Investigation of Oxidation Behavior and Thermal Spray of the Mechanically Milled CoNiCrAlY–YSZ Powders

M. Tahari[a,*], M. Shamanian[a], M. Salehi[a]

[a] *Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran.*

ARTICLE INFO

Article history:

Received 02 November 2014
Accepted 19 December 2014
Available online 15 March 2015

Keywords:

CoNiCrAlY
Oxidation behavior
YSZ
High velocity oxy-fuel

ABSTRACT

In this study, the effects of mechanical milling and YSZ reinforcing on oxidation behavior of CoNiCrAlY coatings were investigated. Various amounts of YSZ particles (0%, 5%, 10% and 15 wt.%) were mixed with commercial CoNiCrAlY powder and milled for 24 h. Then, the mechanically milled and commercial powders were deposited on Inconel 617 substrate using the High Velocity Oxygen-Fuel (HVOF) process. Freestanding bodies of the mechanically milled composit and conventional HVOF CoNiCrAlY coatings were oxidized at 1000 °C for different times to form the thermally grown oxide layer. X-ray diffraction analysis, scanning electron microscopy and X-ray mapping were used to analyze the scales formed on the surface of the oxidized samples. The results showed that the composite coatings exhibited higher porosity due to undesirable morphology of the feedstock powders. This factor accelerated the diffusion rate of oxygen into the coating body. On the other hand, undesirable oxidation of the composite particles during spraying leads to increase in the oxidation rate of the coatings.

1. Introduction

In gas turbine engines, increasing the operating temperature results inhigher efficiency [1-3]. Nevertheless, the increasing temperature may decrease the creep life ofthe turbine componentswhich are usually made of superalloys [4, 5]. Here, air cooling systems and/orthermal barrier coatingssystem (TBCs)can beusedto increase the service temperature of superalloys [6-8]. A TBC system typically consists of two layers; the top (ceramic) coat with low thermal conductivity and the bond coat which provides high temperature corrosion resistance [9]. Another function ofthe bond coat in the TBC systemis to reduce stresses resulted from different thermal expansion coefficient between the top coat andthe substrate [10].

MCrAlY(M=Co, Ni or both) alloys are well-known materials for bond coating [11]. These coatingscreate athermally grown oxides (TGO) layer in the bond/top coat interface which hinders the diffusion of oxygen through the coating. However, a number of researchers believed that the growth of TGO layer introduces mechanical stresses to the top coat which favors the formation of cracks in theceramic top coat. On the other hand, poor mechanical strength of the MCrAlY coatings at high temperatures accelerates the degradation

---

Corresponding author:
E-mail address: Fa.tahari@yahoo.com (Mostafa Tahari).

of the TBC systems [12, 13]. So, improvement ofmechanical strength and oxidation resistance of the MCrAlY alloys canincreasethe service life of TBCs. Previous studies have shown that nanostructured MCrAlY coatings exhibit better oxidation resistance than conventional coatings [10, 14]. It can be due to uniform distribution of aluminum in nanostructured coatingsas well as increased diffusion rate of Al due to the lower grain size. These factors favor the nucleation and growth of a uniform α-Al_2O_3 layer,which can decrease the TGO growth [15, 16]. Fast growing oxides such as NiO, Cr_2O_3, $CoAl_2O_4$, and $NiAl_2O_4$ impose mechanical stress on the top coat and bond coat interface, which can result indecay of TBC [17]. In addition, the nanostructured bond coat improves the adhesion of TGO to the bond coat [16].

Mechanical milling is an interesting method for synthesis of nanostructured and high temperature materials [18]. In this regard, high temperature materials can be strengthenedby dispersion of hard particles such as oxide ceramics [19].

The oxide ceramics, such as alumina and yttria stabilized zirconia (YSZ) are usually used for high temperature materials due to their high thermal stability [4]. On the other hand, due to formation of the oxide layer of active elements such as Hf and Y in the vicinity of YSZ, this ceramic has a good wetting behavior with the supperalloy matrix and MCrAlY [20]

In recent years, due to the increaseof operating temperatures in gas turbines, development of strengthened TBCs is necessary, but research about the strengthening of TBCs is very negligible. In addition to strength, the TBC systems must have a suitable oxidation resistance. In this study, MCrAlY/YSZ powders produced by mechanical milling were used as feedstock to deposit HVOF coatings and the oxidation resistances of the coatings were investigated.

2. Experimental

2. 1. Mechanical milling process

CommercialCoNiCrAlY(Co-38.5.wt%Ni-32wt.%Cr-21wt.% Al-8wt>% Y-0.5wt.%) and YSZ (ZrO_2-92wt.% Y_2O_3-8wt.%) powders with particle sizes of 15-45 µm and 20-120 µm, respectivelywere used as feedstock. The powders were mechanically milled (MM) in a high energy planetary ball mill at a revolution speed of 180 rpm for 24 h at room temperature under argon atmosphere. The milling process was performed with the time intervals of 3 h to prevent sample overheating. The stoppage time of milling was 1 h. The ball to powder weight ratio was 10:1. 10 mm diameter hardened steel balls were used for ball milling. The CoNiCrAlY powders were mixed with 0%, 5%, 10% and 15 wt. % YSZ. In addition, 0.4 wt. % stearic acid was used as a process control agent (PCA) to prevent excessive cold welding of the powders during milling.

2. 2. Thermal spray process

Mechanically milled powders were sieved into the range of 15-52 µm. This distribution of particles is suitable for HVOF. The morphologies of mechanically milled and commercial powdersare shown in Fig1. A Met Jet III HVOF system (Metallisation, UK) using kerosene as a liquid fuel was utilized to spray the CoNiCrAlY/YSZ composite powders. The optimum thermal spraying parameterswere obtained byTaguchi design of experiments (DOE) as shown in Table 1. Inconel 617 was used as substrate which waspolished with 320 SiC paper before spraying. This type of surface preparation resulted in poor adhesion between the coating and the substrate, facilitating the removal of the coating from the substrate after spraying. The goal was to produce a freestanding coating. For comparison, composite and commercial powders were deposited on polishedsubstrates, too.

2. 3. Oxidation process

To investigatethe oxidation resistance ofthe coatings, cyclic oxidationexperimentswere performed at 1000 °C for 100 h onthe freestanding coatingsunder air environment. Then, the samples were placed in the furnace at 1000 °C and held at that temperature for different durations ranging from 2 to 100 hand were cooled down at room temperature. The weight changes of the samples were measured after each cycle with electronic balance with a sensitivity of 1 mg to determine the kinetics of

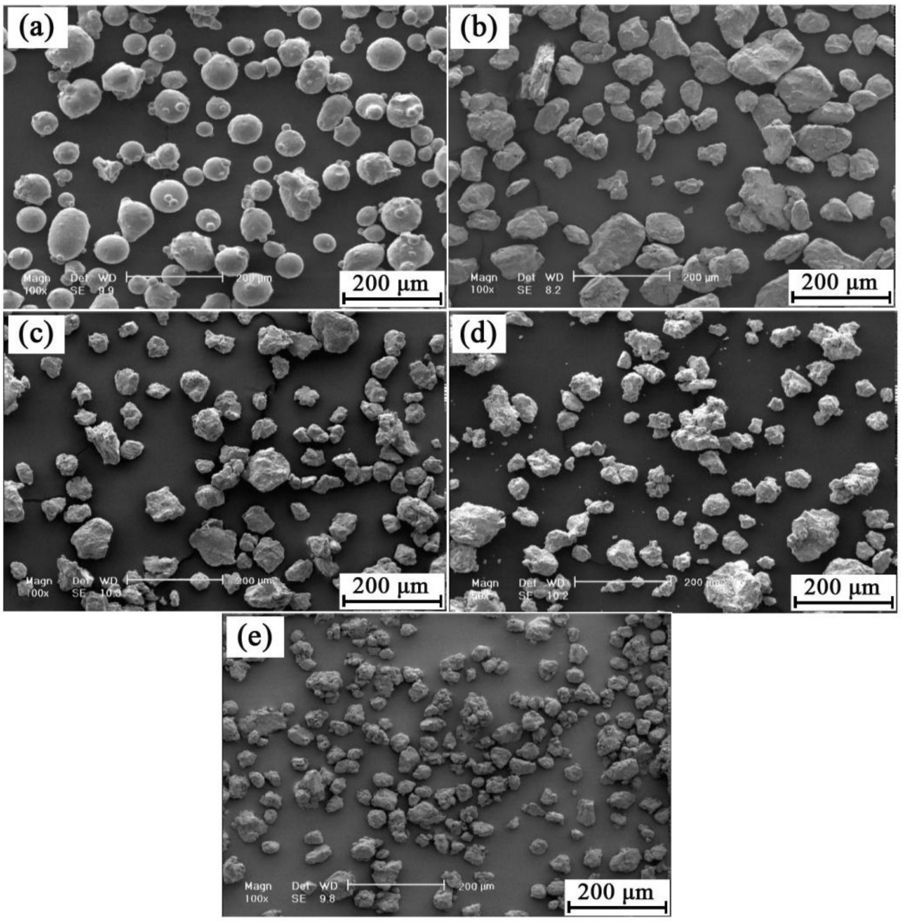

Fig. 1. Secondary electron micrographs of a) commercial CoNiCrAlY b) CoNiCrAlY/0%YSZ c) CoNiCrAlY /5%YSZ d) CoNiCrAlY /10%YSZ e) CoNiCrAlY /15%YSZ powders

Table1. The optimum thermal spraying parameters obtained bytaguchi design of experiments (DOE) method

Coating	Powder feed rate (g/min)	Fuel flow rate (mlit/min)	Spray distance (cm)	Oxygen flow rate (mlit/min)
Commercial	50	250	35	830
0%YSZ	50	250	35	830
5%YSZ	50	250	35	880
10%YSZ	50	250	35	880
15%YSZ	50	250	35	880

oxidation. Toinvestigate theeffect of splats oxidation on the oxidation behavior of the coatings, the surface of the coatingswere polished with 180 SiC paper and then oxidized.

SEM imaging and X-ray mapping wereconducted using a Philips XL30 FEG SEM andX-ray diffraction patterns of the samples were obtained by Philips X'PERT MPD diffractometer using filtered Cu-Kα radiation.

3. Result and discussion

3. 1. Characterization of the powders and the as-sprayed coatings

Fig 2 shows the cross section of the commercial and composite coatings. Ascan be seen, the average thickness of all the coatingsis about 150-200 µm. The gray layer aroundthe splats of the composite coating is the oxide layer. During spraying, a layer of oxide is formed on thesurfaceof splats due to the

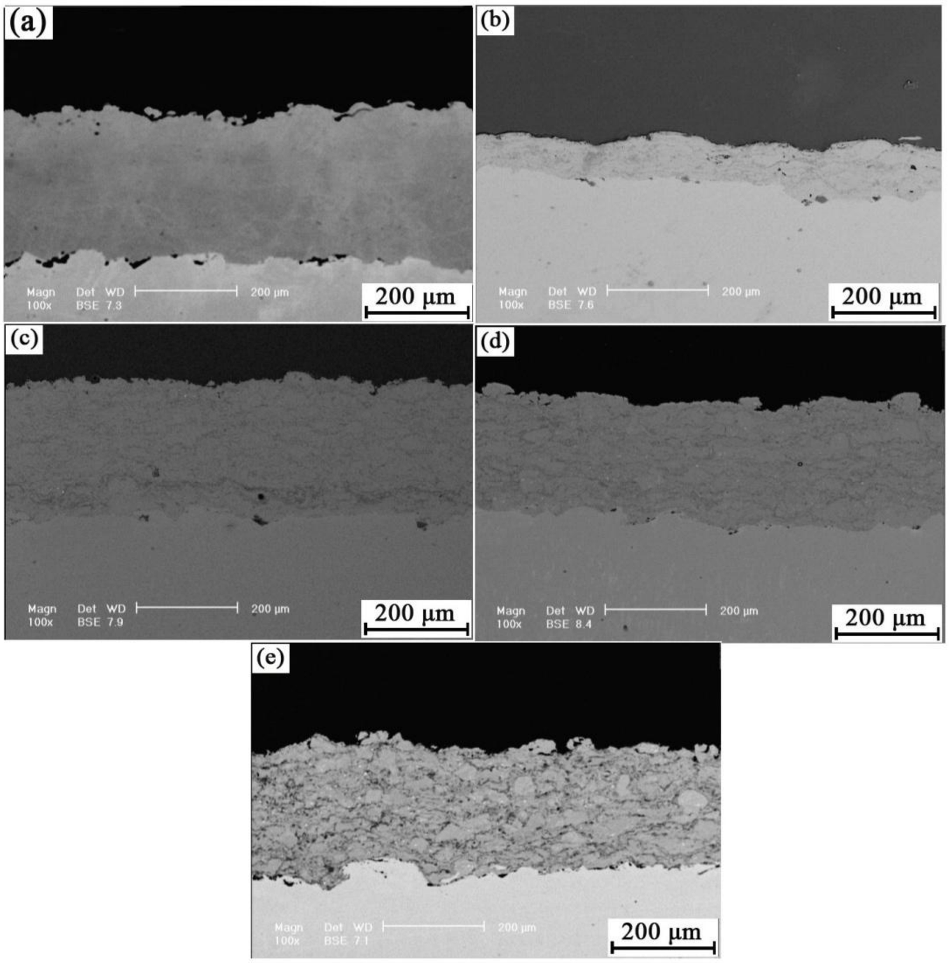

Fig. 2. Cross section of a) commercial CoNiCrAlY b) CoNiCrAlY/0%YSZ c) CoNiCrAlY /5%YSZ d) CoNiCrAlY /10%YSZ e) CoNiCrAlY /15%YSZ coatings

Table 2. Porosity percent of all the coating calculated byimage analysis

Coatings	Commercial	0%YSZ	5%YSZ	10%YSZ	15%YSZ
Porosity %	< 0.2	1.2	1.6	2.9	5.4

chemical reactions between active elements such as Y, Al, Cr and oxygen. But in the commercial coating, the gray layer is not formed. Due to the rough surface of the composite powder, chemical reaction between the powders and oxygen has been favored. On the contrary, the smooth surface of the commercial powder decreased the surface exposed to oxygen. On the other hand, some dark regions are seen in the composite coatings which arepores [21]. Porosity percentage of all the coatingswascalculated byimage analysis software (Table 2). It can be seen that by increasing YSZ content, porosity increased, due to the increaseof the unmelted particles. On the other hand, irregular morphology of the milled powdersincreasedthe porosity content, too, but the porosity content of the commercial coating is negligibledue to spherical morphology of feedstock powder. This morphology is very suitable for thermal spraying [22].

3. 2.Oxidation in air

3. 2. 1. Thermogravimetric analysis

Mass gain versus time curves for all as-sprayed CoNiCrAlY coatings are shown in Fig. 3. Weight gains in various samples are very different. In coating with 15% YSZ, the weight gain is very highcompared to other samples. The gradient curve of this sampledid notvary

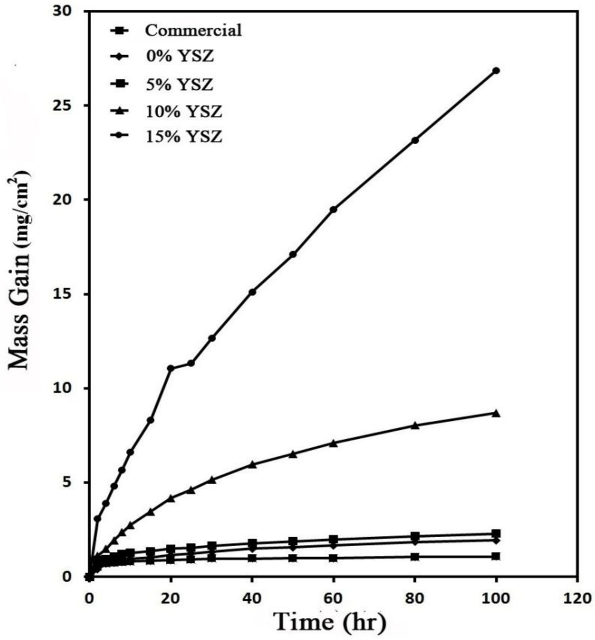

Fig. 3. Mass gain versus time for all as-sprayed coatings oxidized in air at 1000 ◦C for 100 h

Table 3. Parabolic rate constants of the coatings oxidized at 1000 °C for 100 h

Coatings	Commercial	0%YSZ	5%YSZ	10%YSZ
$k_p(10^{-10}\ gr^2\ cm^{-4}\ h^{-1})$	4	17	23	507

with the course of the experiment, whileon the other samples, the weight gain gradually decreasedwith increasing the oxidation time. In these cases, after an initial period characterized by rapid weight gain, all samples followed parabolic growth typical of oxidation reactions. The parabolic growth is related to formation of a barrier oxide layer during theoxidation process. This layer inhibitsdiffusion of the oxygen ions into the fresh metal and decreasestheoxidation rate [23]. Ascan be seen in the commercial and composite CoNiCrAlY coatings containing 0%wt. and 5%wt. YSZ, the oxide layer can be protective, while in theCoNiCrAlY/10% wt. YSZ and CoNiCrAlY/15% wt. YSZ, it cannot.

For further investigation of oxidation kinetics,Kp(oxidation constant) values for the all the coatings subjected to air oxidation at 1000 °C after 100 hare shown in Table 3.

It can be observed that the commercial coating has a lower $k_p$than other coatings. The comparison of Tables 3 and 4shows that by increasing theporosity of the coatings, the $k_p$value also increased. Kai et al. [24] believed that the porosity is a free path for penetration of oxygen and other corrosive ions. Therefore, porous coatings show a high oxidation ratecompared to denseones. On the other hand, interfaces betweenYSZ reinforcementsand the CoNiCrAlY matrix increased penetration of the oxygen ions too. In another study, Mahesh et al. [25] added cerium oxide particles to the MCrAlY coating which decreasedoxidation resistance of the coatings. $k_p$of the coating produced by Mahesh et al. was about 0.28×10^{-10}(g^2 cm^{-4} s-1), which is similar to the 10% YSZ coating in the presentstudy. Coating porosity and the interface between reinforcements and matrix are reportedto be the two main reasons for increasing the oxidation rate.

3. 2. 2. X-ray diffraction

Fig 4 shows the X-ray diffraction patterns of the mechanically milled powders, 0% YSZ, 5%YSZ and the commercial coatingsoxidizedat1000 °C for 2, 15, and 100 h. It can be observed that the β-NiAl phase (bcc- phase) peaksdisappearedat the first two hours of oxidation.

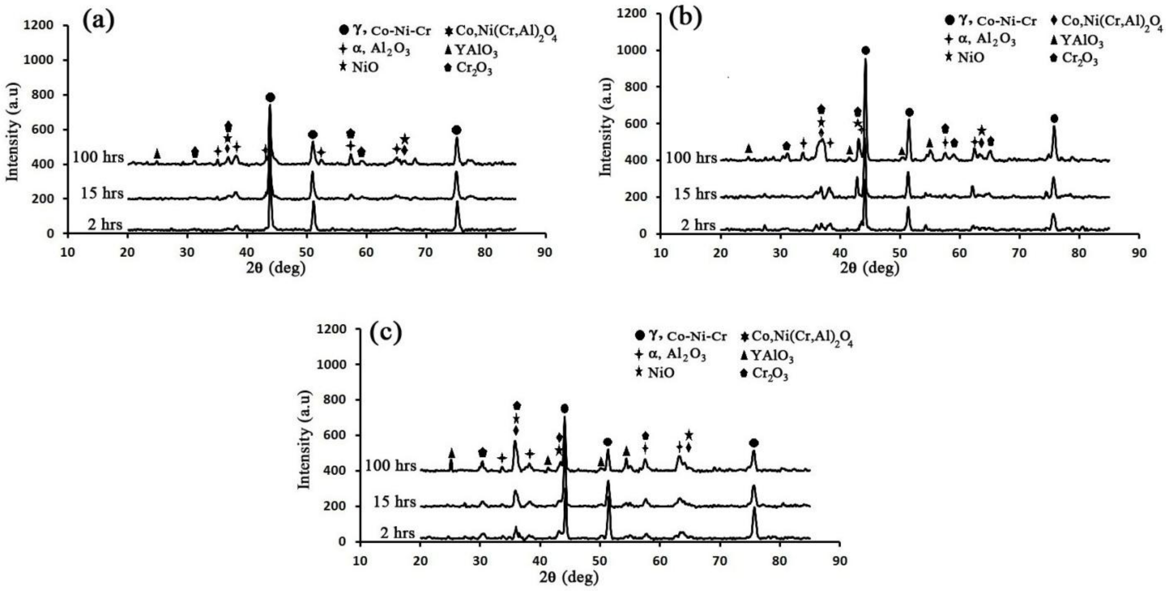

Fig. 4. X-ray diffraction patterns of a) the commercial CoNiCrAlY b) CoNiCrAlY/0%YSZ c) CoNiCrAlY /5%YSZ d) CoNiCrAlY /10%YSZ e) CoNiCrAlY /15%YSZ coatings oxidized at1000 °C for 2, 15 and 100 h

This phenomenonoccurred due to diffusionof Al into theupper layer andformation of oxide layers [14]. The XRD pattern of the commercial coating shows that the main fraction of oxide layer formed on this coating is α-Al_2O_3,NiO and spineloxidesare also present. But in the composite coating the NiO and spinel oxides comprisethemajority of theoxide layer. Choi et al. [26] believed that in the porous coatings the diffusion of oxygen ion into the coating is very high. This phenomena resultsinincreasingthe oxygen activity in the coating. The increasing oxygen activity in the coating leads to NiO and CoOformed mid to Al_2O_3 and Cr_2O_3. NiO and CoO are unstable at 1000 °C;therefore, these oxide phases are combined with $Al_2O_3$and $Cr_2O_3$and form spinel phases such as Co,Ni$(Cr,Al)_2O_4$.

3. 2. 3. Surface-scale analysis

Fig 5 shows the surface morphology of the oxide scales of the commercial, and 0% YSZ and 5% YSZ coatings after 2, 15 and 100 h ofoxidation at 1000 °C. It can be observed that after 2 h, particles with needle-like morphology were formed onthe commercial coating. Researchers believe that this morphology is related to α-Al_2O_3 phase, whichconfirmed the XRD analysis results [27]. This needle shape particles grew fast and after 2 h, oxidation coveredthe entiresurface of the commercial coating, but by increasing the time of oxidation, the growth ratesof theseparticles decreased. This is in agreement with the mass gain changes diagram shown in Fig 3.

In the 0% YSZ and 5% YSZ coatings, the surface of oxide scale contained polyhedral particles. The polyhedral particles startednucleation and growth in the early stages of oxidation. But, in contrast to the commercial coating, the growth rate of polyhedral particles did not decreaserapidly with increasing the oxidation time. Tang et al. [14] believed that this morphology is related to spinel and NiO phases. These phases cannot form a dense layer to inhibit oxygen diffusion into fresh metal. These results confirmthe high mass gain changes of the 0% YSZ and 5% YSZ coatings after 100 hof oxidation. Some researchers believed that the nature and type of the oxide phases formed during thermal spray process affected theoxidation behavior of the coatings [17].

4. Conclusion

The mechanically milledCoNiCrAlY/YSZ and commercial CoNiCrAlY powderswere thermally sprayed on Inconel 617 with HVOF method and high temperature oxidation of the

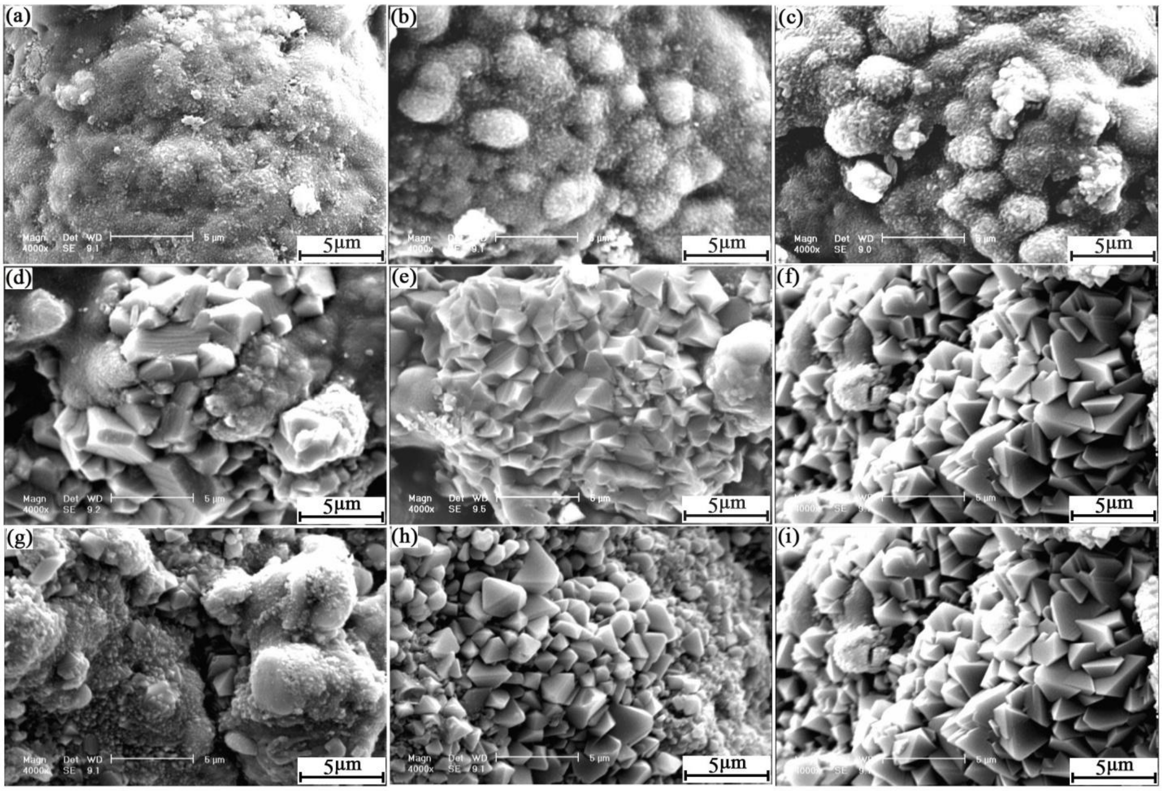

Fig. 5. Morphology of the oxide layer on the surface of the commercial CoNiCrAlY coating oxidized for a) 2 h, b) 15 h and c) 100 h, CoNiCrAlY/0%YSZ coating oxidized for d) 2h , e) 15 h and f) 100 h, CoNiCrAlY/5%YSZ coating oxidized for g) 2 h, h) 15 h and i) 100 h at 1000 ◦C

coatings were studied and the following conclusions were drawn:

- Undesirable morphology and low surface quality of the milled powders caused anincrease in porosity and surface oxidation of splatsinthe composite coatings during the thermal spray process.
- High porosity of the composite coating and surface oxidation of the splats in these coatings caused a decrease in oxidation resistance of these coatings.
- Theinstability of CoO, NiO, and Al_2O_3 phases at 1000 °C and high activity of oxygen caused a stable phase spinelto be formed.
- The surface morphology of the oxide scale in commercial andcomposite coatings showedneedle and polyhedral shapes, respectively.

Acknowledgements

The authors are grateful to the Poudrafshan Company for their financial support and assistance with the HVOF spraying.

References

1. M. Seraffon, N. J. Simms, J. Sumner, J. R. Nicholls, “The development of new bond coat compositions for thermal barrier coating systems operating under industrial gas turbine conditions”, Surf. Coat. Technol. Vol. 206, 2011, pp. 1529-1537.
2. T. Liang, H. Guo, H. Peng, S. Gong,“Microstructural evolution of CoCrAlY bond coat on Ni-based superalloy DZ 125 at 1050 °C”, Surf. Coat. Technol., Vol. 205, 2011, pp. 4374-4379.
3. B. A. Pint, M. A. Bestor, J. A. Haynes, “Cyclic oxidation behavior of HVOF bond coatings deposited on La- and Y-doped superalloys”, Surf. Coat.Technol., Vol. 206, 2011, pp.1600-1604.
4. A. Keyvani, M. Saremi, M. H. Sohi,“Oxidation resistance of YSZ-alumina composites compared to normal YSZ TBC coatings at 1100°C”, J. Alloys Compd.,Vol.509, 2011, pp. 8370-8379.
5. J. H. Lee, Pi-C. Tsai, J. w. Lee, “Cyclic oxidation behavior and microstructure evolution of aluminized, Pt-aluminizedhigh velocity

oxygen fuel sprayed CoNiCrAlY coatings", Thin Solid Films, Vol. 517, 2009, pp. 5253-5260.

6. H. Guo, L. Sun, H. Li, S. Gong, "High temperature oxidation behavior of hafnium modified NiAl bondcoat in EB-PVD thermal barrier coating system", Thin Solid Films, Vol. 516, 2008, pp. 5732-5739.
7. F. Tang, L. Ajdelsztajn, G. E. Kim, V. Provenzano, J. M. Schoenung, "Effects of variations in coating materials and process conditions on the thermal cycle properties of NiCrAlY/YSZ thermal barrier coatings", Mater. Sci. Eng. A, Vol. 425, 2006, pp. 94-101.
8. T. Sadowski, P. Golewski, "The influence of quantity and distribution of cooling channels of turbine elements on level of stresses in the protective layer TBC and the efficiency of cooling", Com. Mater. Sci, Vol. 52, 2012, pp. 293-299.
9. L. Ajdelsztajn, J. A. Picas, G. E. Kim, F. L. Bastian, J. Schoenung, V. Provenzano, "Oxidation behavior of HVOF sprayed nanocrystallineNiCrAlY powder", Mater. Sci. Eng. A, Vol. 338, 2002, pp. 33-43.
10. K. Ma, J. M. Schoenung, "Isothermal oxidation behavior of cryomilledNiCrAlY bond coat: Homogeneity and growth rate of TGO", Surf. Coat. Technol., Vol. 205, 2011, PP. 5178-5185.
11. S. Kamal, R. Jayaganthan, S. Prakash," Mechanical and microstructural characteristics of detonation gun sprayed NiCrAlY + 0.4 wt% CeO2 coatings on superalloys", Mater. Chem. Phys. Vol. 122, 2010, pp. 262-268.
12. M. D. Ferdinando, A. Fossati, A. Lavacchi, U. Bardi, F. Borgioli,C. Borri, C. Giolli, A. Scrivani, "Isothermal oxidation resistance comparison between air plasma sprayed, vacuum plasma sprayed and high velocity oxygen fuel sprayed CoNiCrAlY bond coats", Surf. Coat. Technol., Vol. 204, 2010, PP. 2499-2506.
13. L. Ajdelsztajn, D. Hulbert, A. Mukherjee, J. M. Schoenung, "Creep deformation mechanism of cryomilledNiCrAlY bond coat material", Surf. Coat. Technol., Vol. 201, 2007, PP. 9462-9499.
14. F. Tang, L. Ajdelsztajn, G. E. Kim, V. Provenzano, J. M. Schoenung, "Improvement in oxidation behavior of nanostructured conicra1y bond coat dispersed with nano-size alumina particles", International Conference of Fundamental Science of Energy 004, USA, 2002, P. 293.
15. L. Ajdelsztajn, F. Tang, G. E. Kim, V. Provenzano, J. M. Schoenung, "Synthesis and Oxidation Behavior of NanocrystallineMCrAlY Bond Coatings",J. Therm. Spray Technol., Vol. 14, 2005, pp. 23-31.
16. D. Mercier, C. Kaplin, G. Goodall, G. Kim, M. Brochu, "Parameters influencing the oxidation behavior of cryomilledCoNiCrAlY", Surf. Coat. Technol., Vol.205, 2010, pp. 2546-2552.
17. D. Mercier, B. D. Gauntt, M. Brochu,"Thermal stability and oxidation behavior of nanostructured NiCoCrAlY coatings", Surf. Coat. Technol., Vol. 205, 2011, pp. 4162-4168.
18. M. Krasnowski, T. Kulik, "Nanocomposites obtained by mechanical alloying in Fe–Al–Ti–C system", J. Alloys Compd., Vol. 448, 2008, pp. 227-233.
19. C. C. Koch,"Intermetallic matrix composites prepared by mechanical alloying—a review", Mater. Sci. Eng. A, Vol. 244, 1998, pp. 39-48.
20. F. Valenza, M. L. Muolo, A. Passerone, "Wetting and interactions of Ni- and Co-based superalloys with different ceramic materials", J. Mater. Sci., Vol. 45, 2010, pp. 2071-2079.
21. S. Deshpande, S. Sampath, H. Zhang, "Mechanisms of oxidation and its role in microstructural evolution of metallic thermal spray coatings—Case study for Ni–Al", Surf. Coat. Technol., Vol.200, 2006, pp. 5395-5411.
22. S. Deshpande, A. Kulkarni, S. Sampath, H. Herman,"Application of image analysis for characterization of porosity in thermal spray coatings and correlation with small angle neutron scattering",Surf.Coat. Technol., Vol. 187, 2004, pp. 6-15.
23. D. J. Young, High Temperature Oxidation and Corrosion of Metals, 1rd ed., Elsevier, England, 2008, p. 348.
24. T. Kai, Z. Xiang, C. Hua, Z. J. shan,"Oxidation and hot corrosion behaviors of HVAF-sprayed conventional and nanostructured NiCrC coatings", trans. Nonferrous met. Soc. China., Vol. 19, 2009, pp. 1151-1160.
25. R. A. Mahesh, R. Jayaganthan, S. Prakash, "A study on the oxidation behavior of HVOF sprayed NiCrAlY–0.4 wt.% CeO2 coatings on superalloys at elevated temperature",Mater. Chem. Phys., Vol. 119, 2010, pp. 449-459.
26. T. Y. Choi, J. H. Yoon, K. S. Kim, K. O. Song, Y. K. Joo, W. Fang, S. H. Zhang, S. J. Youn, H. G. Chun, S. Y. Hwang,"A study on HVOF coatings of micron and nano WC–Co powders", Surf. Coat. Technol., Vol.202, 2008, pp. 5556-5564.
27. D. Toma, W. Brandl, U. Koster, "Studies on the transient stage of oxidation of VPS and HVOF sprayed MCrAlY coatings", Surf. Coat. Technol., Vol. 121, 1999, pp. 8-20.