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Laser pyrolysis of an organosilazane-based glass/ZrO_2 composite coating system

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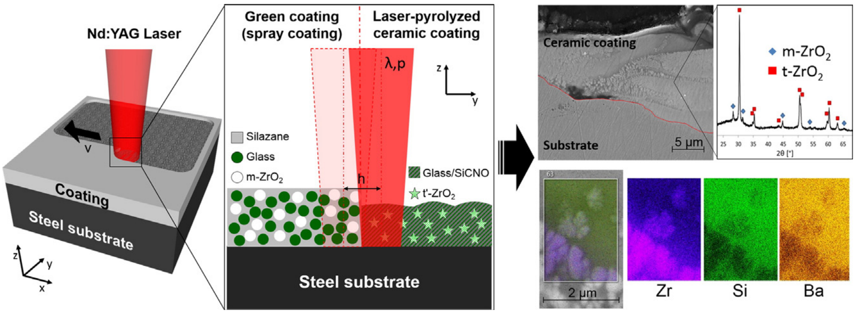
HIGHLIGHTS

- Composite coatings of silazane/glass/passive filler were obtained for the first time by pyrolysis using laser irradiation.
- The applied set of processing parameters for the laser pyrolysis resulted in dense, semi-crystalline and crack-free coatings.
- Laser irradiation induced the transformation of the monoclinic ZrO_2 filler into its high-temperature tetragonal phase.
- Components of the glass fillers stabilized the tetragonal phase of ZrO_2.

GRAPHICAL ABSTRACT



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ABSTRACT

A process for the laser pyrolysis of a ceramic composite coating system composed of an organosilazane (Durazane ™ 1800) with ZrO_2 and glass particles as fillers was developed. Firstly, the mild steel substrates were dip-coated with a perhydropolysilazane (PHPS) bond coat, onto which the composite coating slurry was applied by spraying. After drying, pyrolysis using a Nd:YAG laser led to the formation of a dense semi-crystalline ceramic coating system with a thickness up to 20 µm in a short time. The resulting coatings possess a significantly different morphology compared to the same coating system pyrolyzed in a furnace, due to different forming mechanisms. Laser irradiation led to the unexpected formation of oxygen vacancies in the crystalline lattice of ZrO_2, which increased the absorption of the laser radiation, enabling the transformation into a ceramic coating. Simultaneously, reactions between the glasses and the monoclinic ZrO_2 fillers were activated, resulting in the formation of dendritic tetragonal-stabilized ZrO_2 crystals. The thermal stability of the coating components was analyzed by thermogravimetric analysis (TGA) and the coatings were investigated by attenuated total reflectance infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD).

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1. Introduction

Protective coatings are frequently the most suitable and cost-effective solution for several engineering problems like corrosion, oxidation and wear. Indeed, novel specially tailored polymeric, metallic and ceramic coatings have been developed for specific applications [1–6]. In this context, ceramic coatings stand out due to their oxidation/corrosion resistance in harsh environments. However, the traditional methods for the preparation of ceramic coatings are relatively expensive and have several limitations. As an alternative, the polymer-derived ceramics (PDC) technology has been successfully applied in the last years for the processing of various ceramic coatings [7–15]. In this method, preceramic polymers, usually silicon-based compounds, are converted into amorphous ceramics by a pyrolysis between 500 and 1000 °C in a furnace [11]. The polymers may be applied by conventional lacquer methods like dip, spray and spin coating.

PDC-based coatings can be used for corrosion protection of metal, e.g., in marine, automotive and industrial applications [16]. However, one of the drawbacks of the PDC route is related to the high temperatures required for the ceramization of the precursors. This processing step is usually limited by the thermal resistance of the substrates. Hence, the preparation of thick ceramic coatings by PDC processing on substrates with low melting point is not possible by conventional pyrolysis in a furnace. Therefore, this method has been mostly limited to high-temperature steels, superalloys and ceramic substrates. However, even the properties of temperature-resistant metals may change due to the heat treatment, leading to unwanted characteristics. A possible solution to these issues is the application of laser radiation as energy source for the ceramization. Additionally to the low overall processing temperature, laser pyrolysis has the advantage of fast processing and the selective pyrolysis of the coatings, enabled by the high energy and precision of the laser beam.

Compared to furnace pyrolysis, the laser pyrolysis of preceramic polymers has been much less intensively investigated. Laser pyrolysis was previously used in combination with preceramic polymers for the additive processing of ceramic microcomponents [17]. The samples were produced using a layer-by-layer build-up technique in combination with a pulsed Nd:YAG laser. Small specimen with dimensions varying between 0.4 and 1 mm were prepared. The authors used a commercially available polysilazane precursor and investigated the influence of several laser parameters, e.g., pulse frequency, pulse duration and pulse energy. According to the authors, especially the pulse frequency influences remarkably the quality of the samples due to the presence of bubbles generated by the gaseous products of the pyrolysis. By reducing the frequency below 5 Hz, the refraction of the laser beam caused by the bubbles could be avoided, whereas the use of higher pulse frequencies resulted in undefined ceramic parts.

Müller et al. [18] reported on the comparison between CO_2 laser pyrolysis and pyrolysis in a furnace of liquid polysilazanes to generate nano-sized amorphous SiCN particles. The relative amount of carbon was considerably higher in the laser-pyrolyzed samples. This indicates that less carbon was lost during laser pyrolysis in comparison to furnace pyrolysis. Nevertheless, the authors concluded that, despite the different energy transfer mechanisms during laser and furnace pyrolysis, the decomposition reactions of the molecular precursors were similar in both experimental set-ups.

Also coatings have been prepared by laser pyrolysis of preceramic polymers. Colombo et al. [19] reported on the preparation of thin SiC ceramic films (70–100 nm) on Si and SiO_2 substrates from polycarbosilane coatings by pyrolysis with a pulsed Nd:YAG laser. Laser radiation absorption was enhanced by depositing a carbon layer on the substrate surface or by introducing graphite particles as fillers in the polycarbosilane. This processing method yielded SiC ceramic coatings without damaging the substrate. Laser pyrolysis in air or low vacuum did not result in oxidized coatings, in contrast to furnace pyrolysis. From microstructural point of view, the laser-pyrolyzed films were similar to furnace-treated coatings processed at 1000–1200 °C under high vacuum.

In the present work, the laser pyrolysis of a silazane-based coating system is proposed. The investigated coating system was previously used for the preparation of thick ceramic coatings by furnace pyrolysis in air [13]. The furnace-pyrolyzed coatings were developed to protect mild steel against oxidation and corrosion up to 700 °C. The system is composed of the organosilazane Durazane™ 1800, ZrO_2 and two types of glasses as fillers. The influence of the laser radiation on the precursor and on the fillers was studied. The laser-pyrolyzed coatings were investigated by attenuated total reflectance infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD).

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. [13]. Sheets of steel 13CrMo4-5 were pretreated by sandblasting followed by cleaning in ultrasound bath with acetone before the deposition of the coatings. Subsequently, a bond coat of polysilazane PHPS (Fig. 1a) (perhydropolysilazane, 20 wt% in di-*n*-butylether, Merck KGaA, Germany) was applied by dip coating using a hoisting apparatus (RDC 15, Bungard Elektronik GmbH & Co. KG, Germany) operated with hoisting speed of 0.3 m min^{-1} and immersion time of 10 s. The coated samples were then cured in air at 110 °C for 1 h. A single layer was deposited, resulting in a coating with thickness of ~1 μm [15]. This bond coat improves the adhesion of the top coat and protects the steel against oxidation.

The liquid organosilazane Durazane™ 1800 (Fig. 1b) (Merck KGaA, Germany), previously known as HTT 1800, was used as precursor for the top coat. To improve the cross-linking reactions, 3 wt% DCP (dicumyl peroxide, Sigma-Aldrich Chemie GmbH, Germany) was added to the Durazane™ 1800. Monoclinic ZrO_2 powder (Alfa Aesar GmbH & Co KG, Germany) with particle size between 0.3 and 4 μm and coefficient of thermal expansion (CTE) of 9–13 × 10^{-6} K^{-1} was used as passive ceramic filler to increase the overall CTE and the maximum coating thickness. To densify and seal the coatings, two glass powders with CTE close to that of the steel substrates (~10 × 10^{-6} K^{-1} for the glasses and 11–13.5 × 10^{-6} K^{-1} for the steel 13CrMo4-5) were selected: borosilicate glass 8470 (glass softening temperature: 570 °C) and barium silicate glass G018-311 (glass softening temperature: 750 °C) (Schott AG, Germany). The particle sizes of the glass powders range from 3–10 μm. To prepare the coating suspensions, firstly the dispersant DISPERBYK-2070 (BYK-Chemie GmbH, Germany) was dissolved in di-*n*-butylether (purity > 99%, Acros Organics BVBA, Belgium). Then, the fillers were added and dispersed by ultrasound and magnetic stirring. At last, the precursor was added to the mixture and the suspension was further mixed by magnetic stirring. The final composition of the top coat was calculated by Günthner et al. [13] based on TGA and density of the materials. The starting composition of the system is 37 vol% Durazane™ 1800, 21.5 vol% of glass 8470, 21.5 vol% of glass G018-311 and 20 vol% ZrO_2. After a thermal treatment

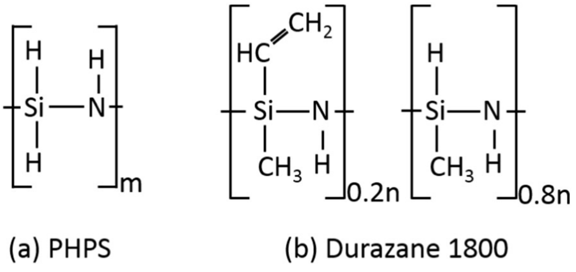

Fig. 1. Basic structure units of the silazanes (a) PHPS and (b) Durazane™ 1800.