Production of CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} Based Plasma Spray Coating Powder

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Abstract

In this study CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} (CAS) based coating powders prepared for plasma spraying coating process. In accordance with this purpose, natural, waste and pure materials were used to prepare composition of compound which contain %57.5 SiO\textsubscript{2}, %27.5 CaO, and %15 Al\textsubscript{2}O\textsubscript{3} by weight. The glasses obtained by melting at 1450°C, then were annealed at 600°C for 1h. Annealed CAS glass samples were crushed, milled and sieved to obtain desired particle sizes. Phase analysis and microstructural properties of prepared powders were analyzed by X-Ray diffraction (XRD), scanning electron microscopy (SEM). The results showed that obtained CAS based glass powders were non-porous, had an angular shape and proper flowability for plasma spray coating process.

1. Introduction

Atmospheric plasma spraying is one of the most commonly used thermal spraying processes because of its flexibility, high deposition rates and multifunction [1]. It consists of a plasma source where a feed material is melted and accelerated until it impacts upon substrate. The high heat energy provided by plasma flame could melt spraying materials quickly and the solidification of the melting materials can obtain a lamellar structure coating preventing the formation of vertical cracks in the coating. Therefore, the coating prepared with plasma spraying often exhibits good thermal shock resistance and outstanding oxidation protective ability [2,3]. Plasma spraying is employed to deposit coatings of almost all materials including metal alloys, ceramics and cermets with a congruent melting point onto the substrate [1,4]. It is known that the properties of plasma spraying coating is related to many parameters of plasma spraying process such as the powder feed rate, the spraying power, spraying distance, gas flow rate and particle size [1,5]. These parameters affect the thermal energy and kinetic energy of the particles. If particles are subjected to an excess of thermal energy, they can be vaporized in the plasma jet rather than arriving at the substrate in the fully molten condition. However, if the particles receive too little thermal energy, they arrive at the substrate in an unmelted condition. It is widely recognized that the hardness increases with the increasing coating density, i.e. decreasing number of pores and microcracks [1].

The deposition efficiency, interface bonding and mechanical properties of sprayed coatings increases with the increase of particle velocity and temperature. It was demonstrated that the as-sprayed coatings show elemental composition different from the initial feedstock powders. Variation of plasma gun power allows changing and controlling the plasma jet temperature and, consequently, to adjust the melting degree of the feedstock powders. Therefore, it is generally considered that the fully melted particles will lead to production of dense with low pore volume coatings. The nature and elemental composition of the initial powders are directly related to the melting temperature. Therefore it is very important to obtain the optimal spraying process parameters for individual feedstock powders [5]. Powder characteristics such as shape, density, and purity also have a significant influence on the thermal-spray process used and resulting coating properties. Thus the end user must have a good understanding of all powder characteristics to be capable of matching powder type, coating rate, deposition efficiency, and price to achieve optimum coating performance [5-7].

The coating material, in powder form, is radially fed into the plasma flux just outside the nozzle exit: the particles are therefore dragged and heated by the plasma itself, so that they melt and accelerate towards the substrate. The melted droplets impact on the substrate, flattening and solidifying in a few microseconds, assuming a typical lamellar (or splat-like) morphology. Among thermal spraying techniques the plasma spraying is probably the fittest to spray glass powders [6].
The torch power is a crucial parameter, because it influences the velocity and temperature of the plasma flow and, in consequence, powder particles directly [5]. These parameters directly influence the heat and mass transfer between particles and plasma jet, and then affect the degree of melting of particles, the temperature and in-flight velocity of droplets before they impact on the substrate [1].

To produce spray powders, precursor materials must be melted or sintered with subsequent size reduced by crushing, grinding and attrition milling. Mixing of powders and classification are also important process steps. Fusing and crushing technique of manufacturing is applied to ceramics and cermet (carbide) powders as well as to brittle metals. Oxide ceramics are manufactured by fusing or sintering followed by crushing. The fused or sintered powders are blocky and irregular and this lowers their flowability [8].

Numerous reports on the ternary system CAS have been issued in the literature [9]. Glasses in the ternary CAS system find their application in printed circuit boards, gems and also glass fibers. Furthermore, they are used as reference material [9]. CAS s ystem glasses are one of the basic silicate systems that have been widely used in many fields of industry [9-11].

In this work, CAS based plasma spraying coating powder was prepared using natural, waste and pure materials. XRD was conducted with a Rigaku-type diffractometer with Cu Kα radiation, to analyse CAS based coating powder over a 2θ range of 10°–90°. A JEOL 6060 SEM-EDS was used for characterization of starting and produced CAS based plasma powders.

### 2. Experimental Procedure

The chemical composition of waste and natural materials that used in this study are given in Table 1. Zeolite raw materials used as a SiO₂ and Al₂O₃ resources both CAS1 and CAS2 compositions. Eggshell powder was used as a CaO resource for CAS1 and marble powder was used in CAS2 composition for same purpose. Table 2 shows CAS compositions that selected according to the CAS ternary diagram which has low melting temperature within this system.

The raw materials mixed by wet ball milling for 24 h and then dried at 100°C for 48h. After drying process the powder mixture was put into an alumina crucible and melted at 1450°C for 2 hours. Then the melt was cast into a graphite mould and placed into preheated furnace (600°C) for 1 hour to annealing. Annealed CAS glass samples were crushed, milled and sieved to 45-125 μm to obtain desired particle sizes. AISI 304 steel was used as substrate material in the dimensions of 5x5 cm. Stainless steel samples were cleaned in ethyl alcohol and acetone, ultrasonically for 15 min and then sand blasted with 24 grit alumina. Atmospheric plasma spray coating technique (Sulzer METCO, F4 Plasma spray gun) was used for coating treatment of the prepared CAS based powder on NiCr (Metco 43F-NS) coated steel samples. Only one surface of each substrate was coated. X-ray diffraction (XRD) analysis was performed with RIGAKU D/Max/2200/PC to determine the crystalline phases occurred in the produced glasses. Scanning electron microscopy (SEM, Jeol 6060LV) and energy-dispersive X-ray spectroscopy (EDS) were used to characterization of starting powders and produced CAS based glass powders.

### Table 1. Chemical Components of Raw Materials (wt %).

<table>
<thead>
<tr>
<th>Components</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>TiO₂</th>
<th>SO₃</th>
<th>P₂O₅</th>
<th>I.L.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite</td>
<td>2.383</td>
<td>13.123</td>
<td>76.972</td>
<td>4.631</td>
<td>0.188</td>
<td>1.669</td>
<td>0.935</td>
<td>0.099</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M. P</td>
<td>71.63</td>
<td>0.111</td>
<td>0.176</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.067</td>
<td>0.427</td>
<td>-</td>
<td>-</td>
<td>27.59</td>
</tr>
<tr>
<td>Eggshell</td>
<td>51.76</td>
<td>0.040</td>
<td>0.109</td>
<td>0.083</td>
<td>0.110</td>
<td>0.122</td>
<td>0.367</td>
<td>-</td>
<td>0.597</td>
<td>0.177</td>
<td>46.63</td>
</tr>
</tbody>
</table>

I.L. (Ignition Loss) M.P. (Marble powder) Eggshell (E.S.)

### Table 2. Composition of CAS glass-ceramics (wt%).

<table>
<thead>
<tr>
<th>Composition (wt%)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite</td>
<td>57.5</td>
<td>15</td>
<td>27.5</td>
</tr>
<tr>
<td>M. P</td>
<td>57.5</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>Eggshell</td>
<td>57.5</td>
<td>15</td>
<td>27.5</td>
</tr>
</tbody>
</table>

### 3. Result and Discussions

Figure 1 showed the XRD pattern of CAS1 and CAS2 coating powders and as-sprayed CAS coatings. XRD pattern of the coating powders and as-sprayed coatings for both CAS1 and CAS2 as presented in the curves showed a complete amorphous material.
The CAS based glass powders particles have the typical shape of a mechanically milled material as seen in Figure 2. SEM micrographs indicate the particles have an irregular morphology. An acceptable particle size distribution has been achieved through sieving. Figure 3 indicates the granulometric distribution: the maximum of the distributive curve lies at around 100 μm, an optimal particle size for plasma spraying, although the distribution is not narrow around this value. It is important to have spray powders with a narrow particle size distribution, since several studies have shown that spray parameters can be optimized only for a narrow particle size distribution [12,13].

The as-sprayed CAS1 and CAS2 coatings (Fig. 4) have much more porosity, which are quite high, but not too different from literature porosity values for plasma-sprayed coatings [14]. Both the coatings show a broad band in the diffraction patterns, with no detected crystalline phase peaks (Fig.1). They both present the lamellar microstructure of plasma sprayed coatings. The defectiveness of as-sprayed coatings might be ascribed to different reasons: the broad particle size distribution, the low thermal conductivity of glasses which hinders heating and melting of the middle region of sprayed particles, the low density of glasses when compared to other engineering ceramics usually employed in thermal spraying (like alumina and zirconia) resulting in lower particle speed (the particle density affects the viscous drag) and lower kinetic energy upon impact.

Consequently, some general conclusions on plasma spraying of glass coatings can be drawn. In the as sprayed conditions the coatings are always defective so they must be thermally treated. In any case, proper heat treatments always improve the coatings mechanical properties. The
highest improvement in mechanical properties is obtained when controlled crystallization of suitably chosen glass compositions is achieved [6].

![Figure 4. SEM micrographs cross-section; a) CAS1 as-sprayed, b) CAS2 as-sprayed coatings.](image)

4. Conclusions

The as-sprayed microstructures were fully vitreous and very defective: pores, cracks due to thermal stresses relaxation and very rough and irregular surfaces were present. Post-process thermal treatment can enhance the microstructure, but the degree of improvement strongly depended on the thermal behaviour of the coating materials. Thus, future developments of this research will focus on the crystallization of glass compositions in order to achieve very high quality glass ceramic coatings (small amount of porosity, high toughness induced by crystallization).

References


