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Thermal cycling assessment of steel-based thermal barrier coatings for Al protection

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There is a strong interest from the transportation industry to achieve vehicle weight reduction through the replacement of steel components by aluminium parts. For some applications, aluminium requires protective coatings due to its limited wear and lower temperature resistance compared to steel. The objective of this study was to assess the potential of an amorphous-type steel as a thermal barrier coating (TBC) through the evaluation of its spalling resistance under thermal cycling. The amorphicity of the coatings produced via plasma spraying of specialised alloyed steel was confirmed through x-ray diffraction (XRD). The thermal cycling behavior of the resulting coatings was evaluated by cycling the coated face of coupons to a maximum cycle temperature of 500°C, with heating rates in the range of 50°C/s. These tests were performed in a custom-designed laser rig, capable of achieving a complete cycle in a few seconds. The stability of the coating amorphous microstructure in this temperature range was established. However, it was found that the spalling resistance of the steel-based amorphous coatings to thermal cycling is well below that of conventional arc-sprayed steel coatings, probably due to the lower initial adhesion of the amorphous coatings.

1 Introduction

In the last years, the transportation industry has been facing increasing pressure to decrease vehicle weight in order to reduce fuel consumption as well as the associated emissions. Significant weight reduction can be achieved by replacing steel components by aluminum (Al) parts. However, as Al exhibits poor wear and lower melting point compared to the current steel parts, there is a rising interest in shielding Al parts with protective coatings to alleviate those issues [1-3].

While ceramics offer good insulating properties and high hardness, their reliability is a major issue for such application. Their poor toughness can lead to catastrophic failure upon mechanical loading or thermal shock. Furthermore, their coefficients of thermal expansion are typically much lower than that of the metallic substrates to be protected, causing a problematic mismatch for high-temperature applications. For example, yttria stabilised zirconia displays a CTE of $10 \times 10^{-6} / ^\circ\text{C}$ while the CTE of Al is $24 \times 10^{-6} / ^\circ\text{C}$ [4]. One possible alternative is to use metal-based thermal barrier coatings (TBCs). Nanostructured or amorphous metals are particularly of interest as they offer low thermal diffusivity and conductivity. For instance, the thermal diffusivity of a plasma-sprayed Fe-based amorphous coating has been measured at $6 \times 10^{-7} \text{ m}^2/\text{s}$ [3], which is half the thermal diffusivity of conventional SS300 series arc-sprayed coatings. Amorphous metals also display high toughness, hardness and wear resistance, all desirable properties for a protective coating [5, 6]. Finally, amorphous, Fe-based coatings present relatively high CTE. The CTE of Fe-based amorphous coating was elsewhere measured at $15 \times 10^{-6} / ^\circ\text{C}$, offering a better match with an Al substrate [3]. This high CTE originates not only from the metallic composition, but also from the amorphous state, that typically displays higher CTE than the crystalline counterpart.

Amorphous-type metal-based coatings have been produced out of most thermal spray techniques. Among those, plasma spray offers a remarkable capability to produce this type of materials as coatings: its high heat input enabling full melting of the alloys is combined with a high cooling rate associated with the rapid solidification of the molten droplets upon impact. This rapid quenching from the melt is necessary to suppress the nucleation and growth of the crystalline phases [7]. As a comparison, it has been shown that complete amorphisation of the feedstock material selected in this study was not possible with HVOF or arc spraying which coatings contained unmelted particles showing borocarbide or carbide precipitates [3, 7-9].

Most of the previous work involving amorphous metal-based coating has focused on corrosion and wear resistance evaluation [5, 6, 9-13]. It has been shown, for instance, that HVOF Fe-based amorphous coatings offer superior wear performance than bulk steel, hard Cr and Al_2O_3 coatings [5, 9]. Fe-based amorphous coatings have also been applied successfully on Al to improve wear performance [13]. However, little has been done regarding heat protection and associated challenges, such as coating resistance to thermal cycling.

The objective of this study was to assess the potential of an amorphous-type steel as TBCs through the evaluation of its spalling resistance under thermal cycling. Specialised alloyed steel powder was deposited via plasma spray and thoroughly characterised through XRD and SEM. The thermal cycling behavior of the coatings was evaluated by a custom-developed laser rig and compared with conventional arc-sprayed steel coatings.

2 Experimental Procedures

2.1 Materials

The powder feedstock selected for the production of amorphous coatings was the SHS-717 (Nanosteel, USA), which is a strongly alloyed steel (Fe-25Cr-8Mo-10W-5Mn-5B-2C-2Si). It was specially designed to maximize glass forming ability, hardness and wear/corrosion resistance. Fig. 1 shows the microstructure and particle size distribution of this powder measured with a laser diffraction particle size analyzer (LS320, Beckman Coulter, USA). Its size distribution between 10 and 100 μm as well as its spherical shape are well-adapted to plasma spraying.

For comparison purpose, two commercial stainless steel (SS) wires were also used, 61T and 80T (Praxair, USA). The two steels have been selected in order to obtain coating with an austenitic FCC crystalline structure of a nominal composition 18% Cr 8%Ni (SS 304, 80T) and a BCC ferritic structure of a nominal composition 14%Cr (SS430, 61T). The coatings were produced using arc spraying.

Fig. 1. SHS-717 powder feedstock characteristics.

The coatings were deposited on degreased and grit blasted 6061 Al cylinders (25.4mm dia X 16 mm height).

2.2 Spraying Conditions

Plasma air spraying was performed using a F4-MB torch (Sulzer-Metco, Switzerland) or an Axial III system (Mettech, Canada). The spraying parameters, detailed in Table 1, were selected to provide a large range of in-flight particle temperatures and velocities.

The stainless steel wires were sprayed using both the BP400 (Praxair, formerly Miller, USA) and the SmartArc systems (SA, Sulzer-Metco, Switzerland). The arc spraying conditions are also detailed in Table 1. All coatings displayed thicknesses between 400 and 600 μm .

The in-flight particle measurements were performed using the DPV-2000 (Tecnar Automation, Canada).

Table 1: Spraying parameters

PLASMA	Sample	Ar (slpm)	H2 (slpm)	I (A)	Power (kW)	SOD (cm)	T (°C)	V (m/s)
	F1	70	5	500	28	12	2230	222
F4-MB	F2	35	12	700	39	12	2400	188
	F3	70	5	300	18	20	2117	148
Axial	A1	0%*	15%*	180	131	20	n/a	n/a
	A2	70%*	20%*	170	79	20	n/a	n/a
ARC	Sample	Wire	GP (psi)	I (A)	SOD (cm)	T (°C)	V (m/s)	
BP400	M80	80T	60	100	10	2178	91	
	M61	61T	60	100	10	2321	96	
SA	S80	80T	60	100	15	2191	160	
	S61	61T	60	100	15	2332	161	

*balance of nitrogen

GP: gas pressure

SOD: standoff distance

2.3 Coating Evaluation

Powder and coating microstructures were observed using either a field emission SEM (S4700, Hitachi Instruments Inc., Japan) or a standard SEM (JSM-6100, JEOL, Japan). Samples were prepared using standard metallographic procedures to produce a polished cross-section. The phases present within the various powders and coatings as well as crystallinity indices (I_c) were determined by XRD using a D8 Discover x-ray diffractometer (Bruker, USA) with Cu-K α_1 radiation at 1.6 kW. I_c is defined in this paper as the ratio of the areas of the Bragg peaks over the total areas of the spectrum between 30 and 55°. Pull tests (ASTM C633-01) were performed to evaluate as-sprayed coating adhesion strength on aluminium.

Three samples per spraying conditions were then cycled thermally until failure, e.g. until coating delamination reached about 25% of the sample surface, and the number of cycles recorded. Thermal cycling was performed using a laser rig developed in-house. The heating of this rig is achieved using a continuous 3.3 kW CO₂ laser (10.6 μm). Sample temperatures are recorded with infrared optical pyrometers and cameras equipped with filters absorbing the 10.6 μm wavelength of the incoming CO₂ laser radiation. The sample is held by a spring loaded 4-point ceramic sample holder. There is an air jet amplifier at the front of the sample for cooling stage, e.g. both heating and cooling are performed on the same sample side. The system is interfaced with a computer using the Labview software to define a temperature profile for the front and back faces. The laser rig configuration is shown in Fig. 2.

At steady state, a maximum coating surface temperature of 500°C was obtained with a heating rate of about 50-55°C/s. The sample was then cooled down during 4 seconds to reach a minimum surface temperature of about 250°C, this cycle being repeated

until failure. Typical cycles are shown in Fig. 3. Coating delamination was easily observed from a local and sudden increase in temperature (hot spot) explained by the apparition of a gap of low thermal conductivity between the coating and the substrate. This criterion for failure has been used in the past [14]. An example of this hot spot is shown in Fig. 2.

Fig. 2. Thermal endurance laser rig configuration. In inset, a failed sample showing hot spot.

Fig. 3. Front temperature of a typical sample during cycling: max T is about 500°C and steady state is reached in about 5 cycles. *Pyrometer calibrated range did not allow T recording below 300°C.*

3 Results and Discussion

3.1 Coating Microstructure

As-sprayed amorphous coating microstructures obtained from plasma spraying are shown in Fig. 4. Coatings F1 and F3 present similar microstructures; splats are well defined and their content is uniform and homogeneous. A2 microstructure also presents typical splats, but their boundaries are less defined. Even if not investigated in this study, it is expected that the number and width of those interlamellar boundaries would affect the coating thermal conductivity. Therefore, it could be envisioned to minimise coating thermal conductivity through an optimisation of spraying parameters.

The microstructures of F2 and A1 coatings are more heterogeneous. There is a darker phase that was identified as oxides with EDS. Some vertical cracks were also seen under SEM in the two coatings: an example is shown in Fig. 2 for coating F2. Lastly, it was visually noticed that the overall color of those coatings was dark brown instead of the typical metallic grey color of the other coatings. Those different findings indicate a higher heat input during spraying. Among the F-series of coatings, the F2 coating was sprayed at the highest (i) H_2 flow, (ii) H_2/Ar ratio and (iii) plasma power. Thereby, the F2 plasma probably exhibited the highest enthalpy and thermal conductivity. This hypothesis is supported by the higher temperature values recorded for the F2 sprayed particles (Table 1). Regarding the A-series of coatings, the A1 particles were sprayed with a nitrogen plasma and at high power. Based on the known high enthalpies of N_2 plasmas, higher oxidation levels of this coating were expected. The A2 coating was sprayed using an Ar-based plasma at low power, i.e., a low enthalpy plasma when compared to N_2 , therefore, lower oxidation levels were observed. It is known that higher H_2 flow rates in plasma torches can help to create a de-oxidizing environment, by combining with oxygen atoms of the surrounding atmosphere to form water. Nonetheless, the higher H_2 flow of F2 plasma was probably outweighed by highest plasma power. In addition, the F4 torch has an external and radial feeding system. Consequently, in order to have a "sufficient degree of melting" to form the coating, the particles must cross over the streamlines of the plasma jet, thereby being more exposed to the atmospheric air and more prone to as-sprayed oxidation.

In spite of the higher heat input for F2 and A2 coatings, their microstructures present spherical features along the splats that could denote unmelted, spherical powder particles (Fig. 4). It is believed that a thick oxide shell is formed around some of the in-flight particles. This oxide shell could have two effects. It could first prevent further heat transfer to the particle core, inhibiting particle melting in spite of the high enthalpy plasma conditions. It could also act as a skeleton and prevent particle deformation upon impact, thus preserving the spherical shape of the semi-molten particle.

The plasma-sprayed coating microstructures can be compared with those obtained for the arc-sprayed samples, shown in Fig. 5. Arc-sprayed coatings present a typical lamellar microstructure with interlamellar cracks and pores (black), chromium oxide phase (dark grey) and the steel phase (light grey). The oxide phase is more abundant in those coatings than in the plasma-sprayed coatings.

Fig. 4. Microstructure/Amorphous plasma-sprayed coatings. In inset, a crack is shown in coating F2.

Fig. 5. Microstructure/Arc-sprayed steel coatings

Fig. 6 shows the XRD spectrum of the powder together with that of the plasma-sprayed coatings produced. The powder presents a variety of peaks corresponding to crystalline phases such as martensite, borides and borocarbide [7]. On the other hand, the coating patterns present an amorphous hump as the main feature, indicating a predominantly amorphous state. The indices of crystallinity of all coatings are also lower than the powder index. F2 and A1 present extra peaks associated to iron oxides, which is consistent with the SEM/EDS findings and the fact that it was sprayed with the highest plasma power.

Fig. 6. XRD/Amorphous plasma-sprayed coatings

3.2 Coating Behavior upon Thermal Cycling

Table 2 displays the coating bond strength (as-sprayed), together with the number of thermal cycles achieved prior to delamination. It can first be seen that the adhesions achieved by the amorphous, plasma-sprayed coatings are much lower than those of the conventional, stainless steel arc-sprayed coatings. This difference could come from both the coating composition and/or the spraying technique. Amorphous steel has a lower thermal conductivity than conventional steel. This lower thermal conductivity limits heat transfer from the coating to the substrate and thus, could accentuate the thermal mismatch and the residual stresses. Furthermore, plasma spraying generates more heat than arc spraying, further increasing the mismatch and the resulting residual stresses. The low adhesion of the amorphous coatings could be problematic for the envisioned application: not only would those coatings be sensitive to spalling, but their low adhesion would also prevent the production of thicker coatings, desirable to provide appropriate heat shielding.

Among the plasma-sprayed coatings, the best adhesion is obtained with F3, which is the spraying condition with the lowest enthalpy and lowest in-flight particle temperature. Again, this seems to indicate that a low heat input during spraying is desirable to decrease residual stresses and thus, improve coating adhesion.

The resistance to thermal cycles is lower for amorphous plasma-sprayed coatings compared to stainless steel arc-sprayed samples. It is believed that the lower initial bond strength of the plasma sprayed coatings is detrimental to the thermal cycle performance. In the case of the arc-sprayed coatings, the thermal cycling performance appears to be proportional to the initial coating bond strength. Interestingly enough, the same trend is not observed for amorphous, plasma-sprayed coatings, at least within the few samples of the study. F2 coating presents vertical cracks that, similarly to ceramic TBCs, could be key to accommodate thermal stresses. This probably explains why this coating present better resistance to thermal cycling than F3

and M80, in spite of the lower coating initial adhesion. It is expected that the variation in the level of crystallinity could also affect coating thermal cycling performance, as it would modify the coating thermal conductivity as well as the coating coefficient of expansion (CTE). Unfortunately, the limited number of samples and the bias of the oxide peaks on the crystallinity indices do not allow us to draw conclusions in this regard.

Since a high CTE mismatch increases the thermal stresses generated in the coating upon thermal cycling, it was expected that some relationship could be found between the coating CTE and the respective number of thermal cycles for failure. Even if the conventional arc-sprayed coatings were produced out of stainless steel feedstock presenting very different CTE: 80T wire with a CTE of $17 \times 10^{-6} / ^\circ\text{C}$, and 61T wire with a CTE of $10 \times 10^{-6} / ^\circ\text{C}$ [4], this difference did not result in different thermal cycling behaviour. By using very short heating time, the high temperature zone was possibly limited to the coating and did not reach the interface, where the difference of CTE would matter [14]. In order to complete the investigation of the effect of CTE mismatch, much longer ramping and holding times at temperature should be used.

Table 2: Coating properties

Sample	As-Sprayed Bond Strength (MPa)	No. thermal cycles for failure
F1	~0	n/a
F2	6.0 ± 2.3	400
F3	11.5 ± 0.2	150
A1	n/a	50
A2	~0	n/a
M80	17.9 ± 1.5	325
S80	27.9 ± 0.5	1800
M61	23.8 ± 3.3	500
S61	26.6 ± 2.2	1450

In order to evaluate the relevance of Fe-based amorphous coatings as TBCs, their stability under high temperature exposure needs to be assessed. Indeed, it has been shown that thermal diffusivity of Fe-based amorphous coating can double with microstructure evolution, going from about 6×10^{-7} to above $1.2 \times 10^{-6} \text{ m}^2/\text{s}$ [3]. Similarly, recrystallization of the coating would detrimentally affect wear performance.

Since SEM observations did not show significant changes in microstructure after thermal cycling, only F2 and F3 are presented in Fig. 7. XRD patterns (Fig. 8) also show little to no phase evolution. The variability in crystallinity indices are attributed to the low peak-to-background ratio and/or the presence of oxide peaks, and not to actual microstructure evolution. This is consistent with results of heat treatments performed on similar coating composition and microstructure and described in literature. In one

case, it was found that an HVOF-sprayed Fe-based coating was still amorphous after a heat treatment at 530°C for 5 h [6]. A TGA performed on a plasma-sprayed coating produced with the same feedstock of our study show that the main nucleation peak was starting at 605°C [8] and another study [3] has shown that a heat treatment at 650°C for 1 hr led to crystallization of a plasma-sprayed coating (ICP) produced with the same feedstock. Those combined results show that those amorphous coatings can be envisioned for Al protection, as the maximum operating temperature of the part will be limited by the maximum structural temperature of the Al substrate, in the range of 250°C . Even when taking into account the temperature gradient through the coating, the maximum operating temperature of the part will not exceed the recrystallization temperature of the coating.

Fig 7. Microstructure/Amorphous plasma-sprayed coatings after thermal cycling

Fig 8. XRD/Amorphous plasma-sprayed coatings after thermal cycling

4 Conclusions

The behavior under thermal cycling of a Fe-based amorphous coating, a key characteristic for a TBC, was assessed in this study. Initial coating amorphicity was confirmed by XRD for all plasma-sprayed conditions. However, it was established that spraying conditions of high enthalpy resulted in significant coating oxidation. The thermal cycling resistance of amorphous plasma-sprayed coatings was found to be lower than conventional arc-sprayed coatings. The lower resistance is attributed to a lower initial coating bond strength. On the other hand, it is believed that some features specific to the amorphous coatings,

e.g. vertical cracks, relatively high CTE, could provide good coating thermal cycling resistance once the low bond strength issue is tackled, either through further spraying parameters optimisation or improved substrate surface preparation. Also, the amorphous coatings showed good microstructural stability for temperature exposure up to 500°C and above. Further work is required to truly assess the potential of amorphous, plasma-sprayed coating as TBC, including coating diffusivity measurements.

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