Glass Coatings By Combustion Flame Spraying: the Microstructure and Properties

F. Al-Hasso

School of Engineering Systems and Design, London South Bank University, London, SE1 0AA, UK

*Corresponding Author: alhassf@lsbu.ac.uk

Copyright © 2013 Horizon Research Publishing All rights reserved.

Abstract Glass coatings on carbon steel substrates have been produced by spraying glass feedstock powders using combustion flame spraying. Glass powders with different compositions and particle size were tested; coatings with increasing soft glass A volume fractions in hard glass B base (0%, 10%, 20%, 30%) were sprayed. Furthermore, two different particle size (53-63 μm and <45 μm) of 30wt%A glass feedstock powders were employed. The microstructures of coatings were examined, characterised and the porosity was quantified. Vickers microhardness, fracture toughness and adhesion strength have been measured. The comparisons between the microstructure of coatings produced by conventional enamelling and thermally sprayed were investigated. Uniform structure and large pores produced in conventional enamels and non-uniform structure with small size pores produced in thermally sprayed coatings. It was observed that adhesion strength increased, hardness decreased and the fracture toughness did not change with increasing glass A content. Refining particle size of 30wt%A glass composition increased the hardness and did not affect the adhesion and fracture toughness of coatings.

Keywords Glass Coatings, Microstructure, Porosity, Properties, Fracture Toughness, Hardness, Pull-Off Strength, Combustion Flame Spraying

1. Introduction

Most of the applications of materials are limited by their resistance to aggressive environments. Industry demands protective coatings that are able to withstand the working conditions required in a wide variety of service situations. Thus, achieving the protection of metals against oxidation at low and high temperatures, against acid and alkaline media, and against corrosive gases is of great scientific, technological and economic importance [1]. Vitreous enamel is gloss hygienic, shock resistant finish and durable and has the hardness of glass and the strength of steel, furthermore when exposed to ultra violet radiation from the sun it has a proven life span of at least four times any other

metal finish. Enamels are impossible to scratch and products of any shape and colour can be enamelled such as baths, washing machines, gas and electric cookers, hot water services, storage tanks, car exhaust systems, street signs, interior and exterior architectural panels, fascias and partitions [2].

This paper concerns an investigation of the use of combustion flame spraying for producing of glass coatings on carbon steel. In principle, combustion flame spraying has advantages over conventional enamelling in terms of energy efficiency and flexibility of manufacture. In conventional enamelling, the glass and the substrate are heated together one or more time in furnace to approximately 850 °C, whereas in combustion flame spraying the glass particles is melted in the flame and the temperature of the substrate is maintained at a relatively low level [3]. This has the potential of avoiding the need to heat the substrate to elevated temperature and evading the formation of fishscales and pinholes defects in coatings. Combustion flame spraying consists of injecting glass powder into a flame, where the particles are melted, accelerated and projected on a substrate to form a coating. A schematic diagram of the process is given in Figure 1. The flame temperature (2800 °C) and velocity ($\sim 70 \text{ ms}^{-1}$) enables glasses to be readily melted and deposited [4]. Combustion flame spraying combines particle melting, cooling and consolidation into a single process unlike the several stages that are required in conventional enamelling. Several attempts have been made to deposit glass on steel and ceramic substrates in the laboratory using plasma technique [5, 6, 7, 8], however, the deposition mechanism is not fully understood, and in particular the effect of the glass composition has not been clarified [5]. The high thermal energy of the plasma jet (Argon - based) can cause thermal shock in the deposited glass during the spraying [9]. Moreover, plasma spraying may generate partially molten large glass particles and decomposed fine particles [4], and these can increase the flaws (porosity and microcracks) in coatings.

The combustion flame technique was selected instead of the plasma because the temperature of the combustion flame spray is much lower [10] and the equipment costs are greatly reduced. A problem encountered during the combustion

flame spraying of the glass is attributed to the thermal stresses developed during processing rising above the adhesion strength of the coating. Moreover, the high melt viscosity of the glass prevents the splats from flattening on the steel substrate and reduces adhesion of coatings. The unmolten particles can also affect coating microstructure by increasing pores in coatings and this can affect the properties of coatings.

The application of thermally sprayed coatings (TSCs) depends mainly on the quality of produced coating such as chemical resistance; wear resistance, corrosion resistance, mechanical properties, etc. Quality is a factor which measures the coating surface finish, mechanical properties, homogeneity, bonding strength, etc, and these depend mainly on material properties and coating microstructure [11]. The quality of thermally sprayed coatings is usually assessed by their adhesion/cohesion strength, defects in coating (i.e. porosity and microcracks) and specified properties [12]. Three major factors can influence the quality of coatings such as material composition, process parameters and substrate conditions, where in this study the last two factors are fixed.

The present work reports about the experimental characterization of the microstructural and mechanical properties of thermally sprayed coatings.

Figure 1. Schematic showing spraying process and the stress measurement device.

2. Material Details and Characterization

Table 1 gives the chemical composition in wt % of Glass A and Glass B. A carbon steel sheet supplied by Corus Group

Figure 2. SEM micrographs showing the particles of the glass powders using size range of 32-45 μm, A: Glass B powder and B: Glass-A powder (magnification 150X).

Ltd and two glass powders supplied by Escol Products Ltd (Huntingdon, UK) of properties listed in Table 2 were used in experiments. Figure 2 shows as-received Glass-A and Glass B powder particles of size range 32-45 μm examined by the scanning electron microscopy (SEM) Hitachi S-530. The examination shows that both particles have irregular shapes, solid, and were agglomerated.

The glasses were mixed using different contents of Glass A in Glass B base, sintered using optimal temperatures, crushed and classified to 28±5 μm to provide uniform feedstock powders for combustion flame spraying. The optimal sintering temperatures obtained for densest samples produced. Table 3 shows the weight percentages (wt %), volume fractions (vol. %) for the prepared glass compositions, which calculated using Equation 1. Table 3 also gives the calculated thermal expansion coefficient and melt-flow index using rule of mixture equation [Equation 2] and the measured optimum sintering temperature for the prepared glass feedstock powders of different compositions.

$$V_B = \frac{\frac{W_B}{\rho_B}}{\frac{W_B}{\rho_B} + \frac{W_A}{\rho_A}} \times 100 \quad \text{Equation 1}$$

$$\text{Specific property (K)} = \sum_{i=1}^n V_i X_i \quad \text{Equation 2}$$

Where, V is the volume fraction for the glass constituent, W is the weight percentage of the glass, X is the constant of the properties for each constituent and ρ is the density.

The glass powders were classified to 53-63 μm and 45-32 μm using BS 410-1986 sieves and a Metco vibrator machine for 15 minutes and characterized by means of particle size distribution analysis (Image-Pro plus 5.1 and ACD Fotoslate 3.1 software) and optical microscope (Nikon 50WAD equipped with Hitachi video camera model KP-161 CCD). The surfaces of the steel substrates (50 mm×40 mm×1.5 mm) were degreased and roughened by blasting using alumina grit "Metcolite C" and a Sulzer-Metco grit blasting machine equipped with pressurized air (2 bar) for 2 minutes for each sample before spraying to avoid oxidation. The substrates were preheated to 300 °C prior of spraying.

Table 1. Chemical composition of Glass A and Glass B in wt%.

Glass	SiO ₂ , Al ₂ O ₃ , ZrO ₂	P ₂ O ₅ , B ₂ O ₃ , F ₂	TiO ₂ , K ₂ O, Na ₂ O	Li ₂ O, CaO, BaO	MgO, Co, Ni, Mn, Cu, W, Fe
A	35	21	35	6	3
B	60	20	15	3	2

Table 2. The as received glass properties and carbon steel materials used in experiments.

Materials	Thermal expansion coefficient $\alpha \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$	Melt-flow index / mm	T _g / $^{\circ}\text{C}$	E / GPa
Glass A	17.3	280	360	
Glass B	8.4	29	473	
Commercial carbon steel	11.7	-	-	205

Table 3. The contents of the glass mixtures prepared for combustion flame spraying and the calculated properties of the glass of different compositions.

Glass composition	Glass-A / wt%	Glass B / wt%	Glass B / vol%	Thermal expansion coefficient $\alpha \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$	Melt flow index / mm	Optimal Sintering temperature / $^{\circ}\text{C}$
100wt%B	-	100	100	8.7	29	-
10wt%A	10	90	89.5	9.3	55	630
20wt%A	20	80	79.02	10.3	82	580
30wt%A	30	70	68.72	11.2	108	570

Combustion flame spraying was undertaken using Metco spray gun and Oxy-acetylene fuel gas. The powder feed unit available in the laboratory of London South Bank University was used to feed the glass feedstock powder horizontally into the flame. The glass powders were sprayed onto the steel substrates of dimensions 50 mm $\times$ 40 mm $\times$ 1.5 mm using process parameters given in Table 4.

Table 4. The process parameters used to deposit the feedstock powders on the steel substrates.

Pressure (bar)		Flow rate (lit/min)		Gas ratio (Moles) O ₂ /C ₂ H ₂	Powder feed rate g/min	Spraying	
Oxygen	Acetylene	Carrier air	Cooling air			Distance / cm	Angle
2-2.1	1-1.1	45-55	50-55	1.6-1.64	50-55	10-11	90 $^{\circ}$

Basically, four groups of coatings were produced: 100wt % Glass B, 10wt %, 20wt % and 30wt % Glass A in B using particle size $28 \pm 5 \text{ } \mu\text{m}$ (53-63 μm) and one coating of 30wt % using particle size $9 \pm 0.2 \text{ } \mu\text{m}$ (45-32 μm).

These process parameters were selected as it can deliver molten particles on the substrates. The number of torch passes on a substrate can reflect the coating thickness, which was measured using "Combo Posi Test DFT" tester.

The coating microstructures were examined by optical microscope (OM) Nikon 50WAD equipped with Hitachi video camera model KP-161 CCD. The porosity in coatings was analysed and quantified using image analysis (Image-Pro plus 5.1 and ACD Fotoslate 3.1 software).

Cross-sectional samples were cold mounted in resin, ground with 60, 120, 240, 800, 1200, 2400 μm SiC abrasive papers, and polished with 3 and 1 μm diamond paste. The Mitutoyo MVK-tester model VL-M55 equipped with Vickers indenter and video image-capture camera connected to Mitutoyo video line micrometer type VL-101 was

employed to measure Vickers microhardness on polished cross-sections; high load cracked Vickers microindentations on the cross-sections were employed in fracture toughness measurement (according to Anstis formulae [13]). Eight indentations were performed for the indentations and cracks measurement. The splats shapes, boundaries and unmolten particles were examined by etching the cross-sections of coatings for 90 seconds using the Buffered Hydrofluoric acid solution (BHF) [(HCl-HF₂O solution)] with etching rate of 1 $\mu\text{m}/\text{min}$.

The pull-off test (using 50 kN AVERY universal tensile test machine) was carried out for adhesion strength measurement of coatings following the British Standard EN ISO 4624:2003 [14]. The flat surface of the steel cylinder (20 mm diameter and 60 mm height) and the surface of glass coating were roughened ($R_a = 5 \pm 0.8 \text{ } \mu\text{m}$ and $1.5 \pm 0.75 \text{ } \mu\text{m}$, respectively) using grit blasting and SiC paper (Grade 60 μm), respectively to increase the area of contact between the adhesive-cylinder and adhesive-coating surfaces. The

coating and cylinder surfaces were cleaned with acetone to remove the stains and grease and left to dry. The steel cylinder of normalized geometry and flat surfaces was then glued to the coating surface using resin. The prepared samples were then cured in the oven at 150 °C for 2 hours and left 24 hours at room temperature to dry. Samples were then subjected to a progressive tensile loading until the coating is detached from the substrate or fractured within the coating. Four coating samples have been tested for each glass composition and the average value was considered.

3. Results and Discussion

3.1. Microstructure

3.1.1. Effect of glass composition

The microstructural features (porosity, microcracks, structure, splat boundaries and unmolten particles) produced in glass coatings of different compositions (increase Glass A content) as well as using different particle size of 30 wt%A was studied and the porosity in coatings was quantified.

Figure 3 shows the optical micrographs of polished cross-sections of different glass compositions deposited on

50 × 40 × 1.5 mm steel substrates using size range of 53-63 μm.

Results in Figure 3 show that the pores were located at the interface for all glass coatings, but the pores at the interface and total porosity in glass coatings were decreased with Glass A content in the glass mixtures. This is closely linked with the splat flattening on the substrate that increased with Glass A content and thus 30wt%A coating is expected to give better adherence with the substrate compared to other glass compositions. Decreasing of the pores in glass coatings of the same composition is expected to increase the hardness of glass coatings (increase the wear resistance) as the harder the material is the more wear resistant will be. In addition, dense coatings are expected to enhance higher adhesion strength with the substrates and to protect the substrates from corrosion.

Figure 4 illustrates the polished cross-section of 30 wt%A glass coatings produced on 50 × 40 × 1.5 mm thickness carbon steel substrates using the flame spraying and enamelling processes (fusing the glass in furnace for 2 hours at 750 °C). The cross-section surfaces of both coatings were then etched for 90 seconds using the Buffered solution and are illustrated in Figure 5.

Figure 3. Optical micrographs of polished cross-section for coatings of different glass compositions produced on 1.5 mm steel substrate using powder size range of 53-63 μm showing pores in coatings.

Figure 4. Optical micrographs of polished cross-section for 30wt%A glass coating deposited on 1.5 mm steel substrates using size range of 53-63 μm, showing the pore size generated in coatings produced by: A: combustion flame spraying and B: conventional enamelling.

Figure 5. Optical micrographs of etched cross-section surfaces for 30wt%A glass coating A: produced by the principle of enamelling showing glass matrix and pores, and B: produced by combustion flame spray process showing the lamellar structure and small pores.

Figure 6. Optical micrographs of polished cross-section for the 30wt%A glass coatings showing the pore size and the porosity generated in coatings: A: using size range 32-45 μm , and B: using size range 53-63 μm

The results in Figure 5/A show that the coating produced by fusing the glass in a furnace contains a number of large pores compared to that of the same coating produced by flame spraying. This suggests that the moisture from such sources in glass structure (combined water) reacted with the carbon content in the steel substrate at the high temperature in the furnace and generating gasses. The gasses trapped in the coating generated large pores. The microstructure examination in **Figure 5/A** also shows that the glass coating produced by fusing has one matrix phase and a non-layered uniform structure due to sufficient fusing temperature (750 °C) and time (2 hours) in the furnace. This is attributed to the glass particles melted completely onto the substrate in the furnace under the same temperature. In the same figure/B, the results show that the 30wt%A coating produced by the combustion flame spraying process contains small size pores (globular pores) and has a layered structure due to rapid solidification of the flattened splats. Small pores are voids between splats generated in the coating due to poor splat flattening resulting from partially-molten particles and air entrapped between splats during the spraying.

The different size of particles (large size) deposited on the substrate can explain different colours generated in the coating microstructure (**Figure 5/B**), suggesting different viscosities. In addition, Glass A and Glass B have different softening temperatures and viscosities (Table 3) and thus Glass B particles will solidify first.

Therefore, the microstructure of coating produced by The microstructure observation shows that coatings

fusing is characterized as coating with one matrix contained large size pores. The microstructure of the glass coating produced by combustion flame spraying shows layers of accumulated flattened splats due to rapid solidification, and small pores, and thus, the coating is characterized as a layered structure coating containing small pores.

Table 5 gives the summary of the measured mean pore diameter and the total porosity using Image analysis resulted from analyzing 10 photomicrographs for each glass coating of different compositions. Results show that the porosity in coatings decreased with increased Glass A content, suggesting reasons mentioned earlier.

Table 5. The mean pore size and the porosity generated in glass coatings of different compositions using size range 53-63 μm , as determined from image analysis.

Coatings	Mean pore diameter / μm	Total porosity / %
100wt%B	10.8 $\pm$ 2.5	18.8 $\pm$ 5
10wt%A	13.4 $\pm$ 3.4	12.1 $\pm$ 3.5
30wt%A	10.5 $\pm$ 2.7	10.4 $\pm$ 1.6

3.1.2- Effect of Particle size

Figure 6 shows the photomicrographs of polished cross-section of 30wt%A glass coatings produced on steel substrates using both fine (32-45 μm) and medium (53-63 μm) glass powders.

produced using fine powder (32-45 μm) is less porous

compared to that coating produced using medium powder (53-63 μm). Table 6 gives the determined mean pores size and total porosity formed in 30wt% glass coating produced using fine and medium powders.

Table 6. The porosity and mean pore size of 30wt%A glass coating using size range 53-63 μm and 32-45 μm , as determined from image analysis.

Powder size range / μm	Total porosity / %	Mean pore diameter / μm
53-63 (medium)	10.39 $\pm$ 1.6	10.5 $\pm$ 2.7
32-45 (fine)	5.57 $\pm$ 1.3	8.9 $\pm$ 1.5

The results in Table 6 show that the porosity formed in 30wt%A glass coating is reduced from 10.4 $\pm$ 1.6% to 5.57 $\pm$ 1.3% when coatings produced using medium and fine powders, respectively. This is likely linked to the splat-flattening ratio (mean of splat diameter/mean of particle size), which increased with fine particles, increased the area of contact between splats, and consequently reduced the porosity in coatings. It is obvious that the small pores of size range 1-5 μm increased in the coatings (produced using fine powder) due to non-fully contact between the splats. The

globular pores (pore size 3-10 μm) generated in coatings produced using 32-45 μm are approximately 70%, and in coating using 53-63 μm are 34%. The globular pores produced due to viscous deposited splats caused by partially-molten particles. The large size particles and agglomerated particles in the glass powder increased the number of partially-molten particles, reduced the splat flattening and this likely increased the pores in coatings.

3.2. Properties of coatings

3.2.1. Vickers microhardness

Table 7 gives the average values of eight indentations of the measured diagonals and the hardness for glass coatings of different compositions using medium powders (53-63 μm). The reduction in the hardness (H_V) resulted from increasing Glass A content was calculated using the Equation below, and the results are included in the same table.

$$(H_{\text{Glass B}} - H_{\text{glass mixture}}) \times 100 / H_{\text{Glass B}}$$

Table 7. The mean indentation size and the hardness under 1N indentation load for 15 sec and the reduction in hardness for glass coatings of different compositions using size range of 53-63 μm .

Coatings	Mean indentation size / μm	Hardness (MPa)	Coating thickness / μm	Reduction %
100wt%B	17.6 $\pm$ 0.2	5755 $\pm$ 80	70 $\pm$ 14	0
10wt%A	18.1 $\pm$ 0.08	5605 $\pm$ 70	190 $\pm$ 16	2.61
20wt%A	18.3 $\pm$ 0.04	5443 $\pm$ 75	180 $\pm$ 19	5.41
30wt%A	19 $\pm$ 0.07	5037 $\pm$ 84	190 $\pm$ 23	12.5
100wt%A	23 $\pm$ 1.08	3454 $\pm$ 32	120 $\pm$ 12	

Figure 7 shows the plot between the measured hardness given in Table 7 versus Glass A content in the glass mixture and the best-fitted line between points was drawn.

Figure 7. The measured hardness for the glass coatings of different composition using size range of 53-63 μm deposited on 1.5 mm steel substrate, showing the hardness decreased with increasing Glass A content.

Results in Figure 7 show that Glass-A coating is soft ($H_v=3455$ MPa) and Glass B coating is hard ($H_v=5756$ MPa).

MPa), and increasing Glass A content to 30wt% in B, decreased the hardness of coatings by 12.5% (Table 7), and thus, the coating became softer and this degraded one of the coating properties. This suggested that increasing the soft Glass A in the glass mixture increased the glass softening and reduced the glass viscosity and this increased the deformation of the glass locally underneath the indenter. This can explain why the indentation size increased from 17.6 μm to 19 μm for Glass B and 30wt%A glass coatings, respectively, and this reduced the hardness of coatings from 5756 MPa to 5037 MPa.

Effect of particle size

Table 8 gives the mean value (eight indentations) of the measured hardness and the indentation size of 30wt%A glass coating produced using both fine (32-45 μm) and medium (53-63 μm) powders.

Table 8. The measured mean indentation size and the Vickers hardness values under 1N indentation load for 15 sec for 30wt%A glass coatings ($t_c=180 \mu\text{m}$).

Coatings	Mean indentation size/ μm	Hardness / MPa	Size range / μm
30wt%A	19 $\pm$ 0.1	5037 $\pm$ 84	53-63
30wt%A	18.2 $\pm$ 0.2	5542 $\pm$ 20	32-45

Results in Table 8 show that with reducing the powder size range from 53-63 μm to 32-45 μm , the hardness of 30wt%A glass coating increased from 5037 to 5542 MPa, and the standard deviation decreased from 84 to 20. This is likely due to the increased homogeneity of the coatings resulted by the increase in melt-flow of fine particles, which produced dense coatings (Table 6).

Reducing the porosity has two effects; first decreased the pores located underneath the indenter, and second increased the cohesive strength between splats, decreased the indentation size and increased the hardness of coatings. Moreover, producing dense coatings can increase the stiffness of the glass coating, increase the load required to yield the glass and hence increase the hardness.

3.2.2. Fracture toughness

The fracture toughness (K_{IC}) of glass coatings has been determined using Anstis Equation 4. The crack length (C) under different indentation loads 1-5N (P) has been measured from the indentation centre. The Elastic modulus (E) value was selected to be 56 GN/m² and the hardness (H_V) was measured using 1N indentation load.

$$K_{IC} = 0.016 \left[\frac{E}{H_V} \right]^{\frac{1}{2}} \left[\frac{P}{C^{\frac{3}{2}}} \right] \dots \dots \dots \text{Equation 3}$$

$$C^{\frac{3}{2}} = \frac{0.016 \times E^{0.5}}{K_{IC}} \left[\frac{P^2}{H_V} \right]^{\frac{1}{2}}$$

$$\text{Slope} = \frac{C^{3/2}}{\left(\frac{P}{\sqrt{H_V}} \right)} = \frac{0.016 \times \sqrt{E}}{K_{IC}}$$

$$K_{IC} = \frac{0.016 \times \sqrt{E}}{\text{slope}} \dots \dots \dots \text{Equation 4}$$

Table 9 represents the average of five indentations (under each indentation load) of the hardness and the crack lengths, which measured from the indentation centre.

Table 9. The measured hardness, indentation loads, and the measured crack length under different indentation loads for glass coatings of different compositions using size range of (53-63) μm .

10wt%A, coating ($t=170 \mu\text{m}$)		
Hardness / GPa	Load (P)/ N	Average crack length (C)/ μm Centre
5.7 $\pm$ 0.03	1	22.6 $\pm$ 7
5.66 $\pm$ 0.06	2	26.6 $\pm$ 3.2
5.57 $\pm$ 0.02	3	39.4 $\pm$ 8
5.7 $\pm$ 0.06	5	64.4 $\pm$ 9
30wt%A coating, ($t=160 \mu\text{m}$)		
5.6 $\pm$ 0.01	1	15.8 $\pm$ 3
5.4 $\pm$ 0.02	2	24.4 $\pm$ 3.2
5.34 $\pm$ 0.01	3	33.2 $\pm$ 9
5.26 $\pm$ 0.02	5	58.9 $\pm$ 8

Figure 8 shows the best-fitted lines were plotted between the crack lengths ($C^{1.5}$) versus the load/hardness ($P/\sqrt{H}$) for 10wt%A and 30wt%A glass coatings using data given in Table 9. The equations of the best-fitted lines and the correlation coefficients (R^2) were calculated from the graphs, the fracture toughness was calculated using Equation 4 and the results are given in Table 10.

Figure 8. The relation between the average values of the measured crack length and (load/hardness) under different indentation loads for the glass coatings using size range 53-63 μm .

Table 10. The calculated line equation, the correlation coefficients and the calculated fracture toughness of 10wt%A and 30wt%A glass coatings.

Coating Composition (53-63 μm)	Coating thickness / μm	Correlation coefficient (R^2)	Line equation	K_{IC} / $\text{MPa}\cdot\sqrt{\text{m}}$ using Eqn. 4
10wt%A	170 $\pm$ 10	0.9617	$C^{1.5} = 0.0079 P/\sqrt{H} - 2 \times 10^{-8}$	0.509 $\pm$ 0.13
30wt%A	160 $\pm$ 8	0.9721	$C^{1.5} = 0.0070 P/\sqrt{H} - 8 \times 10^{-8}$	0.538 $\pm$ 0.1

Results in Table 10 show that the fracture toughness of coatings has high standard deviation due to the cracks and hardness variations and thus, increasing Glass A content in the mixtures has no effect on the calculated fracture toughness, suggesting non-radial cracks were formed under different indentation loads due to residual stress in coating, pores and splat boundaries in microstructure. Moreover, experimental results also show that reducing the particle size of the same glass composition (30wt%A) gives no effect on the fracture toughness of coatings.

3.2.3. Coating adhesion strength

Table 11 gives the mean value of the calculated pull-off strength (three samples) as well as the calculated splat-flattening ratios of different glass compositions.

Table 11. The mean bonding strength and the splat-flattening ratio for the glass coatings of different compositions produced on 1.5mm steel substrates using size range of 53-63 μm .

Glass composition	Pull-off strength / MPa	Splat flattening ratio
100wt%B	3 $\pm$ 1.6	1.14 $\pm$ 0.01
10wt%A	5.1 $\pm$ 1.1	1.31 $\pm$ 0.106
20wt%A	6.2 $\pm$ 1.2	-
30wt%A	7.7 $\pm$ 1	1.57 $\pm$ 0.02

The pull-off strength data given in Table 11 was plotted versus increasing Glass A content in Glass B base and the result is illustrated in Figure 9. The best-fitted line for the graph was plotted, and the correlation coefficients (R^2) was calculated (0.9771).

The results in Figure 9 show that the pull-off strength of glass coatings increased with increasing Glass A content. For example, increasing Glass-A content from 0wt% to 30wt% in Glass B increased the pull-off strength of coatings from 2.7 $\pm$ 1.6 to 7.7 $\pm$ 1 MPa.

From the results analysis, the main observation was that the load of fracture increased with increased Glass A content to 30wt%, and hence increased the pull-off strength of coatings. The key point of the adhesion mechanism is that the adhesion strength increased with the area of contact between the glass splats and the substrate. The contact area increased with splat-flattening ratio (Table 11), and the latter increased with reducing the glass viscosity. The viscosity of the glass reduced with increasing Glass A content in the glass mixtures (Table 3). Thus, splat-flattening ratio of the glass has direct effect on adhesion strength and the viscosity has an indirect effect on the adhesion. Moreover, as the splat flattening increased with Glass A content, the porosity in coatings reduced and this suggested increased cohesive strength i.e. decreased cohesive mode failure.

Figure 9. The calculated pull-off strength for glass coatings of different compositions deposited on steel substrates showing the pull-off strength increased with Glass A content.

4. Conclusions

Glass feedstock and simply mixed powders of compositions 10wt%A, 20wt%A and 30wt%A in Glass B using size range 53-63 μm as well as glass feedstock powder of 30wt%A composition using size range 32-45 μm have been thermally sprayed on plain carbon steel substrates ($50 \times 40 \times 1.5$ mm) using combustion flame spraying. Glass compositions of 20wt%A and 30wt%A were successfully produced giving crack-free coatings of 250 μm and 300 μm thickness, respectively, while 10wt%A glass composition failed to produce crack-free coatings above 200 μm thickness.

The microstructural examination of glass coatings showed that thermally sprayed glass coatings have a layered structure, which attributed to flattening of the molten glass particles as they strike the solid substrate during the deposition process. The coatings were also found to contain pores of a much smaller size than those in conventional enamel. The pores in the flame-sprayed coatings are attributed to air being entrapped during deposition, partially-molten large size particles resulted from agglomerated particles and particle size distribution, and the growth of pores being suppressed by the rapid solidification rate inherent in the process.

The results showed that mixing two glasses with very different viscosities in different proportions promoted the melt-flow of the glass mixture, reduced the porosity and increased the pull-off strength of glass coatings. For example, increasing Glass A content in a Glass B from 0wt% to 30wt% increased the melt-flow rate and increased the splat-flattening ratio from 1.1 to 1.6. This increased flow enabled a much greater the area of contact between splats and splats-substrate and reduced the coating porosity from 19% to 10 % but did not change the pore size (10.5 μm) due to agglomerated particles. As a result, the pull-off strength (cohesive and adhesion strength) increased from 2.7 to 7.7 MPa, the hardness reduced from 5755 to 5040 MPa, and the fracture toughness remained unchanged ($0.54 \text{ MPa}\cdot\text{m}^{0.5}$).

The results showed that reducing particle size of the glass feedstock powder decreased the porosity, increased the hardness and unchanged the fracture toughness of coatings.

REFERENCES

- [1] A. Conde, J. de Damborenea, Monitoring of vitreous enamel degradation by electrochemical noise, *J. of Surface and Coatings Technology*, vol. 150, (2002), pp 212–217.
- [2] Glass metal industries P/L, <http://www.glassmetal.com.au/enamelling.html>, 25-11-08.
- [3] Y. Bao, T. Zhang and D. T. Gawne, The Mechanism of Crack formation in Plasma sprayed Enamel, *Trans IMF*, Vol. 76, (1998), pp. 213-216.
- [4] Mitchell R. Dorfman, 2002, *Advanced Materials & processes*, Sulzer Metco (US) Inc, New York.
- [5] J. Schrooten and J. A. Helsen, Adhesion of bioactive glass coating to Ti6Al4V oral implant, *Journal of Biomaterials*, Volume 21,

(2000), pp 1461-1469.

[6] C. Gabbi, A. Cacchioni, B. Locardi and E. Guadagnino, *Journal of Biomaterials* 18, Bioactive glass coating: physicochemical aspects and biological findings, Vol. 16, (1995), p. 515.

[7] Bessmertnyi, N.I. Min'ko, P.S. Dyumina and N.A. Dridzhd, Evaluation of the Competitiveness of Household Glassware Decorated by Plasma Spraying, *Journal of Glass Ceram.* Vol. 59, (2002), p. 251.

[8] Bessmertnyi, V.P. Krokhn, V.A. Panasenko, N.A. Drizhd, P.S. Dyumina and O.M. Kolchina, Plasma Rod Decorating of Household Glass, *Journal of Glass Ceram.*, vol. 58 (2001), p. 214.

[9] Bao Y., Gawne D. T. , Zhang T, Qiu Z., Zhang K., Influence of secondary phase on residual stress of plasma sprayed glass coatings, *Surface engineering*, Vol. 16, (2000), pp 473-479.

[10] Lech Pawlouski, *The Science and Engineering of thermal spray coatings*, John Wiley and Sons Ltd, 1995, UK.

[11] Shaw K., *Technology of Enamels* (ed. & Trans.), V. Vargin (London: Maclaren & Sons Ltd.), 1968, PP. 179-206.

[12] William D., Callister Jr, *Material Science and Engineering, An Introduction*, 6th edition, John Wiley & Sons Inc, 2003, USA.

[13] G. R. Anstis, P. Chantikul, B. R. Lawn and D. B. Marshall, A critical evaluation of indentation techniques for measuring fracture toughness, *J. Am. Ceram. Soc.*, Vol 64, (1981), p 533.

$$K_C = 0.016 \pm 0.004 \left(\frac{E}{H_v} \right)^{\frac{1}{2}} \left(\frac{P}{C^{\frac{3}{2}}} \right)$$

[14] BS 3900-E10:2003: Paints and varnishes-Pull-off test for adhesion.