

High temperature oxidation of HFPD thermal-sprayed MCrAlY coatings

F.J. Belzunce ^{a,*}, V. Higuera ^b, S. Poveda ^b

^a *Department of Materials Science, University of Oviedo, 33203 Gijón, Spain*

^b *Department of Energy, University of Oviedo, 33203 Gijón, Spain*

Received 4 January 2000; received in revised form 6 June 2000

Abstract

NiCrAlY and CoNiCrAlY powders were thermal-sprayed using the high frequency pulse detonation method (HFPD) onto AISI 310 austenitic stainless steel samples in order to obtain dense, adherent high temperature oxidation resistant coatings. The cyclic oxidation behaviour in air of both types of coatings was determined at a maximum temperature of 1273 K. The porosity, internal oxidation (after the first 8-h oxidation cycle), hardness, coating thickness and substrate-coating adherence were not significantly modified by the high temperature oxidation cycles. The surface phase composition was evaluated throughout the tests using X-ray diffraction and scanning electron microscope techniques revealing the formation of a continuous and highly protective alumina layer. The oxidation kinetics of both coatings can be characterized by parabolic rate constants, which are very similar to those of pure alumina. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: MCrAlY coatings; Air oxidation; HFPD; Thermal-sprayed coatings

1. Introduction

Gas-fired gas turbine combined-cycle systems are expected to account for a significant proportion of the projected new electricity generation units to be constructed over the next 10 years. Such plants are available in sizes of up to > 200 MW per turbine. Current combined-cycle plants have professed cycle efficiencies in the order of 49% and are capable of achieving environmental compliance for SO₂ and NO_x with minimal effluent streams. The ultimate goal of these new systems is to reduce the cost of electricity by at least 10% [1].

In order to achieve the aforementioned goals, the gas turbine industry is making the utmost effort to allow increased operation temperatures to improve engine efficiency using a reduced cooling air/fuel ratio. At the same time, reduced fuel consumption is obtained and lower emission rates of nitrogen oxides (NO_x), carbon monoxide (CO) and hydrocarbons (HC) are achieved in

order to meet the expected lower limits for pollution in the future [2].

The main requirements for industrial land-based gas turbines are long life, maximum efficiency, reliability and minimum cost. The durability of a gas turbine is limited by components operating at high temperatures [3]. Ni-based superalloys are the materials normally used to make the blades of the first stages of gas turbines, which are the ones operating at the highest temperature. However, these high performance alloys are not able to withstand oxidation and high temperature corrosion caused by the surrounding atmosphere and have to be coated with protective coatings. MCrAlY coatings (M = Ni, Co or both) are used worldwide for this purpose. They owe their protective effect to the fact that aluminum forms a continuous oxide layer on the coating surface that is thermally very stable. The remaining elements control the aluminum activity, hold the oxide layer in place and adapt the coating to the properties of the base material. These coatings are usually applied using the vacuum plasma-spray process, a method which produces a dense coating (low porosity) with excellent adherence to the substrate and which prevents oxidation during the application.

* Corresponding author. Tel.: +34-985-182024; fax: +34-985-182022.

E-mail address: belzunce@etsiig.uniovi.es (F.J. Belzunce).

Table 1
Composition and grain size of the spherical powders

Powder	% Ni	% Co	% Cr	% Al	% Y	Grain size (μm)
Amdry 962	Balance	–	25	10	1	–106+56
Amdry 9954	32	Balance	21	8	0.5	–62+11

Recently, other thermal-spray processes have been developed, such as the high velocity oxygen fuel (HVOF) and the detonation gun methods, both able to produce dense coatings with a high adherence to the substrate. These spray processes are also much more economical and convenient than the vacuum plasma-spray process. Finally, the new high frequency pulse detonation (HFPD) thermal-spray process represents a cost-effective alternative for the production of premium quality coatings [4].

In this paper, the high temperature oxidation behaviour in air of two MCrAlY coatings produced by the HFPD process is analysed.

2. High frequency pulse detonation spray process (HFPD)

The HFPD spray system is based on a carefully designed gun, able to produce a discontinuous behaviour (cycled explosions) from a continuous supply of the detonable gases and powders. The system lacks mechanical moving parts, being designed with aerodynamic valves that allow the self-generation of discrete batches of gases and powders for each cycle opening up the possibility of working in a wide range of explosion frequencies (up to > 100 Hz) and gas mixtures. In the HFPD process, the flow of gaseous products from cycled explosions in the gun is used to accelerate and heat the sprayed particles. Typically, these particles attain very high speeds and sufficiently high temperatures leading to quite dense, well-bonded coatings from most commercially available powders (cermets, metallic alloys and ceramics) [5].

One of the most important consequences of the particular physical process involved in the HFPD cycled explosions is the low consumption of gases, especially when compared to alternative continuous HVOF systems, mainly due to two factors: the different oxy-fuel ratios (low oxygen) and the pulsed nature of the process. Another important economic consideration is its extended operating time and low maintenance needs [4].

3. Materials and experimental procedure

Two types of commercial MCrAlY powders were sprayed onto the AISI 310 austenitic stainless steel by

means of the HFPD thermal-spray method. The specimens were cylindrical with a diameter and height of 25 mm, in agreement with the ASTM C-633 standard [6]. Table 1 shows the chemical composition, morphology and grain size of both powders. A PK 200 Aerostar Coatings HFPD thermal-spray apparatus was used to spray both powders. The most relevant spraying parameters are listed in Table 2 along with the final coating thicknesses. Samples were first cleaned and blasted with alumina grit (F-24) at 0.7 MPa and their flat surfaces ($\phi 25$ mm) were automatically thermal-spray coated immediately after cleaning.

Table 2
Spraying parameters

Spraying system:	NiCrAlY	CoNiCrAlY
HFPD-PK200		
Gun length: 250 mm (Φ 20 mm)	(Amdry 962)	(Amdry 9954)
Oxygen (l min^{-1})	135	110
Nitrogen (l min^{-1})	25	120
Fuel (l min^{-1})	47 (propilene)	80 (natural gas)
Carrier gas, N_2 (l min^{-1})	20	20
Frequency (Hz)	45	75
Spraying distance (mm)	150	150
Powder feeding (g min^{-1})	26	30
Translation velocity (cm s^{-1})	10	10
Displacement (cm)	1	1

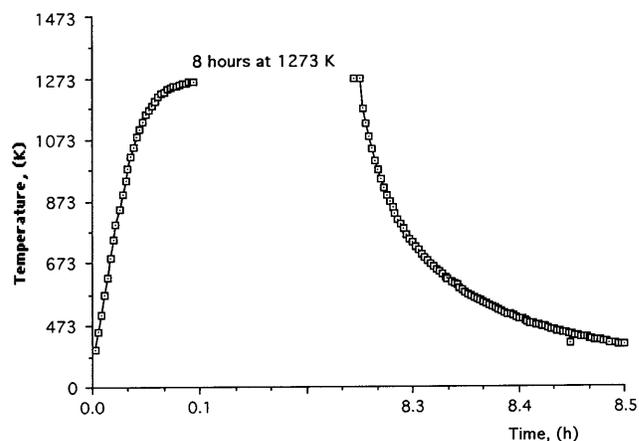


Fig. 1. Thermal cycle (maximum heating rate: 6 K s^{-1} , maximum cooling rate: 4 K s^{-1}).

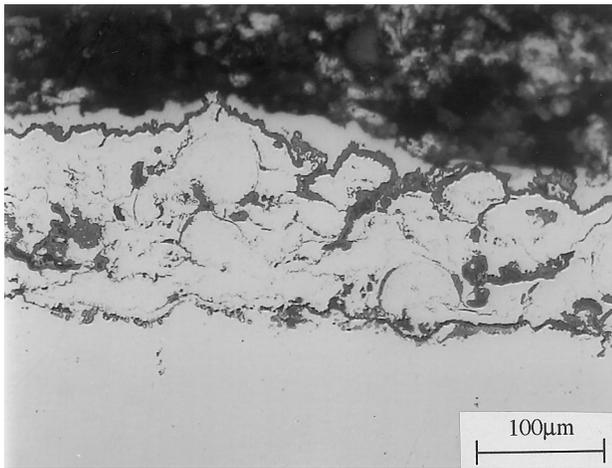


Fig. 2. NiCrAlY coating after 20 cycles of air oxidation.

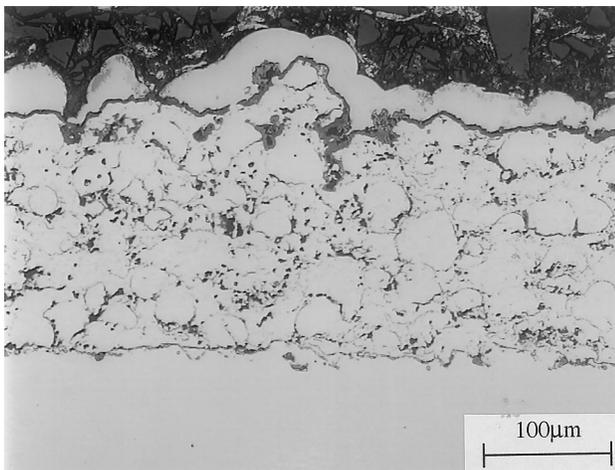


Fig. 3. CoNiCrAlY coating after 20 cycles of air oxidation.

The thickness of the coatings, along with their microstructure, porosity and oxide content were determined by means of optical microscopy techniques. The porosity and oxide content of the coatings were evaluated by point

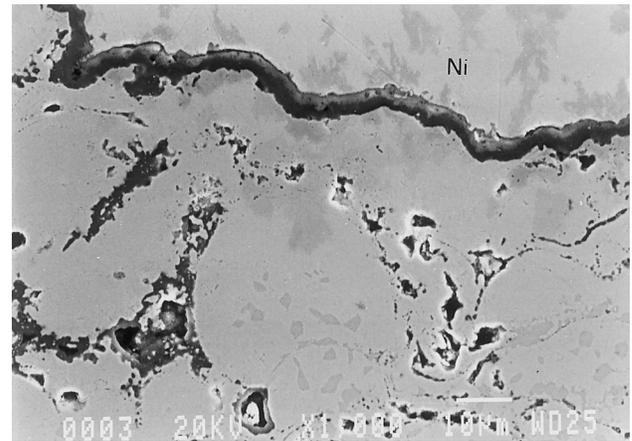


Fig. 4. Al_2O_3 and CoAl_2O_4 layers built up on the surface of the CoNiCrAlY coating after 20 cycles of air oxidation.

counting under an optical microscope, according to the ASTM E-562 Standard [7]. The substrate-coating adherence test (in accordance with the ASTM C-633 Standard [6]) and the Vickers microhardness test (using a load of 300 g) were also performed on the coating layers. The phase composition of the coatings was determined by X-ray diffraction analysis using a Philips PW 1729-1710 device equipped with a copper anode. High temperature cyclic oxidation tests were carried out in air, using a laboratory furnace maintained at 1273 ± 5 K. Fig. 1 shows a typical thermal cycle characterized by an annealing period of 8 h at 1273 K followed by air cooling. These experiments were performed until a maximum of 160 h (20 cycles) with the ultimate aim of determining the oxidation kinetic behaviour of these coatings. The samples were taken out of the furnace several times during the first cycle and then after every cycle to determine the weight gain due to surface oxygen intake. Weight measurements were carried out using a balance with a sensitivity and an accuracy of 0.1 mg. High temperature cyclic oxidation tests of the steel substrate were carried out as a reference.

Table 3

Coating parameters modification after different oxidation times in air at 1237 K (\pm S.D.)

	As-sprayed	1 cycle	2 cycles	5 cycles	10 cycles	20 cycles
<i>NiCrAlY</i>						
Thickness (μm)	182 ± 20	155 ± 17	149 ± 24	165 ± 20	165 ± 24	140 ± 20
Porosity (%)	2.6 ± 0.8	2.5 ± 1.1	1.4 ± 0.5	1.6 ± 0.8	1.7 ± 0.4	2.1 ± 0.5
Internal oxid. (%)	0.4 ± 0.2	7.3 ± 1	8.3 ± 1.3	8.6 ± 1	10.8 ± 1.6	6.4 ± 0.8
HV ₃₀₀	433 ± 40	443 ± 31	405 ± 26	410 ± 38	392 ± 31	382 ± 17
Adherence (MPa)	>70	>68	–	–	>54	>63
<i>CoNiCrAlY</i>						
Thickness (μm)	178 ± 24	190 ± 17	177 ± 15	176 ± 19	160 ± 17	166 ± 16
Porosity (%)	0.8 ± 0.2	1.1 ± 0.3	1.1 ± 0.6	1.0 ± 0.4	1.1 ± 0.3	1.3 ± 0.2
Internal oxid. (%)	1.4 ± 0.3	7.6 ± 0.7	10.7 ± 1.2	8.2 ± 0.6	7.1 ± 0.8	6.5 ± 1.1
HV ₃₀₀	320 ± 26	364 ± 20	348 ± 23	346 ± 23	362 ± 20	336 ± 10
Adherence (MPa)	>66	–	–	–	>62	>54

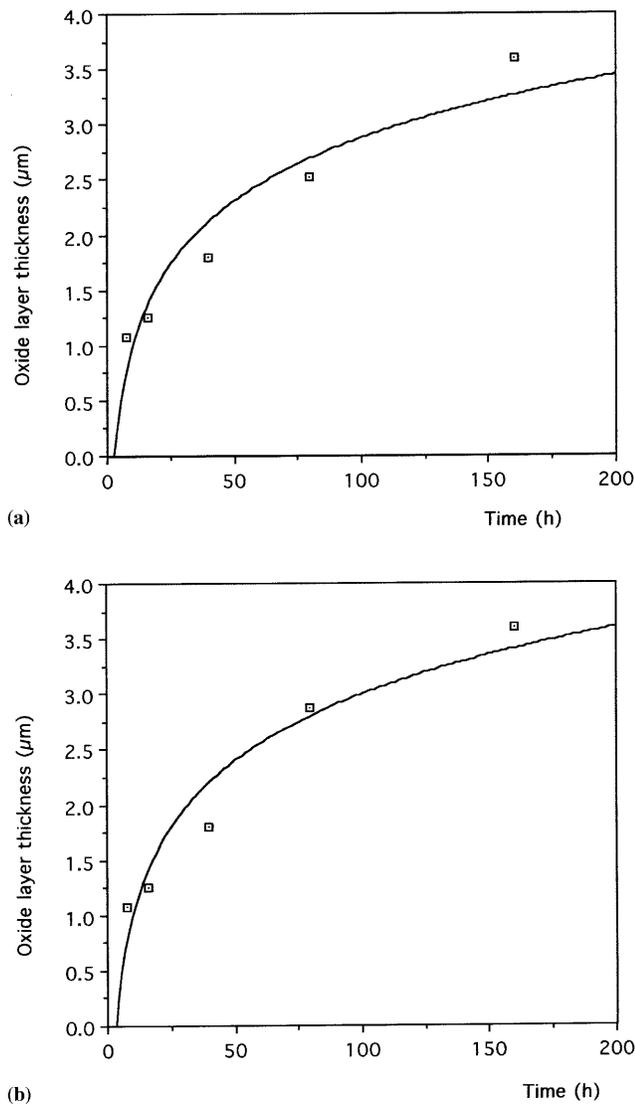


Fig. 7. Coating oxidation kinetics in air at 1273 K (thickness of alumina layer versus time). (a) NiCrAlY and (b) CoNiCrAlY.

Table 4
Oxidation parabolic constants of HFPD thermal-sprayed coatings

Parabolic constants	NiCrAlY	CoNiCrAlY
K_1 ($\mu\text{m}^2 \text{h}^{-1}$)	0.0765	0.0806
K_2 ($\text{g cm}^{-2} \text{s}^{-1}$)	$3.17 \cdot 10^{-12}$	$3.34 \cdot 10^{-12}$

ings increases significantly after a very low oxidation time (first cycle, < 8 h), but then does not change any more. The oxidant atmosphere penetrates into the coatings through their open porosity until all the accessible internal surfaces have been oxidised. Subsequently, the oxidation phenomenon takes place only on the external surface of the coating, so that the presence of a surface

protective layer is needed in order to avoid further oxidation. Taking these facts into account, the most important limitation of the HFPD thermal-sprayed coatings is the loss of aluminium to internal oxides. Fig. 4 shows the continuous oxide layer built up on the surface of these coatings and also on internal surfaces connected with the exterior via the open porosity. Two continuous layers of oxides can be detected under the scanning electron microscope (Fig. 4) according to the analysis carried out using the electron microprobe, the dark-contrast inner layer, which has a uniform thickness is alumina and the lighter-contrast exterior layer, which was intermittently present and also has a more irregular morphology, is the corresponding mixed spinel-type oxide (NiAl_2O_4 and CoAl_2O_4 , respectively). Similar results were obtained by other authors when characterizing the oxidation behaviour of low pressure plasma-sprayed MCrAlY coatings [8–10]. The presence of alumina and mixed spinel-type oxides was also revealed from the diffraction pattern of the surface of these samples, as can be seen in Fig. 5, which stems from the CoNiCrAlY sample after 20 thermal oxidative cycles (160 h). It is the dense and continuous alumina layer that avoids inward diffusion of oxygen and explains the excellent resistance of these coatings against oxidation. It must be remarked also that no surface or internal cracks were detected after any of the high temperature cyclic oxidation tests.

Fig. 6 represents the weight gain per unit surface of the NiCrAlY and CoNiCrAlY coatings and the 310 steel substrate measured during the 1273 K cyclic oxidation tests. As only the flat surface of the samples were spray-coated ($\Phi 25$ mm), the net weight gain of the coatings was obtained after correcting the measured data taking into account the oxidation behaviour of the substrate and its exposed surface. Nonetheless, these data can be used only qualitatively, since at this temperature (1273 K) the chromium oxide (Cr_2O_3) developed on the steel surface transforms into the volatile oxide CrO_3 [11]. This fact may explain the weight loss observed in all the samples after long exposure in air at 1273 K.

Since the kinetics of the oxidation reaction cannot be obtained by means of weight measurements, the thickness of the Al_2O_3 layer was accurately measured under the scanning electron microscope after different oxidation periods (Fig. 7). The oxidation kinetics of both coatings is parabolic and quite similar, giving rise to the parabolic rate constants shown in Table 4. K_1 expresses the oxidation behaviour in terms of the alumina thickness and K_2 in terms of oxygen gain per unit coating surface (the density of pure alumina used in the calculation of K_2 was, in accordance with [12], 3.86 g cm^{-3}). The parabolic rate constants obtained in this study present values very close to those for the bulk material (pure alumina) [13,14].

5. Conclusions

NiCrAlY and CoNiCrAlY coatings may be thermal-sprayed using the HFPD process. The coatings are dense and exhibit interconnected porosity along droplet boundaries. They adhere well to the substrate and the adherence is not affected by cyclic oxidation. During high temperature cyclic oxidation, the oxidant atmosphere penetrates into the coatings through their open porosity; this internal oxidation occurs until all the accessible internal surfaces are oxidised. Subsequently, the oxidation takes place only on the external surface, where a continuous and uniform layer of alumina protects the coating from further oxidation.

The porosity, hardness and thickness of NiCrAlY and CoNiCrAlY coatings are not significantly altered by cyclic oxidation.

The kinetics of the oxidation reaction can be determined only indirectly by measurement of the thickness of the Al₂O₃ layer. The oxidation kinetics of the coatings is parabolic and can be characterized by parabolic rate constants that are very similar to those of pure alumina.

Acknowledgements

Funding for this work was provided by FICYT (Asturias, Spain), Project Reference Number PB-MAT 98-03. The authors would also like to thank Aerostar Coatings for the provision of the coated samples.

References

- [1] W.P. Parks, E.E. Hoffman, W.Y. Lee, I.G. Wright, *J. Ther. Spray Tech.* 6–2 (1997) 187.
- [2] T. Haubold, J. Wigren, C. Gualco, Proceedings of the Fifteenth Thermal Spray Conference, Nice, France, ASM International, 1998, p. 1617.
- [3] N. Czech, W. Esser, F. Schmitz, *Siemens Power J.* 4 (1994) 22.
- [4] I. Fagoaga, G. Barykin, J. De Juan, T. Soroa, C. Vaquero, Proceedings of the United Thermal Spray Conference, Düsseldorf, Germany, DVS-Verlag, 1999, p. 282.
- [5] I. Fagoaga, G. Barykin, J. De Juan, T. Soroa, C. Vaquero, Proceedings of the United Thermal Spray Conference, Düsseldorf, Germany, DVS-Verlag, 1999, p. 726.
- [6] ASTM C-633, Standard test method for adhesion or cohesive strength of flame-sprayed coatings, in: *Annual Book of ASTM Standards*, American Society for Testing and Materials, 1979.
- [7] ASTM E-562, Standard test method for determining volume fraction by systematic manual point count, in: *Annual Book of ASTM Standards*, vol. 03.01, American Society for Testing and Materials, 1990.
- [8] J.A. Haynes, E.D. Rigney, E.D. Ferber, W.D. Porter, *Surf. Coat. Tech.* 86–87 (1996) 102.
- [9] N. Czech, V. Kolarik, W.J. Quadakker, W. Stamm, *Surf. Eng.* 13 (1997) 384.
- [10] E.A.G. Shillington, D.R. Clarke, *Acta Mater.* 47 (1999) 1297.
- [11] N. Birks, G.H. Meier, *Introduction to High Temperature Oxidation of Metals*, Edward Arnold, London, 1983, p. 80.
- [12] ASM International, *ASM Engineered Materials Reference Book*, ASM International, Metals Park, OH, 1989, p. 168.
- [13] H. Iwamoto, T. Sumikawa, K. Nishida, T. Asano, M. Nishida, T. Araki, *Mater. Sci. Eng. A241* (1998) 251.
- [14] R. Peraldi, D. Monceau, A. Malie, B. Pieraggi, Proceedings of the Fifteenth Thermal Spray Conference, Nice, France, ASM International, 1998, p. 1561.