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Revealing mechanical properties of a suspension plasma sprayed coating with nanoindentation

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Abstract
Solution and suspension thermal spraying is providing a more economic approach to the production of thin coatings. Advances in this new promising technology require accompanying tools to assess micro and nanosized areas within these deposits. Hydroxyapatite was deposited in an r.f. plasma using a powder and a suspension. The powder feedstock produced a dense, oriented coating, whereas the suspension led to a porous randomly oriented coating. The porosity leads to a decrease in the hardness and elastic modulus of the bulk coating, but site specific indentations on dense areas in the SPS coating revealed greater values (5±0.2 vs 4±0.2 GPa), possibly due to the finer grain size and crystal orientation. Nanoindentation presents a valuable tool for the assessment of the mechanical properties in solid areas of porous materials, and when used with microscopy will be valuable for the further development of SPS coatings.

Keywords: Coating, Hydroxyapatite, Nano-indentation, Scanning electron microscopy, Suspension plasma spraying

1. Introduction

Developments in thermal spraying have centred on new processes that extend the range of coating properties. Half a century ago, plasma was utilized for a higher throughput of particle feedstock as well as enabling the manufacture of high melting temperature materials [1]. Progress in feedstock technology in line with an interest in powder metallurgy gave rise to better control of powders leading to smaller particle size and spherical powder with better feeding characteristics. Finer particles initially used for D-gun spraying [2], were readily adopted for new processes such as high velocity oxyfuel spraying [3] and cold spraying [4]. The latest development includes the use of suspensions and solutions in arc plasma [5], r.f. plasma [6], flame [7] and high velocity oxy-fuel [8] spraying.

Suspension thermal spraying led to various departures from traditional thermal spray processing. Established knowledge from the spray drying industry provided an insight into the drying stage [9]. The carrier liquid is evaporated and the agglomerated nanoparticles are then molten. Material deposition is more complex, as revealed by the first deposits from alumina sols [10]. It became difficult to draw the comparison to the simple flattened droplet or particle microstructures from traditional thermal spray coatings. New properties were revealed leading to new applications, some of which are presently being assessed.

Liquid thermal spraying is a related technique, but requires more processing steps. Despite the increased complexity, the range in properties could be readily improved by the use different metals from soluble metal salts. Thermal processing required the removal of the solvent and then the salt to finally produce the desired metal or metal oxide [11]. This approach was first developed for glass colouring [12] in the thermal spray industry. Deposition of submicron sized deposits onto hot glass minimized the time for metal ion diffusion into the surface of the hot glass to produce very thin coloured layers. Other source materials such as organic precursors could also be used.

Thinner coatings produced by suspension/solution thermal spraying are well suited to mechanical assessment by nanoindentation. The ability to select the site of the indentation will enable testing on the coating surface, within the coating or at the coating-substrate interface. Previous work has revealed the ability to make indentations on the cross-section [13]. This technique presents a new tool for determining mechanical properties from different chemical phases and as well as ascertaining the presence of residual stresses within the coating.

This paper will investigate the differences between powder plasma sprayed (PPS) and suspension plasma sprayed (SPS) coating. The testing conditions for the determination of true hardness will be determined for both coatings. A comparison will provide insight into the differences between coatings both in terms of chemical phases and mechanical properties.
2. Materials and methods

2.1. Sample production

Hydroxyapatite \([\text{Ca}_{10}(\text{PO}_4)_{6} (\text{OH})_2]\) from CeramTec (Plochingen, Germany) was injected at a rate of 4.5 g/min into a vacuum induction plasma spray unit operating with Argon/Helium (5%), at a power level of 28 kW and a pressure of 60 kPa. A hydroxyapatite suspension was produced from the addition of an orthophosphoric acid solution into a calcium hydroxide suspension to provide a 40 wt.% solid content. This suspension was injected through a pressure nozzle at a rate of 5 g/min into a plasma using a Argon/Hydrogen (10%), at a power level of 38 kW and a pressure of 40 kPa. Both samples were produced at the Plasma Technology Research Centre at the Faculty of Applied Science, University of Sherbrooke, Canada. Further details of the spray process are detailed in a review article on r.f. plasma spraying [14].

Samples were embedded in epoxy resin (Aka-Resin & Aka-Cure, Denmark) to provide support for cutting the cross-section and then metallographically prepared to produce the smooth surfaces for nano-indentation testing. Fine grinding was conducted with silicon carbide abrasive papers of decreasing grit size (800, 1200 and 2400 grit) and polishing involved a 3 micron diamond suspension on a Largo surface followed by a 0.05 µm colloidal silica on an OPS cloth.

2.2. Coating characterization

The phase composition was determined with a Philips PW 1800 X-Ray diffractometer (XRD) system with Cu-Kα radiation at 40 kV and a current of 30 mA. The diffracted signal was collected over a two-theta range of 20°–60° with the step size of 0.02° and a fine slit. MicroRaman spectroscopy (with a Renishaw RM1000 microspectrometer) was used to detect the presence of an amorphous phase and dehydroxylated regions. Microstructural features were identified on a microscope with a 100x microscope objective. Analyses were conducted with an excitation wavelength of 514 nm and a spectral resolution of 1 cm\(^{-1}\). Spectra were recorded within the range of 800 and 1200 cm\(^{-1}\) where the most intense peaks for the amorphous/crystalline phases appear.

Surface topography was determined with a XL30 Philips scanning electron microscope (SEM). The samples were gold coated with an Edwards S150B Sputter Coater for examination with the SEM at 2 kV. Each sample was viewed at 200×, 700× and 1000×.

3. Results and discussion

X-ray diffraction of the coating surface produced with radio frequency spraying revealed preferred crystal orientation of hydroxyapatite, Fig. 1. This was apparent from the intense (002) and (004) peaks positioned at 26.1 and 54.4°. A small shoulder to the left of the 26.1 peak [16] suggests the loss of hydroxyl ions from hydroxyapatite. A peak at about 30° reveals \(\beta\)-tricalcium phosphate. This is in accordance with hydroxyapatite coatings manufactured at the Plasma Technology Research Centre, University of Sherbrooke, Quebec, Canada [17].

The microRaman spectra from the cross-section and the coating surface revealed a peak at 960 cm\(^{-1}\), Fig. 2. The small shoulder at a
lower wavenumber, also indicated dehydroxylation from hydroxyapatite, as observed in the XRD pattern. The less intense peak in the SPS coating suggested less dehydroxylation than the PPS coating. Water as a carrier liquid provides a high concentration of water vapour within the plasma and this lowers the degree of dehydroxylation within the hydroxyapatite.

The amount of dehydroxylation is lower at the surface of the SPS coating, than the core of the coating. This could be attributed to the more porous structure facilitating easier access of surrounding water vapour to the crystallites on the surface of the coating, Fig. 3.

The coating produced from the powder showed good melting of the individual particles, Fig. 3. This produced droplet flattening over the underlying contours to form a dense coating. The mechanical preparation of the cross-section produced isolated pores, representative of pull-out. The cross-section of the SPS coating revealed pores as large as 20 µm. These pores arose from what appears to be particulate containing agglomerates deposited during the build-up of the coating. Some areas remained sufficiently dense to assess the micromechanical properties.

Indentations were made on both coatings to reveal the critical load for reporting the true hardness. Fig. 4 shows a constant hardness at larger loads and higher hardness values at loads less than about 125 mN. A comparison of the three materials revealed the largest hardness for

![Fig. 3. The cross-section and surface of the coatings produced from a powder and suspension.](image)

![Fig. 4. The hardness and elastic modulus for different indentation loads. The deflection in the hardness curve reveals that critical load below which higher hardness value will be observed.](image)
sintered hydroxyapatite, followed by a lower hardness on both PPS and SPS coatings. The indentation size effect was seen in hardness, and not in the elastic modulus that exhibited a constant value at all indentation loads. This suggests that the calibration was sound.

All indentations reported in Fig. 5 were made on selected areas with full density. A grid of indentations placed on the coating showed the variation with location within the coating. Indentations 5, 8, 11 on fully dense areas showed a hardness of 4–4.5 GPa. Other areas appear to be surrounded by cracks and pores. The hardness from indentations 5–11 all show similar values, and so the surrounding cracking has had little affect on the hardness. The reported hardness is in agreement with that of hydroxyapatite coatings made by flame spraying [13].

Indentations 10 and 17 placed in a dense flat area of the SPS coating provided hardness values of 5 GPa, Fig. 6. The large variation in hardness and reduced elastic modulus at other locations was due to the indentation in surface pores and epoxy regions.

The SPS coating revealed a slightly higher hardness of 5 GPa in the solid areas compared to 4 GPa in the PPS coating. Three contributing factors could lead to this change. Firstly, the SPS coating with the faster cooling would produce a finer grain size that will lead to higher hardness values. Secondly, the indentation on the side of the crystals in the preferably oriented PPS coating will lead to lower hardness values [18]. Finally, a residual stress can influence the value of the hardness, where a lower hardness results from a tensile residual stress. Despite the presence of tricalcium phosphate in the SPS coating, this will have a hardness of 5 GPa [19] and will not lead to an increase in the hardness observed. To determine the cause of the increased hardness of the SPS coating, one would need to isolate the contributions from grain size, crystal orientation and residual stress.

The careful assessment of the indentation location together with the reported value provides an approach to determine the mechanical properties of dense areas in porous materials. This can be extended to rigid areas in porous materials such as filters, heat insulation materials and tissue engineering scaffolds. The mechanical properties will then provide a useful feedback for the design and manufacture of porous materials.

The development of SPS requires new tests to assess microdeposits and thin coatings. Traditional tests, such as tensile adhesion testing, are not suitable due to the adhesive penetration into the pores [20]. Nanoindentation presents a new approach for testing of the deposited material. This study has reported the mechanical properties of the material within the coating. Future studies will investigate further potential of nanoindentation by assessing the mechanical properties of the first layer adjacent to the substrate.

Fig. 5. Nanoindentation with 150 mN in a powder plasma sprayed coating, as seen in (a) a cross-section showing the indentation locations, and (b) the corresponding values of hardness and elastic modulus.

Fig. 6. Nanoindentation with 150 mN in a suspension plasma sprayed coating, as seen in (a) a cross-section showing the indentation locations, and (b) the corresponding values of hardness and elastic modulus.

4. Conclusions

Higher power levels are required for processing of SPS coatings. Despite the presence of water, the high heating level is sufficient to remove the hydroxyl ions from the hydroxyapatite feedstock, leading to a dehydroxylated coating.
Suspension plasma sprayed coatings are more porous than powder plasma sprayed coatings. The porosity leads to a decrease in the hardness and elastic modulus of the bulk coating, but site specific indentations on dense areas in the SPS coating revealed greater values, possibly due to the finer grain size and crystal orientation. Nanoindentation presents a valuable tool for the assessment of the mechanical properties in solid areas of porous materials, and will be valuable for the further development of SPS coatings.

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