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# Structural evolution of ceramic coatings produced by mechanical alloying technique

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The article researches formation of ceramic coatings of zirconium dioxide ( $ZrO_2$ ) on the X12CrNi1810Ti steel surface after mechanical alloying. Study of coatings' surface showed coalescence of defected coating's particles with created subgrains and this process is more representative due to different toughness of zirconium oxide and steel. It is suggested that adhesive bond between the coating and support structure is provided by strain welding of the powder on the support structure coating. When using X-phase analysis neither diffusive mixing of coating/support structure components or formation of new compounds and phase changes was revealed. Surface contamination of the coating with carbon was found out and it was getting less towards the border between the coating and support structure. It could be due to mechanical sorption of carbon dioxide from the environment.

**Keywords:** MA process, X-phase analysis, ceramic coatings.

## Introduction

X12CrNi1810Ti is an attractive material for applications in nuclear power reactors, boilers, automobile exhaust systems, pressure vessels, carburetors and furnace parts [1]. Improving performance of X12CrNi1810Ti is an actual problem and its solution using coating application seems to be promising approach. Application of thermal barrier coatings on most heat-stressed components of various devices is one of the widely used ways to maintain their performance under

high temperature exposures. Zirconium dioxide is often used for thermal barrier coating owing to its lowest coefficient of thermal conductivity (up to  $2\text{W}/(\text{mK})$ ) among all high-temperature materials and it is chemically resistant compound with melting point of  $2680^\circ\text{C}$  degrees. Decrease in thermal conductivity will increase thermal resistance of thermal barrier coatings and reduce thickness of the coating and mass of defended fittings. Zirconium oxide as coating can be produced by various methods of deposition [2]. The given work investigates the possibility to employ mechanical alloying technique (MA) for application of  $\text{ZrO}_2$ -based ceramic coatings on X12CrNi1810Ti surface.

The MA technique is relatively new method used for coating application. The idea behind of this method is to use striking energy of moving balls for coating on metal surface. The work [3] describes usage of mechanical-chemical technique as new method of metal coating application on steel and aluminum surfaces. Today MA technique has been successfully used to obtain intermetallide, nanostructured, composite and complex-synthesized ( $\text{LaPO}_4$  and hydroxapatite) coatings [4-8].

## Experimental procedure

The application of coatings by the method of mechanical alloying was carried out in the SVU-2 (stand vibration universal) vibrational mechanical activator. A plate made of X12CrNi1810Ti measuring ( $70 \times 70 \times 3$ ) mm was used as the substrate. The average initial roughness  $R_a$  of the plates was less than  $0.8 \mu\text{m}$ .  $\text{ZrO}_2$  powder with size of fraction 60 to 80 nm and purity of 99.9% was used as reference material. To apply coating the following MA parameters were defined: amplitude of oscillation of vibration chamber is 3.5 mm; oscillation frequency is 50 Hz; rate of chamber filling is 80 to 85%; ratio of powder mass to the balls' weight is  $m_p:m_b=1:30$ . Steel balls with a diameter of 6.7 mm weighing 360 g were loaded into the vibration chamber. The steel plate was fixed at the top of the vibration chamber (Figure 1). The temperature of the chamber walls during MA processing did not exceed  $70^\circ\text{C}$  degrees. The MA process was carried out in an ambient atmosphere. MA process took 2 h.

Phase composition of the specimens was examined by X-phase analysis using diffractometer Shimadzu XRD6000. Coating surface was studied with application of atomic-force microscope JSPM5200, scanning electron microscope JSM-6390 with detector of energy-dispersive spectrometry and 3D contactless profile meter MicroMeasure 3D. Elements distribution through the specimen-in-depth was made by Auger electron spectrometer Shkhuna-2. Specimens were tested on endurance by friction gage THT-S-AX0000 using disk-ball technique. VK6M ball with diameter of 2mm was used as a counterbody. Testing parameters were the same for all the specimens: load 2 N, velocity 2 cm/s and carried out at room temperature..

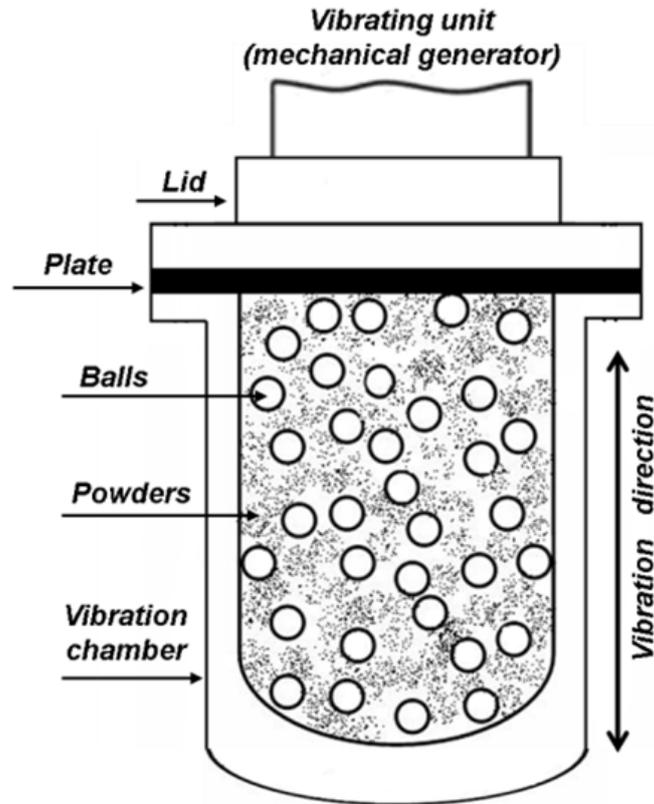


Figure 1. Schematic illustration of the MA process.

## Results and Discussion

During MA process, formation of coating structure depends on how efficient powder components exist in the region of dynamic loading of balls' strike. Figure 2 shows the structure of  $ZrO_2$  coating on the steel surface. The deposition of pure  $ZrO_2$  coatings on the steel substrate by method of MA was not so successful. The sample has some uncoated regions on the surfaces (Figure 2b). The thickness of the coatings is about 450 nm (Figure 3). Identification of the coating's thickness by preparation of cross-section for investigation was associated with some troubles occurred while processing and data interpretation. Surface potentials and strong electric fields are created because of dielectric properties of  $ZrO_2$  affected by electron beam exposure. This led to the image defocusing and made it hard to identify the border between the substrate and coating. Coating thickness of tested specimens was defined by element distribution through the specimen-in-depth by Auger spectrometry. Relative concentration of coating components is virtually constant in the main part of the coating. Concentration of carbon was found there that was getting lower towards the border between coating and support structure (Figure 3). It might be due to mechanical sorption of carbon dioxide gas released from the environment. The idea of this processes in absorption of  $CO_2$  from the environment by almost inert-to- $CO_2$  particles while mechanical treatment owing to mechanical-chemical processes [9]. It should be noted, that interaction between defected solid body and ambient medium ( $N_2$ ,  $O_2$ ,  $CO$  etc.) with phase formation of reaction product solid body-gas (corresponding nitride,

oxide and other compound) can be used to modify properties of solid surfaces, namely their hardening, improving corrosion resistance, etc [10].

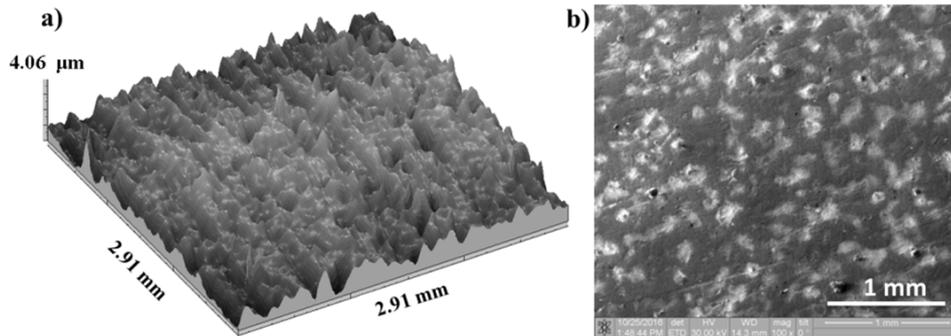


Figure 2.  $ZrO_2$  coating on X12CrNi1810Ti surface: a) surface profile; b) the SEM images of the surface of the coating.

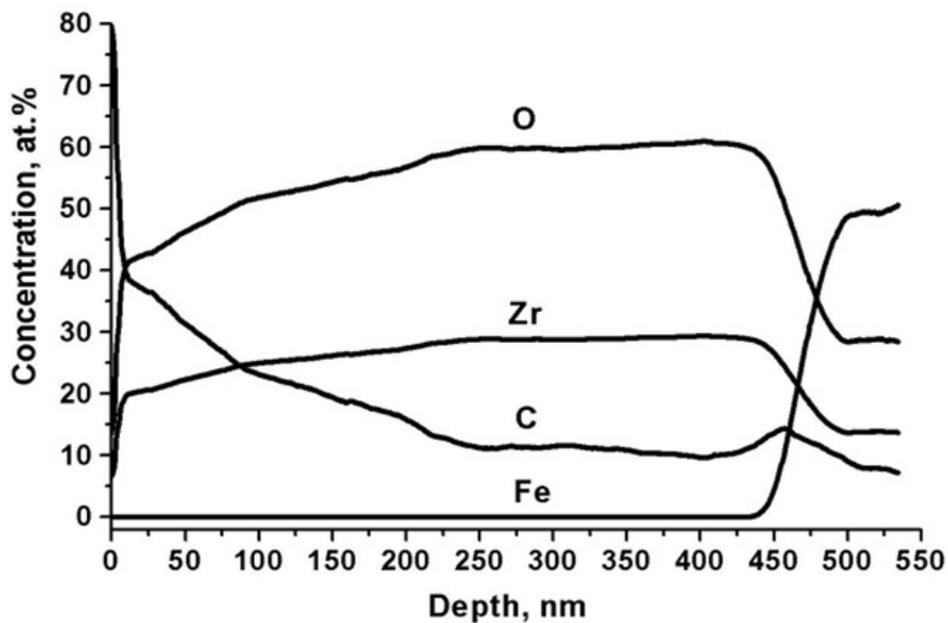


Figure 3. Depth profile of Auger electron spectroscopy of the  $ZrO_2$  coating on X12CrNi1810Ti surface.

3D image of coating surface makes it possible to get amplitude parameters of the surface which are helpful to characterize vertical surface ribbing. The ball size is critical to coating formation and structural changes; the different effects are associated with the impact energy. A larger milling ball transfers higher impact energy in a single impact due to its higher mass and velocity. When small balls are used, the coating was smoother because of the higher impact frequency [11]. Dimensions of ball should be selected depending on chamber volume.

Increase in size of the balls at a constant fill factor in most cases leads to raising intensity of energy supply and temperature. However, in case of camera overfilling by increasing of ball size, free path of the balls is reduced and the frequency of ball strike is reduced respectively. This leads to an increase in the roughness of the coatings. To that end, chosen size of the ball with a diameter of 6.7 mm seems to be most representative for the coating. Average arithmetic roughness  $S_a$  of coating surface equals to  $0.46 \mu m$  (Figure 2a).

Figure 4 shows local microstructure of the surface and elements' distribution on the coatings' surfaces. Compositional structure of the coatings is heterogeneous. On the surface, there are some zirconium-enriched accumulated coatings and regions without coating with high concentration of iron (Figure 4b). Coalescence of defected particles of the coating might take place due to cold welding (in our case it's a powder accumulation) and this process is more representative because of solidity of zirconium oxide (5.5-15 GPa) and X12CrNi1810Ti steel ( $\approx 2$  GPa). Alloying will start only after softer material gets solid like second component due to mechanical hardening [12]. To that end, particles' coalescence is more probable process on the coatings' surface. However, there is a critical velocity of balls' impacting, and in case of its excess, alloying efficiency does not depend on combination of mechanical properties of the components. Atomic-force microscope was used to examine specimen's surface in detail (Figure 5). Topographical expression of the specimen clearly shows hillock-type defects i.e. regions of accumulated powder. This image also shows subgrains formation due to particles coalescence of the coatings that confirms our assumption.

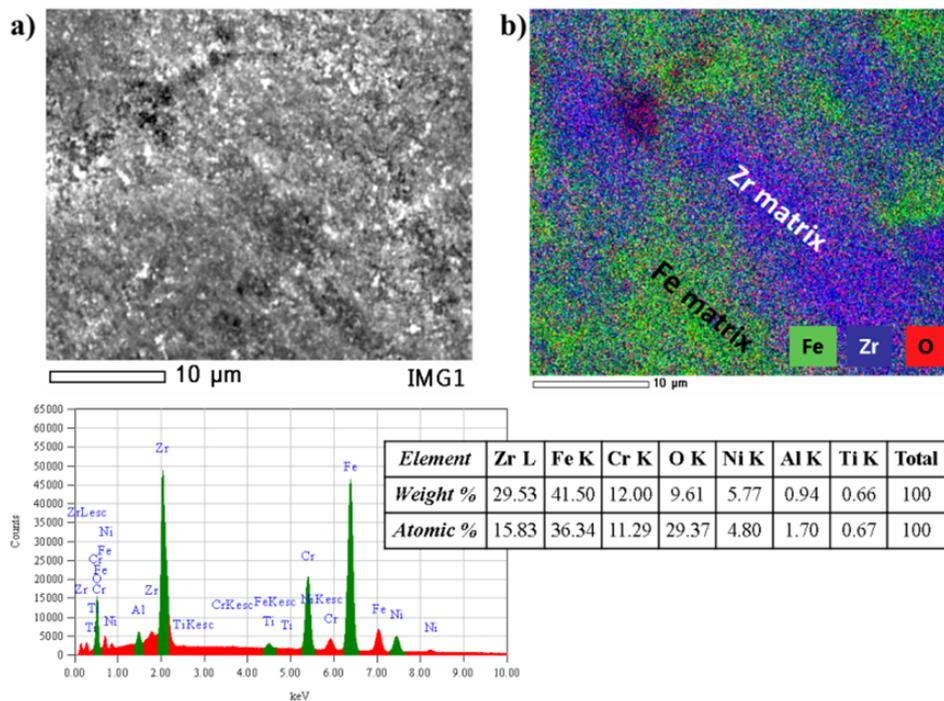


Figure 4. Microstructure of the  $ZrO_2$  coating on X12CrNi1810Ti surface: a) SEM image, b) EDS analysis of the surface.

It is known that intense impact of the balls on the surface leads to change of surface properties and phase composition of the specimen. Given the idea of MA technique, X12CrNi1810Ti surface was exposed to surface mechanical treatment using balls (without coating). Mechanical surface treatment and coating was implemented under the same parameters of MA process. Figure 6 shows diffractogram of  $ZrO_2$ -coated reference steel X12CrNi1810Ti and this steel after mechanical treatment. X12CrNi1810Ti consists of austenite phase ( $\gamma$ -Fe) and martensite phase ( $\alpha$ -Fe) (Figure 6c). After MA treatment, martensite transformation takes place underaction of plastic deformation and  $Fe_3O_4$  formation is observed (Figure 6b).

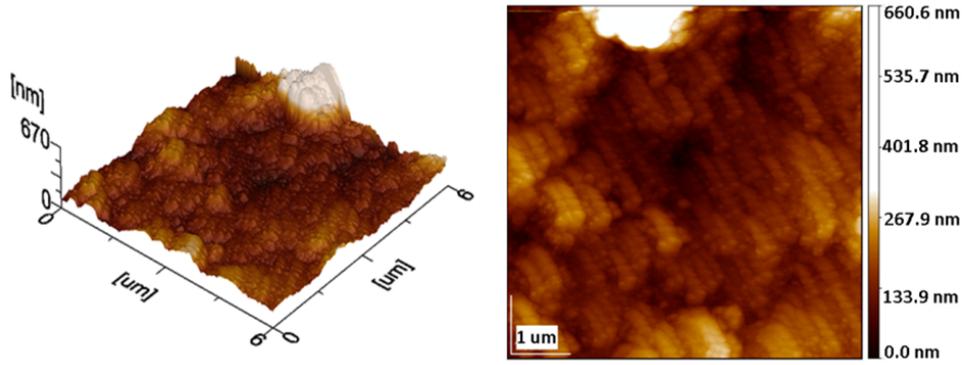


Figure 5. AFM image of the  $ZrO_2$  coating on X12CrNi1810Ti surface.

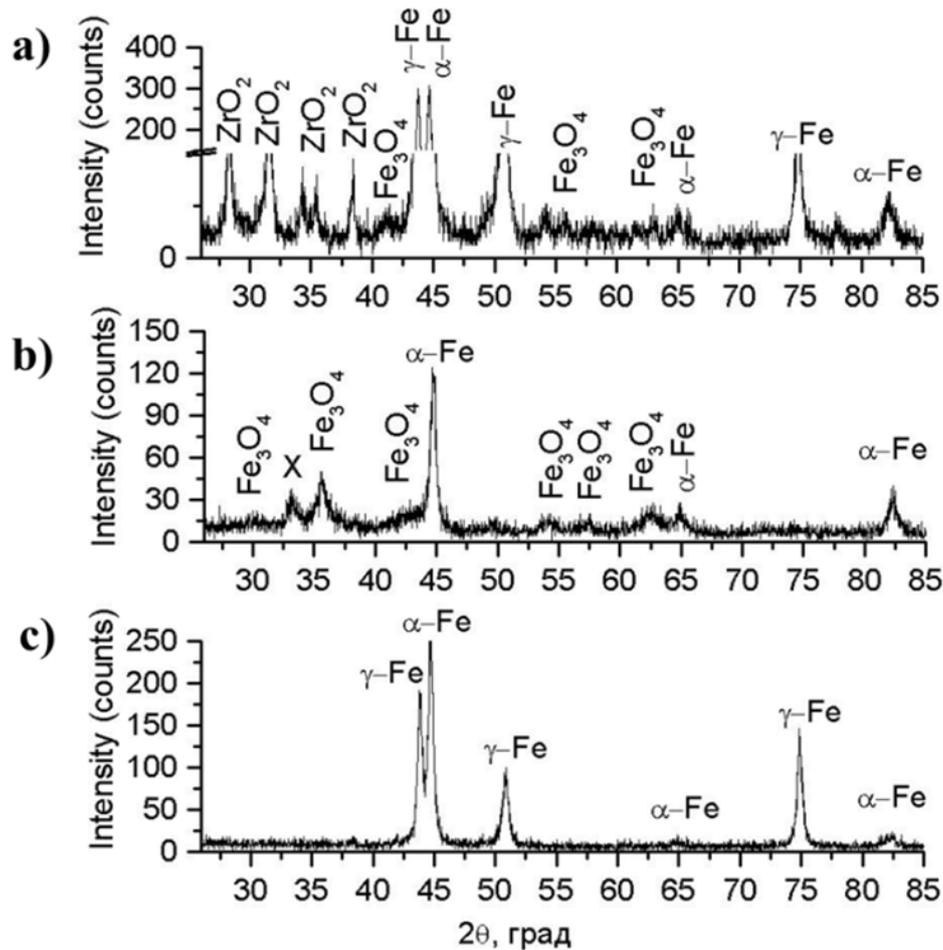


Figure 6. X-ray diffractogram, a)  $ZrO_2$  coating on X12CrNi1810Ti surface, b) X12CrNi1810Ti after mechanical treatment, c) initial X12CrNi1810Ti.

X-ray diffractogram of coated specimen corresponds to phase composition of the system under examination. Lines  $\gamma$ -Fe (fcc),  $Fe_3O_4$ -Fe (bcc),  $ZrO_2$  with monoclinic structure and  $Fe_3O_4$  are registered. No formation of carbides is revealed despite the high carbon content in the coating (Figure 3). The work [13] investigated the interaction of reaction mixture components with the atmosphere where mechanical alloying occurs. Research results showed that the oxygen acts as reaction reagent and absorbed mainly at the grain boundaries and encourages formation of oxide compounds. In case of coating with oxide ceramics, oxide

connections can positively impact on adhesion strength of the coatings.

Today there is no unified theory that can determine condition of the coating by MA technique. In the course of MA, high local internal stress of defected structures is assumed to be an important channel for accumulation of strain energy, which plays a significant role in the phenomena of increasing reactivity of treated material, anomalous high-mass transfer and solid-phase mechanical alloying [14]. However, conditions for application of ceramic coatings by MA technique can be different. According to A. Pincus theory, the processes of metal components oxidation and interactions between new oxides and ceramic oxides make the basis for formation of strong connection between the metal and ceramics [15]. It was thought that a good adhesion of zirconium-bearing ceramics to the metal could be explained by chemical reaction between zirconium oxide and intermediate (alloying) metal. The work [16] addresses theoretical background for an increase of adhesion at the boundary of the metal and  $ZrO_2$ . It is shown that strong adhesion can be achieved at the boundaries of bcc-metals in the middle of d-periods on oxygen end of polar surface  $ZrO_2$  (001). High values of bcc-metals film adhesion in comparison with fcc-metals are associated with a high charge transfer from the metal to support structure that leads to increased contribution of ionic component into the chemical mechanism at the boundaries.

Figure 7 presents results of tribological testing of the specimens. According to the analysis of given dependences,  $ZrO_2$  coating on the surface of X12CrNi1810Ti has low adhesive strength because of coating breakdown in the beginning of the test. Mechanical surface treatment largely reduced friction coefficient compared to reference steel. Improvement of steel wear resistance is caused by the formation of deformation martensite on the specimen's surface after balls striking. X-ray phase analysis data confirmed formation of  $\alpha$ -martensite resulted from martensitic transformations affected by deformation (Figure 6b).

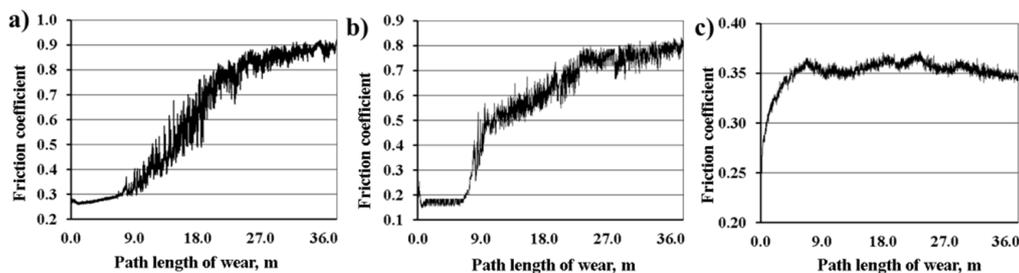


Figure 7. Change in the coefficient of friction, a) initial X12CrNi1810Ti, b)  $ZrO_2$  coating on X12CrNi1810Ti, c) after mechanical treatment X12CrNi1810Ti.

Thus, MA technique can be used to apply  $ZrO_2$  coating on the surface of X12CrNi1810Ti. However, it is required to use a complex of various techniques to achieve desired mechanical and adhesive strength of  $ZrO_2$  coating on the X12CrNi1810Ti surface. Thermal annealing, for instance, could be used after MA to make diffusing faster or steel surface pre-oxidation could be utilized to create adhesive  $\alpha$ - $Fe_2O_3$  layer of special morphology for  $ZrO_2$  coating [2]. Then, before coating surface pre-treatment with the balls will be applied to improve adhesion strength of the coatings. Based on the results of the experiments conducted by surface treatment there can be achieved structure-phase transfor-

mations, creation of oxide layer and hardening of X12CrNi1810Ti surface that will assist to good adhesion at the  $ZrO_2$ -metal boundary according to above mentioned theories.

The given work assumes that the adhesive bond between the coating and support structure is ensured by powder deformation welding on the surface of support structure. No diffusive mixing of coating/support structure components was found with formation of new compounds and phase transformations by using of X-ray phase analysis. Formation of oxidic iron compounds in the coating after MA can serve as the beginning of further chemical reactions between coating and support structure. However, to create chemical bond at the boundaries, diffusion plays a key role which is accelerated due to equally overweighted vacancies (generated during the deformation). This requires high power density (i.e. a large amount of energy transferred by working medium to treated material while mechanical treatment), which can be achieved by controlling MA process taking into account technical specifications of SVU2 machine.

## Conclusion

When analyzing experimental results achieved in the course of the work the following was concluded:

- Mechanical alloying technique has been proposed to apply  $ZrO_2$ -based ceramic coating on the X12CrNi1810Ti surface;
- It is found out that formation of coating surface depends on mechanical properties of alloying components. Study of coating surface structure showed coalescence of defected coating particles with subgrains' creation;
- Surface coating contamination with carbon has been revealed but it was getting less towards the border between the coating and support structure. It can be attributed to the mechanical sorption of carbon dioxide released from the environment. No ferric carbide was found out when using X-phase method;
- It is suggested that adhesive bond between the coating and support structure is provided by deformation welding of the powder on the support structure surface. When using X-phase analysis, neither diffusive mixing of the components coating/support structure nor formation of new compounds or phase changes were observed;
- According to tribological testing, low adhesive durability of  $ZrO_2$  coating has been revealed on X12CrNi1810Ti surface. It is proposed to do mechanical surface pre-treatment by the action of ball strikes to improve adhesive durability.

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