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Microstructural and tribological studies of as-sprayed and heat-treated HVOF Cr_3C_2–CoNiCrAlY coatings with a CoNiCrAlY bond coat

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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 Cr_3C_2–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 75Cr_3C_2–25CoNiCrAlY coating with a CoNiCrAlY bond coat 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 Cr_3C_2–CoNiCrAlY coating was analysed.

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 are hard chrome plating. This is very effective at improving wear resistance, but hard chrome coatings seriously lose their wear protectiveness by increasing temperature, both because the mechanical properties decrease due to the metallic nature of the coating and because the coating loses hydrogen with a great decrease in hardness. Furthermore, there are increasing concerns over the environmental and social acceptability of the process, as consequence that all commercial plating baths use hexavalent chromium (CrVI), which is both highly toxic to the user and hazardous to the environment [6]. Additionally, 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 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 coating 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

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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 Cr_3C_2–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, Matthews [17] showed that in certain conditions the oxidation of Cr_3C_2–25%NiCr coatings is more pronounced than expected due to preferential oxidation of the Cr_3C_2 carbide-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 coatings for high temperature oxidation resistance [19,20].

In addition to these features, the coefficient of thermal expansion of Cr_3C_2–20%Ni ($10.3 \times 10^{-6}\ K^{-1}$) [21] is nearly similar to that of iron ($11.4 \times 10^{-6}\ K^{-1}$) that constitutes the base of most hot working tool materials [22]. 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 [23], with a coefficient of thermal expansion of $11.6 \times 10^{-6}\ K^{-1}$ [24], and accordingly in this work the same alloy was used both as binder phase in the top coating and as bond coat.

Even if the Cr_3C_2–CoNiCrAlY powder is commercially available, not many papers dealing with its mechanical or wear properties have been found [25]. 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 $75Cr_3C_2$–25CoNiCrAlY coating with a CoNiCrAlY bond coat and to explore 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 Cr_3C_2–CoNiCrAlY 75/25 powder (K-880.23), supplied by Flame Spray Technologies, were employed as the feedstock powders to produce the bond and top coatings respectively. The agglomerated and sintered powders were received with a nominal size distribution within the range of 22 μm to 45 μm and 15 μm 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 $l \cdot h^{-1}$; oxygen flow rate 944 $l \cdot min^{-1}$, and for the Cr_3C_2–CoNiCrAlY powder were: spray distance 360 mm; fuel flow rate 25.3 $l \cdot h^{-1}$; oxygen flow rate 900 $l \cdot min^{-1}$. 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 coat effect in the wear resistance and in thermal shock resistance behaviour of coatings, some monolayer Cr_3C_2–CoNiCrAlY coatings were deposited directly on the steel substrate.

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

	Co	Ni	Cr	Al	Y	C
M-427.25	Bal.	32	21	8	1	–
K-880.23	9.5	7.5	Bal.	1.75	0.2	10

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) Kα (λ = 0.15406 nm) radiation. The analysis depth of XRD is a function of the incidence angle which depends to the diffraction angle and material. For Cr_3C_2–CoNiCrAlY coatings the analysis depth can fluctuate between 3 and 15 μm, and consequently the obtained spectra give an idea about the phase 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 coating samples was evaluated by heating the samples at several temperatures for 1 h, 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 0.2 μm.

The microhardness was measured on a polished cross-section of the HVOF coatings and in the oxidised coating 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 oxidised surface of the coated samples was 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.

Tribological evaluation of coated substrates was carried out, under dry conditions, using a pin-on-disc tribometer, manufactured by CSM Instruments (Switzerland), according to ASTM wear testing standard G-99. Samples were prepared for wear testing by grinding and diamond polishing up to average surface roughness levels (Ra) near 0.2 μm. Wear tests were carried out by sliding a 6 mm diameter WC–6Co sintered pin against the polished samples at a constant linear speed of 0.10 $m \cdot s^{-1}$ with an applied load of 30 N. All the tests were performed at 25 °C