JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **11** No 6, 06025(4pp) (2019)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **11** № 6, 06025(4cc) (2019)

Layered Structure of CoCrAlY/$ZrSiO_4$/Al_2O_3 Coatings Before and After Thermal Treatment

M.G. Kovaleva[1,*], V.V. Sirota[2], V.M. Beresnev[3], Yu.N. Tyurin[4], O.N. Vagina[1], I.A. Pavlenko[1]

[1] *Belgorod National Research University, 85, Pobedy St., 308015 Belgorod, Russia*
[2] *Belgorod State Technological University named after V.G. Shoukhov, 46, Kostyukov St., 308012 Belgorod, Russia*
[3] *V.N. Karazin Kharkiv National University, 4, Svobody Sq., 61000 Kharkiv, Ukraine*
[4] *E.O. Paton Electric Welding Institute, NASU, 11, Bozhenko St., 03650 Kyiv, Ukraine*

(Received 27 September 2019; revised manuscript received 02 December 2019; published online 13 December 2019)

In work, dense CoCrAlY/$ZrSiO_4$/Al_2O_3 coatings have been prepared on nickel based superalloy substrates by a new multi-chamber gas-dynamic accelerator. The coatings were subjected to thermal treatment in vacuum at a temperature of 950 °C for 2 hours. Scanning microscope with an EDX microprobe was used to analyze the chemical composition. Analysis of structural changes, mainly from the aspect of porosity, was also carried out using an optical microscope. Measurement of the microhardness of coatings was done with a microhardness tester DM-8B using a Vicker's hardness tester at a test load of 50 g. A positive impact of thermal treatment on the coating microstructure and microhardness was observed. The CoCrAlY/$ZrSiO_4$/Al_2O_3 coatings after thermal treatment were observed to be continuous, without cracks, and well bonded with the substrate. The absence of discontinuities in the interfaces among the different layers was indicative of good adhesion between them. Thermal treatment resulted in an increase in the coating hardness.

Keywords: Microstructure, Microhardness, Multi-chamber gas-dynamic accelerator, Nickel alloys, Thermal barrier coatings.

DOI: 10.21272/jnep.11(6).06025 PACS numbers: 68.37.Hk, 68.37.Yz, 62.20.Qp

1. INTRODUCTION

TBCs are finding increasing application in engines which operate with low quality fuels containing vanadium and sulfur. During service at a temperature of 600-1000 ºC, vanadate salt and sulfate condense on the surface of TBCs [1]. TBCs have a two layered structure consisting of a bond coat and yttria stabilized zirconia (YSZ) topcoat [2]. Zirconia itself shows good resistance to the attack of the molten sulfate or vanadate compounds arising, yttria is leached out of the zirconia causing the structural destabilization of ZrO_2 (i.e., transformation of the zirconia from the tetragonal and/or cubic to monoclinic phase). The structural destabilization of ZrO_2 is accompanied by a large destructive volume change, leading to large stresses within the YSZ, which eventually results in the delamination and spalling of the coating [3, 4]. Many kinds of ceramic were tested as alternative thermal barrier coating material of the thermal barrier coating system in decades. The zircon ($ZrSiO_4$) is also chosen as the suitable ceramic material for the thermal barrier coatings [5-7]. It shows excellent thermal shock resistance as a result of its very low thermal expansion coefficient [1]. Over the years attempts have been made to seal the surface of zirconia TBCs using ion and laser beams [8] or various "seal coats" [9] to prevent the penetration of molten deposits into the porous YSZ coating [10]. Alumina has a high melting point and stability without showing phase transition at high temperatures like the ZrO_2 ceramics. Al_2O_3 has a small solubility particularly in molten salt and is expected to show an excellent corrosion resistance. It seems that the use of fine alumina particles as a dense layer over the YSZ and zircon-based coatings can decrease oxygen diffusivity and salt penetration through this layer [10].

In our study, both the dense zircon-based ceramic coating [11] as TBC and alumina as overlay coating were obtained by a new multi-chamber gas-dynamic accelerator (MCDS) [11, 12]. The effect of thermal treatment (in vacuum) on the microstructure and microhardness of CoCrAlY/$ZrSiO_4$/Al_2O_3 coatings was investigated using optical microscopy (OM), scanning electron microscopy (SEM), and Vickers hardness tester.

2. EXPERIMENTAL PROCEDURE

Nickel based superalloy (Ni-20Cr-11.5Co-0.6Mo-3W-0.5Ni-3.5Ti-21Al-0.5Fe, all in wt. %) ($30 \times 30 \times 5$ mm^3) which grit blasted with alumina particles was used as substrate. Three types of powders were selected (see Fig. 1): Co-25Cr-11Al-1Y (CoCrAlY) as bond coat, zircon sand ($ZrSiO_4$) (naturally available) powder and AMPERIT 740.0 Al_2O_3 powder as TBC. Table 1 indicates the characteristic of the powders, and the parameters of coating spraying are listed in Table 2. In the present study, a vertically mounted multi-chamber and a gas-dynamic accelerator (MCDS) were employed to deposit the coatings on nickel based superalloy substrates. The coatings were deposited with a frequency of 20 Hz. MCDS was equipped with several combustion chambers serially connected by channels. These channels were intended for the expiration of the combustion products. They were converged in the central chamber – nozzle. Filling of all chambers by the combustible mixture was carried out simultaneously. MCDS was equipped with a standard powder feeder (by Metco). Continuous gas-powder jet was supplied along the conduit (4-8 m) divided into portions and inserted into the nozzle [11].

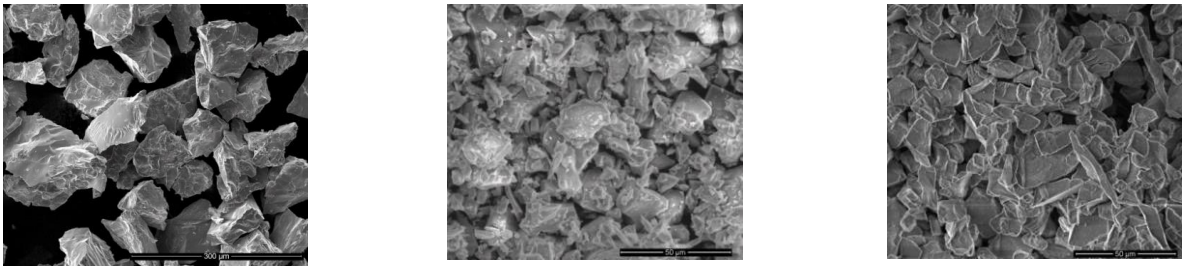
To determine the microstructure and elemental composition of the powders and coatings, scanning electronic

*Kovaleva@bsu.edu.ru

microscope (SEM) (Quanta 200 3D, Nova NanoSEM 450) and Optical Microscope Olympus GX 51 were performed. Investigations were carried out on polished cross-sections that were normal to the surface. Specimens were transversally cut by spark erosion, mechanically polished and prepared by standard metallographic sample preparation: sectioning, mounting and polishing methods. Porosity was determined by the metallographic method with elements of the qualitative and quantitative analysis of the geometry of the pores using an optical inverted Olympus GX51 microscope [13]. Ten arbitrarily selected micrographs for each experimental point were registered with an optic microscope (bright field, magnified 1000×) using the "SIAMS Photolab" program. Phase composition of the powders was determined by the X-ray phase analysis method (diffractometer Rigaku Ultima IV). Crystalline phases were identified by the ICDD PDF-2 (2008) powder diffraction database. Microhardness of the coatings was determined by an automatic microhardness tester DM-8B (Affri) by Vickers's test at a test load of 50 g. Indentation was carried out on the cross-sections of the samples of the coatings. On average, 10 tests were used as an indicator of the coating hardness. A high-temperature vacuum furnace (VHT 8/22-GR, Nabertherm GmbH) was used for heat treatment of coatings in vacuum. The samples were placed in the furnace, air was evacuated, and the furnace was heated at 8 ºC/min from 23 to 950 ºC. The coatings were cooled to 50 ºC at a rate of 7.5 ºC/min for 2 h, and then allowed to cool to room temperature outside the furnace.

3. RESULTS AND DISCUSSION

In some cases, heat treatment of thermally sprayed deposits can release residual stresses, decrease their porosity, and improve their microstructure and properties [14]. Heat treatment of thermally sprayed coatings can effectively improve their corrosion resistance by changing their microstructure from lamellar one to a bulk-like, by removing such defects as pores and lamellae boundaries, which are known to impair their performance [15, 16].



a b c

Fig. 1 – Morphology of the CoCrAlY (a), $ZrSiO_4$ (b), and Al_2O_3 (c) powders (SEM)

Table 1 – The chemical, phase composition, and particle size of the powders

	Powder			
Chemical composition, all in wt. %	Element	CoCrAlY	$ZrSiO_4$	Al_2O_3
	Co	59.88	–	–
	Cr	23.24	–	–
	Si	2.66	8.23	0.12
	Fe	1.13	0.46	1.10
	Al	13.10	0.07	54.94
	Zr	–	77.48	–
	O	–	13.77	35.84
	C	–	–	8.00
Particle size distribution, μm				
d (0.1)		6.6	2.6	7.6
d (0.5)		62.7	18.3	15.8
d (0.9)		123.4	46.7	29.4
Identified major phases		$Al_{0.94}Co_{1.06}$, Cr	Z-zircon ($ZrSiO_4$)	γ-Al_2O_3, a-Al_2O_3, Fe_2O_3, SiO_2

Table 2 – Spraying parameters of coating layers

Spraying parameters	Coating layer		
	CoCrAlY	$ZrSiO_4$	Al_2O_3
Spray distance, mm	55		
Barrel length, mm	500		
Barrel diameter, mm	18	16	16
Powder feed rate, g/h	1400	550	700
Flow rate of fuel mixture components, m^3/h			
Oxygen	*2.9/**2.6	*4.3/**3.2	*4.3/**3.2

Propane (100 %)	*0.7/**0.7	*0.8/**0.7	*0.8/**0.7
Air	*1.6/**1.1	*0.1/**0.3	*0.1/**0.3
Oxygen/fuel ratio	4.4	5.3	5.3
*Cylindrical form combustion chamber. **Combustion chamber in the form of a disk			

Fig. 2 presents SEM micrographs (back-scattered electron mode) of the polished cross-sections of the $CoCrAlY/ZrSiO_4/Al_2O_3$ coatings both after deposition and after heat treatment. The dense coatings were formed through the intensive plastic deformation resulting from the impact of a particle moving with high velocity and the tamping effect on the source side of the following particles. The coating thickness is approximately 140 micron; coatings are dense and show a good adherence to the substrate. The thickness of coating layers varied in the range of 25 to 65 microns (Table 3). No major cracking was observed in the microstructures of these coatings both after deposition and after heat treatment. As shown in Fig. 2, the sample had a wavy and stratified structure with piled-up flattened particles. The lines of laminations are often quite diffuse and poorly defined. The contrast in Fig. 2 indicates that each layer has different chemical compositions. The «coating – substrate» interface and interface between coating layers had no visible macro defects both after deposition and after heat treatment. The metallographic porosity levels in the as-sprayed and heat-treated coatings were very low (see Table 3).

Fig. 2b presents SEM images showing the microstructure of heat-treated coatings. It was found that during high-temperature annealing, the porosity of the $CoCrAlY/ZrSiO_4/Al_2O_3$ coatings did not change much (see Table 3).

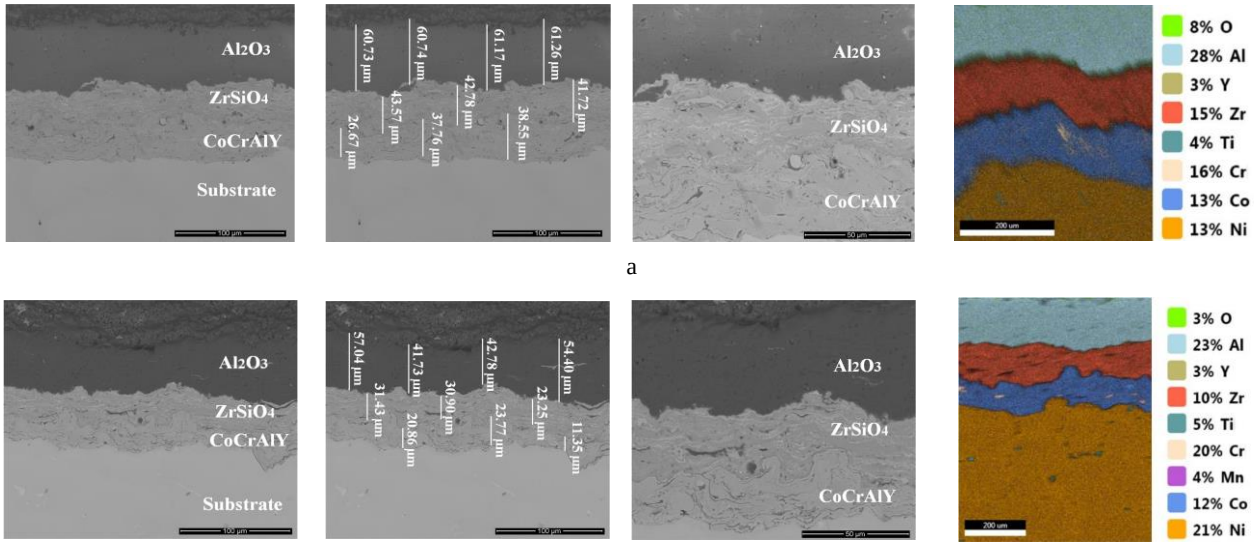


Fig. 2 – SEM micrographs of cross-sections of the $CoCrAlY/ZrSiO_4/Al_2O_3$ coatings (back-scattered electron mode, Quanta 200 3D) before (a) and after (b) thermal treatment and SEM EDX element distribution maps (NanoSEM 450)

Table 3 – The thickness, porosity, and microhardness of coating layers before and after thermal treatment

Coating layers	Thickness, micron		Porosity, %		Microhardness, $HV_{0.05}$	
	Thermal treatment					
	Before	After	Before	After	Before	After
Al_2O_3	55 ÷ 65	38 ÷ 60	0.7	0.5	1419 ± 197	1447 ± 253
$ZrSiO_4$	30 ÷ 45	15 ÷ 40	0.5	0.3	693 ± 124	829 ± 161
CoCrAlY	25 ÷ 40	11 ÷ 25	0.2	0.1	686 ± 91	788 ± 122

Heat treatment gives rise to no changes in the area of the coating that adjoins the substrate. The absence of cracks or other discontinuities in the interfaces among the different layers of heat treated coatings was indicative of good adhesion between them. The decrease in thickness of coatings (Table 3) owing to heat treatment was due to the active dislocation sources and decrease in the residual stress. The increased compactness with the heat treatment was also predicted to be main reason for good appearance and high hardness [17]. The results showed that the thermal treatment of the coatings led to an increase in the microhardness of $CoCrAlY/ZrSiO_4/Al_2O_3$ coatings.

4. CONCLUSIONS

It was experimentally demonstrated that the $CoCrAlY/ZrSiO_4/Al_2O_3$ coatings could be manufactured on nickel based superalloy substrates using a new multi-chamber gas-dynamic accelerator with subsequent thermal treatment of the deposits. The main results can be summarized as follows:

1) The coatings presented dense microstructure and porosity below 1.0 % both after deposition and after heat treatment.

2) The «coating – substrate» interface and interface between coating layers had no visible macro defects

both after deposition and after heat treatment.

3) The thermal treatment of the coatings leads to an increase of microhardness.

In our next study, both the zircon-based ceramic coating and the $ZrSiO_4/Al_2O_3$ system will be exposed to the molten salt ($Na_2SO_4 + V_2O_5$) at 950 °C. The role of Al_2O_3 in the hot corrosion environment will be examined in greater detail in a forthcoming publication.

AKNOWLEDGEMENTS

The studies were carried out on the equipment of the Joint Research Center of Belgorod State National Research University «Technology and Materials» and the High Technology Center at BSTU named after V.G. Shoukhov. This research work is financially supported by the Ministry of Education and Science of Russian Federation in the framework of State Assignment No 11.9329.2017/8.9.

REFERENCES

1. R. Rajendran, *Eng. Fail. Anal.* **26**, 355 (2012).
2. C. Zhou, N. Wang, H. Xu, *Mater. Sci. Eng. A* **452-453**, 569 (2007).
3. N. Eliaz, *Eng. Fail. Anal.* **9**(1), 31 (2002).
4. R.L. Jones, *Surf. Coat. Technol.* **37**, 271 (1989).
5. D.R. Clarke, S.R. Phillpot, *Mater. Today* **8**(6), 22 (2005).
6. R. Vassen, X. Cao, F. Tietz, D. Basu, D. Stover, *J. Am. Ceram. Soc.* **83**(8), 2023 (2000).
7. H. Lehmann, D. Pitzer, G. Pracht, R. Vassen, D. Stover, *J. Am. Ceram. Soc.* **86**(8), 1338 (2003).
8. Z. Liu, *Appl. Surf. Sci.* **186**, 135 (2002).
9. S. Ahmaniemi, P. Vuoristo, T. Mantyla, *Surf. Coat. Technol.* **151-152**, 412 (2002).
10. N. Wu, Z. Chen, S.X. Mao, *J. Am. Ceram. Soc.* **88**(3), 675 (2005).
11. M. Kovaleva, M. Prozorova, M. Arseenko, Y. Tyurin, O. Kolisnichenko, M. Yapryntsev, V. Novikov, O. Vagina, V. Sirota, *Coatings* **7**, 1 (2017).
12. M. Kovaleva, Yu. Tyurin, N. Vasilik, O. Kolisnichenko, M. Prozorova, M. Arseenko, M. Yapryntsev, V. Sirota, I. Pavlenko, *Ceram. Int.* **41**, 15067 (2015).
13. G.J. Moskal, *JAMME* **20**(1-2), 483 (2007).
14. H.-T. Wang, C.-J. Li, G-J. Yang, C.-X. Li, *Vacuum* **83**, 146 (2009).
15. N.N. Ault, *J. Am. Ceram. Soc.* **40**, 69 (1957).
16. H. Herman, *Sci. Am.* **259**(3), 112 (1988).
17. M. Pushpavanam, S.R. Natarajan, K. Balakrishan, L.R. Sharma, *J. Appl. Electrochem.* **21**, 642 (1991).

Структура покриття $CoCrAlY/ZrSiO_4/Al_2O_3$ до та після термічної обробки

М.Г. Ковальова[1], В.В. Сірота[2], В.М. Береснев[3], Ю.Н. Тюрін[4], О.Н. Вагіна[1], І.А. Павленко[1]

[1] *Бєлгородський національний дослідницький університет, вул. Перемоги, 85, 308015 Бєлгород, Росія*
[2] *Бєлгородський державний технологічний університет імені В.Г. Шухова, вул. Костюкова, 46, 308012 Бєлгород, Росія*
[3] *Харківський національний університет імені В.Н. Каразіна, пл. Свободи, 4, 61000 Харків, Україна*
[4] *Інститут електрозварювання імені Є.О. Патона НАН України, вул. Боженка, 11, 03650 Київ, Україна*

У роботі щільні покриття $CoCrAlY/ZrSiO_4/Al_2O_3$ були підготовлені на підкладках із суперсплавів на основі нікелю за допомогою нового багатокамерного газодинамічного прискорювача. Покриття піддавали термічній обробці у вакуумі при температурі 950 °C протягом 2 годин. Для аналізу хімічного складу використовували скануючий мікроскоп з мікрозондом EDX. Аналіз структурних змін, в основному з точки зору пористості, проводили за допомогою оптичного мікроскопа. Вимірювання мікротвердості покриття проводили за допомогою мікротвердоміра DM-8B з використанням пірамідки Вікерса при навантаженні 50 г. Встановлено, що термічна обробка позитивно впливає на мікроструктуру і мікротвердість покриття. Покриття $CoCrAlY/ZrSiO_4/Al_2O_3$ після термічної обробки суцільні, без тріщин і добре пов'язані з підкладкою. Відсутність пор на межах розділу між різними шарами свідчить про хорошу адгезії між ними. Термічна обробка призвела до підвищення твердості покриття.

Ключові слова: Мікроструктура, Мікротвердість, Багатокамерний газодинамічний прискорювач, Нікелеві сплави, Термобар'єрні покриття.