Protective Coatings Obtained By Dynamic Metallisation: Stress Investigation

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Abstract

The annual cost of metallic corrosion in industrialised countries is estimated to be 3-4% of the Gross National Product. Though the problem of corrosion is as old as civilisation, it is not surprising that the search for more effective and economically efficient protective measures continues. Dynamic metallisation is one of the relatively novel surface protection methods based on cold spray technology. This technique has been used in a variety of applications ranging from repair and corrosion protection of metal structures to high-tech and art. This paper presents the quantitative assessment of the factors important for the mechanical integrity of the coatings made by dynamic metallisation.

Introduction

The idea to spray molten metals, mostly aluminium and zinc, on a surface of engineering components for the purpose of corrosion protection dates back to the 1910's. This idea led to the development of a wide range of thermal spray techniques such as the electric arc spray, plasma spray, high-velocity-oxy-fuel (HVOF).

Nowadays, when it has reached its maturity, the thermal spray is widely used in many industrial applications such as corrosion protection of bridge structures, offshore constructions, splash-zone and submerged areas of sea vessels and other applications in marine, mining, oil and gas and manufacturing industries. The main advantage of the metallised coatings is their long-term performance: some 200 μm thick aluminium coatings can serve as long as 50 years in harsh conditions such as the sea-water environment. The major drawback of metallisation is the relatively high initial cost when compared, for example, with painting. In the long-term, however, when considering life-cycle costs, metallisation definitely outperforms painting technologies. The most popular metallisation coating systems are aluminium, zinc or a mix of the two combining higher mechanical performance of aluminium and better anodic protection provided by zinc (Sulit, 1993; Leclercq, 1980)

One of the technical issues related to high temperature metal spray techniques is the residual stresses in the deposited coating caused by the large temperature differences. The tensile residual stresses might reduce the reliability and durability of the coatings and therefore decrease their technical and economic efficiency.

Cold Spray Techniques

A new class of spraying process has been put into practice since the late 1980s (Papyrin et al., 2006). This method has been named "gas-dynamic deposition" as it uses the kinetic energy of the powder particles for binding them in deposit. Unlike thermal spraying methods, it does not rely on the metallurgical kind of adhesion made when a molten particle binds with a surface. Instead, it rather forms the mechanical interlock of the particle with the surface as the result of the particle's kinetic impact. Because of the lower working temperatures in comparison with thermal spraying methods, this technique is also called "cold spray".

For this technique the working temperature does not exceed the melting point of the sprayed metal powders. Therefore the deposition of metal coatings under such conditions should not create significant thermal stresses. The previous results of the stress measurement of some coatings confirm this fact (Luzin, Valarezo and Sampath, 2008).

The sprayed material particle velocity for cold spray varies from sonic (~300m/s) to supersonic (>1200m/s) while temperature can be just near ambient. The current interest in use of this technology in the industrial scale is due to the following advantages of the produced metal coatings:

- Cold spray can produce metal coatings of higher density than coatings obtained by other spraying techniques. This factor ensures a better integrity (void free) of the cold spray coatings as well as their mechanical properties close to the properties of the bulk material.
- Because the spraying process is carried out at temperatures well below the melting point of the sprayed metals, the produced coatings are oxide-free which eliminates any deteriorating influence of oxides on the coating performance.
- In contrast to high temperature spraying techniques, cold spray does not involve high temperatures or any fuels and therefore is generally safer from the point of view of a health and safety requirement and can even be used in fire hazardous environments.
- There is a difference in the mechanism of the deposit formation between thermal and cold spraying techniques. This results in the fact that the coatings produced by the cold spray process are in a slight compression stress state, while the thermally sprayed coatings are usually in tension. Slight compression is considered to be beneficial because it creates unfavourable conditions for crack formation and propagation and therefore contributes to an extension of the service life.

One of the cold spray techniques is called Dynamic Metallisation (DM) (Kashirin, Klyuyev and Buzdygar, 1997; Kashirin et al. 1998). DM utilises a rather low supersonic range of the particle velocities (300-700 m/s) by using the Laval nozzle with compressed air as a carrier. What makes DM different from other cold spray systems is the usage of a mixture of metal and ceramic powders (usually-alumina, Al_2O_3) in different proportions to suit various applications. The utilisation of a mixture of hard ceramic particles and soft metal powder serves for two purposes: it provides unique conditions for forming dense coatings by creating a stronger kinetic impact while entrapped ceramic particles play a role in deposit reinforcement and hardening due to its micro-composite structure. As a result, a dense, high quality coating with desired properties can be produced by selecting a regime of operations (temperature, particle velocity) and optimising a combination of materials.

It was shown (Spiridonov, et al. 2007) that combining rather soft metals with hard metals and ceramics enables the production of coatings superior to solid metals such as mild and stainless steel. It was also demonstrated that the corrosion resistance of DM coatings is high. The salt spray test conducted by an independent organisation showed that the sprayed coatings are equal or superior to hot dip zinc galvanised coatings. The best results were achieved by spraying a nickel-zinc compound.

Figure 1 Dymet equipment

Residual Stress Factors

Residual stress is a direct result of the spraying process and depends on the spraying conditions and materials in use. High residual stress can lead to coating failure due to peel-off or delamination. In order to control residual stress in coatings it is essential to understand the microscopical behaviour of material leading to the formation of residual stress. The stress formation process is a complex phenomenon that at the microscopical level involves a dynamical (plastic and elastic) response of the material to the conditions of a shock wave. Alternatively, for practical purposes, empirical relationships between physical spraying parameters and the resultant stress can be established.

There is a variety of experimental methods of different natures available to assess the residual stress. Some of them are destructive (layer removal, hole drilling, slitting) and some are non-destructive (x-ray diffraction, neutron diffraction, synchrotron radiation). When it comes to two-phase materials, diffraction techniques are more universal since they can provide experimental results not only on macrostress (equivalent to mechanical stress) but can shed light on microstress because different phases can be examined independently. X-ray diffraction is rather a surface technique (first 100 µm) compared to neutron diffraction which be used for stress profiling through coating's thickness with special resolution of 0.5mm and better.

A research case

A series of samples has been sprayed using DM portable spraying equipment Dymet 403 (Figure 1) with a thickness of approximately 1 mm. Two samples were produced using a mixture of pure aluminium and alumina (Al_2O_3) powders and another pair was produced with the addition of Zn powder. In a standard setup, there are 5 temperature modes varying from 300°C (M1) to 400°C (M5) measured inside the spraying gun. Elevated temperatures are for the purpose of enhancement of the ductility and cohesion that improve the overall spray efficiency. A low temperature is used for spraying low melting point metals (e.g. lead, tin), whereas a higher temperature is used for copper, nickel and titanium. For aluminium or aluminium-zinc coatings intermediate regimes, M2 – M4 give the best result.

Samples have been studied in order to evaluate the effect of coating composition and the temperature regime on resultant stress in the coating system. Exact volume fraction of each constituent in the coatings has been determined by x-ray diffraction phase analysis and shown in Table 1. The microstructure of metal and ceramic phases is shown in Fig. 2; the phases can be distinguished readily by the colour difference. The aluminium substrate is seen on the left hand side.

Table 1. Phase composition of the sprayed coatings (vol. %)

Spraying mode	M2	M3	M4
Air temperature	~325C	~350C	~375C
Al coatings	-	75%Al_1	73%Al_1
		25%Al_2O_3	27% Al_2O_3
Al-Zn coatings	68%Al	68%Al	-
	12%Zn	12%Zn	
	20% Al_2O_3	20% Al_2O_3	

Residual stresses were measured in all samples (coating + substrate) by neutron diffraction with a spatial resolution of 0.5 mm using a neutron diffractometer BT8 at the NIST Center for Neutron Research (NIST, 2003.). A typical stress profile obtained experimentally for one sample is shown in Fig. 3(a). A corresponding fitting profile calculated within the frame of a certain empirical model of stress formation, the progressive coating deposition model

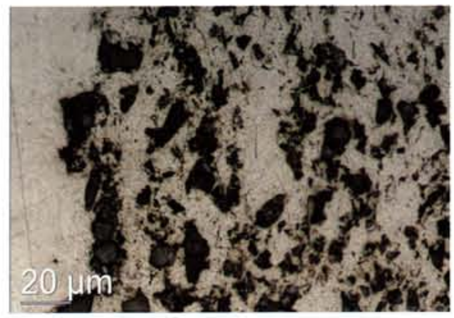

Figure 2 Microstructure of a sample with aluminium coating (mode M3) with 25% of alumina. Light colour area is aluminium and dark inclusions are alumina particles.

(Tsui, and Clyne, 1997), is also shown. For coating material, the macro-stress is a stress averaged over all phases weighted with their volume fractions and this is the quantity that is comparable with mechanical stress in the coating provided by the model.

A good agreement between the experimental results and the model validates the applicability of the empirical model that can be used effectively for stress predictions. The main fitting parameter of the model is the "deposition stress", that characterises quantitatively the stress with which (infinitesimal) the coating layer is deposited on the surface during the spraying process.

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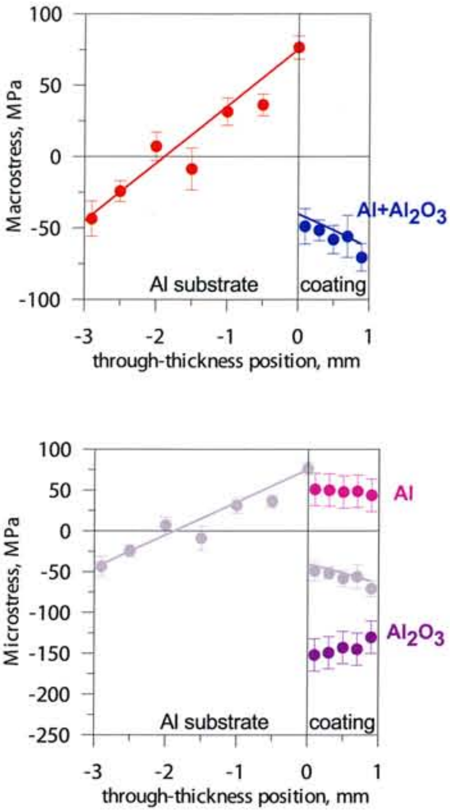

(a) Experimentally determined macro-stress or average stress profile (dot symbols) with the profile calculated within the model assumptions (solid lines) for "Al-M3" sample. (b) Deviatoric part of the micro-stress tensor for both Al and Al_2O_3 phases in "Al-M3" sample.

It has been found that for the given series of samples it is compressive (negative deposition stress), which is typical for cold spray and desirable for the coating performance. Comparison between the pair of samples sprayed under the same temperature conditions but using different compositions,"Al-M3" and "AlZn-M3", shows that the deposition stresses have approximately the same values, _d = -45 MPa for "Al-M3" and _d = -35 MPa for "AlZn-M3". The absolute value of the deposition stress is significantly larger then for analogous coatings sprayed without (alumina) hard particles with _d = -10 MPa, even when particle velocities were higher (Choi, et al, 2007). It demonstrates the peening (or forging) effect of by the hard phase particles. It can be noted that the deposition stress in aluminium coatings sprayed by thermal spray techniques is tensile (Luzin, Valarezo and Sampath, 2008). On the contrary, it seems that zinc can slightly decrease the absolute value of the stress. In this case, by varying the two opposite factors the residual stress in the coating can be minimised to the desired value.

Further insight into the details of stress formation can be gained by analysing microstresses (inter-phase stresses) which usually exist due to a discrepancy in properties, e.g. thermal expansion coefficient. In isotropic composites this type of stress is a hydrostatic tensor while in the case of coatings the deviatoric part of the micro-stress tensor can be evaluated as shown in Fig. 3(b). This is due to specific features of the microstructure, like oriented cracks and pores, and make-ups of the interfaces.

It should be mentioned that other coating properties can be of importance for the integrity of a coating system: cohesive strength between the coating and substrate can be a limiting factor, coating-to-substrate thermal expansion coefficient discrepancy can shift stress balance when the spraying is carried on at elevated temperatures.

Conclusions

Dynamic metallisation is an available and effective method for producing corrosion protection coatings in small scale applications and industrial usage. Coatings produced by this method in many aspects are superior to ones made by thermal spray techniques. Residual stresses created in the coatings during the DM spraying process are favourable and can be effectively controlled. Thus, the residual stress factor can contribute to an extension of the coating service life.

Neutron diffraction is a suitable tool for the experimental assessment of the residual stresses in coatings. A combination of mechanical tests and diffraction methods enables a very detailed quantitative characterisation and a better understanding of the mechanisms of stress formation during cold spraying.

Specifically to Australia, the residual stress instrument, stress diffractometer Kowari (Kirstein and Luzin, 2008), is available at OPAL research reactor (ANSTO) through a proposal system.

The equipment for dynamic metallisation is commercially available from InnovEco Australia.

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