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Processing of an organosilazane-based glass/ZrO_2 composite coating system by laser pyrolysis

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Abstract

Protective ceramic-based coatings are frequently the most suitable and cost-effective solutions for problems like corrosion, oxidation and wear. It has been shown, that the polymer-derived ceramics technology is suitable for the preparation of ceramic coatings by pyrolysis in a furnace. However, the required high temperatures for the preparation of the ceramic coatings only allow the use of temperature-resistant substrates. A very innovative approach to overcome this restriction is the use of laser radiation as an energy source for the pyrolysis of the preceramic polymer. For this reason, a composite coating system composed of an organosilazane with ZrO_2 and glass particles as fillers was developed suitable for pyrolysis with a Nd:YVO_4 laser. The composite coating slurry was applied onto stainless steel substrates by spraying and afterwards irradiated with a Nd:YVO_4 laser. Finally, the microstructure, chemical composition, abrasions resistance as well as the mechanical properties and the corrosion behavior was investigated.

Keywords: Polymer-derived ceramic; Laser pyrolysis; Nd:YVO_4 laser; environmental barrier coating

1. Introduction

Protective coatings are the most suitable and cost-effective solutions for many engineering problems like corrosion, oxidation and abrasion. Ceramic based coatings are promising candidates due to their oxidation and corrosion resistance in harsh environments. Moreover, due to their high hardness they stand out as wear protective coatings. However, the traditional methods for the preparation of ceramic coatings are usually expensive and have some limitations. A promising alternative for the preparation of ceramic coatings is the polymer-derived ceramics (PDC) technology. Preceramic polymers, usually silicon-based compounds, are

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converted into amorphous ceramics by a pyrolysis between 400 and 1000 °C in a furnace. A major advantage of this technique is that the coatings can be applied by simple methods like spraying or dip coating.

However, one drawback of the PDC route is related to the high temperatures required for the ceramization, whereby it is limited by the thermal resistance of the substrate. A very innovative approach to overcome this restriction is the use of laser radiation as analternative energy source for the pyrolysis of the preceramic polymers. Additionally, laser pyrolysis enables fast processing and the selective pyrolysis of the coatings, due to the high energy and precision of the laser beam.

2. Experimental procedure

The procedures for the preparation of substrates and coating suspensions, and for the deposition of the coatings were reproduced from the work of Günthner et al., 2011. The coatings consist of the two commercially available polysilazanes Durazane 2250 and Durazane 1800 (both Merck KGaA, Germany). Monoclinic ZrO_2 powder (Alfa Aesar GmbH & Co. KG, Germany) was used as a passive ceramic filler. In order to densify and seal the coatings, the two glass powders borosilicate glass 8470 and barium silicate glass G018-311 (both Schott AG, Germany) were selected as additives. The preparation of the suspension is described in detail by Günthner et al., 2011 and Horcher et al.,2020. According to Günthner et al., 2011, the starting composition of the coating system is 37 vol.% Durazane 1800, 20 vol.% ZrO_2 and 21.5 vol.% of each glass.

Stainless steel AISI 304 was used as the substrate for the coatings. The Durazane 2250 bond-coat was applied by dip-coating. The top-coat was applied by spraying onto the bond-coat. The laser pyrolysis was conducted using a Nd:YVO_4 laser (EasyMark 10E, ROFIN-BAASEL Lasertech GMBH & Co.KG, Germany) in a continuous wave operating mode as described by Tangermann et al., 2016.

The microstructure was investigated by scanning electron microscopy (SEM) (Merlin, Carl Zeis AG, Germany). The adhesion strength of the coatings has been evaluated by using a pull-off tester (PosiTest AT-A, DeFelsko Corp., USA) and the microhardness was determined by using a hardness tester (TYP KB 30S, KB Prüftechnik GmbH, Germany). The wear behaviour of the coatings has been investigated using a testing procedure based on a pin-on-disk-method. The corrosion behavior of the coating was evaluated by salt spray test according ASTM B117.

3. Results

The laser pyrolysis of the glass/ZrO_2-filled organosilazane-based composite coating has been described in detail by Tangermann et al., 2016. By using a laser, the coatings were successfully pyrolyzed. Fig.1 shows a representative SEM image of the cross-section of the composite coating after laser pyrolysis. Ceramic coatings with thickness of 20 µm were generated by laser pyrolysis of 50 µm thick green coatings.

By using a laser, dense and crack-free ceramic coatings were generated. The absorption of the laser radiation caused complete melting of both glass fillers. The melting of the glass fillers leads to a densification and infiltration of pores. Moreover, Tangermann et al., 2016 and Horcher et al.,2020 described the formation of ZrO_2 dendrites. It can be attributed to the melting of the ZrO_2-fillers.

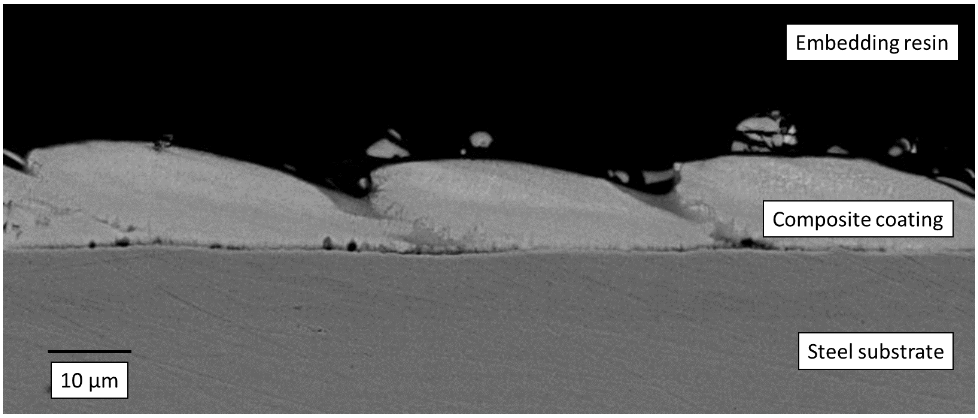

Fig. 1. Cross-section SEM micrograph of the glass/ZrO_2-filled organosilazane composite coating after laser pyrolysis

The adhesion strength of the laser pyrolyzed coating was examined by pull-off adhesion tests. The average pull-off adhesion of the coatings was 23.8 MPa (n = 3, SD = 1.3 MPa). For comparison, the adhesion strength of an oven-pyrolyzed coating (700 °C) amounted to only 8.7 MPa (n = 3, SD = 1.7 MPa). For the laser pyrolyzed coatings, mainly adhesion failure was observed. This indicated a good bonding between the substrate and the top-coat and within the top-coat. The strong adhesion results from the absence of pores and defects inside the coatings. In addition, the silazane forms chemical bonds with the substrate and fillers, which improves the adhesion. This mechanism is described in detail by Horcher et al., 2020.

The surface hardness has a significant influence on the abrasion resistance. The average Vickers hardness (load 0.01 kg) of the coating was 1324 ± 164 HV. The hardness of the steel substrate was 312 ± 22 HV. Therefore, the coating exhibit higher surface hardness than the substrate, whereby the coating is suitable for wear protection. The high hardness results from the dense coating structure and the hardness of the used fillers.

The abrasion resistance of the coating was determined by pin-on-disc method. Next to the hardness, the coefficient of friction (COF) plays a crucial role in development of wear protection coatings and should be kept as low as possible in order to avoid sliding wear. The roughness of the coating has also a significant effect on the sliding behavior. The arithmetic mean height (R_a) of the coating was 2.09 µm. By a double irradiation of the coating, the roughness was reduced to 1.02 µm. The influence of surface roughness has also been reflected in the coefficient of friction. For the single irradiated coatings, the COF is 0.33. By a double irradiation of the coating a levelling of roughness peaks has been achieved and therefore, the friction resistance and interlocking mechanism were minimized, which is indicated by reduction of the COF to a value of 0.10. No traces of abrasion were observed on the surface which has been double irradiated. On the surface of single irradiated coatings some small traces of abrasion were visible, which can be related to the higher surface roughness. During the wear test these roughness peaks were levelled by the applied pressure and resulting shear forces. Since the steel pin has a lower hardness compared to the coatings, the removal by penetration of the steel pin into the coating can be excluded.

The corrosion resistance was determined by salt spray testing for 168 h. The laser pyrolyzed coatings were characterized by only minor signs of corrosion and the coating adhere very well on the substrate. The good corrosion behavior can be explained by the dense structure of the coating and the corrosion-resistance nature of the silazane and the used fillers. The weight loss rate of the laser pyrolyzed coating was 0.013 g/h·m², whereby it can be considered as corrosion resistant.

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