clusters – pockets. These clusters are changing to reach a stable position. Gradually, as they accumulate, a continuous surface of the film is formed, which subsequently becomes the basis for the formation of its crystal structure.

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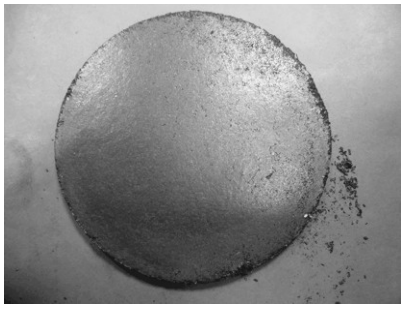
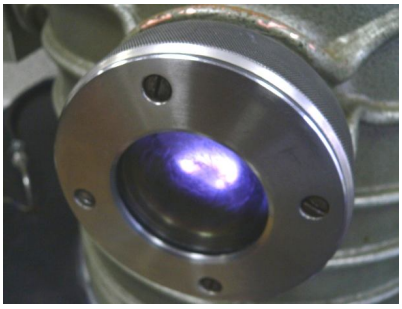


Fig.4. Composite pellet from Ti +WS_2



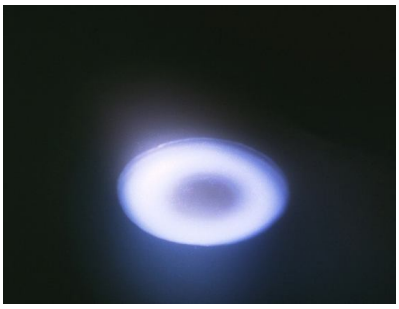


Fig.5. A pellet during operation of magnetron

Thus, the process of interaction of a particle with a base coat is fundamentally different from the processes considered by the authors of [8, 12]. In these works, the interaction and destruction of solids under impact is studied differently. The interaction processes considered in this article are carried out on the bodies approaching the size of nanoscale levels. Due to the departure (knocking out) of particles from the pellet and getting them onto the base coat, the particles perform a building process and from a durable coating on the part or technological tool. A comparison of this process with the processes described in [8, 12] showed that a part having a magnetron-deposited coating can be more resistant to dynamic action during impact from another body.

The pellet of the magnetron prior to its application, made from powder material, is shown in Fig.4. A sample of the pellet during the operation of the magnetron is shown in Fig.5.

Formation and effectiveness of wear-resistant self-lubricating coating. The coating was formed using the following sequence and modes: degassing of the pellet for 3 hours; preparation of surface samples in an ultrasonic bath, degreasing and ion-beam etching of 30 min; coating at an argon pressure of 0.1 Pa, a discharge voltage on a magnetron of 800 V, a discharge current of 0.6-1.6 A, a distance to the samples of 180 mm, and a particle deposition rate of up to 5 nm/min.

Data on the value of the dry friction coefficient of the manufactured parts show that the coating obtained from the composition Ti + WS_2 (pure titanium powder and tungsten disulfide) provides a reduction in the coefficient of friction by a factor of 2 compared to the uncoated sample. In the case of the composition TiN + WS_2 (powder from ground chips [4, 6] and tungsten disulfide) it decreases in 2.3 times. The surface of the part before coating can go through preliminary water-jet machining [7].

The task of pressure treatment solved by self-lubricating coating is alternative to usage of actively directed contact friction forces between the workpiece and the tool to increase the efficiency of the production process [10]. Also note that in addition to magnetrons technology, pressure treatment specialists have other tools [9] for controlling the microstructure and, therefore, the mechanical properties of deformed metals.

A technique for studying the molding magnetron pellet based on titanium dioxide. The production of the pellets shown in Fig. 4 from titanium dioxide-based powders can be carried out by two methods: 1) cold molding of the powder in a closed matrix; sintering; hot stamping of the porous preform in a closed matrix; 2) hot molding of the pellet from the powder in a closed matrix. The disadvantage of the first method is the difficulty in ensuring an even density distribution in the pellet volume. In the absence of this type of distribution, uneven shrinkage occurs during sintering. As a result, the pellets become warped and cracked. Additional processing equipment is required for sintering and subsequent hot stamping of the molded and sintered porous billet. In view of these shortcomings, the second technology is preferred. In this case, it is necessary to ensure that the powder is heated to the specified temperature directly in the matrix.

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The installation unit for implementing the second technology is shown in Fig.6.

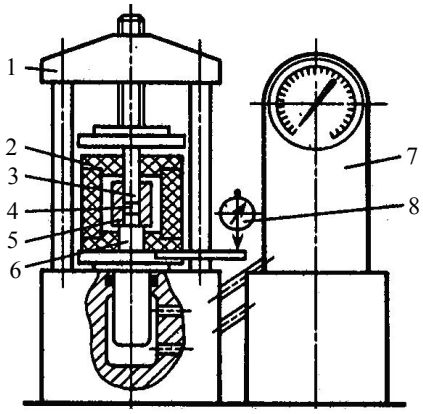

Fig.6. Layout of a unit for heating powder and plate molding

1– testing machine Instron-350;
2 – furnace; 3 – upper punch; 4 – part;
5 – matrix; 6 – lower punch;
7 – unit hydraulic drive;
8 – tool movement indicator

Between the plates of the press there is an oven with silicate heaters. The design of the furnace allows its quick disassembly for installation and extraction of the matrix with the workpiece. The furnace has openings through which forming punches enter, as well as an opening for mounting a thermocouple. The temperature in the oven is controlled by changing the voltage on the silicon heaters. Since the heating of ceramic powders is carried out directly in the matrix installed inside the heating plant, their compaction can be considered isothermal. The temperature range for hot molding of the plates is 1200-1300 °C.

The need to maintain a high temperature causes specific requirements for heat resistance of the materials from which tooling is made. Silicon carbide is used for making working details of the tooling. It has high compressive strength, wear and heat resistance, and retains high mechanical properties at elevated temperatures. Silicon carbide has a high thermal stability and thermal conductivity, its melting temperature is 2600 °C. The working parts of the silicon carbide die withstand 40 or more load cycles at a temperature of 1300 °C. Preventing the welding of the powder die to the tool is provided by a zirconia separating layer. The thickness of the separation layer is approximately 1 mm.

Hot molding of the TiO_2 powder pellet consists of two steps. At the first stage, short-term deformation occurs, and on the second stage – plastic deformation in time. The second stage N.N. Malinin called a short-term creep flow. The duration of the second stage in the molding of pellets is measured in tens of minutes.

In the conducted research, the hot isostatic molding of the TiO_2 powder is provided with the help of the tracking system of the Instron-350 test machine. It was aimed at determining the dependence of the product density on the temperature at which the molding is performed, the powder compression pressure, the holding time under pressure, and the powder dispersion.

The dispersion of the powder (grain size) was considered as a variable parameter, since in [11] hot stamping of titanium indicates a significant effect of this size. The molding was carried out at a temperature corresponding to the greatest plasticity of the material. The upper limit of the maximum plasticity interval for the studied material is 1300 °C. In the study, the lower limit of the hot-molding temperature range was determined from 1100 °C. Stamping equipment made of silicon carbide can withstand specific forces (averaged pressures) up to 40 MPa. The range of pressure changes is 20-40 MPa. The upper limit of the range of exposures under pressure is 50 minutes. The lower limit of the investigated range is 10 min. The study uses powders with a grain size of 2.2; 2.7; 3.5; 4.3; 4.54 μm.

The dimensions of the powder particles were controlled by sieving through electromechanical batch screen, driven by screw vibrations. The sieve had an option of sealing and using fine grids to sift the powders of fine fractions. The frequency of the sieve oscillation was 20-50 Hz, the amplitude of the oscillations was 2 mm. In the process of sifting, the oscillation frequency was changed stepwise. During the first 10 minutes it was 20 Hz, the next 10 minutes – 25 Hz, the final 10 minutes – 50 Hz. In the preparation of powders for the experiment described, sieving began through the smallest mesh, 2.2 μm. The powder fraction with a predetermined size after passing through the mesh poured into the tray, and the powder of larger fractions moved along the ring. After finishing the sifting, the non-milled powder of larger fractions was removed from the screen and the mesh was replaced in the sieve by a larger one. In this study, in

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b	d \ a	1100	1150	1200	1250	1300
20	2.2	15.0	11.5	10.9	3.2	0.34
	2.7					
	3.5					
	4.3					
	4.54					
25	2.2	14.7	9.3	9.96	5.75	0.13
	2.7					
	3.5					
	4.3					
	4.54					
50	2.2	10.8	10.5	8.2	5.8	0.18
	2.7					
	3.5					
	4.3					
	4.54					
35	2.2	11.5	10.5	6.4	1.36	0.27
	2.7					
	3.5					
	4.3					
	4.54					
40	2.2	9.5	7.4	7.97	4.9	0.17
	2.7					
	3.5					
	4.3					
	4.54					

Fig.7. Combination square showing values of four studied parameters in each 25 experiments

the second stage, 2.7 μm. The sieve was loaded with the powder seized after the first sifting, and sieving resumed through the second mesh. Thus, the powders of the five fractions used in the experiment were prepared. We note that along with the values of the particle fractions given, insignificant inclusions of smaller fractions were observed in all the experiments. These minor inclusions did not have any noticeable effect on the result of the study, described in the discussion of the results of the article.

The research is aimed at finding the process parameters at which the highest density of the pellet is achieved. The density was estimated from the value of the weight water absorption in percent. For this purpose, the product, previously weighed to within 0.0001 g, was boiled for 15 minutes and then cooled in water. After cooling, the item was re-weighed, the difference in weights before and after the boiling was counted, and this difference was referred to the weight of the dry sample.

The authors of the article used the method of planning the experiment and processing its results, proposed by M.M. Protodiakonov and R.I. Teder (Fig.7).

The large cells of the combination square shown in Fig.7 have the values of the water absorption measured according to the method described above (in per cent) of the samples formed with the combination of parameters corresponding to small cells, where *a* is the temperature, °C; *b* – specific force (averaged over the sample surface pressure), MPa; *c* – time of holding under pressure, min; *d* – the grain size, μm.

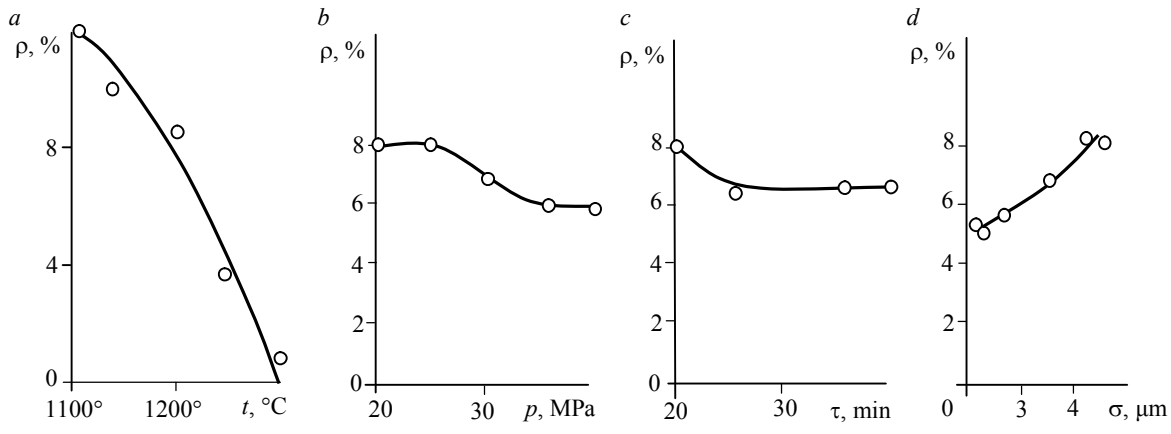

Fig.8. Dependencies of water absorption ρ of pellets samples from molding temperature (*a*), pressure (*b*), pressure holding time (*c*) and grain size (*d*)

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Results of the study of hot molding of TiO_2 powder pellets. The results of the experiments, the method of processing the data and the dependence of the water absorption (ρ) of the product on each of the four process parameters with an average effect of three are given in Tables 1 and 2. Based on the results of processing the experimental data, the dependences shown in Fig.8.

Table 1

Results depending on temperature and pressure values

Pressure, MPa	Water absorption, %						
	t = 1100 °C	t = 1150 °C	t = 1200 °C	t = 1250 °C	t = 1300 °C	Row sum	Row average
20	15.0	11.5	10.9	3.2	0.34	40.94	8.188
25	14.7	9.3	9.96	5.75	0.13	39.84	7.968
30	10.8	10.5	8.2	5.6	0.18	35.28	7.056
35	11.5	10.5	6.4	1.36	0.2	29.96	5.992
40	9.5	7.4	7.97	4.9	0.17	29.94	5.988
Column sum	61.5	49.2	43.43	20.81	1.02	175.96	–
Column average	12.3	9.84	8.686	4.162	0.5044	–	35.392

Table 2

Results depending on the time of exposure to pressure and the grain size

Grain size, μm	Water absorption, %						
	τ = 20 min	τ = 20 min	τ = 30 min	τ = 40 min	τ = 50 min	Row sum	Row average
2.2	0.18	9.5	3.2	9.3	6.4	28.58	5.716
2.7	9.96	1.36	7.4	0.34	10.8	29.86	5.972
3.5	4.9	0.13	8.2	11.5	11.5	36.23	7.246
4.3	10.5	10.9	14.7	5.6	0.17	41.87	8.374
4.54	15.0	10.5	0.2	7.97	5.75	39.42	7.884
Column sum	40.54	32.39	33.7	34.71	34.62	175.96	–
Column average	8.108	6.478	6.74	6.942	6.924	–	35.392

Discussion of the results. The greatest influence on the pellet water absorption, i.e. on its density, has a hot-molding temperature (Fig.8). As the temperature approaches 1300 °C, an increase in temperature by several degrees substantially increases the density of the product. At the same time, the change in compression pressure of the powder from 35 to 40 MPa practically does not affect the density of the product. Therefore, during the hot molding, the pressure can be maintained less thoroughly than the temperature. Increasing the holding time under pressure during molding for more than 20 minutes practically does not affect the density of the items. The average grain size of the moldable powder has a significant effect on the density of the product. In the obtained dependence this effect decreases with a grain size of less than 2.5 μm.

Conclusion. By combining the four parameters (temperature 1300 °C, pressure 40 MPa, time 20 min, and grain size 2.2 μm), which makes it possible to mold the pellet with the highest density, we estimated the dependence of the density on the shape and dimensions of the designed item. An additional experiment showed that planned shape and dimensions practically do not affect the product density.

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