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Fracture of Nanostructured Ceramic Coatings on Metal Substrates under Thermal and Mechanical Loadings

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Characteristic features of fracture of nanostructured Si-Al-N and Zr-Y-O ceramic coatings on metal substrates subjected to thermal cycling, uniaxial tension and wear tests are studied. The effect of elemental composition of the coatings on their fracture and delamination from the substrate is shown. The effect of bombardment of the Cu substrate by low-energy Zr+ ions on adhesion and fracture of the Si-Al-N heat resistant coatings is investigated. The dependence of the wear resistance of Si-Al-N / Zr-Y-O multilayer coatings on the number of Si-Al-N and Zr-Y-O layers and on their thickness is revealed. It is found that the coating consisting of 6 bilayers is characterized by minimal wear.

Keywords: Protective Coatings, Fracture, Thermal Cycling, Mechanical Loading, Wear.

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1. INTRODUCTION

The main problem under deposition of protective coatings is to gain strong adhesion between the ceramic layer and the metallic substrate that provides for maintenance of coating continuity during all its durability. Considerable difference in coefficients of thermal expansion of the coating and the substrate, their elastic characteristics, etc. results in high thermal, mechanical, phase stresses in the coatings. Stress relaxation leads to intensive cracking of ceramic coatings under thermal and mechanical loadings as well as their delamination. Moreover, currently used protective coatings are characterized by limited stability of structural-phase condition and properties and have narrow operation ranges. Considerable progress in increasing operation characteristics and reliability of protective coatings is expected of introduction of new class of nanostructured Si-Al-N / Zr-Y-O multilayer coatings [1]. The use of such composite coatings is supposed to provide high reliability and increased physical and mechanical characteristics of new generation of aerospace products. To solve this issue it is necessary to study the characteristic features of fracture of the composite ceramic coatings under different loadings. This work contributes to the insight into the mechanisms of fracture of the Si-Al-N and Zr-Y-O ceramic coatings subjected to thermal cycling, uniaxial tension and wear tests.

2. RESULTS AND DISCUSSION

2.1 Thermal Cycling

Thermal cycling test of the Si-Al-N coatings on the Cu substrate showed that during heating surface layers of the substrate were subjected to biaxial compression, while the coating undergoes tension. The mechanism of stress relaxation to a great extent depends on chemical and phase composition of the coatings. It is evident on thermal cycling of the coatings with different Si/Al ratio. In the case of high Si concentration in Si-Al-N coating (90 % Si -10 % Al), tensile stresses result in quasi-periodical cracking and fragmentation of the coatings. In turn, relaxation of compressive stress in the surface layers of a Cu substrate during annealing occurs by means of uphill diffusion of copper atoms upwards to coating surface. The most of diffusing copper atoms reacts with silicon atoms resulting in formation of copper silicides. It is clearly revealed in investigations of the coatings by electron microscopy and energy dispersive X-ray spectroscopy (EDS). Fig 1 shows that the atomic flux through the coating-substrate interface is predominantly localized in the central part of the coating fragments. It is due to that the coating-substrate system is strained inhomogeneously, so that compressive stresses in the substrate and correspondingly tensile stresses in the coating reach maximum values in central parts of coating fragments and fall to zero near their edges.

On annealing Si-Al-N coatings with high Al content (10% Si - 90% Al) stress-induced diffusion of Cu atoms from the substrate into the coating results in formation of copper agglomerates (Fig. 2a). During cooling relaxation of compressive stress in the coating leads to its bending in the areas of underlying substrate with reduced material density revealed as collapsed regions. Multiple heating-cooling cycles give rise to even more embedding of the coating into the substrate. When reaching critical curvature of the interface, delamination and spalling of coating fragments around the embedded region take place (Fig. 2b). On increasing a number of thermal cycles, the total area of coating spalling gradually raises (see Fig. 2c) results in degradation of its heat-resistant properties.

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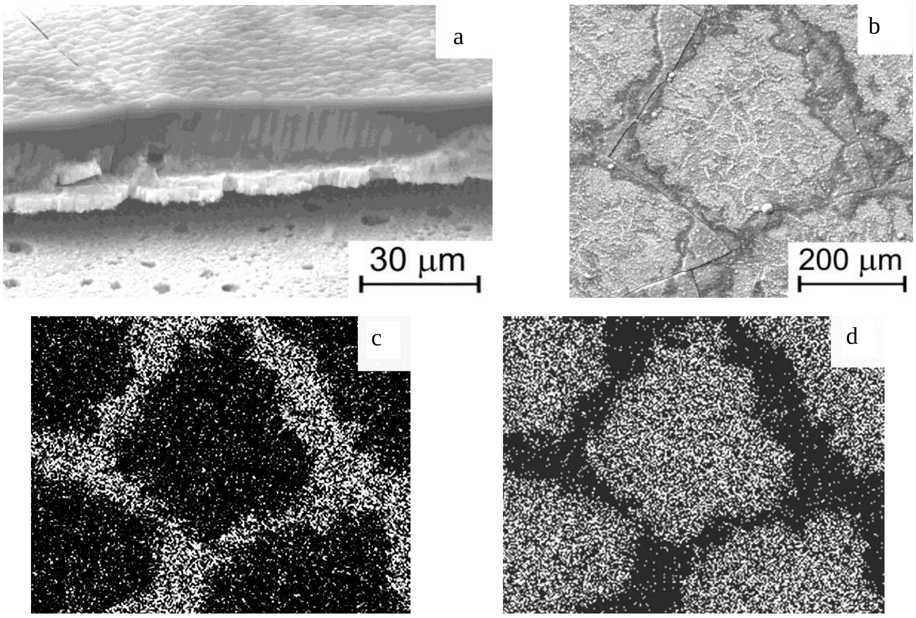

Fig. 1 – Cross-section (a) and plane view (b) of Si-Al-N coating as well as maps of Si (c) and Cu (d) distribution on this surface area after annealing during 1 min at a temperature of 1000 °C

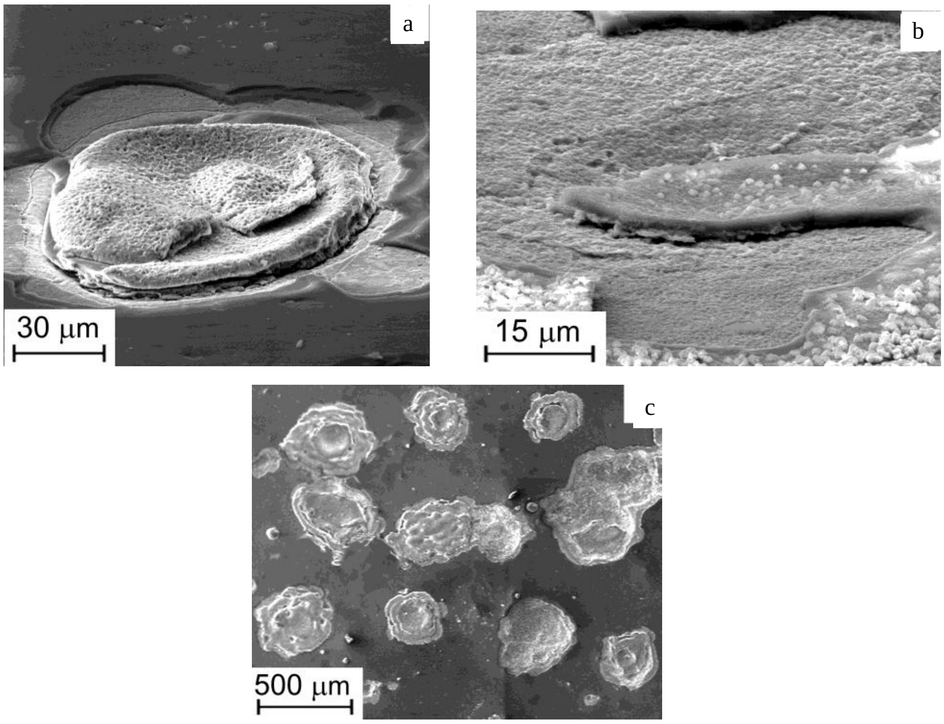

Fig. 2 – SEM-images of Si-Al-N coating after 50 min cyclic annealing (1 min each cycle) at 1000 °C

2.2 Uniaxial Tension

Fracture of Si-Al-N coatings on Cu substrates subjected to uniaxial tension takes place by means of transverse cracking. Both transcrystalline and intercrystalline cracks are observed. Increasing strain results in gradual crack opening that is accompanied by secondary cracking. At the same time, localized strain of the surface layer of the Cu substrate in the form of non-crystallographic shear bands oriented along the directions of maximum tangential stresses leads to weakening bonding between the coating and the substrate and, therefore, to partial coating delamination. The necessity of strain compatibility between the Si-Al-N coating and the Cu substrate, which are characterized by different Poisson's ratios, causes development of transverse compressive stresses under uniaxial tension of the coating-substrate system. Relaxation of the stresses gives rise to buckling of debonded fragments of the coating bordered by transverse cracks (Fig. 3a).

Further loading results in dislocation gliding all over the test portion of the Cu substrate and the coating delaminates everywhere. Under the influence of the compressive stresses delaminated coating stripes bordered by transverse cracks buckle and spall from the substrate. As a result, the Si-Al-N coating almost completely delaminates at 15% strain of the Cu substrate (Fig. 3b).

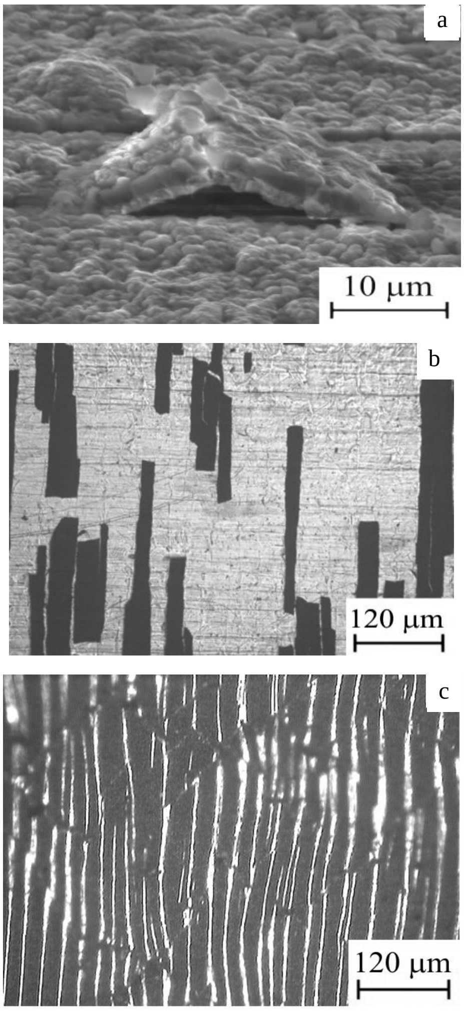

Fig. 3 – Cracking and delamination of Si-Al-N coatings deposited on untreated Cu substrates (a,b) and the substrate subjected to Zr^+ ion bombardment (c); uniaxial tension, ε = 5 (a) and 20% (b,c)

Nanostructuring of the metal substrate is the advanced technique of increasing interfacial shear strength of heat-resistant coatings because it provides the best agreement between their crystal lattices, mechanical properties, thermal expansions, etc. In the case of treatment of a Cu substrate by Zr^+ ion beams, the Si-Al-N coating does not delaminate even at 20% strain (Fig. 3c). It is due to the fact that ion implantation leads to enriching the substrate surface layer by zirconium that apparently causes formation of zirconium nitrides at the coating-substrate interface. According to [2], intermixing of Zr, Cu and N atoms results in the formation of a layer consisting of ZrN and Cu nanocrystallites. The latter considerably increases adhesion of the heat-resistant coatings. Coatings deposited on ion-beam treated substrates remain in contact with them until complete fracture of the substrate. Even on necking of the extended metal substrate, only coating cracking at an angle of 45° to the loading axis and shift of coating fragments in a lateral plane are observed (Fig. 3c).

2.3 Wear Tests

Wear tests of Si-Al-N / Zr-Y-O multilayer coatings performed on conditions of dry friction using cylinder-on-plate geometry revealed intensive abrasion of initial surface roughness of the coatings as well as formation of grooved surface topography of wear tracks at the running-in stage (Fig. 4a). In addition to abrasive wear, further tests revealed adhesive wear, which intensity considerably depends on a number of Si-Al-N / Zr-Y-O bilayers in the coating. Due to adhesive bonding between the rider and the coating, rider rotation leads to tearing of large coating fragments (Fig. 4b). In case of a bilayer ceramic coating, debonding occurs along the coating-substrate interface and results from fatigue damage of surface layers of the substrate. The latter is confirmed by formation of shear cracks in nanostructured surface layer of the substrate.

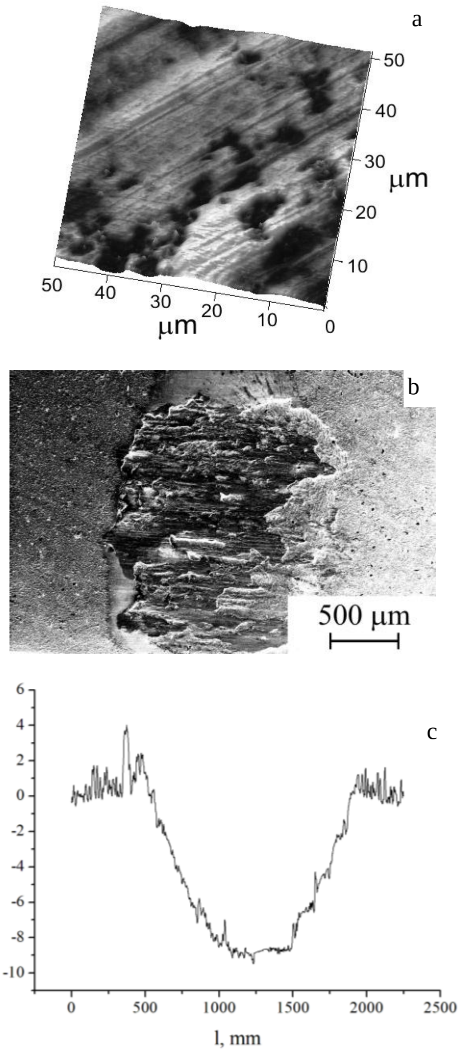

Fig. 4 – AFM- (a) and SEM-images (b) of a wear track on a Zr-Y-O / Si-Al-N bilayer coating after wear test during 12 (a) and 16 min (b). c – cross-section profile of a wear track on a multilayer coating (6 Zr-Y-O / Si-Al-N bilayers) after wear test during 40 min

Increase of a number of bilayers in the coating and, therefore, appearance of additional interfaces prevents from extension of strain deep into the specimen. Thus the rate of adhesive wear of the coatings consisting of 6 Si-Al-N / Zr-Y-O bilayers considerably decreases as compared with the one of the bilayer coating. However, increase in the number of bilayers providing constant total coating thickness leads to diminishing layer thickness. Therefore, tests of the coatings consisting of 17 bilayers showed increasing wear rate caused by quick tearing of bilayers due to debonding along the Si-Al-N / Zr-Y-O interfaces. It is clearly evident as stepped surface of the wear track (see Fig. 4c), with step height well agreeing with the bilayer thickness.

3. SUMMARY

Peculiarities of fracture of nanostructured Si-Al-N and Si-Al-N / Zr-Y-O multilayer ceramic coatings on metal substrates subjected to thermal cycling, uniaxial tension and wear tests are studied. High stress arising in the coatings during thermal cycling is found to induce cracking and spalling of the coatings with high Si content as well as uphill diffusion of metal atoms upwards to coating surface. In the case of coatings with high Al content degradation their heat-resistant properties is caused by stress-induced diffusion of Cu atoms from the substrate through the coating and formation of copper agglomerates.

The delamination of the Si-Al-N coatings deposited onto an untreated Cu substrate during uniaxial tension is related to transverse contraction. At the first stage, local folding and spalling of square coating fragments occur, which is caused by the development of slip bands in substrate grains. At the second stage, a coating spalls over the entire sample surface in the form of stripes bounded by longitudinal and transverse cracks and, then, separates from the substrate. Modification of the Cu substrate surface layer by means of Zr^+ ion bombardment inhibits coating delamination because of an increase in the coating adhesion due to the formation of zirconium nitrides at the film-substrate interface.

Wear tests of Si-Al-N / Zr-Y-O multilayer coatings showed that due to simultaneous action of abrasive and adhesive mechanisms their wear resistance is governed not only by the total coating thickness but also by the number and thickness of bilayers. The dependence of the wear resistance on the bilayer number has an extremum, so as the coating consisting of 6 Si-Al-N / Zr-Y-O bilayers is characterized by minimal wear.

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