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Development of Ti-Al-Cr-based thermobarrier coatings on titanium alloys

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The behavior of Ti-Al-Cr heat-resistant coatings during high-temperature oxidation was shown to depend on the structure of the substrate, which, in turn, defines the nature of the diffusion processes occurring at the coating-substrate boundary. When the substrate was made from titanium-rich alloys, active diffusion of Al and Cr from the coating, as well as Ti into the coating was observed. Thus, due to the change in the Al/Ti activity ratio, a mixed TiO_2 and Al_2O_3 oxide layer is formed on the coating surface. In the case of γ-TiAl substrate, only an Al_2O_3 oxide layer is formed on the surface of the TiAlCr coating.

Keywords: thermal barrier coatings, titanium aluminides, oxidation, zirconium dioxide

Створення термобар'єрних покриттів на основі Ti-Al-Cr на титанових сплавах. *В.Л.Сироватка, В.Є.Шелудько, А.В.Міницький.*

Показано, що поведінка жаростійких Ti-Al-Cr покриттів в процесі високотемпературного окислення залежить від складу підкладки, яка в свою чергу визначає характер дифузійних процесів, що мають місце на межі розподілу покриття-підкладка. У випадку коли підкладка виконана з титан-збагачених сплавів, має місце активна дифузія Al та Cr з покриття, а Ti – в покриття. При цьому зі зміною відношення активності Al/Ti на поверхні покриття формується оксидний шар з суміші TiO_2 и Al_2O_3. У випадку, коли підкладка зроблена з γ-TiAl, на поверхні покриття TiAlCr формується тільки оксидній шар Al_2O_3.

1. Introduction

Thermal barrier coatings (TBCs) are used in various industries to protect parts of gas turbine engines, diesel engines, and various space devices from environmental influences at elevated temperatures. The use of TBC together with cooling of parts allows reducing the temperature of the metal surface by 100 – 150 °C. Traditionally, a TBC consists of a metallic bonding layer (MeCrAl, where Me - Ti,Ni or Co) and an outer layer of yttria-stabilized zirconia (YSZ). Its service life largely depends on the ability of the bonding layer to form a continuous oxide layer of Al_2O_3 at the boundary with the outer ceramic coating, protecting the base from oxidation.

Statement of the problem

It has been experimentally established, that γ-TiAl retains stability from 49 to 66 wt. % [1] in the temperature range of 750-800 °C according to equilibrium diagram. Typically, at these temperatures TiO_2 and Al_2O_3 mixed oxide scale forms in the surface layer of materials of this class. The presence of rutile is undesirable, since this porous oxide is not able to protect the metal sublayer from oxygen penetration, and also quickly deteriorates.

One of the promising ways to increase the heat resistance of TiAl-based alloys to 900–1100 °C while ensuring satisfactory crack resistance is the partial replacement of Al with Cr. The production of a heat-resistant alloy with acceptable properties based on the Ti-Al-Cr system can be realized in two directions. The ***first*** way involves using γ-titanium aluminide as a base, which has fairly good mechanical properties, and increasing the heat resistance of the alloy from 800 to 1100 °C by alloying.

As for the first direction, it has been established that excess Cr content in materials leads to their embrittlement. So, in [2] it is reported that the Ti-50Al-20Cr coating was recognized as brittle due to the high content of the extremely brittle Laves phase – $Ti(Cr,Al)_2$ in the two-phase structure. It is this phase, containing 37-42 at. % Al, that plays a key role in the formation of a continuous protective Al_2O_3 layer on the surface of the oxidized alloy. In addition, reactionary Cr-enriched zones leading to a decrease in crack resistance were found at the boundary of the coating with the γ-substrate (Ti-47Al-2Cr-2Ta). Subsequent studies in this area were aimed at finding a composition with lower Cr content in order to improve the fatigue characteristics of the coating-substrate composition.

The studies showed that a coating with a reduced Cr content up to 12 at. % (due to an increase in the Ti content to 37 at. %, and, accordingly, the γ-phase) deposited by the plasma spraying, provides successful protection of the Ti-48Al-2Cr-2Nb substrate after hold at 1000 °C in air for 500 hours. Nevertheless, from the dependencies given in this work it is evident that the increase in the mass of oxidized samples at both 800 °C and 1000 °C due to the penetration of oxygen into the coating still continued. The crack resistance of the coating after hold at a temperature of 1000 °C was assessed by measuring the microhardness using an indenter imprint. Unlike the first generation alloys, whose structure consisted mainly of the Laves phase with intense cracking already at a load of 100 g, the new coating had a higher crack resistance. In the Vickers indenter print at a load of 1000 g/15 s, only small isolated cracks of 1-3 μm in length were recorded using scanning microscopy. In addition, no chromium-containing brittle inclusions were found in the adhesion zone of the coating to the substrate. However, this result was not considered final and work on reducing the Cr content in the alloy was continued.

The Ti-52Al-5Cr composition was identified as the most promising. This alloy, with a minimum amount of Cr, retains a structure in the form of a γ-phase with a tetragonal face-centered lattice (Ll_2). This favors the achievement of satisfactory strength characteristics with oxidation resistance at 1000 °C in an air environment. However, this result was assessed only as promising, since the air environment in this experiment was subjected to special drying (reduction of air humidity). Without this procedure, areas rich in rutile and titanium, as well as aluminum oxide, were found in the resulting scale, which are conductors for oxygen penetration into the alloy (sources of rapid scale cracking). It should be emphasized that the object of the study was casting alloys. The coatings applied to them contain pores, which can have a significant negative effect on both strength characteristics and oxidation resistance.

It has been shown that microalloying of Ti-52Al-5Cr alloy with scandium provides the necessary oxidation resistance, at least not lower than at 900 °C in air without additional drying [3].

The ***second*** direction involves the use of titanium trialuminide, which has acceptable heat resistance. Unlike γ-TiAl having an ordered face-centered lattice (Ll_0) with a small degree of tetragonality (c/a=1.02), the intermetallic compound $TiAl_3$ has a tetragonal lattice (D022) [4] and is extremely brittle. However, it is possible to obtain an alloy with the required mechanical properties based on it by alloying. Attempts to develop materials in this direction are mainly reduced to the transformation of the ordered tetragonal crystal lattice of $TiAl_3$ (D022) into a cubic one (Ll_0) with an increased number of slip systems due to alloying with Cr. Many studied titanium trialuminide-based alloys contain 66-67 at.% Al and 8-10 at.% Cr, which is close to the minimum for this phase. For example, in [5], an ingot with the composition Al-8 at.% Cr-25 at.% Ti was subjected to oxidation (200 cycles of one hour) in a furnace in air at 1200 °C. High oxidation resistance was noted, confirmed by the formation of scale mainly in the form of α-Al_2O_3. However, X-ray studies of the scale made it possible to record the presence of rutile in it. Throughout the experiment, there was a decrease in the specific weight of the oxidized sample, associated with the chipping of the scale material.

In the review [6] devoted to gas-thermal cubic titanium trialuminide-based coatings, the results of oxidation at 815 °C (500 hours/

cycles) of AL153 coatings with a composition 66Al-9Cr-25Ti very close to that indicated above for the ingot are presented. The coating was sprayed by the LPPS-method onto a substrate made of Ti-47Al-2Cr-2Nb alloy. During cyclic tests, the structure of the "coating-substrate" system was homogenized and Al diffused into the substrate, converting the α_2+γ phase of the TiAl alloy into an Al-rich γ-phase at the boundary with the coating. The work notes that this coating did not provide absolute protection due to the formation of a crack network due to local mechanical stresses during thermal cycling. This phenomenon was observed during the spraying process or the first thermal oxidation cycles for Ti- and TiAl-alloy substrates. Subsequently, cracks did not develop during the formation of scale from an oxide mixture enriched with Al_2O_3, and thus the overall level of protection was maintained. The coating thickness was about 200 µm. The results of controlling the change in the specific weight of the coated samples indicated high stability of the coating properties.

Nevertheless, it should be noted that during oxidation, there was a continuous increase in the specific gravity of the samples. The use of the APS method of spraying the coating in air instead of LPPS method made it possible to obtain, according to the authors, an exceptionally high-quality coating, which after spraying contained less than 0.1 at.% oxygen in the form of Al_2O_3. This coating on Ti- and TiAl- substrates was found to be more crack-resistant, but, nevertheless, after 25 cycles, crack development took place. The use of another widely used spraying method (HVOF) made it possible to obtain coatings with a phase composition close to that obtained by the APS method, although in some cases the intensity of the X-ray peaks of the Al_2O_3 phase was weaker for HVOF coatings. In the conclusion to the work, it is indicated that the developed coatings provide exceptional protection against oxidation of substrates made of various Ti-based alloys. It can be noted that these methods differ in the production modes and properties of the coatings (adhesion, cohesion, porosity, microhardness) [7-9].

The aim of this work was to study the relationship between the processes occurring during high-temperature oxidation of TBCs at the boundaries of the bonding layer with the substrate and the outer ceramic layer during the formation of a heat-growing layer of protective scale.

2. Experimental

The bonding layers were AL153 and TiAlCrSc detonation-sprayed coatings onto γ-TiAl and VT-16 titanium alloy substrates. The thermal barrier layer (TBL) was formed by the plasma method in air from YSZ, which is widely used in industry. Local chemical analysis and element distribution assessment in the coating were carried out using a SEM CamScan 2000 (Camscan Electron Optics Ltd, Cambridge, UK) equipped with an ENERGY 200 attachment.

AL153 and TiAlCrSc powders for spraying the coatings were obtained from an ingot by mechanical crushing. The ingots were smelted in an electric arc furnace with a tungsten non-consumable electrode on a copper water-cooled substrate in a purified Ar environment, after which they were annealed in a vacuum at 1300 °C for 10 hours. The particle size of the powders was 10-60 µm. The "Dnepr-5MA" gun developed by the Frantsevich Institute of Problems of Metallurgy of the National Academy of Sciences of Ukraine was used for spraying the powders. A mixture of acetylene with oxygen (C_2H_2/O_2 = 1/1.5) was used as a combustible gas. Compressed air was used as a gas transporting the powder in the barrel of the unit to the zone of action of the detonating mixture. Thermal cycling tests of the samples with coatings were carried out in air in the SNOL 2.3.1.3/11I2 furnace at T = 900 °C, each cycle included an 8-hour hold at a given temperature, the total oxidation time was 56 hours.

3. *Results and discussion*

The ***first*** series of experiments consists in testing the effect of TBL on the behavior of AL153 and TiAlCrSc cast alloys, selected to obtain a heat-resistant bonding coating. The first alloy is a representative of the group of $TiAl_3$-based alloys. The second is based on γ-TiAl. It was established that the presence of TBL does not fundamentally affect the nature of oxidation of cast γ-TiAl; in this case, as usual, a scale layer is formed from a mixture of Al_2O_3 and TiO_2 oxides. In our experiment, no significant effect of TBL was found either; in both cases a continuous, so-called, thermally growing oxide layer (TGO) consisting mainly of Al_2O_3, was formed at the boundary "base-TBL". Fig. 1 shows the cross-section of the coating microstructure before and after thermal cyclic oxidation, the thickness of the continuous TGO at the "TiAlCrSc base – TBL" boundary was 2-5 µm.

Table 1 – Results of local chemical analysis of TiAlCr–coating on VT-16–substrate after oxidation at 1000 °C

Spectrum	Element, wt.%					Total
	O	Al	Ti	Cr	N	
2	6.44	7.31	72.44	0.32	13.48	100.00
3	37.5	23.09	26.81	7.05	5.55	100.00
4	48.97	19.45	24.43	7.16		100.00
5	24.13	0.45	74.36	1.06		100.00
6		2.86	96.74	0.4		100.00

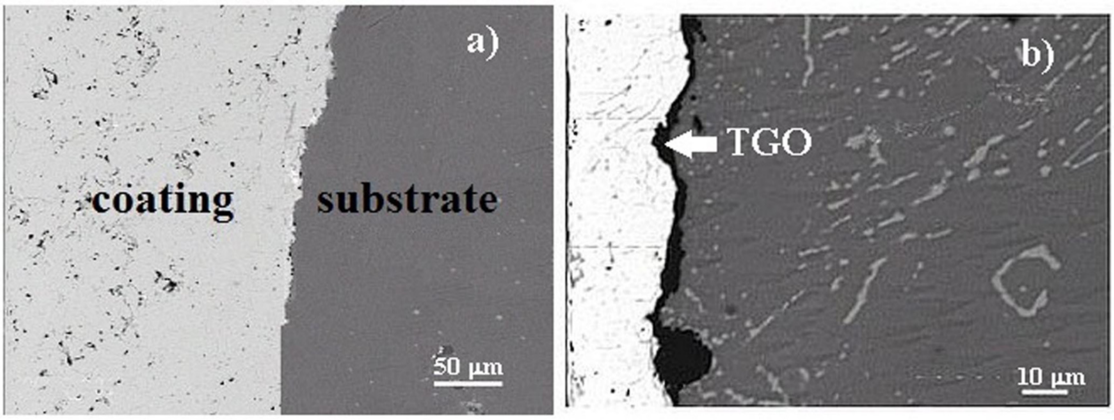

Fig. 1 – Microstructure of ZrO_2–TB-coating on TiAlCrS–substrate at 900 °C: a- before oxidation; b- after oxidation

As is known, the porosity of the material on which the GO is formed can significantly affect the nature of its oxidation. Therefore, in the ***second*** series of experiments, an intermediate bonding layer of AL153 was first deposited on the γ-TiAl substrate, followed by GO. Fig. 2 shows the microstructure of the ZrO_2 - AL153 - γ-TiAl system and the distribution of Zr, Ti, Al, Cr, O elements across its thickness before oxidation. The layers sprayed in air, as expected, contained oxygen.

After thermocyclic oxidation, a GO from Al_2O_3 was formed at the “AL153–TBL” boundary (Fig. 3), and the oxygen content in the AL153 layer remained virtually unchanged, indicating high protective properties of the GO. It should be noted that the thickness of the GO formed in this case on the porous coating is approximately twice as large as on a cast alloy of similar composition. In addition, as can be seen from the element distribution curves, Ti diffusion from the Ti-rich base into the bonding layer took place at the AL153–γ-TiAl boundary.

Based on the fact that in the case of manufacturing a base from an alloy with an even higher Ti content, diffusion processes can affect the formation of GO more significantly, the ***third*** series of experiments was carried out for studying the oxidation processes in the system of “an aluminide coating AL153 (66 at.% Al-9 at.% Cr-25 at.% Ti) - a substrate made of titanium alloy VT-16 (1.6-3.8 Al; 4.0-5.0 V; 4.5-5.5 Mo, rest Ti, wt.%)”, widely used in aircraft building. The coating thickness was 200-250 µm (Fig. 4). A photo of the microstructure indicates a high degree of its homogeneity and density. Visually, the structure looks like consisting of wavy veins, which is typical for the structure of a detonation coating, since its thickness is increased by serial shots. After oxidation, significant changes were recorded in the structure of the “coating-substrate” system under consideration. Local chemical analysis shows (Table 1) that the outer scale layer at the early stage of thermal cyclic oxidation (after 17 hours) at a temperature of 900 °C consists of a mixture of TiO_2 and Al_2O_3 (Sp 4, Table 1). The priority of formation of these oxides is due to the fact that the equilibrium partial pressure of oxygen for them is less than the actual partial pressure of oxygen in the air on the surface of the coating. As oxygen moves deeper, its activity decreases and, as a result, the formation of aluminide phases Ti-Al-Cr-O takes place (Sp 5-6, Table 1).

The “substrate-coating” system consists of at least 4 layers (Fig. 4). The outer layer, about 10 µm in thick (Sp 5, Table 1), can be identified

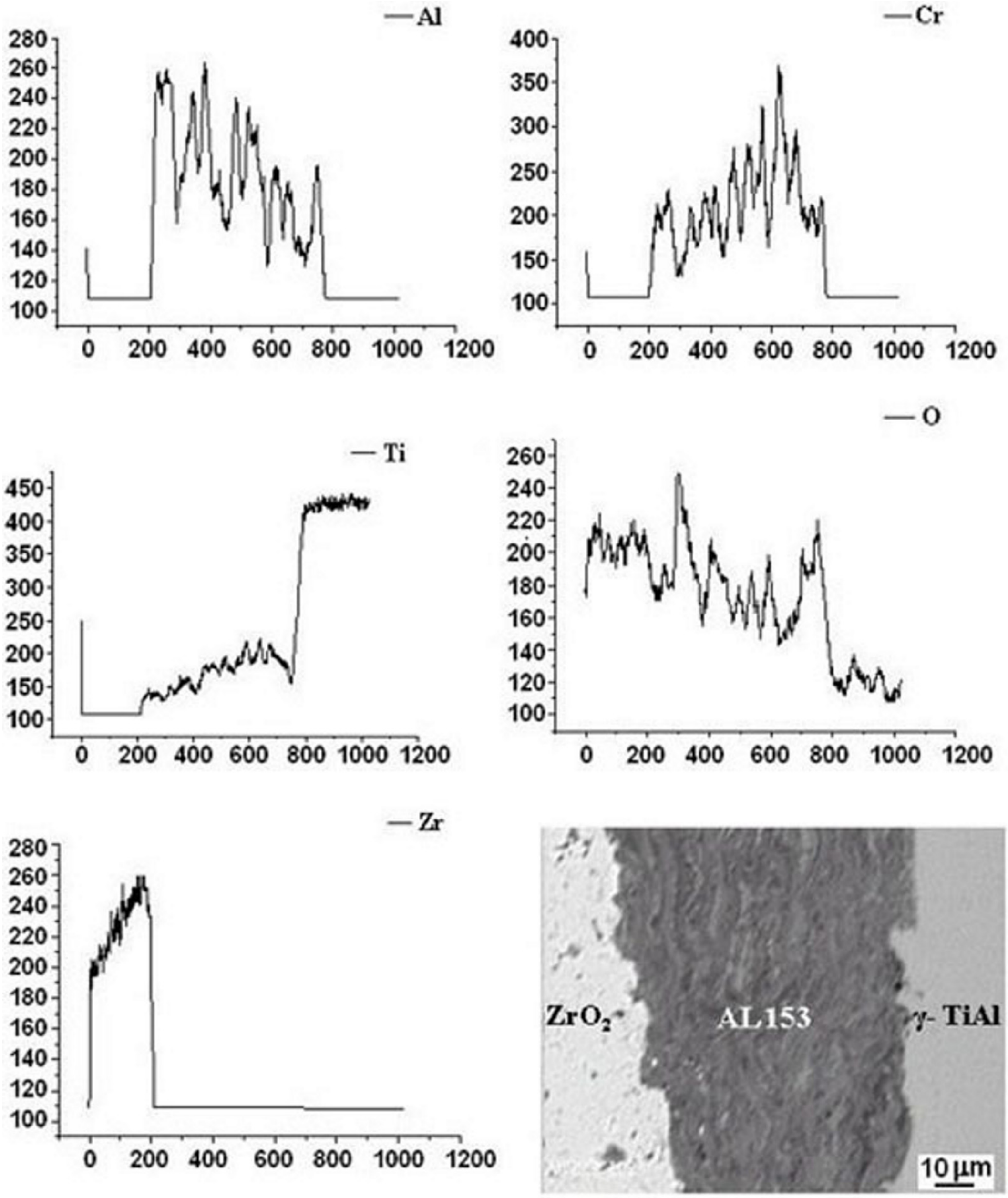

Fig. 2 – Microstructure and distribution of elements in AL153-coating before oxidation

as Ti-rich oxide – TiO_2. The Cr content in this layer is only about 1 wt.%. The second layer can be represented as a finely dispersed mixture of two oxide phases based on TiO_2 and Al_2O_3 with a Cr content of ~7 wt.% (Sp 4, Table 1). The standard free energy of formation of these oxides in air at elevated temperatures differs insignificantly. At the early stage of oxidation, Cr oxide is believed to form [8], since it has the highest oxidation rate among the elements of the Ti-Al-Cr system. However, this oxide subsequently dissolves completely in aluminum oxide upon their contact, forming a more thermodynamically stable oxide $(Al,Cr)_2O_3$. The third layer in the coating has approximately the same thickness (5-10 μm) as the second one. The oxygen content in this layer, although somewhat less than in the previous one, is nevertheless large (36-38 wt.%) (Sp 3, Table 1). The results of chemical analysis and visual examination of the structure indicate that this layer contains two intermetallic phases TiAlCr (light and dark) with different ratios of Ti to Al at practically the same amount of Cr, as well as oxides.

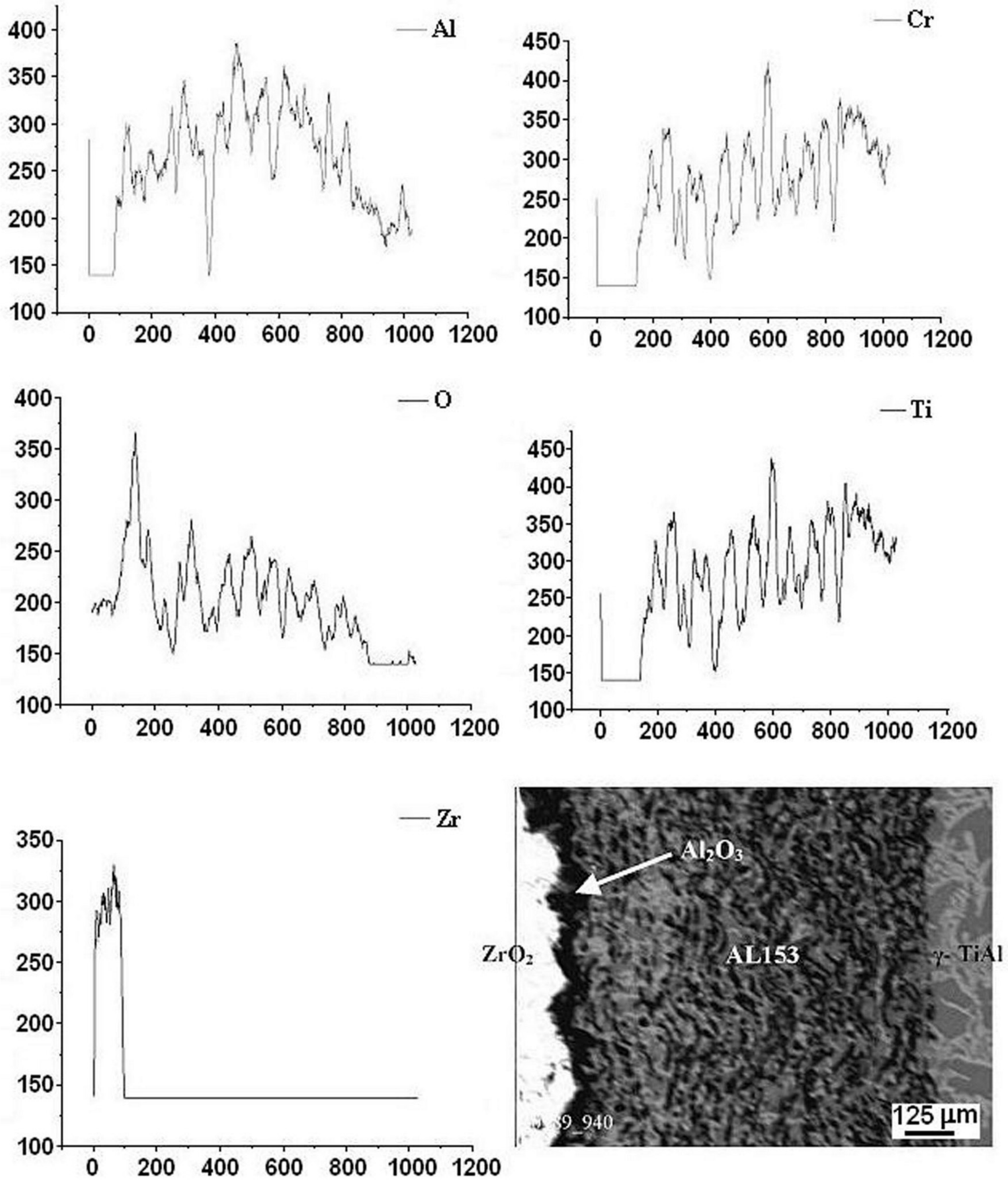

Fig. 3 – Microstructure and distribution of elements in AL153 coating after oxidation at 900 °C

The fourth layer (its thickness is about 50 µm), formed in the substrate at the boundary with the coating, unlike the substrate, contains more Al - 7.31 wt. % (Sp 2, Table 1). Taking into account that the Al content in the coating after oxidation became much less than it was in the initial state, it can be stated that active diffusion of Al from the coating into the substrate occurred. The result of such depletion of the coating in Al was the formation of Ti oxide phases in it, which do not provide protection of the substrate from oxidation, as evidenced by the presence of oxygen in it (6.44 wt. %) (Sp 2, Table 1). Obviously, the diffusion of Al from the coating, the penetration of oxygen into it, as well as the diffusion of Ti from the substrate into the coating due to the formation of microcracks as a result of thermal stresses during thermal cycling outpaced the formation of Al oxide on its surface. The consequence of this is a relatively uniform distribution of a significant amount of oxygen over the entire thickness of the coating. It is necessary to note such an important fact as the presence

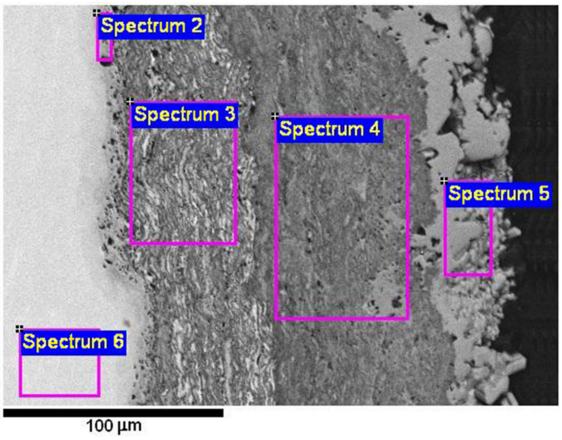

Fig. 4 – Microstructure of TiAlCr–TB-coating on VT-16–substrate after oxidation at 1000 °C with the results of local chemical analysis

of nitrogen in the substrate and the adjacent coating layer (Sp 2 and 3, Table 1). It should be noted that the maximum nitrogen content (13.48 wt. %) was recorded exactly in the surface layer of the substrate, where the activity of Ti is the highest. The local chemical analysis shows that nitride phases are formed. The transport paths of nitrogen to the "metal–oxide layer" boundary, where nitride-containing phases are found, are unclear, although grain boundary diffusion and gas transport through pores in TiO_2 are usually considered the most likely mechanism for their formation. In this case, rutile acts as a "conductor" through which oxygen and nitrogen from the air penetrate deep into the alloy, leading to its embrittlement and, ultimately, to early failure. Taking into account the difficulty of accurately identifying the phases formed under metastable conditions, it can be assumed that the studied alloys contain phases of the oxynitride TiN_zO_y, similar to what occurs in the case of Ti oxidation. The formation of oxynitride from a saturated solid solution of oxygen and nitrogen in α-Ti is estimated to be more probable than the formation of the nitride phase TiN_z and oxide TiO_x from it. The occurrence of the TiN_zO_y oxynitride phase from a saturated solution of oxygen and nitrogen in Ti is due to the formation of a continuous series of solid solutions in the TiO-TiN system. At the same time, the opinion is expressed that with an increase in the duration of oxidation, as a result of partial oxidation of the TiN_zO_y phase, TiO_x is formed from it with the release of nitrogen.

Comparison of the scale structure formed after 52 hours with the scale structure obtained in a shorter period of time (after 17 hours), i.e. at an earlier stage of oxidation, allows us to note a number of differences that are important for understanding the oxidation mechanism. In the first case (Fig. 3), this is the absence of both the inner layer containing nitrides (nitrogen is not recorded) and the outer TiO_2 layer. During continuous oxidation, when the oxygen activity in the inner layers of the coating becomes quite low, nitrides are formed. This process occurs at the boundary with the substrate (Fig. 5), where the Ti activity is highest, and the ratio of partial pressures PO_2/PN_2 is minimal. Nevertheless, the presence of oxygen is recorded even in the substrate. The absence of the outer TiO_2 layer in the first case is explained by the fact that the diffusion of Al deep into the Ti substrate does not have time to complete. In principle, the observed layered structure of scale on the coating largely coincides with that previously described for oxidation of cast TiAl. The formation of diffusion porosity occurs in the structure, especially at the "substrate-scale" boundary. However, it should be taken into account that in our case, the object of study is a sprayed coating with an initial porosity of 1-2%, which undoubtedly has an accelerating effect on diffusion processes. During oxidation, diffusion porosity is added to the initial porosity of the coating. The nature of the porosity in different areas of the coating thickness can be judged from images of the structure at high magnifications (Fig. 5). As can be seen, the greatest porosity occurs in the coating in the border areas with the substrate.

Considering that the local chemical composition was determined by the device from an area of about 1 μm^2, an assessment of the sizes of structural components in different layers of the coating after oxidation shows that in many cases we are dealing with relatively finely dispersed phases, at least of submicron order.

Thus, to solve the problem of protecting Ti alloys from oxidation using a coating, it is necessary to minimize the diffusion of Al from it into the substrate. One way may be to spray an intermediate layer that reduces the concentration gradients of Ti and Al, leading to the appearance of additional diffusion porosity and, as a consequence, to a decrease in the protective properties of the coating.

4. Conclusions

It was established that the presence of a ceramic layer does not change the oxidation nature of TiAlCr coatings. The working capacity of a BC with an outer ZrO_2 layer on substrates

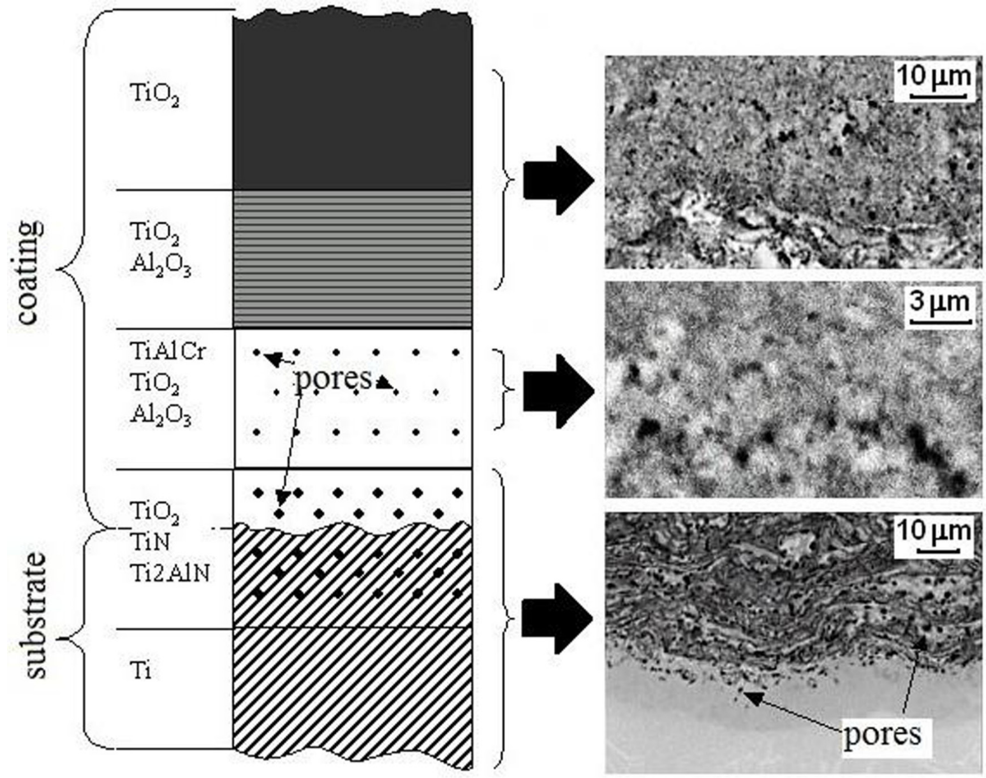

Fig. 5 – Formation of diffusion porosity in the structure at the “substrate-scale” boundary

made of Ti and γ-TiAl alloys depends on the oxidation features of the TiAlCr aluminide bonding layer, as well as on the nature of the diffusion processes occurring at the “coating-substrate” boundary. When the substrate is made of Ti-enriched alloys, Al and Cr diffuse from the coating, and Ti diffuses into the coating. In this case, an oxide layer consisting of TiO_2 and Al_2O_3 is formed on the coating surface. In the case of a γ-TiAl substrate, a protective layer of only Al_2O_3 is formed on the surface of the TiAlCr coating.

The oxidation process of TiAlCr coatings occurs in several stages, which determine the layer-by-layer distribution of phase-forming elements in it – Ti, Al, Cr, O, N. Under the surface layer-scale of TiO_2 and Al_2O_3 there is a layer of Al-depleted intermetallides, and at the “coating – substrate” boundary a layer containing nitrides is formed.

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