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Characterisation of three-dimensional porosity in an Fe-based amorphous coating and its correlation with corrosion behaviour

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ABSTRACT

Porosity, an important and inevitable property of thermally sprayed coatings, considerably influences the corrosion resistance of the coated materials. In this work, the correlation between porosity and corrosion of an Fe-based amorphous coating was investigated. The volume fraction, size and distribution of the coating porosity were measured and analysed via 3D XRT technique. Direct evidence for preferential substrate corrosion caused by the through-porosity was obtained. It was found that through-porosity is sensitive to the coating thickness. The critical coating thickness for the presence of through-porosity was determined, which could provide a guide for the design of corrosion resistant coatings.

1. Introduction

Thermal sprayed coatings are frequently used to protect surfaces of metals and alloys against corrosion and wear, and have been widely used in industry [1–3]. Thermal spraying comprises a group of coating processes, in which finely divided metallic or non-metallic materials are deposited in a molten or semi-molten condition to form a coating [4]. The formation of the coating from individual deformed particles produces a distinctive lamellar microstructure, frequently referred to as "splats". Such microstructural features inevitably introduce porosity in the thermally sprayed coatings. The most common source of the coating porosity is trapped unmelted, partially melted or resolidified particles [1,2]. Besides, the angle of impingement of the spray stream and thermal stresses can also cause the formation of porosity. Porosity is an important property, which considerably influences the mechanical, chemical and thermophysical properties of the coated materials [1,2,5].

It is well known that the corrosion resistance of the coated base materials is strongly related to the coating porosity [6–16]. The coating delamination and peeling off caused by corrosion is one of the most commonly encountered failure types. However, the correlation between the porosity and the corrosion behaviour of the thermally sprayed coating still remains ambiguous. Porosity can be categorised as through-porosity and non-through porosity according to its role in corrosion behaviour of the coated materials. Compared with non-through porosity, through-porosity demonstrates much more sensitive to the corrosion resistance as it forms direct paths between the corrosive environment and the substrate [7,8]. In recent years, a number of attempts have been made to explore the role of porosity in the corrosion behaviour of the thermally sprayed coatings [6,9–13]. For the thermally sprayed Inconel 625 coating, a distinct difference between the corrosion resistance of coating and the equivalent bulk materials was observed [6]. Furthermore, Zeng et al. [9] have evaluated the corrosion resistance of a high velocity air fuel (HVAF) sprayed 316L stainless steel coating by salt spray test. They found that much more corrosion products formed on the unsealed coatings compared with the sealed ones. Note that, both porosity and other crystalline defects (*e.g.* grain boundary and dislocation) exist in the crystalline coating systems. Such defects are argued to be an important origin of the reduced corrosion resistance in the crystalline coatings. However, to clarify the intrinsic effect of the porosity on corrosion, ruling out the effect of structural defects in crystalline solids by selection of amorphous metallic coating becomes premier. In a Ni-based amorphous metallic coating system, Wang et al. [13] have found that the corrosion resistance of the coatings increases as the coating thickness increases from 120 μm to 400 μm, reflected by the variations of the current density in anodic polarisation curves of the coatings. The reduced corrosion resistance for the thinner coating was speculated to be associated with the formation of the through-porosity by the connection of individual porosity along the thickness of the coating. It seems that through-porosity is sensitive not only to the

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volume fraction of the porosity, but also to the coating thickness. However, the direct evidence demonstrating the intrinsic feature of the through-porosity in the coating still lacks. Accordingly, quantifying the coating porosity accurately is highly needed.

Measuring porosity accurately has been a major goal over recent decades for the thermally sprayed coatings. Several methods have been used to characterise the coating porosity [17–22]. Image analysis method is widely used for the assessment of the coating porosity due to its simplicity, accessibility and the ability to measure the surface porosities [18,23]. This method quantifies porosity by image analysis on the cross-sectional views of the coated sample obtained by an optical microscope (OM) or a scanning electron microscope (SEM) [18,19]. Note that, in essence, porosities are distributed in three-dimensional (3D) space in the coating. However, the image analysis method belongs to two-dimensional visualisation regime. It could hardly resolve the complex geometries of the porosities as well as their distribution in 3D space. In this regard, to accurately and quantitatively characterise the coating porosity, a novel approach applied in 3D space is highly desirable. Lab-based high resolution X-ray tomography (XRT) is a newly-developed 3D technique that could nondestructively detect and analyse the internal microstructure of materials [24,25]. This feature has advanced its applications in various aspects, *e.g.* the tortuosity calculations of percolating pore networks [26], the quantification of reflow porosity in Sn-rich alloy/copper joints [27], the analysis of 3D-microstructure of cast Mg alloys [28] and fuel cell anode [29]. But so far, characterisation of the porosity in thermally sprayed coatings using XRT technique has rarely been reported in the literature.

This paper attempts to ascertain the correlation between the porosity and the corrosion behaviour in a thermally sprayed Fe-based amorphous coating via selecting distinctive amorphous coating system and effective porosity characterisation method. On one hand, the HVAF sprayed Fe-based amorphous coating (SAM2X5) has been selected, since this alloy system has a high glass forming ability and the HVAF process with a high cooling rate is favourable for forming amorphous coating. In addition, Fe-based amorphous coating has received increased considerations for many engineering applications due to its good wear and corrosion resistance, high thermal stability and relatively low material cost. Although the corrosion resistance of the thermally sprayed SAM2X5 coating has been extensively studied by Farmer and co-workers [30–32], the deep study of the role of porosity in the corrosion behaviour of the coated materials is still lacking. On the other hand, 3D XRT technique was used to characterise the coating porosity at a micron level spatial resolution. In terms of 3D tomography reconstruction of the coated sample, the volume fraction, size and distribution of the porosity in the coating were presented, and the preferential corrosion of the substrate at coating–substrate interface was directly observed. The critical coating thickness for the presence of through-porosity was determined, which could provide a guide for the design of new corrosion resistant amorphous metallic coatings.

2. Experimental

2.1. Material and sample preparation

The material used in this work is $Fe_{49.7}Cr_{18}Mn_{1.9}Mo_{7.4}W_{1.6}B_{15.2}C_{3.8}Si_{2.4}$ (at.%) alloy. The master alloy ingot with the above nominal composition was prepared by arc-melting appropriate amounts of high-purity elemental constituents (Fe: 99.9%, Cr: 99.9%, Mo: 98.5%, Mn: 99.7%, W: 99.9%, FeB: 99% (20.06 wt.% boron), C: 99.9%, Si: 99.9%) in a water-cooled copper crucible under a Ti-gettered argon atmosphere. In order to ensure a homogenous chemical composition, the ingot was flipped and remelted at least five times. The amorphous ribbons were fabricated by induction melting the master alloy ingot in a silica crucible under an argon atmosphere, and ejecting it onto a copper wheel rotating with a speed of 40 m/s using a Bühler melt spinner (Hechingen, Germany). The amorphous powders were prepared by high-purity argon gas atomisation at a dynamic pressure of 7 MPa after heating up to about 1350 °C using a close-coupled annulus nozzle. The atomised powders were sieved according to conventional sieve analysis and divided into different size ranges. The powders with diameters of 22–45 μm were used for coating preparation. The type 304 stainless steel plate with dimensions of 100 mm × 40 mm × 5 mm was selected as the substrate. The steel was analysed by energy dispersive X-ray analysis (EDX) coupled to a SEM (Quanta 600). Such analysis gave (in weight percent): Fe 69.86, Cr 19.9, Ni 8.56, Mn 1.22, C 0.26, Si 0.26, P 0.03. No sulphur was detected. All the substrates were ground to a 800 grit finish by using SiC paper, degreased by acetone, dried in air, and subsequently grit-blasted prior to deposition. The $Fe_{49.7}Cr_{18}Mn_{1.9}Mo_{7.4}W_{1.6}B_{15.2}C_{3.8}Si_{2.4}$ amorphous coating was fabricated by AcuKote HVAF thermal spray system with AK-07 spray gun (Kermetico, USA). The detailed spraying parameters for the HVAF process are summarised in Table 1.

The coated sample with a thickness of about 5.8 mm (coating thickness ~800 μm) were sectioned into two kinds of cylindrical rods (5 mm and 1 mm in diameter) and rectangular bar with a coating cross section of 1 mm × 1 mm for subsequent investigations. The sectioned cylindrical rods and rectangular bar are perpendicular to the coating surface. The cylindrical rods of 5 mm in diameter were electrically connected to an isolated wire and cold mounted using epoxy resin leaving the round coating surface exposed. The mounted samples were ground to various coating thickness and then polished to a 0.5 μm diamond finish for electrochemical experiments. In order to find a tiny coating region free of porosity, the tip of the cylindrical rods with a diameter of 1 mm was ground into fine point using 2000-grit SiC paper whose tip diameter was tens of micrometres. Then the samples were mounted and polished as described above. The amorphous ribbons, with a thickness of about 45 μm and a width of about 3 mm, were cut into coupons with a length of 10 mm. The coupons used for electrochemical measurements were electrically connected to an isolated wire and embedded in an epoxy resin. The exposed cross-section surface area is 0.001–0.002 cm^2 (~3 mm × 45 μm). To characterise the coating porosity, the rectangular bar specimens with a cross section of 1 mm × 1 mm were measured using 3D XRT system after each surface of the specimens was mechanically ground with SiC paper. The specimen used for investigating the substrate corrosion at coating–substrate interface by XRT technique was embedded in an epoxy resin after being ground with 2000-grit SiC paper. Then the coating surface (~1 mm × 1 mm) of the mounted specimen was ground until the coating thickness reduced to ~150 μm. The evolution of internal microstructure of the coated sample was measured using XRT system before and after electrochemical measurements.

Table 1
Spraying parameters employed in the HVAF process.

Parameter	Value
Spray distance (mm)	178
Air pressure (MPa)	0.627–0.634
Fuel pressure (MPa)	0.519
Fuel flow rate (m^3/min)	0.127–0.132
Hydrogen flow rate (m^3/min)	0.035
Nitrogen flow rate (m^3/min)	0.027
Powder delivery rate (rpm)	9
Traverse velocity (mm/s)	500