Advances in Science and Technology Research Journal
Volume 13, Issue 2, June 2019, pages 46–50
https://doi.org/10.12913/22998624/106161

Received: 2019.03.25
Revised: 2019.04.12
Accepted: 2019.04.26
Available online: 2019.05.17

Features of Formation Stress State of Amorphized Detonation Coatings of the Zr-Al-B Systems

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ABSTRACT

The results of experimental studies on the dependence of the thickness of amorphous-crystalline Zr-Al-B coatings on the value and level of distribution of type 1residual stresses were presented. It was demonstrated that residual compressive stresses arise in the surface layers of coatings, which in absolute value are not significant for its integrity and quality. It was established that the amorphous-crystalline composition, under the conditions of minimizing residual stresses and the optimal combination of the volume fraction of components, the structure and morphology of their components, has the best surface strength and wear resistance under friction compared to tungsten carbide and iron coatings.

Keywords: amorphous coatings, residual stresses, annealing temperature, wear resistance, detonation spraying.

INTRODUCTION

One of the topical methods in world practice to increase the durability of structural materials for friction parts is the use of protective coatings [1, 6, 7]. Amorphous coatings obtained by high-speed detonation spraying and their ability to protect materials from wear are of particular engineering interest [1].

The problem of creating amorphous coatings is mainly studied in two aspects: firstly, the selection and improvement of the technology of their formation to ensure the optimal combination of mechanical and physicochemical properties; secondly, the study of the contact interaction of particles with the base and with each other, which causes the implementation of a certain stress state, which depends on the value and distribution of residual stresses [4].

However, despite the formal representations of the basic physical processes, the available theoretical and practical research results are contradictory to a certain extent. Therefore, generalizing conclusions are mostly premature. According to the authors, this refers to the issues of correlation between the value of technological residual stresses, the level of their distribution and sign, which significantly determine the performance and durability of coatings.

Typical representatives of amorphous materials are transition metal alloys with boron, which are obtained by the gas-thermal method, in particular, by detonation spraying. Thus, the aim is to investigate the level of a certain stress state during the spraining of detonation coatings of the Zr-Al-B system, which has a significant impact on the wear resistance properties.

METHODS

Experimental evaluation of technological residual stresses in the Zr-Al-B coatings under study [8] was determined by studying the sample deflection due to layer-by-layer etching of the surface layer using an electrochemical method. The samples had the form of plates: a thickness of 2–3 mm, a width of 10–12 mm and a length of 50–60 mm.

The studies determined type 1 stresses (macrostresses), which occur in coatings as a result of the interaction of technological parameters of spraying. Coatings were sprayed onto one of the sample surfaces. In the process of electrochemical etching in the samples with coatings, the equilibrium of stresses is disturbed and their deformation and bending occurs. The residual stress is determined from the strain value. Electrochemical etching and boom deflection measurement of the samples was carried out at the installation of the type NI-1 (IPMS NASU). The study of the surface layer, in which friction activation processes occur, affecting the main type of wear, was provided by probe scanning electron microscopy («Camskan», accelerating voltage 25 kW, beam current 200 mA). The ZAF-L/FLS program was used for chemical analysis of surface structures as well as localization zones of their components. Additionally, the electron diffraction method was used to study the state of the friction surface. The studies were conducted on an EMR-100electron diffractometer.

Tests for wear were made under friction conditions without lubrication according to the butt-end scheme on annular samples of heat-treated steel 45 (D×d = 25×17.5), equipment of the UMT-1 type. While studying the processes of friction and wear for the same conditions, detonation coatings VK15 (“BK15”) and Fe-Ti-SiC were tested. The thickness of the sprayed coatings in all cases was 0.18-0.25 mm. Hardness was measured on a PMT-3 type microhardometer (0.5 N load).

RESULTS AND DISCUSSION

The value and level of distribution of residual stresses across the thickness of wear-resistant composite coatings based on tungsten carbide (WC-Co), iron (Fe-Ti-SiC type) and amorphous-crystalline Zr-Al-B coating were determined and analyzed. According to the test method, three samples were studied to build the stress distribution curve over the depth of the coating. This is due to the fact that the discrepancy between data within one part largely depends on the sprayed materials (Fig. 1). The samples of amorphous zirconium-based coatings (curve 2) have the smallest discrepancy when tested, as confirmed. The largest discrepancy within the parts corresponds to the iron-based coatings (curve 1). It is logical to assume that the small discrepancy in residual stresses depends on the action of active diffusion redistributions at the initial stage of coating formation, which is confirmed by the results of structural and phase studies [6]. For the coatings based on iron, the opposite is true, i.e. their materials are most quick-response to the technological parameters of spraying.

According to the study, the distribution of stresses across the thickness substantially depends on the structure of the materials. In some materials compression stresses prevail, in others – stretching, with significant convergence in absolute values. The best distribution, in terms of performance properties, characterizes the zirconium-based coatings. On the surface of the above-mentioned coatings, compression stresses up to 130 MPa exist, monotonously decreasing in thickness, and tend to zero at a depth of about 150 μm. The tungsten carbide-based coatings (curve 3) also have compression stresses, but their value is at most nearly halved, and they also tend to zero to a depth of 200 μm. In addition, we note that the general stress distribution in the coatings under study is of the same type, that is, there are some residual stresses on the surface that decrease in depth. In most cases, exploitation should aim at the compression stresses in coatings as the safest.

Heat treatment (annealing) is one of the most accessible and efficient technological operations under production conditions to reduce residual

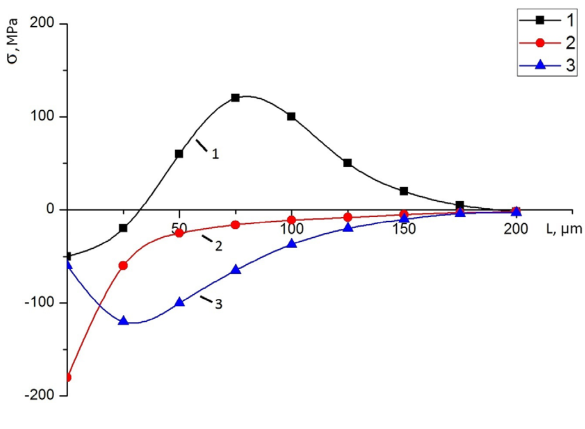

Fig. 1. Distribution of residual stresses over the coating depth: 1 – based on Fe doped with Ti, SiC; 2 – containing WC type VK15; 3 – amorphous Zr-Al-B system

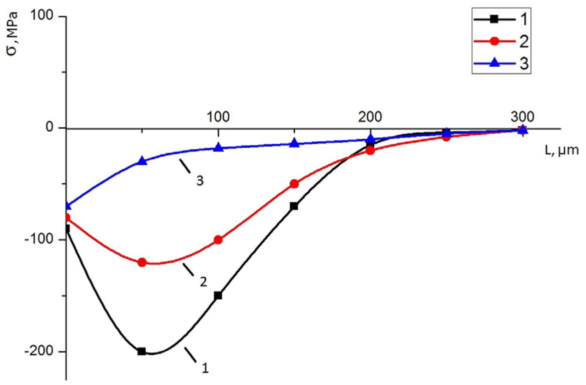

Fig. 2. Distribution of residual stresses in depth of the Zr-based coatings on after annealing (250°C): 1 – 100 µm; 2 – 200 µm; 3 – 300 µm

stresses, due to a change in the value and level of stress distribution. Changes in the distribution of stresses are increasingly distinguishable, the higher the annealing temperature. Annealing of the investigated samples of amorphous Zr-based coatings was done at temperatures of about 250°C and 400°C.

The distribution of residual stresses after annealing at a temperature of 250°C is shown in Figure 2. The value of compressive stress over the depth of the coatings decreases monotonously. Additionally, the greater the value of compressive stress , the smaller the thickness of the coatings. With an increase in the depth, the stress decreases and near the surface it tends to a minimum. It should be noted that there is a tendency to a decrease in the proportion of the amorphous component with increasing thickness of the coatings. The effect of such a parameter as the coating thickness on the residual stresses is very significant.

An increase in the annealing temperature to 450°C redistributes the residual stresses in the direction of decreasing their absolute values.

The sign of the residual stresses largely depends on the combination of the thermal expansion coefficients of the template and coating materials. If the thermal expansion coefficient of the sprayed material is equal to or greater than the thermal expansion coefficient of the template, tensile residual stresses appear in the sprayed coating. In other cases, compressive residual stresses may occur [5]. While spraying a zirconium-based coating on a sample of carbon structural steel 45, the difference in thermal expansion coefficients is negligible. The thinner the coating layer, the smaller the difference in the adjacent layers of the coating and the template. Consequently, with an increase in the thickness of the sprayed layer, there will mainly be a difference in the coefficients of thermal expansion in the sizes of the heated and cooled particles, and in the previously sprayed, significantly cooled layers. Therefore, with increasing coating thickness, the residual stresses increase.

Figure 3 shows the functional dependence of wear intensity on speed under a constant load of 5.0 MPa.

In the study of structural changes, which determined the high resistance to wear of the Zr-Al-B coatings (curve 3), the microanalyzer examined the distribution of the elements along the thickness of the spray layer. The analysis was done with a probe diameter of 2 and 10 microns. The obtained results revealed the presence of a transitional diffusion zone of the order of 20–25 µm, with a variable concentration of the elements that make up the coating. While comparing the prints taken in absorbed electrons and in X-rays, it is not possible to determine these structures, which indicates the heterogeneity of their composition. The discrepancies in the chemical composition prove the irregularities of the dispersed structure, which corresponds to the current knowledge about the nature of amorphous and amorphous-crystalline composites [3,5]. The X-ray studies of the phase composition determined that the coating contains α-solid solution based on Zr, finely dispersed borides ZrB_2 and AlB_2, and aluminides Zr_2Al. Moreover, Al_2O_3 and an oxide of complex composition (such as ZrAlO) were found in the sur-

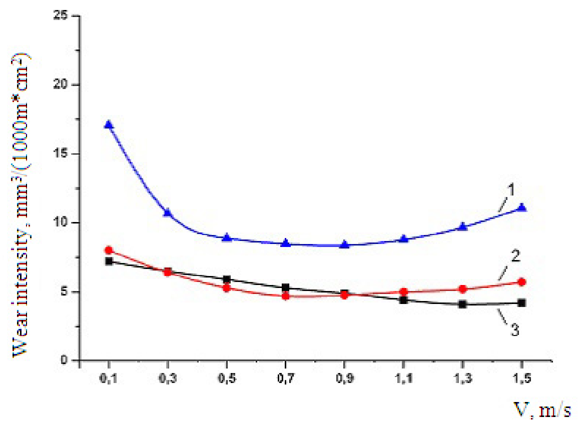

Fig. 3. Dependence of wear intensity on the sliding speed of the coatings: 1 – Fe-Ti-SiC; 2 – type VK15; 3 – amorphous-crystalline system Zr-Al-B

Table 1. Mechanical properties of Zr-Al-B coatings

Content of components, %				E, H/mm	σT, H/mm2	m	HV, MPa
Zr	Al	B	admixture				
80	12	6	2	162900	3980	2,20	1390
70	19	9	2	173700	4190	2,28	1460
60	27	11	2	187800	4860	3,15	1580

face layer. According to the experimental curves, the wear resistance of the Zr-Al-B system at almost the entire speed range under load exceeds the values for VK15 and FeTi-SiC coatings. This is due to the creation of optimal heterogeneous durable thin-film structures with a high level of self-organization and structural adaptability. The amount of amorphous phase is from 75 to 82%. Micrographs of the cross-section of the Zr-Al-B system are shown in Figure 4.

Table 1 presents the results of studies on the mechanical properties of the Zr-based detonation coatings with fine particles of crystalline refractory borides and aluminides.

According to the method [2,3], the yield strength (σT) was determined by the angle of residual bending of flat samples with a sprayed coating, strain hardening was found. In this case, the hardening (m) was determined in the case of a linear dependence for amorphous materials as m < 2.5. Thus, the increase in σT should not exceed 2.5% with an increase in plastic deformation by 1%. Table 1 shows the m values calculated for the tested coatings. The analysis of the data in the table shows that the hardness of the coatings increases along with the decreasing Zr content, and that of aluminum (together with B) sudden increases. At the same time, the addition of up to 20% Al and 10% B increases the value of σT, the Young's modulus and the strain hardening coefficient. The strain hardening coefficient increases and exceeds the limit values for amorphous alloys (E = 180,000 H/mm2 and m = 2.5), which proves the presence of crystalline phases in the structure.

Figure 4 illustrated the microstructures and electron diffraction patterns, which have diffused rings and point reflections of crystalline phases. The studies in dark and bright fields enabled to establish that the test coatings of the Zr-Al-B system consist of an amorphous matrix with crystalline inclusions. The size of the inclusions is 0.10–0.25 μm, most often globular shape. According to the structural-energetic hypothesis, the presented microstructures and electron diffraction patterns reflect the destroy kinetics of structures on the friction surface of Zr-based detonation coatings. An increase in the temperature activates the processes of coagulation and recrystallization, which develop at different scale levels. This is proven by the gradual disappearance of the rings and the appearance of point reflections on the electron diffraction patterns.

Thus, this transformation of secondary structures can be considered as the corresponding elementary mechanisms of adaptation of the surface layers in the process of structural adaptability of the friction system. Therefore, firstly, due to the statistical regularities of the phase of formation and fragmentation of secondary structures in different parts of the contact surfaces do not correlate, but their additive distribution represents a stable structural-temporal state. Secondly, the formation of the structure of the surface layer is not indeterministic, but depends on the minimal principles of dissipative processes. Otherwise, it can be argued that if the structure can adapt to these friction conditions, then it will definitely be indeterministic. In more detail, if there is any

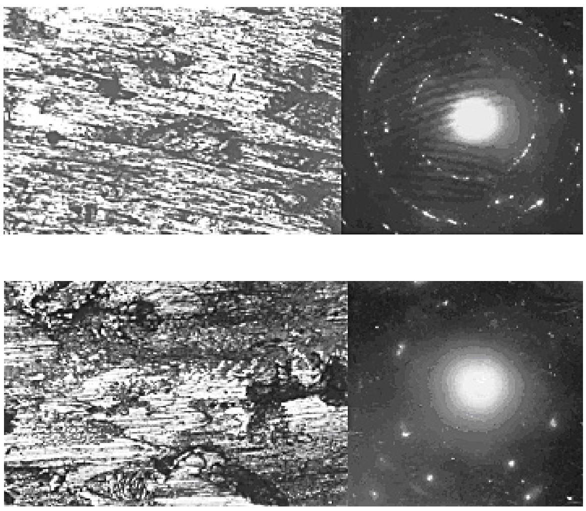

Fig. 4. Microstructures and electron diffraction patterns of friction surfaces of Zr-Al-B coatings: a) V= 0.5 m/s; b) V= 1.5 m/s

distribution of secondary structures corresponding to the state of adaptability, the system will do this, and the friction parameters will be minimal.

The stability of the coating with increasing sliding speed indicates a high performance of the tested Fe-Ti-SiC detonation coatings, a hard alloy of the type VK15 and amorphous-crystalline system Zr-Al-B. The Fe-Ti-SiC coating has a lower wear resistance than the VK15 coating, and according to phase analysis there is a solid solution based on Fe and a fine mixture of strengthening phases, mainly in the form of titanium and silicon carbides.

As a result of the research, it was confirmed that internal compression stresses are an important parameter of the state characterizing the surface layers of machine parts and contribute to an increase in endurance strength and wear resistance. Thus, residual stresses arise in the surface layers of amorphous-crystalline coatings, which in absolute value are not significant for its integrity and quality. It was established that the optimum thickness of the sprayed amorphous coatings of the Zr-Al-B system, which corresponds to the maximum wear resistance, equals 150-250 μm. With increasing thickness of sprayed coatings, the increase in residual stresses can be significantly reduced by heat treatment. During heat treatment, tensile stresses turn into compressive stresses, which has a positive effect on the performance characteristics of the considered coating.

CONCLUSION

Residual stresses, taking into account their features and specific loading scheme, can be adjusted by:

1. Control of temperature and kinetic parameters of spraying during the optimization of the technological process of forming amorphous coatings.
2. Coordination of the properties of the components of coatings and, especially, their coefficients of thermal expansion.
3. The use of amorphous coatings with optimal thickness.

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