PLASMA ZrO_2 COATINGS WITH METALLIC BOND COAT OF ALLOY AlCuFe

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The article present results of investigations of structure, phase composition and microhardness of thermal barrier plasma coatings produced by using quasi-crystalline alloy AlCuFe with a different content of the ψ-phase as a bond coat material instead of traditional alloy MeCrAlY (Me–Ni, Co, Fe). Formation of phases in the ceramic ZrO_2 layer was studied depending upon the ψ-phase content in the bond coat of a thermal barrier plasma coating.

Keywords: *thermal barrier plasma coatings, powders, zirconia, alloy AlCuFe, quasi-crystalline phase, structure, coating properties*

To increase power of internal combustion engines it is necessary to raise temperature and degree of compression of a working gas formed in fuel combustion. One of the efficient methods to address the above problem is to apply thermal barrier coatings (TBC). This makes it possible either to increase the working temperature of the gas and, thus, engine power, or to reduce losses of the engine power in combustion chamber through decreasing consumption of cooling air. Moreover, TBCs allow reducing cost of the engine owing to utilisation of less expensive and scarce materials, other parameters being equal.

TBC is a multilayer system, which consists of a metallic bond coat, external ceramic and transition cermet layers [1–3]. The external ceramic layer performs heat-protecting functions in TBC. The system based on partially stabilised zirconia has received the widest acceptance as a thermal barrier layer. Wide application of ZrO_2 is provided by low thermal conductivity coefficient ($1\ W\cdot m^{-1}\cdot K^{-1}$) and high values of linear thermal expansion coefficient (LTEC) ($9.5\cdot10^{-6}\ K^{-1}$), heat resistance and fracture toughness.

Zirconia is susceptible to reversible polymorphic transformation, which is a negative factor when it is used as a coating material. In heating to 1000–1050 °C, its low-temperature monoclinic modification ZrO_{2M} transforms into the tetragonal one ZrO_{2T}, which is accompanied by volumetric compression (by 7.7 %) [4]. Cooling to a temperature below 1000 °C causes reverse transformation into the monoclinic modification and, accordingly, increase in volume and decrease in density of a coating, this leading to its fracture and deterioration of performance. Polymorphic transformation is suppressed by using partial or complete stabilisation of structure of ZrO_2 by oxides which are close to it in structure (Y_2O_3, MgO, CaO, CeO_2, Yb_2O_3), form solid solutions with ZrO_2 and decrease thermal conductivity of ceramics approximately by half [5]. The most efficient stabilising addition to zirconia is yttrium oxide.

The key function of the bond coat in TBC is plastic relaxation of stresses in the coating, which form because of unmatched changes in volumes of ceramic and metallic materials in heating and cooling of a part [2, 3]. As ductility of alloys catastrophically falls as a result of their high-temperature oxidation, and a layer of ceramics is permeable for gases, the bond coat material should be characterised by high heat resistance. Alloys of the type of metal (Ni, C, Fr)–Cr–Al with additions of reactive elements (Y, Yb, Zr, Hf, etc.) are used as such bond coats. Fracture of such a coating occurs in diffusion interaction with the substrate metal, this leading to decrease in the concentration of alloying elements in the coating and formation of phases with lower oxidation resistance [2].

In this study the authors used alloy AlCuFe [6–9], corresponding in its chemical composition to a range of existence of the quasi-crystalline ψ-phase ($Al_{63}Cu_{25}Fe_{12}$), instead of MeCrAlY, which is a traditional bond coat material. This alloy is characterised by high hardness (up to 10 GPa), corrosion resistance and heat resistance (up to 500 °C), while in LTEC (about $1\cdot10^{-5}\ K^{-1}$) and thermal conductivity (1–$2\ W\cdot m^{-1}\cdot K^{-1}$) it is close to ceramics ZrO_2. The presence of aluminium as a main element in the alloy indicates to a high potential of using it as a bond coat material for protection from high-temperature corrosion, e.g. in manufacture of internal combustion engines.

The main method for deposition of zirconia thermal barrier coatings is plasma spraying (up to 90 % of developments) [9]. Plasma spraying of the ZrO_2–6–8 % Y_2O_3 ceramic layer provides formation of coatings, which may contain up to 99 wt.% of the tetragonal phase [3] or meta-stable T′-phase also with the tetragonal lattice [10]. It is characterised by an increased content of stabiliser, low degree of tetragonality and non-transformability into a monoclinic phase under the effect of stresses. So, investigations were

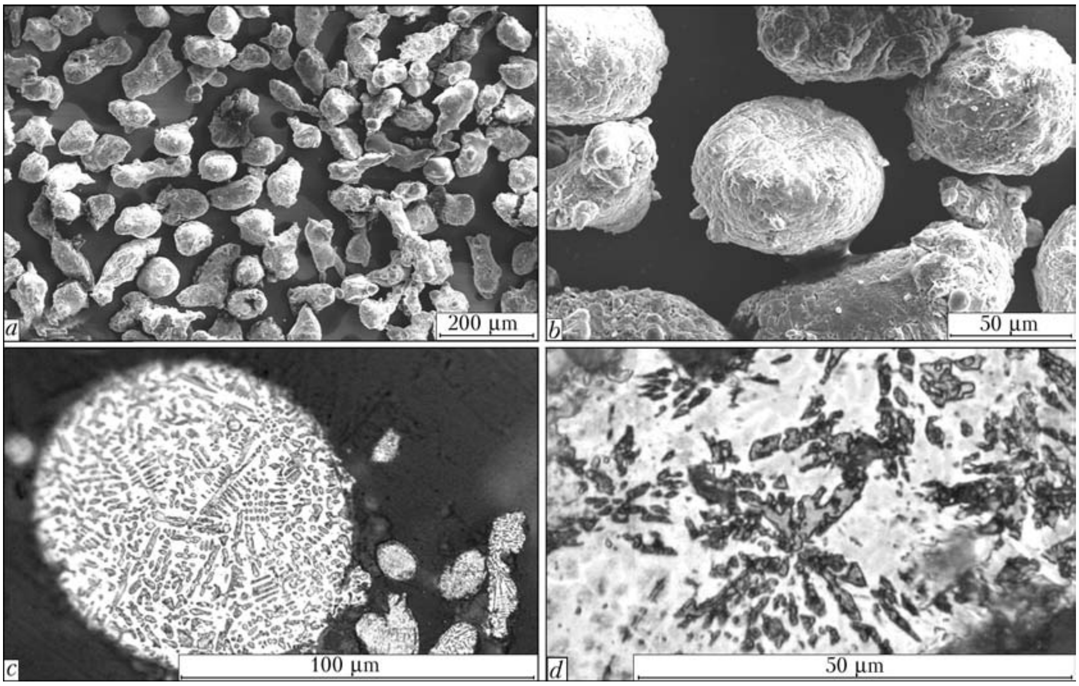

Figure 1. Appearance (*a, b*) and typical structure (*c, d*) of particles of the AlCuFe powder produced by high-pressure water atomisation of melt

conducted to study the effect of a new material of the bond coat, i.e. powder of quasi-crystalline alloy AlCuFe, and its ψ-phase content on structure and phase composition of the ZrO_2 external ceramic layer.

The ZrO_2 powder stabilised by 6.2 wt.% Y_2O_3 (external ceramic layer), as well as powder of alloy AlCuFe with a different content of the quasi-crystalline ψ-phase (metallic bond coat) were used as initial materials for deposition of thermal barrier coatings. The AlCuFe powder was produced by high-pressure water atomisation of the melt [11, 12]. Its ψ-phase content is determined by cooling conditions (quenching). It depends upon the size of the powder particles and may vary from 24 (for a faction of −160 + 120 μm) to 55 wt.% (for a fraction of −40 + 25 μm). Powders of three compositions were used in this study for spraying of the bond coat of thermal barrier coatings: powder with a 24 wt.% content of the ψ-phase was produced by milling and separation of the required fraction (−63 + 40 μm) from the powder with a particle size of 120−160 μm; powder of the −63 + 40 μm fraction with the 52 wt.% content of the ψ-phase was produced by atomisation; and to provide the 80 wt.% content of the ψ-phase the same powder was subjected to annealing in argon at a temperature of 700 °C for 2 h.

Table 1. Parameters for plasma spraying of coatings

Spraying powder	I, A	U, V	Plasma gas		Spraying distance, mm
			Composition	Flow rate, l/min	
ZrO_2	500	65	N_2	25	100
AlCuFe	500	40	Ar + N_2	25	140

The integrated procedure was employed to examine powders and coatings:

- metallography (microscope «Neophot-32» equipped with a digital photography attachment);
- scanning electron microscopy (scanning electron microscope JSM-840);
- durometry analysis (LECO hardness meter M-400 with a load of 0.25, 0.5 and 1 N);
- X-ray diffraction analysis (XRDA) (diffractometer DRON-UM1 with monochromated radiation Cu_{K_α}). The graphite single crystal placed on a path of the diffracted beam was used as a monochromator. Diffraction patterns were produced by step-by-step scanning in a $10 < 2\theta < 120°$ angle range. The content of the quasi-crystalline ψ-phase in the powders and coatings based on alloy AlCuFe was determined by the Sordelet method [13].

As established by the morphology examination, the main mass of the AlCuFe powder consists of particles of an irregular rounded or elongated shape with the developed surface (Figure 1, *a, b*). The XRDA results (Figure 2, *a*–*c*) showed that the powders contained a mixture of two phases, i.e. metallic β- and quasi-crystalline ψ-phases.

Microstructure of the particles revealed by etching is a heterogeneous and two-phase one. Polyhedral crystals of the ψ-phase in the form of dendrites or rosettes (see Figure 1, *c, d*) can be seen in the light crystalline matrix (β-phase).

According to the XRDA results (Figure 2, *d*), the ZrO_2 powder stabilised by 6.2 wt.% Y_2O_3 contained 89.8 wt.% ZrO_{2T} and 10.2 wt.% ZrO_{2M}.

TBCs from the AlCuFe and ZrO_2 powders with a particle size of 40−63 μm were deposited on a steel

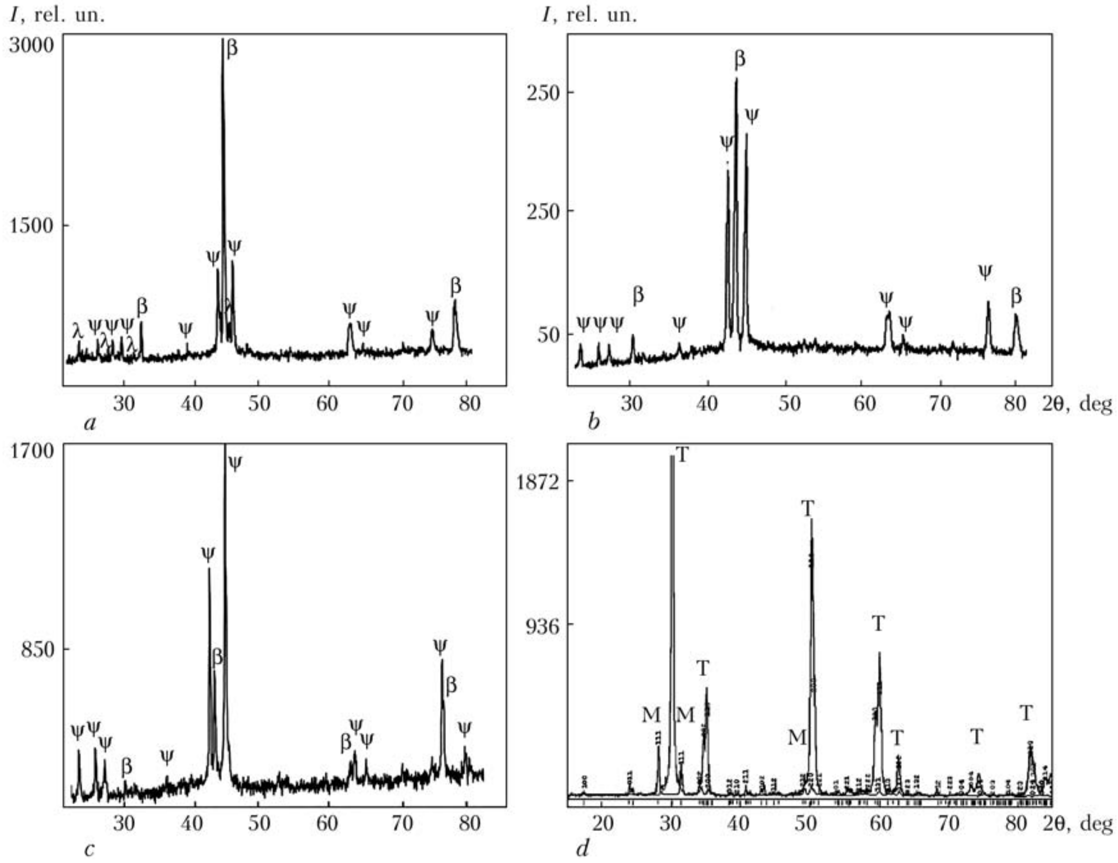

Figure 2. Diffraction patterns of AlCuFe powders with ψ-phase content of 24 (*a*), 52 (*b*) and 80 wt.% (*c*) and ZrO_2 + 6.2 % Y_2O_3 (*d*)

substrate by the plasma method using the UPU-8M unit. The plasma spraying parameters providing formation of dense coatings without defects and exfoliations are given in Table 1.

As found by examination of coatings of the AlCuFe powder containing different amounts of the ψ-phase, its content in the coatings decreased to 15, 23 and 54 wt.%, compared with 24, 52 and 80 wt.% in the initial powders. Traces of aluminium-base oxides α- and γ-Al_2O_3 and $CuAl_2O_4$ were detected in the coatings, in addition to the β- and ψ-phases. Microhardness of the metallic AlCuFe bond coat grew from (5620 ± ± 920) to (6820 ± 900) MPa with increase in the ψ-phase content (Table 2).

Metallography of the two-layer coatings (Figure 2) showed that they were free from cracks and exfoliations both at the interface with the substrate and at the ceramic coating–bond coat interface. Microhardness of the external ceramic layer grew to some extent when it was spayed on the bond coat with an increased ψ-phase content (see Table 2).

As established as a result of XRDA (Figure 4), the content of the monoclinic phase in the external ceramic layer (5.00–6.38 wt.%) was lower than in the initial powder (10.2 wt.%). The ZrO_2 tetragonal phase dominated in the ceramic layer. The calculations showed that the degree of tetragonality c/a (where c and a are the crystalline lattice parameters) also decreased and equalled c/a = 1.0103–1.0107 (see Table 2), while in the powder it was c/a = 1.0122.

Therefore, the ZrO_2 ceramic coating that forms on the AlCuFe metallic bond coat is close in structure to the non-equilibrium T′-phase, which is, according to [10], is oversaturated with the stabiliser and does not

Table 2. Characteristics of two-layer thermal barrier coatings

Sample No.	Layer	Microhardness *HV*, MPa	Phase composition, wt.%	Degree of tetragonality of ZrO_2
1	Metallic	5620 ± 920	15 ψ, 85 β, traces of oxides α-, γ-Al_2O_3 and $CuAl_2O_3$	1.0107
	Ceramic	11090 ± 1150	94, 98 ZrO_{2T}, 5.02 ZrO_{2M}	
2	Metallic	5950 ± 930	23 ψ, 77 β, traces of oxides α-, γ-Al_2O_3 and $CuAl_2O_4$	1.0103
	Ceramic	11200 ± 500	95 ZrO_{2T}, 5 ZrO_{2M}	
3	Metallic	6820 ± 900	54 ψ, 46 β, traces of oxides α-, γ-Al_2O_3 and $CuAl_2O_4$	1.0104
	Ceramic	11990 ± 1400	93, 62 ZrO_{2T}, 6.38 ZrO_{2M}	

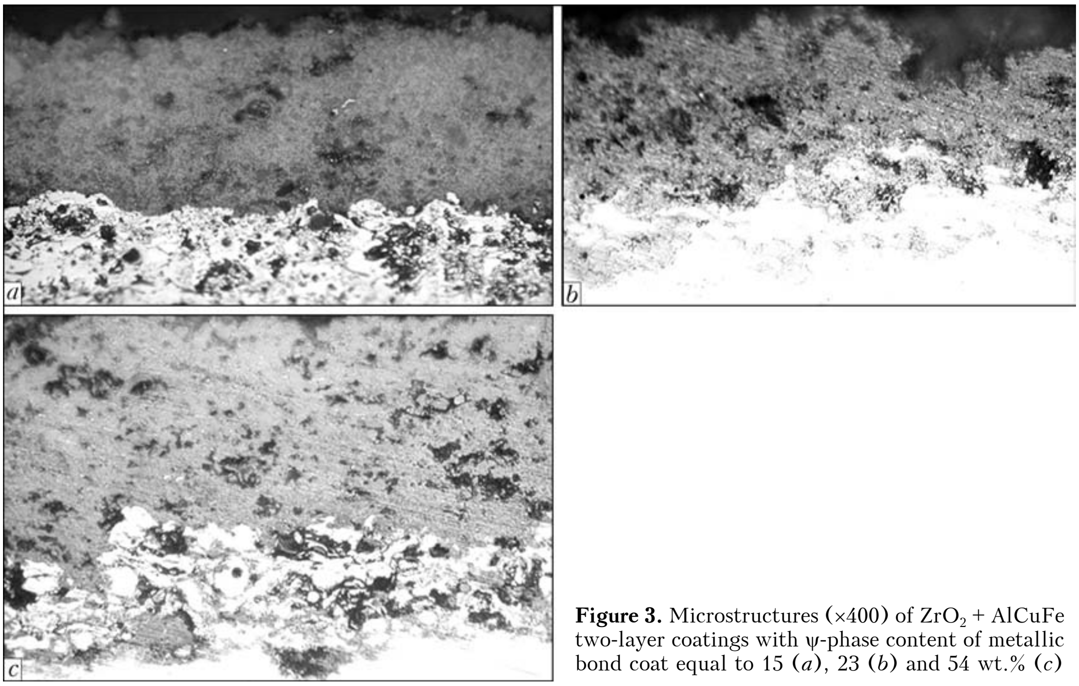

Figure 3. Microstructures (×400) of ZrO_2 + AlCuFe two-layer coatings with ψ-phase content of metallic bond coat equal to 15 (*a*), 23 (*b*) and 54 wt.% (*c*)

readily transform into the monoclinic one, like the equilibrium ZrO_{2T} phase. Only as a result of diffusion of the stabiliser in high-temperature (over 1200 °C) and long-time annealing the T′-phase transforms into the cubic and equilibrium tetragonal phase. The latter transforms into the monoclinic modification of ZrO_2 in cooling, which is accompanied by degradation of strength properties of ceramics and causes reduction of service life of the TBC [3]. In other words, the T′-phase plays an important role in production of coatings with high fracture resistance in thermal cycling.

Investigations of heat resistance of the two-layer TBCs* sprayed on aluminium alloy showed that in heating with flame of a gas torch to 400 °C for 3 s,

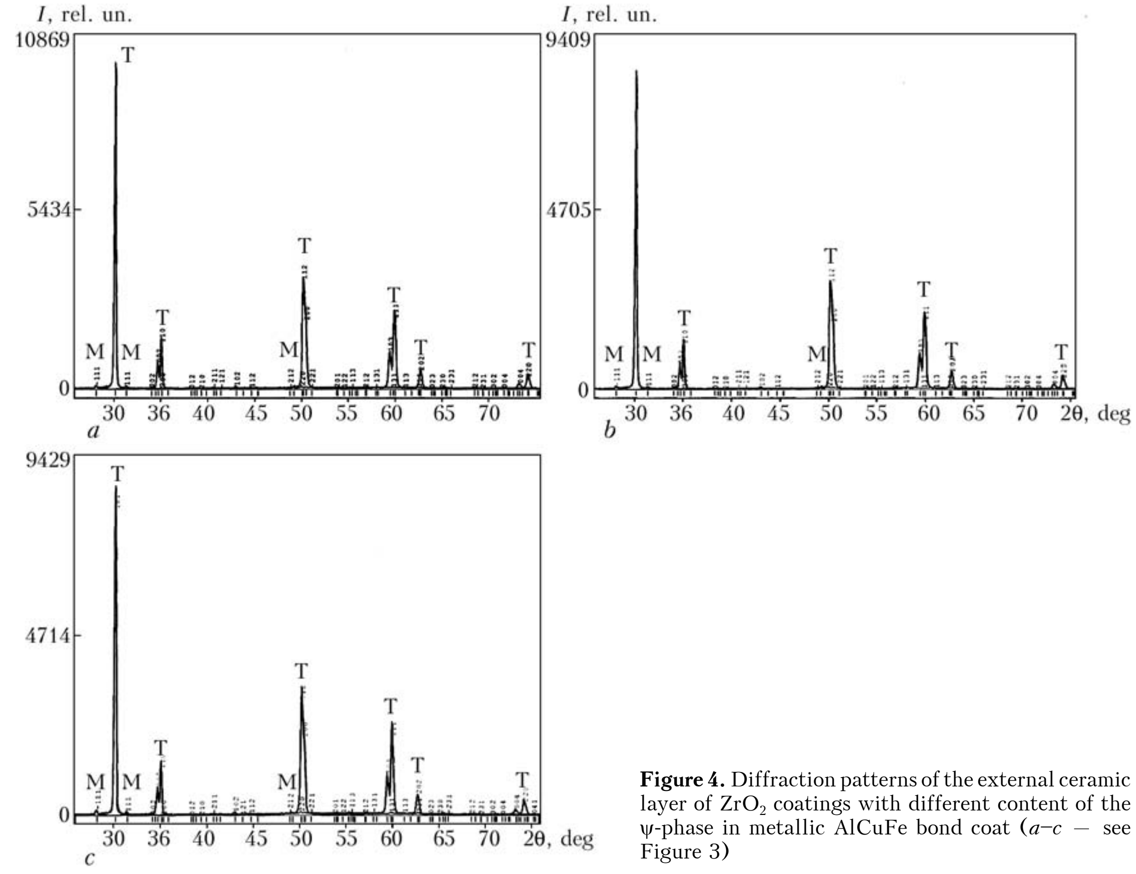

Figure 4. Diffraction patterns of the external ceramic layer of ZrO_2 coatings with different content of the ψ-phase in metallic AlCuFe bond coat (*a*–*c* — see Figure 3)

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[*] Engineers A.N. Burlachenko and N.V. Virgilyanskaya took part in the investigations.

followed by cooling with compressed air to a temperature of 70–80 °C, the coatings had no signs of fracture for 600 cycles. Analysis of cyclograms of heating of the coated samples indicated that the use of alloy AlCuFe as a bond coat allowed decreasing the substrate temperature by 87 °C, whereas the use of NiCrAlY as a bond coat allowed this temperature to be decreased only by 70 °C.

Therefore, the ZrO_2 + AlCuFe two-layer coatings can be of interest as thermal barrier coatings for parts of aluminium alloys, e.g. components of internal combustion engines.

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