*Highlights (for review)

Highlights

- 1. The heat treatment of the coating produced a hardness decrease inside the coating.
- 2. The coating heat treatment caused a hardness increase on the top coating surface.
- 3. The oxidation of the top coating surface produces a reduction of the wear rate.
- 4. The use of a bond coat improves the thermal shock resistance of the system.
- 5. The proposed HVOF coating can prolong the life of dies in hot-working processes.



Microstructural and tribological studies of as-sprayed and heat-treated HVOF Cr₃C₂-CoNiCrAlY coatings with a CoNiCrAlY bond coat

J.A. Picas*, M. Punset, S. Menargues, E. Martin, M.T. Baile.

Light Alloys and Surface Treatments Design Centre. Department of Materials Science and Metallurgy. Universitat Politècnica de Catalunya. Rambla Exposició, 24; 08800 Vilanova i la Geltrú; Spain.

*Corresponding author: Tel: +34938967213, Fax: +34938967201, E-mail address: josep.picas@upc.edu.

Abstract

Die wear is an important problem for manufacturers in hot-working processes, e.g. metal die casting, hot extrusion and thixoextrusion of aluminium, magnesium or steel, as well as glass and plastics processing. The dies have to be capable of withstanding complex thermal and mechanical loads, while giving a sufficient wear resistance against abrasion and adhesion at very high temperatures. In order to improve the wear resistance and reduce the heating of the extrusion die it can be protected with a hard cermet coating. The purpose of this work is to study the high-temperature performance of Cr₃C₂-CoNiCrAlY coating and explore the potential application of this coating to prolong the life of tooling and dies while reducing maintenance and increasing shelf life and dimensional control. A wo-layer 75 Cr₃C₂-25CoNiCrAlY coating with a CoNiCrAlY bond-coating was sprayed by HVOF thermal spray process on a steel substrate. Coatings were heat-treated at a range of temperatures between 900 °C and 1100 °C. The mechanical and tribological properties of coatings were determined as a function of the temperature of heat treatment. The bond coat effect on the thermal shock resistance of Cr₃C₂-CoNiCrAlY coating was analysed.

Keywords: Thermal spray coatings; HVOF; Chromium carbide; Heat treatment; Wear.

1. Introduction

Hot-working processes provide means of producing a desired shape of metal products, but the high temperature and complex atmospheres of these industrial processes have a large effect on dies lifetime. The cost of the dies is generally high and therefore long die life is necessary in order to reduce the production costs.



Attempts carried out in order to obtain suitable die materials with extended service life have been concentrated on treatment of die surface or by deposition of protective coatings. These surface treatments can be done in a variety of ways and techniques depending on the end result desired. The right die has to be resistant to wear, heat cycling, plastic deformation, corrosion and must have high hardness, yield strength, creep resistance and toughness at elevated temperatures.

Gas nitriding has been one of the most successful methods of surface treating of H13 aluminium

extrusion dies for many years [1]. In the past various other surface treatments like plasma nitriding, plasma spray techniques, and chemical vapour deposition (CVD) were used to improve the die wear resistance [2, 3]. Some of these processes, like CVD techniques, have a limitation related to application temperatures, because distortion may occur in parts coated by high temperature CVD coatings. Therefore, steel tools are not widely coated by CVD. In recent years PVD coatings, as well as duplex treatment (nitriding followed by PVD coating) have been also developed for protection of dies, but are severely limited by the size of the PVD chamber size [4, 5]. Another coatings used for the protection of steel tooling is hard chrome plating. This is very effective at improving wear resistance, but there are increasing concerns over the environmental and social acceptability of the process. All commercial plating baths use hexavalent chromium (CrVI), which is both highly toxic to the user and hazardous to the environment [6]. Furthermore, electrodeposited Cr coatings are inherently microcracked, which can result in poor corrosion resistance and spalling. A well-established hard chrome replacement for mechanical components in the automotive and aerospace industry is the high-velocity oxyfuel (HVOF) deposition of tungsten carbide-cobalt (WC-•Co) cermet coatings but the application of this process (and other thermal spray processes) to tooling has been limited. A major drawback for thermal spray coatings can be the resistance to impacts, in particular in areas where sharp edges are presents and this could be the case in geometrically complex dies. Consequently, it's difficult to use these coatings in those processes in which the coating is exposed to impacts, like hot forging processes, but it could be considered as a viable replacement for hard chrome plating in other applications, like metal die casting, hot extrusion and thixoextrusion of aluminium or steel, as well as glass and plastics processing, in which the load distribution would be very different.

HVOF Coatings of various types can be used effectively to combat abrasive, adhesive or erosive wear, including applications that combine wear and corrosion, either at ambient or elevated temperatures. Carbide coatings have proven themselves an excellent choice for wear and corrosion applications. These coatings are composed of small carbide particles reinforcing a metallic binder phase, combining the properties of ceramic-carbide type materials, high hardness and toughness and ductility of metals. WC-Co coatings provide excellent performances at ambient temperature, however, in corroding environment or at elevated temperatures, the synergistic effect of mechanical



attack and chemical attack degrades its performance, restraining the application of this coating up to 450 °C[7]. In contrast, HVOF thermal spray coatings based on the cermet Cr₃C₂-NiCr are commonly employed at elevated temperature up to 900 °C for its good oxidation resistance and reasonable wear resistance [8-15]. This coating also finds application at ambient temperature where wear resistance in corroding environment is required [16]. However, Mathews [17] shown, that in certain conditions the oxidation of Cr₃C₂-25%NiCr coatings is more pronounced than expected due to preferential oxidation of the Cr₃C₂ carbides-matrix boundaries. One possibility to improve the oxidation and corrosion resistance of the cermet coatings is change the binder phase by a matrix having improved properties. In this sense, the MCrAlY coatings show a better corrosion resistance and oxidation resistance than NiCr coatings at high temperatures. MCrAlY coatings represent a family of corrosion resistant alloys designed for high-temperature surface protection (TBC's). MCrAlY overlays used as a TBC's are usually Ni- and/or Co-based with high Cr content to provide hot corrosion resistance, Al contents between 5-15 wt.% to provide oxidation resistance and Y addition around 1 wt.% for stability during cyclic oxidation [18]. Within the family of the MCrAlY coatings, the CoNiCrAlY alloy is one of the best coating for high temperature oxidation resistance [19, 20].

In addition to these features, the coefficient of thermal expansion of Cr_3C_2 (10.3 × 10⁻⁶ °C⁻¹) and nickel (12.8 × 10⁻⁶ °C⁻¹) are nearly similar to that of iron (11.4 × 10⁻⁶ °C⁻¹) that constitute the base of most hot working tool materials [21]. However, in some cases, the use of a bond coat between the top cermet coating and the substrate could be necessary in order to reduce these differences in their thermal expansion coefficients, minimising the stress generation during thermal cycles and improving the wear resistance and the thermal shock resistance of these coatings at high temperatures. Again the CoNiCrAlY coating is widely used as a bond coat for plasma sprayed thermal barrier coatings [22], and accordingly in this work the same alloy was used both as binder phase in the top coating and as bond coating.

Even if the Cr₃C₂-CoNiCrAlY powder is commercially available, not many papers dealing with its mechanical or wear properties have been found. For this reason, the main goal of this work was to investigate the evolution in microstructure, hardness and wear resistance of the heat treated HVOF 75Cr₃C₂-25CoNiCrAlY coating with a CoNiCrAlY bond-coating and explores the potential application of this coating to improve the dies used in hot working processes.

2. Experimental details

2.1 Materials and Thermal Spraying Process

Conventional gas atomized CoNiCrAlY powder (M-427.25) and Cr₃C₂-CoNiCrAlY 75/25 powder (K-880.23), supplied by Flame Spray Technologies, were employed as the feedstock





3

powders to produce the bond and top coatings respectively. The agglomerate powders were received with a nominal size distribution within the range of 22 μm to 45 μm and 15 to 45 μm respectively, and were sprayed accordingly. Table 1 shows the chemical composition of the sprayed powders (provided by Flame Spray Technologies).

A Sulzer Metco WokaJet 400 HVOF thermal spray facility was used for the thermal spraying of powders on a 1.2344 hot work steel substrate, using kerosene as liquid fuel. The spray parameters used for the CoNiCrAlY powder were: spray distance 260 mm; fuel flow rate 18.2 l·h⁻¹; oxygen flow rate 944 l·min⁻¹, and for the Cr₃C₂-CoNiCrAlY powder were: spray distance 360 mm; fuel flow rate 25.3 l·h⁻¹; oxygen flow rate 900 l·min⁻¹. All coatings were deposited onto rectangular steel specimens, which were grit-blasted before spraying. All specimens were mounted on the circumference of a horizontally rotating turntable and cooled during and after spraying with compressed air jets. The gun was attached to an ABB IRB 2400/16 robot controlling the vertical movement. In all cases the orientation of the spray gun is perpendicular to the substrates. In order to evaluate the bond coating effect in the wear resistance and in thermal shock resistance behaviour of coatings, some monolayer Cr₃C₂-CoNiCrAlY coatings were deposited directly on the steel substrate.

2.2 Characterization

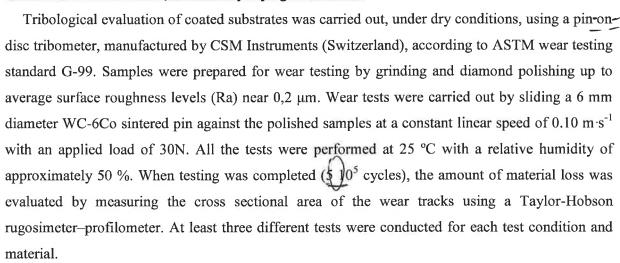
The coating microstructure was examined by means of a scanning electron microscope (SEM, Jeol JSM-5600). Observations were carried out on polished cross-sections normal to the surface. The metallographic preparation was done by first grinding, followed by polishing with 1 μm diamond suspension. Coating porosity was determined by means of optical microscopy techniques, and were evaluated on transversal sections by image analysis technique (Leica Qwin) using a Leica optical microscope.

The phase characterization of the as-received powder and the coatings was conducted by XRD using a Siemens D500 diffractometer with copper (Cu) K α (λ = 0.15406 nm) radiation. The analysis depth of XRD is function of the incidence angle which depends of the diffraction angle and material. For Cr₃C₂-CoNiCrAlY coatings the analysis depth can fluctuate between 3 and 15 microns, and consequently the obtained spectra gives an idea about the phases evolution only on the superficial layers of the coating.

Sprayed coatings were heat-treated in stationary atmospheric conditions at a range of temperatures between 900 °C and 1100 °C. Samples were removed after 4 h of heat treatment and cooled in air. After the heat treatment, the surface oxidation of the coatings was examined by means of a scanning electron microscope (SEM, Jeol JSM-5600). Furthermore, thermal shock resistance of coatings samples was evaluated heating the samples at several temperatures for 1 hour, followed

with water quenching at 20 °C. To perform the heat treatments and thermal shock tests, the samples were previously prepared by grinding and diamond polishing up to average surface roughness levels (Ra) near (μ) μm.

The microhardness was measured on a polished cross-section of the HVOF coatings and in the oxidized coatings surface using a Duramin 5 microhardness tester (Struers) with a Vickers diamond indenter under a load of 300 gf, according to ASTM E384 standard. Fifteen data points were collected and averaged for each hardness value. The samples were mechanically polished with decreasing grain-size abrasive paper and finally finished with a 1-µm diamond paste in order to eliminate surface imperfections. Before measurement, all samples were carefully cleaned by ultrasound in acetone bath, followed by drying in warm air.



The heat treatments described in this work intended to represent the coating work life in high temperature conditions. However, one can notice that the microhardness and tribological tests were carried out at room temperature instead of high temperature. Yet the structure of the coating given by the heat treatment should be similar. For these reasons, the presented results should be considered as an estimation of the coating performance. Nevertheless, it can not be excluded that at real temperature of the hot metal forming processes, the wear mechanisms might be somewhat different. It is very feasible that in real working conditions superficial changes take place varying the mechanical properties of the coating and modifying the surface layer in direct contact with the counterpart (oxides, depletion of the matrix of oxide formers elements, etc...).

3. Results and discussion

3.1 Morphology and Microstructure of the Powders

The morphology of the CoNiCrAlY and Cr₃C₂-CoNiCrAlY powders is shown in Figures 1a and 1b, respectively. In both cases the powder morphology is predominantly spherical. The particle surface is smooth in CoNiCrAlY powders and quite irregular in the Cr₃C₂-CoNiCrAlY powders.







Figures 2a and 2b show the internal microstructure of polished powders. The CoNiCrAlY powder (Fig. 2a) shows the presence of two metallic phases: light γ-matrix Co-Ni-Cr solid solution and dark β-CoNiAl phase [18, 20]. On the other hand, the Cr₃C₂-CoNiCrAlY powder (Fig. 2b) shows the presence of carbide grains, which exhibit dark contrast, embedded in different binder phase regions, which exhibits several grey and black shades. Fig. 3b shows the EDX analysis of the different regions observed in the Cr₃C₂-CoNiCrAlY powder (Fig. 3a): zone 1 (dark grey areas) consists of chromium carbide particles, zone 2 (light grey areas) consists of a Cr-Co-Ni solid solution, zone 3 (light grey-white areas) consists of a Ni-Co-Cr solid solution and zone 4 (black areas) consists of a Cr-Al-Ni-Co solid solution. Furthermore, there are some black areas that correspond with powder porosity (zone 5).

3.2 Microstructural Characterization of the Coatings

SEM image of the polished cross-section of the as-sprayed HVOF 75Cr₃C₂-25CoNiCrAlY top-coating with a CoNiCrAlY bond-coating is shown in Fig. 4a. The compositional distribution of top-coating shows an essentially two phase structure of dark carbides in a bright metallic matrix (Fig. 4b). The retained carbide concentration remained high, being evenly distributed throughout the coating with no bands of carbide free zones. As in the starting powder, the metal matrix displays zones of different colours (Fig. 4b): Cr-Co-Ni solid solution (light grey areas), Ni-Co-Cr solid solution (white areas) and Cr-Al-Ni-Co solid solution (black areas). The porosity value content of as-sprayed coatings was around 0.74 % (value calculated by means of optical microscopy technique).

The bond-coating shows a single-phase microstructure and has not retained the typical two-phase microstructure: γ -matrix Co–Ni–Cr solid solution and β -CoNiAl phase. The absence of visible β -phase in the as-sprayed HVOF coating had been reported to be caused by the dissolution of the β -phase into the γ -matrix due to severe plastic deformation of the particles upon impact with the substrate or as consequence of the rapid solidification of sprayed particles on impact, not giving enough time for the β -CoNiAl phase to precipitate out, resulting in the formation of a single γ phase [23, 24].

After heat treatment at 900°C, precipitation of fine carbides occurred throughout the top coating (Fig. 5a). This precipitation is a consequence of the carbide dissolution in the metallic binder phase produced in-flight during the HVOF thermal spray process. Carbide dissolution occurs when the matrix becomes molten in-flight, leading to supersaturation of Cr and C into the metallic phase which is trapped within the coating due to the high rate of cooling. This supersaturation involves a rapid nucleation upon heat treatment and generates widespread carbide precipitation in the supersaturated binder phase. This process is in accordance with the related for other authors [9, 11,







29]. Continued carbide precipitation and growth of the particles occurred during the thermal exposure at 1000 °C, with an average particle size larger the lower the temperature of heat treatment (Fig. 5b). Moreover, one can observe the formation of small black Cr₂O₃ regions inside the coating and black Cr₂O₃ layers near the coating surface. Finally, the carbide particle tends to coalesce and form larger carbides of complex morphologies at a temperature of 1100 °C. The carbide growth leads to increasing degrees of carbide coalescence and bridging and as a result provides a carbide skeletal structure, with the presence of higher quantity of black Cr₂O₃ regions (Fig. 5c). The porosity values of all as-sprayed and heat treated coatings were very similar, always lower than 1%, being representative of the high density values obtained through high velocity sprayed coatings.

Fig. 6a shows the microstructure of HVOF-sprayed CoNiCrAlY bond-coating after heat treatment in air at 900 °C. After 4 h of heat treatment the typical two-phase γ/β microstructure is now clearly visible. The reappearance of the β -phase is attributed to the fact that the heat treatment alleviates the stresses that were initially responsible for the dissolution of the β -phase or the fact that the coating was held at 900°C for a enough time to allow diffusion and the excess of Al in the γ phase caused the nucleation and growth of the β phase and the system reached its equilibrium state [22, 24]. Furthermore, one can observe the formation in the splat boundaries of an oxide scale composed of Al_2O_3 as well as mixed spinel-type oxides. At higher temperature of heat treatment (1100 °C) the oxidation of the coating progresses and one can observe an increase of the oxide scale thickness, both in the inter-splat boundaries as in the bond coat-top coat interface (Fig. 6b).

Fig. 7 shows the comparison of XRD patterns for the sprayed powder and for the Cr₃C₂-CoNiCrAlY coatings (as-sprayed and thermal treated at different temperatures). In the as-sprayed coating, Cr₃C₂ and γ-CoNiCr matrix diffraction peaks were the major phases identified. As the heat treatment temperature increases, the γ-CoNiCr peaks get increasingly sharper and there is a greater degradation of the Cr₃C₂ phase. New Cr₂O₃ peaks appear as consequence of carbide oxidation. Furthermore, the presence of α-Al₂O₃ and spinel-type mixed oxides was observed. As suggested by Tang et al. [25], peaks indicated as "spinel" are believed to be spinel-type oxides and represent either a mixture of some/all of other spinel mixed oxides such as NiCr₂O₄, NiAl₂O₄, CoAl₂O₄, CoCr₂O₄ and NiCo₂O₄, or a substitutional solid solution of (Ni,Co)(Al,Cr)₂O₄. Fig. 8 shows the oxide layer produced in the HVOF coating surface after 4 h of oxidation at 1100 °C. NiCr₂O₄ spinel forms as a result of solid state reaction between NiO and Cr₂O₃ particles in the scale gradually and forms the external oxide layer. The formation of spinels on the top scale may further enhance the oxidation resistance due to their much smaller diffusion coefficients of the cations and anions than those in their parent oxides [26].

The high temperature oxidation process has followed a diffusion controlled mechanism at 1000 and 1100 °C. It is noticed from the visual observation that the scale formed on the surface of the





coating was uniform and free from cracks. EDS analysis indicates that the oxidised scale was mainly composed by oxide of chromium (Cr₂O₃) (Fig. 9a) and spinels of nickel and chromium/cobalt/aluminium (Fig. 9b). Tang et al. [27] have reported the formation of pure alumina in the beginning stage of oxidation (1 hour exposure at 1000°C) for HVOF sprayed CoNiCrAlY coatings. However, a dual oxide layer spinel outer layer and alumina sublayer has been observed for longer exposure times at 1000°C. They have discussed their observations such that at the beginning stage of oxidation (1 hour) the Al activity on the surface of the coating is high enough to form Al₂O₃, but they have mentioned that as Al is consumed in the coating surface the Al depletion near surface becomes so severe that Al activity in the surface drops lower than a certain threshold level where spinel type oxide forms (instead of alumina) as a result of outward diffusion of Cr, Ni, Co from the alloy through the previously formed alumina layer.

3.3 Microhardness evolution of sprayed HVOF coatings as a consequence of heat treatment,

The microhardness values, measured in the polished cross-section of the Cr₃C₂-CoNiCrAlY and CoNiCrAlY coatings and in the polished top coating surface, are shown in Table 2. Although there is some dispersion of the results, a trend in the evolution of microhardness values could be observed.

The hardness measured in the cross-section of the top coating shows a maximum value at 900 °C of heat treatment and a slight softening at higher temperatures. This response was attributed to the precipitation of chromium carbides through the heat treatment, with the maximum hardness achieved when the carbide nucleus reached the optimum size to strengthen the structure. High density of fine, hard and dispersed precipitates in the matrix, as shown in Fig. 5b, significantly increase the coating microhardness. The trend to softening at high temperature was the result of the carbide structure coarsening [28, 29]. However, after heat treatment, the micro-hardness measured in the surface coating has been enhanced and presents an upward trend with increasing the heating temperatures, firstly as a consequence of the chromium carbide precipitation and secondly on account of the formation of a harder oxide layer developed on the top coating surface. These results are in agreement with the previous results published by Mattews and Guillemany in the study of heat treated CrC-NiO HVOF coatings [9, 29].

3.4 Tribological performance and thermal shock resistance of the sprayed HVOF coatings

The wear behaviour of the top coating as a consequence of heat treatment is shown in Table 3. In order to see the bond coat effect in the tribological performance of the top coating, the wear performance of the monolayer coating deposited directly on the steel substrate was compared with the wear behaviour of the bi-layer coating. For all coated samples the range of the dynamic friction

coefficient was within the range of 0.66 to 0.79. No correlation was detected between the friction coefficient and the wear resistance.

For the monolayer coating, the heat treatment at 1000 °C and 1100 °C causes microcracking in the coating surface that involves an increase in the wear rate. The presence of these cracks is probably due of significant differences between coating and substrate thermal expansion coefficients that results in large increases in the residual stresses into the coating which reduces its integrity. The use of CoNiCrAlY bond-coating minimizes this effect concerning a better wear performance of the system. Furthermore, the adhesive and protective oxides formed on the coating surface sustained the abrasion without spalling and is claimed to be responsible for the improved wear resistance of the coatings heat treated at higher temperatures. The plasticity of the oxides, essential to sustain abrasive wear, has been reported to be adequate for Cr_2O_3 at high temperatures [30]. However, the presented results are an approach of the wear behaviour under high temperature conditions, since in the real work conditions the surface oxidation and the chemical surface can change with the high temperature and consequently can vary the wear mechanism.

Thermal shock resistance tests showed the benefits of using CoNiCrAlY as a bond-coating, assuring a correct coating/substrate adhesion avoiding delamination or spallation phenomena of the HVOF coating at temperatures close to $1100~^{\circ}$ C and maybe higher. The multi-layer Cr_3C_2 -CoNiCrAlY + CoNiCrAlY shows a better performance than the monolayer Cr_3C_2 -CoNiCrAlY coating (see Table 3). These results can be related with the thermal expansion differences between the coatings and the steel substrate.

4. Conclusions

In the present work, influence of heat treatment on mechanical and tribological performance of HVOF sprayed 75 Cr₃C₂-25CoNiCrAlY coating with a CoNiCrAlY bond-coating on hot work steel substrate has been investigated and the following conclusions are made:

- 1. Heat treatment of the top coating at 900°C produces the precipitation of fine carbide particles in the matrix phase, increasing the coating hardness. Higher temperatures of heat treatment led to growth of the carbide particles, with coalescence of grains leading to the formation of an extensive carbide structure that caused a hardness decrease inside the coating. However, one can observe a hardness increase on the top coating surface and a reduction of the wear rate as a result of the formation of a harder Cr₂O₃ phase produced by the oxidation of the chromium carbide particles.
- 2. The use of a bond coating (CoNiCrAlY coating) between the Cr₃C₂-CoNiCrAlY top-coating and the steel substrate reduced the difference in their thermal expansion coefficients,

- minimising the stress generation and improving the thermal shock resistance, the coating adherence and the wear resistance at high temperatures.
- 3. The results from this work show that multilayer HVOF Cr₃C₂-CoNiCrAlY + CoNiCrAlY coatings can be a potential solution to prolong the life of tooling and dies in hot-working processes. Nevertheless, long term exposure of these coatings in real industrial conditions needs to be studied for estimating the protection capabilities of these coatings.

Acknowledgments

The authors wish to express their gratitude to Spain's Ministerio de Eonomía y Competitividad for its financial support under project nº MAT2010-15913.

References

- [1] Y. Sun, T. Bell, The role of oxidation in the wear of plasma nitrided and PVD TiN coated steel, Wear 166 (1993) 119-125.
- [2] Y. Madorsky, M. Thompson, New Developments in Wear-resistance Tool Coatings for Stamping Applications. 2nd annual STAMPING Journal Forum, 2004, Detroit.
- [3] G.J. Gibbons, R.G. Hansell, Down-selection and optimization of thermal-sprayed coatings for aluminum mould tool protection and upgrade, J. Therm. Spray Technol. 15 (2006) 340-347.
- [4] M. Richert, A. Mazurkiewicz, J. Smolik, Chromium carbide coatings obtained by the hybrid PVD methods, JAMME 43/1 (2011) 145-152.
- [5] L.A. Dobrzański, K. Gołombek, J. Mikuła, D. Pakuła, Multilayer and gradient PVD coatings on the sintered tool material, JAMME 31/2 (2008) 170-190.
- [6] G. Cushnie, Pollution Prevention and Control Technologies for Plating Operations, (2nd edn), National Center for Manufacturing Sciences (NCMS): Ann Arbor, MI, USA, 2009.
- [7] V.A.D. Souza, A. Neville, Corrosion and synergy in a WC-Co-Cr HVOF thermal spray coating-understanding their role in erosion–corrosion degradation, Wear 259 (2005) 171–180.
- [8] S.S. Chatha , H. S. Sidhu, B. S. Sidhu, High temperature hot corrosion behaviour of NiCr and Cr_3C_2 -NiCr coatings on T91 boiler steel in an aggressive environment at 750 °C, Surf. Coat. Technol. 206 (2012) 3839-3850.
- [9] S. Matthews, B. James, M. Hyland, The role of microstructure in the mechanism of high velocity erosion of C 3(2) NiCr thermal spray coatings: Part 2 Heat treated coatings, Surf. Coat. Technol. 203 (2009) 1094-1100.
- [10] S. Matthews, B. James, M. Hyland, The role of microstructure in the mechanism of high velocity erosion of C13(2)NiCr thermal spray coatings: Part 1. As-sprayed coatings, Surf. Coat. Technol. 203 (2009) 1086-1093.

- [11] S. Matthews, M. Hyland, B. James, Long-term carbide development in high-velocity oxygen fuel/high-velocity air fuel Cr₃C₂-NiCr coatings heat treated at 900 °C, J. Therm. Spray Technol. 13 (2004) 526-536.
- [12] S. Matthews, B. James, M. Hyland, Erosion of oxide scales formed on Cr₃C₂-NiCr thermal spray coatings, Corros. Sci. 50 (2008) 3087-3094.
- [13] S. Matthews, B. James, M. Hyland ,The effect of heat treatment on the oxidation mechanism of blended powder C NiCr coatings, , J. Therm. Spray Technol. 19 (2010) 119-127.
- [14] C.T. Kunioshi, O.V. Correa, L.V. Ramanathan, High temperature oxidation and erosion-oxidation behaviour of HVOF sprayed Ni-20Cr, WC-20Cr-7Ni and Cr₃C₂-Ni-20Cr coatings, Surface Eng. 22 (2006) 121-127.
- [15] L.M. Berger, M. Woydt, S. Zimmermann, H. Keller, G. Schwier, R. Enzl, S. Thiele, Tribological behavior of HVOF-sprayed Cr₃C₂-NiCr and TiC-based coatings under high-temperature dry sliding conditions. Proceedings of the International Thermal Spray Conference, 2004, pp 468-477.
- [16] S. Frangini, A. Masci, A.D. Bartolomeo, Cr₇C₃-based cermet coating deposited on stainless steel by electrospark process: structural characteristics and corrosion behavior, Surf. Coat. Technol. 149 (2002) 279-286.
- [17] S. Matthews, B. James, M. Hyland, High Temperature-Oxidation of Cr₃C₂-NiCr Thermal Spray. Coatings under Simulated Turbine Conditions. Corros. Sci. 70 (2013) 203-211.
- [18] L. Ajdelsztajn, J.A. Picas, G.E. Kim, F.L. Bastian, J. Schoenung, V. Provenzano, Oxidation behavior of HVOF sprayed nanocrystalline NiCrAlY powder, Mater. Sci. Eng. A 338 (2002) 33-43.
- [19] F.W. Bach, L. Engl, C. BAC, E. Lugscheider, E. Parco, T. Duda, Evaluation of modern HVOF systems concerning the application of hot corrosion protective coatings, International Thermal Spray Conference 2003, Orlando, Florida, 2003, ASM International, Materials Park, OH, USA, 2003.
- [20] S. Saeidi, K.T. Voisey, D.G. Mccartney, The Effect of Heat Treatment on the Oxidation Behavior of HVOF and VPS CoNiCrAly Coatings, J. Therm. Spray Technol. 18 (2009) 209-2016
- [21] S. Kamal, R. Jayaganthan, S. Prakash, S. Kumar, Hot corrosion behavior of detonation gun sprayed Cr₃C₂-NiCr coatings on Ni and Fe-based superalloys in Na2SO4460% V2055 environment at 900° C, J. Alloys Compd. 463 (2008) 358-372.
- [22] J.M. Roy, L. Richter, L. Beauvais, B. Jodoin, Oxidation behavior of CoNiCrAlY bond coats produced by PS, HVOF and CGDS at temperatures of 1000 °C and 1100 °C, International Thermal Spray Conference 2011, Hamburg, Germany, 2011, DVS Media GmbH, Düsseldorf, 2011, pp. 779-784.

(94)

- [23] P. Richer, M. Yandouzi, L. Beauvais, B. Jodoin, Oxidation behaviour of CoNiCrAlY bond coats produced by plasma, HVOF and cold gas dynamic spraying. Surf. Coat. Technol. 204 (2010) 3962-3974.
- [24] S. Saeidi. Thesis: Microstructure, Oxidation & Mechanical Properties of As-sprayed and Annealed HVOF & VPS CoNiCrAly Coatings. December 2010. University of Nottingham.
- [25] F. Tang, L. Ajdelsztajn, J.M. Schoenung, Influence of Cryomilling on the Morphology and Composition of the Oxide Scales Formed on HVOF CoNiCrAlY Coatings, Oxid. Met. 61 (2004) 219-238.
- [26] U.K. Chatterjee, S.K. Bose, S.K. Roy, Environmental Degradation of Metals. Corrosion Technology Series/14. Marcel Dekker, New York, 2001.
- [27] F. Tang, L. Ajdelsztajn, G.E. Kim, V. Provenzano, J.M. Schoenung, Effects of surface oxidation during HVOF processing on the primary stage oxidation of a CoNiCrAlY coating, Surf. Coat. Technol. 185 (2004) 227-233.
- [28] F. Otsubo, H. Era, T. Uchida and K. Kishitake, Properties of Cr₃C₂ -NiCr cermet coating sprayed by high power plasma and high velocity oxy-fuel processes. J. Therm. Spray Technol. 9 (2000) 499-504.
- [29] J.M. Guilemany, J.M. Miguel, S. Vizcaino, C. Lorenzana, J. Delgado, J. Sanchez. Role of heat treatments in the improvement of the sliding wear properties of Cr₃C₂-NiCr coatings. Surf. Coat. Technol. 157 (2002) 207-213.
- [30] Y. Birol, High-temperature abrasive wear testing of potential tool materials for thixoforming of steels, Tribol. Int. 43 (2010) 2222-2230.

TABLE 1. Nominal composition of feedstock powders [wt. %].



	Co	Ni	Cr	Al	Y	C
M-427725	Bal.	32	21	8	1	2000)
K-880.23	9.5	7.5	Bal.	1.75	0.2	10

TABLE 2. Microhardness evolution of the coatings

Coating	Condition	HV0.3	HV0.3	
		Cross-section	Surface	
Top coating	As-sprayed	1043 ± 46	1108 ± 74	
Cr ₃ C ₂ -CoNiCrAlY	Heat treated at 900 °C	1153 ± 68	1181 ± 68	
	Heat treated at 1000 C	1147 ± 65	1242 ± 54	
	Heat treated at 1100 °C	1139 ± 59	1231 ± 56	
Bond coating	As-sprayed	504 ± 29	3 55 0	
CoNiCrAlY	Heat treated at 900 °C	445 ± 25	3 313 27	
	Heat treated at 1000 C	483 ± 19	(44):	
	Heat treated at 1100 °C	473 ± 14	(

TABLE 3. Tribological properties and thermal shock resistance of the coatings

Coating	Condition	Friction coefficient	Spècific wear rate [m ³ ·(m.N) ⁻¹ x10 ⁻¹⁶]	Thermal shock resistance
Bilayer	As-sprayed	0,76	5.5	1000
Cr ₃ C ₂ -CoNiCrAlY/	H.T. at 900 °C	0,66	3.9	good
CoNiCrAlY	H.T.at 1000 C	0,73	2.9	good
	H.T.at 1100 °C	0,74	2.8	good
Monolayer	As-sprayed	0,79	7.2	***
Cr ₃ C ₂ -CoNiCrAlY	H.T. at 900 °C	0,68	5.4	good
	H.T.at 1000 C	0,73	10.1	delamination
	H.T.at 1100 °C	0,66	10.5	delamination