Wear mechanisms of 13Cr steel thermally sprayed coatings

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Résumé :

La projection arc-fil est une méthode très utilisée pour produire des revêtements à partir des fils métalliques, pour protéger les pièces mécaniques contre l'usure et la corrosion. Les revêtements en acier 13Cr ont été produits par projection arc-fil. La microstructure des revêtements a été examinée par MO et MEB. La composition et la structure ont été définies par EDS et DRX. Les revêtements obtenus présentent une microstructure lamellaire avec la présence des oxydes, pores, et particules non fondues. Les propriétés mécaniques ont été évaluées par microdureté Vickers. Le test d'usure a été réalisé par un tribomètre bille-sur-disque conformément à la norme ASTM G99. L'objectif de ce travail est d'étudier le mécanisme d'usure par observation MEB des pistes d'usure.

Abstract :

Arc wire spray is a well established method to deposit metallic wires to protect mechanical components from wear and corrosion. 13Cr steel coatings were produced using arc wire spray method. Microstructure of coating was investigated by MO and SEM. Composition and structure were determined using EDS and RDX. Coatings present a lamellar microstructure with the presence of oxides, pores, and unmelted particles. Mechanical properties were evaluated by microhardness Vickers. The wear test was conducted by ball-on-disc apparatus according to ASTM G99. The aim of this work is to study the wear mechanism by SEM observation of worn tracks.

Key words: Arc wire spray, splat, resolidified particle, microhardness, wear mechanism...
1 Introduction

Thermal spraying is a general term for a group of coating techniques such as air plasma spraying (APS), vacuum plasma spraying (VPS), high velocity oxygen fuel (HVOF), and wire arc spraying. These techniques are used to deposit various materials available in powder or wire forms as molten or semi molten particles onto the surface of a substrate.

Machine parts, such as pump parts (sealing, impellers, bodies, etc.), hydraulic pistons, petrochemical valves, shafts and journal bearings, components for the food and packaging industry and for the aeronautical industry and others, are often protected against wear by thermal spray coatings [1, 2].

Wire arc spray (electric arc spray) is a well-developed technology to deposit coating layers up to a few millimetres in thickness. Wire arc spraying is a flexible, rapid, and relatively cheap method compared to the other deposition techniques. In this process, an electric arc forms between two wires as consumable electrodes made from the desired coating material. Thermal energy resulting from the arc melts both wires, which continuously are fed into the system. Molten metal in the form of droplets is broken up (atomized) into finer particles and accelerated toward the substrate by a high-velocity air stream. [1] Coatings are built up from the impact, flattening, and solidification of fine molten particles, splats, connected to each other by mechanical and metallurgical bonding, forming a layered structure with anisotropic behaviour. The coatings exhibit different thermo mechanical properties in longitudinal and transverse directions. [3, 4] The structural integrity of coatings depends highly on microstructural properties of the deposition. Therefore, the microstructural characteristics are more critical in thermal sprayed depositions and require thorough investigation. Porosity, oxidation, microcracks, and voids are the most important microstructural characteristic features of arc-sprayed coatings.

In recent years, FeCr alloys have received much attention as high-temperature oxidation and wear resistance materials for the requirement of the utilities to increase the thermal efficiency of power generation plants. A number of high strength 9–12% Cr steels have been developed for application as construction materials in such advanced power plants[5]. In addition, the FeCrNi and FeCrAl coatings have been successfully applied in the contexts of corrosion, wear and oxidation resistance at elevated temperatures[6].

Thermal-sprayed coatings of chromium steel are being employed to decrease the coefficient of sliding frictional behaviour between various sliding components [7] the splat morphology plays an important role in the nature of the deposit build-up process and consequently affects the microstructure and properties of the sprayed materials [8]. The generation of residual stress at the interface may cause failure due to plastic deformation, fracture; delamination and/or surface wear [9]. The complex microstructure of this kind of materials affects on the mechanical properties and consequently on the wear resistance.

It has been found that the main wear mechanism related to the lamellar structure of the coating is the splat delamination. Oxide layers between splats are the weak links in many spray coatings. [10] Delamination was shown to be easier when the splats were parallel to the coating surface and more difficult when they were wavy and not parallel to the interface [11].

A-Edrisy et al in their study on wear of thermal sprayed low carbon steel coating on aluminum substrates in sliding distance [12], the wear mechanism at high loads was the fracture of splats due to severe plastic deformation at the tips of splat, and porosity or roughness in the surface makes this mechanism worse.

In general, the self-mated pairs show low life cycles compared to dissimilar pair due to the adhesive wear. Thus nonmetal-on-metal or nonmetal couples show the lowest coefficient of adhesion.
Adhesive-wear-resistant material is normally based on a dissimilar materials pair or a similar-materials pair with dissimilar surface properties.

In this study metal-on-metal couple was used to investigate the wear mechanism under dry sliding between two chromium alloys with different microstructure and surface properties: the first is wrought ball made in 100Cr6 steel and the second is 13Cr steel thermally sprayed coating on mild steel. The aim of this work is to investigate the microstructure of 13Cr arc spray coating and its influence on wear mechanism by SEM observation.

2 Materials and experiment details.

13Cr steel wires were used as the spraying feedstock. A METALLISATION 123 type arc spraying device was applied to form about 400 µm thick layer on the surface of commercial carbon steel C35 of Ø25 mm x 8 mm discs. The wire arc spray process parameters are showed in table.1

Substrates discs were cleaned and roughened by blasting with corundum grits prior to spraying, degreased ultrasonically in acetone, then immediately sprayed due to their rapid oxidation. To ensure a good adhesion coating, substrates are coated primarily by a thin inner bonding coating of nickel/Aluminium.

Table 1 parameters of arc wire spray

<table>
<thead>
<tr>
<th>Current (I)</th>
<th>voltage (V)</th>
<th>Spray distance (mm)</th>
<th>Air pressure (Bar)</th>
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<tr>
<td>100</td>
<td>35</td>
<td>100</td>
<td>3,5</td>
</tr>
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To determine the main characteristics describing 13Cr particles in-flight properties from the arc wire gun to the surface of the substrate, Oseir's (Oseir Ltd., Tampere, Finland) SprayWatch 2i diagnostics system was used.

SprayWatch is an optical camera based system that uses a high-resolution, 12-bit fast shutter CCD array camera to create digital images of the spray and measures the particle properties in-situ[13]. The most important properties are, among others, particle flux, velocity and temperature.

Samples were sectioned and mounted in resin epoxy, they were then ground using silicon carbide followed by polishing with a sub-micron alumina suspension. The Examination of coating microstructure was carried by MO and SEM on cross-sectional samples. Porosity was evaluated by using image analysis technique (Imagej software), element analysis were examined using Jeol JSM 6360LV scanning electron microscope (SEM) coupled with an energy dispersion spectroscopy (EDS). XRD analysis of as-sprayed coatings was performed by means of a Brukers D8 Advance diffractometer, employed at ambient temperature a CuKα.

The friction tests were conducted with a ball-on-disk test machine in accordance with the procedures recommended in ASTM G99 and using a different loads ranging from 2 N to 12 N. The counter body was 6-mm diameter ball made of 100Cr6 steel. Both coated disc and counter body were cleaned in acetone and dried in air prior to wear test. The relative humidity and temperature were held constant during the test (Hr=15–20% and 20 °C, respectively). The track diameter of d=16 mm and a sliding speed of v=0.1 m s⁻¹ were used.

Every worn morphology surface of the samples was observed, and wear rate was calculated from the following equation assuming without ball wear [14]:

\[
disk \text{ volume loss} = 2πR[r^{2}\sin^{-1}(d/2r) - (d/4)(4r^2 - d^2)^{1/2}] \quad (1)
\]

Where \( R = \) wear track radius, \( r = \) ball radius, \( d = \) wear track width
3. RESULTS AND DISCUSSION

3.1. Phase structure.

Figure 1-a. shows the XRD pattern of present phases formed in 13Cr sprayed coating. Fe and Cr phases are the main constituent of the coating. Due to the fact that the coating was deposited on plain carbon steel substrate in air, some oxides including FeO with low intensity were determined, which it can be confirmed by EDS microanalysis of cross section samples (figure 3): That is to say, it can be pointed out that oxide phases are formed during the interacting process of air with melted particles. Chromium steel alloys have received much attention as high-temperature oxidation resistance materials [15].

![XRD pattern](image1)

![Micrograph](image2)

Figure 1 a) RDX pattern of as-sprayed 13Cr coating, b) Micrograph of cross section 13Cr coating obtained by MO

The spray process makes the particles to crystallize when they solidify from molten state. As figure 2-a shows the plot of average temperature obtained by SprayWatch system. The temperature is varying from 1200°C to 1500°C which confirms the melting state of particles in-flight.

![Temperature plot](image3)

![Velocity plot](image4)

Figure 2 In-flight particle velocity (a) and temperature (b) of projected in-flight particles as a function of the monitoring time
3.2. Microstructure

Microstructural characterization of thermal spray coatings involves quantitative measurements of geometrical features such as porosity (in the form of voids, cracks and other defects) and analysis of material aspects in coatings such as splat structure, interfaces, phases, etc.[1, 16] Depending on these properties, microstructural features can be elucidated. Figure 1-b and figure 3 show a typical cross-sectional microstructure of the arc sprayed 13Cr coating on Ni-Al bond coating deposited on carbon steel substrate.

![Figure 3](image)

All coating layers contain porosity, oxides, cracks, unmelted particles and inclusions. Figure 3 shows the SEM micrographs of the polished cross-section of the coatings, showing typical aspect of thermal sprayed lamellar structure. Where the very dark contrast corresponds to porosity, and the gray contrast corresponds to fine oxide layers (FeO). [1]

Generally speaking, coatings deposited by arc wire spray exhibit a significant amount of unmelted particles, resolidified particles, and porosity, the latter and notably the interconnected pores (figure 5-b) may influence the wear and corrosion resistance.

Coating thicknesses of 13Cr coating was determined by SEM. The thickness of 13Cr was found about 400µm. The volume fraction of porosity of 13Cr was about 7±1%.
Figure 4  a) fractured debonded coating   b) high magnification

Figure 4-a show fractured debonded coating and observed via SEM, most splats appear separated from their neighbours especially splats with smooth surface (Figure. 4-b), evidence of a lack of metallurgical bonding between them. Thermal spray deposits microstructure is strongly depending on the size, chemistry, phase, and trajectory of sprayed particles in the spray jet, arriving particles will be either fully or partially molten, resolidified, or unmelted. The coating layer contains microcracks (figure. 5-a). This can be attributed to thermal residual stresses. The nature of the residual stresses significantly influences various types of coating property, such as the bond strength, hardness and wear resistance.

Figure 5  Sem micrographs showing   a) microcraks   b) interconnected pores

Microhardness

Vickers microhardness values of 13Cr are presented in Figure. 6. Microhardness values that were taken along the cross-section of the sample were not uniform due the inhomogeniety of microstructure. But mainly the microhardness is increased according to the microhardness of 13Cr wire ( 320 Hv0.2) thanks to the rapid cooling of deposited particles, as shown in figure 2-b, molten particles leave the gun with 50 m.s$^{-1}$ to cross the spray distance of 120mm, so very short dwell time of particles in-flight : solidification takes place since the particle have impacted on the surface of substrate or the flattened particles with rapid cooling leading to ultrafine grain size ( about 1µm of size )[1] It was observed that some spherical particles in the coating exhibit very high microhardness which makes them not unmelted particles but resolidified ones.
In the electric arc spray process, the wires are melted into particles by an electric arc formed between them. There are no hot gas jets associated with electric arc spray. Unlike other thermal spray processes, droplet/particle temperatures begin to decrease immediately after the particles are formed or atomized in the arc zone, leaving the wire tips as they melt. The dwell time that produces increased heating in other processes only serves to cool particles in electric arc spray, because the atomizing jets are only used to accelerate the particles toward the surface to be coated. However, since the particles are still hot from the melting process, interactions between air and the hot particle surfaces do still occur. The oxides disperse on impact and become included in the deposit, as with the other processes.[17] It is to note the interlamellar areas exhibit microhardness relatively higher than the inner of splat.

### 3.2. Wear testing

Coated samples have rough surfaces like a characteristic property of arc wire spray coating, as shown in figure 7-a. The top surface was observed by SEM figure 7-b, the rough surface is evident due to coating forming by stacking of flattened particles, showing a good melting state at the impact, some of them are unmelted ones, this latter can contribute to form more pores and roughen the surface. That’s why samples must be polished to eliminate the effect of roughness on wear test. Roughness Ra of as-sprayed surface of coatings was measured by TAYLOR HOBSON Surtronic Duo instrument, it was reduced from 20 µm to 5.10¹ µm. Some defects can be observed in top surface as porosity or pull of particle during polishing operation figure 7-c.
The most important governing parameters for sliding wear are load and sliding velocity. The influence of load on coefficient of friction of 13Cr coating is presented in Figure 8-a. It is observed that coefficient of friction decrease with increase in applied load.

Based on the classical theory of adhesion, the frictional force is defined as:

\[ F = \tau_a A_r \quad \text{and} \quad \mu_a = \frac{F}{L} = \frac{\tau_a A_r}{L} \]  

(2)

Where \( \tau_a \) is the average shear strength during sliding and \( L \) is the applied load. \( \mu_a \) is adhesion induced friction coefficient.

For elastic contact of a spherical indenter and a homogenous half-space, the contact area \( A_r \) can be estimated as:

\[ A_r = \pi \left( \frac{3L R}{4E} \right)^{2/3} \]  

(3)

Where \( E \) is the effective elastic modulus and \( R \) is the effective radius of curvature.

Combining equations. (2) and (3), the friction coefficient corresponding to the pure elastic adhesion is given by

\[ \mu_a = \pi \tau_a \left( \frac{3R}{4E} \right)^{2/3} L^{-1/3} \]  

(4)

Where \( \mu_a \) is the coefficient of friction, \( \tau_a \) is the average shear strength during sliding and \( L \) is the applied load. \( E \) is the effective elastic modulus and \( R \) is the effective radius of curvature. Thus the coefficient of friction is inversely related to the cube root of the applied load and the observation of Figure. 8-c well conforms to this relation. The adhesion is the dominant friction mechanism [19], where the coefficient of friction decreases with the applied load.

Figure 7  a Top a) photo of coated disc used in test wear b) top surface of 13Cr coating as-sprayed observed by SEM  c) top surface of polished coating observed by MO
The increase of the wear with the rise of load (figure 8-b) can be explained in the following way: when a sphere is loaded against a plane, the maximum stress occurs at the centre of the contact circle. The mean pressure over the area of contact will be proportional to $L/A_r$ where $A_r = \pi a^2$, where $A_r$ the Hertz area of contact, and $a$ is the radius of area contact.

Combining this equation with the following Hertz equation (3). It can be observed that the mean normal stress will vary as $L^{1/3}$, both the area of contact and the depth below the surface at which the maximum normal and shear stresses will occur, will increase with an increase in load. The coating’s elastic and/or plastic deformation will also affect the stress. At higher loads the adhesive effect of cold welding will also increase, this will cause a higher degree of material removal from the coatings. The higher the load, the higher the level of shear stress responsible for plastic flow, so this causes more material to be displaced. The tensile stress will also go up with the load, which will favour cracking and hence higher levels of fracture in the coatings. The abrasive effect of wear debris is also expected to increase with the load, since these debris will penetrate deeper into the coating.

Figure 8  a) Evolution of the friction coefficient along the sliding distance for the loads tested. b) wear rate of coating under different loads. c) Influence of applied load on the coefficient of friction of 13Cr steel coatings.
It is generally difficult to clearly establish the dominant sliding wear mechanism; given that this wear is known to occur mainly by adhesion [20, 21], delamination [22] and/or fretting [23]; in the present case, to identify wear mechanism, worn surfaces were observed by SEM. The wear of wrought mild steel (uncoated sample) was observed in figure 9. It can be seen the grooves made by the abrasion of hard ball under load of 2N due to the big difference of microhardness of two bodies. However for coatings with higher hardness and their complex microstructure will certainly behave differently.

At lower load 2N, there is no full contact between the ball and coated disc. Because of this, near the worn region as seen in Figure 10-a, it is possible to observe unworn depth region under the surface. However fracture of splats can take place near the macropore as it is observed in Figure 10-b.
At 5N of load the surface worn presented in the figure 11-a show the debris wear produced during friction. The dominant mechanism in this wear process is the delamination of splats which form the coating. Debris appear like-flake produced by this mechanism has high dimensions because it comes from the detachment of single splats, though in other cases it could be generated by the elimination of bits of coating containing more than one splat. [24]

Debris are namely the fraction of delaminated splats of 13Cr coating into ultrafine particles due to their different primary grain size (figure 11-b). This may lower the friction coefficient and decrease the wear rate.

It was reported that the sliding wear of thermal spray coatings could be attributed to splat delamination [11] due to the weak links caused by the oxides veins [10], as it is described in microstructure section and confirmed by EDS microanalysis, and RDX.

At load of 8N, It can be seen that worn track has a scale-like appearance (figure 12-b): splat in contact with the counter ball will be subjected to shear stress, leading to delamination figure (12-c) within oxide veins.

Figure 11: a) worn track of coating under 5N  b) worn track of under high magnification
Figure 12-a shows that some cracks distribute around the scaling pits, and a few slight plows exist on the coating surface.

As shown in Figure 13-a, the wear rate is the highest for the 12N of load. The wear process of 13Cr coating mainly involves the brittle splat delamination (figure 13-b).

It's well known that the wear rate is tribo-system property, this is for what, worn surface of ball was investigated. figure 12-d shows worn surface of the counter ball at 5N of load with the presence of grooves that can be explained by the complexity of coating microstructure especially inhomogeneity of microhardness in the coating constituents including hard oxides and resolidified particles with a relatively rough surface, this latter can be understood from the oscillation of COF evolution curves at loads ranging from 2N to 8N.
However the sphere of counter body 106Cr at 12N was subjected to an adhesive wear, Figure 14-a shows particles adhered into surface detached from coating, due to cold welding between the two surfaces in contact. Figure 14-b Shows a removal area from the surface of ball may due to adhesion with the coating.

**Conclusions:**

- 13Cr steel wire was sprayed on mild steel substrates using arc wire spray process. The produced coating exhibit a lamellar microstructure, with different constituents: splats, oxides, pores, unmelted and resolidified.
- It has been found that the microhardness of coating was increased according to their wrought material. The main reason of rising hardness is the ultra-fine grain size of coating resulting from the rapid cooling of molten state to solidification on the impact on substrate.
• Friction coefficient decrease with to the applied load. So the friction is governed by adhesion theory.
• The presence of oxide increases also the hardness of the coating, which may be beneficial to improving the wear resistance. But the oxide layers mainly originate in the inter-splat boundaries, thus it detrimentally decreases the cohesive strength between splats. Moreover, the micro-cracks often initiate from inside of the oxide layers with the action of concentrated stresses. As a result the main mechanism of wear in this case, is delamination of splats. Porosity may affect the wear to become worse not to only increase cracking propagation but cause splat tips fracture near the macro-pores.
• The wear rate increase with load. It is very common that in a real contact more than one wear mechanism is acting at the same time. Abrasion mechanism can act as wear mechanism especially at loads ranging from 2N to 8N. At high load 12N, a transfer of small particles appears between the two bodies in friction leading to an adhesive mechanism of wear accompanied by delamination.
• The wear behaviour of 13Cr coating samples depends on the microstructure, microhardness, friction characteristics and environmental conditions.

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