Original article

High performance environmental barrier coatings, Part I: Passive filler loaded SiCN system for steel

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Abstract

A novel environmental barrier coating system for steel consisting of a perhydropolysilazane (PHPS) bond coat and a polysilazane-based glass/ceramic composite top coat has been developed. After stabilising the coating slurries, double layers were applied on mild and stainless steel substrates by the dip-coating technique. Parameters like pre-treatment of the steel substrates, filler systems, particle size of the fillers or coating thickness were varied to optimize the coatings. The thermal treatment was performed in air at temperatures up to 800 °C. Microstructural analysis by SEM and XRD revealed the formation of a coating system consisting of a SiNO bond coat and a ZrO_2-filled glass/ceramic top coat. A uniform, well adherent, dense and crack-free coating system with a noteworthy thickness up to 100 μm was achieved. Even after cyclic oxidation tests on coated samples at 700 °C the coating system was still undamaged and no oxidation occurred on the mild steel substrates.
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1. Introduction

Due to the increasing costs for metals, there is currently a need to enhance the performance and lifetime of steel, for example, those employed in exhaust systems, waste incineration plants, metal or glass casting and forming or for applications in the chemical industry.

Thermal and environmental barrier coatings (TBCs/EBCs) have been developed to improve the stability in aggressive environments. Non-oxide and oxide ceramic coatings are well suited to improve the resistance against corrosion and oxidation of metals due to their superior properties at elevated temperatures and in chemically harsh environments. Deposition methods like thermal spraying or CVD and PVD processes are commonly used to make ceramic coatings.[1,2]

Recently polymer derived ceramics (PDCs) have gained attention. They offer a number of advantages compared to traditional methods of ceramic processing like easy application on substrates of any shape, low temperature processing and the potential to tailor the properties via microstructure and composition design.[3]

The precursor technique exhibits a relatively low-cost and easy approach to produce polymeric and ceramic coatings. The coatings are mainly based on silicon containing precursors like polysiloxanes,[4] polycarbosilanes[5] or polysilazanes.[6,7] These coatings combine the processing ease of polymer derived ceramics and the favourable properties of the resulting ceramics like thermal stability, thermal shock resistance, high temperature strength or oxidation and corrosion resistance.[8–10]

The greatest disadvantage of polymer derived ceramics is the shrinkage of the polymer during pyrolysis, which can be higher than 50% by volume.[11] Residual stresses caused by

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the high volume shrinkage lead to the formation of defects, cracks or even delamination of the coatings. By adding passive fillers like SiC, BN, ZrO_2, Al_2O_3[11–14] and/or active fillers like Nb, Ti, $TiSi_2$, Hf[15–18] the volume change from polymer to ceramic conversion can be significantly reduced. Furthermore, – depending on the properties of the substrate – the thermal expansion coefficient of the coatings can be adjusted by an adequate filler material. By incorporation of fillers it is also possible to generate coatings with additional functionalities like special friction properties, electrical or thermal conductivity or catalytic activity.[8]

A critical thickness exists for polymer derived ceramic coatings. Below this thickness value, the coatings remain intact, dense and adherent. If the thickness exceeds this value, cracking and delamination of the coatings occur during pyrolysis.[4,8] For unfilled PDC coatings, this critical thickness value lies in the range of a few micrometers. For composite coatings (active or passive fillers), the critical coating thickness can be increased up to about 20 μm. Thicker coatings can only be realized by a repeated coating and pyrolysis procedure. In Table 1 some coating systems and their critical coating thicknesses are summarized.

The main limitations of composite coatings are often an inhomogeneous distribution of the filler material, the limited coating thickness, the formation of cracks, defects or residual porosity in the coatings and the relatively low adhesion, which can lead to delamination, especially under thermal cycling conditions.

Thus an effective oxidation or corrosion protection of steel by unfilled or composite PDC coatings is difficult to achieve. The aim of this work is the development of a relatively thick (about 100 μm), protective, dense and well adherent coating system on steel. Therefore, two approaches were conducted. In the first approach, a double layer composition with a bond coat and a top coat was investigated. This assembly is generally used in environmental or thermal barrier coatings for instance on turbine blades.

Secondly, glass powders were added as filler materials in order to densify and seal the coatings as well as to improve the coating thickness and adhesion. Vitreous enamels made of melted and fused glass powders are widely used as smooth, durable, dense and thick coatings on metals, glasses or ceramics. They provide high chemical stability, good mechanical properties, gas tightness, superior adhesion, sealing and self-healing properties. However, enamels are limited in their temperature stability and high temperature strength. They are also sensitive to mechanical deformation and thermal shock loads due to their poor fracture toughness.[19,20]

The combination of preceramic polymers with glass materials has already been investigated. Scheffler and co-workers for instance developed a cellular glass foam by the use of a polysiloxane filled with a glass powder and a glass former.[21] However, polysilazane-based glass filled coating systems have not been developed. In this work, different polysilazane systems, ceramic fillers and glass additives were selected and investigated as coating materials. The slurry preparation as well as the processing, microstructure and cyclic oxidation behavior of the novel coating systems are presented in this paper.

2. Experimental procedure

Based on the goal of the work, two different commercially available polysilazanes PHPS (perhydropolysilazane) and KiON HTT1800 (both Clariant Advanced Materials GmbH, Germany) were studied as precursor materials. The PHPS system is supplied as a 20 wt.% solution in di-n-butylether. KiON HTT1800 is a liquid polysilazane-based coating system.[22]

BN (Henze BNP GmbH, Germany), Si_3N_4 (H. C. Starck GmbH, Germany) and ZrO_2 (Alfa Aesar, USA) fillers with a particle size between 0.3 and 4 μm were tested as passive fillers. As discussed in the next section, ZrO_2 powder was selected as the best passive filler material.

Four glass powders whose coefficient of thermal expansion is close to that of the steel substrates were selected as additives (all Schott, Germany). The glass systems are: 8472 (lead borate glass), G018-198 (lead-free passivation glass), 8470 (borosilicate glass) and G018-311 (barium silicate glass). The average particle size of the glass powders is between 3 and 10 μm. Selected properties of the ceramic and glass filler materials are summarized in Table 2.

Parameters like the precursor, the filler and glass systems, the volume fraction of the components, the dispersant and the dispersing methods (stirring, ultrasonic treatment, ball milling) were varied to optimize the composite coating system.

Mild steel (13CrMo4) and stainless steel (AISI 304) plates were cut into 2.5 cm × 8 cm sheets. In order to achieve well adherent coatings, the pre-treatment of the steel substrates and the application of a bond coat were investigated. Therefore the influence of different sandblast parameters, cleaning procedures and bond coatings was examined. The pre-treated substrates were dip-coated with a hoisting apparatus and the coating thickness was controlled by varying the hoisting speed between 1.5 and 8 mm/s. The curing of the PHPS bond coat was done in air at 110 °C for 1 h. The thermal treatment of the composite coatings was performed in air (Nabertherm® LH 60/14, Nabertherm, Germany) at temperatures up to 800 °C with heating and cooling rates of 3 K/min and a holding time of 1 h. In Fig. 1, the processing scheme of the coatings is presented.

Cyclic oxidation tests were performed on pyrolyzed samples. The samples were heated to 700 °C in three consecutive cycles with heating and cooling rates of 10 K/min and holding times of 30 min at 700 °C as well as at room temperature.

The coating thickness before and after thermal treatment was measured with a Fischerscope® MMS (Helmut Fischer GmbH & Co. KG, Germany) by the eddy current method (ASTM B244). Microstructural and interfacial analyses were performed with a light microscope and a scanning electron microscope with EDS (1540EsB Cross Beam, Carl Zeiss AG, Germany). X-ray diffraction measurements were done with a Bragg–Brentano Diffractometer "XRD 3000 P" (Seifert, Germany) to investigate the crystalline phases. The cyclic oxidation behavior of coated and uncoated samples was analyzed by scanning electron microscopy.

Table 1
Polymer derived coatings and critical coating thickness values.

Precursor/system	Filler material	Critical coating thickness (μm)	References
Polycarbosilane	–	1	[5]
Poly(carbo)silazane PHPS/ABSE	–	1	[7]
Polycarbosilane	Al_2O_3	10	[12]
Polysilazane PHPS	BN (hexagonal)	12	[13]
Polysilazane ABSE	BN (cubic)	15	[14]
Polysiloxane PHMS	$TiSi_2$	18	[17]

Table 2
Comparison of some properties of selected filler materials (manufacturer's data).

Material	Average particle size d_{50} (μm)	Thermal expansion coefficient α (10^{-6}/K)	Softening point (°C)	Density (g/cm³)
BN	0.7	3.5–4	–	2.25
Si_3N_4	0.6	2.5–3.5	–	3.2
ZrO_2	1	9–13	–	5.7
Glass 8472	9.7	12	360	6.7
Glass G018-198	9.9	9–10	444	6.6
Glass 8470	3.3	10	570	2.8
Glass G018-311	3.1	10	770	3.8

(mild steel substrate 13CrMo4 11–13.5)

Ceramic and glass powders, PHPS and HTT1800 poly(carbo)silazanes and composite coating mixtures were analyzed by TGA measurements according to the thermal treatment of the coatings in air with a heating rate of 3 K/min (Linseis L81 A1550, Linseis, Germany). For sample preparation, the solvent of the PHPS solution and of the composite coating mixtures was removed by distillation. The resulting solids were milled and sieved to a grain size smaller than 32 μm for better comparisons with the behavior of the coatings during pyrolysis.

3. Results and discussion

3.1. Materials

Previous work has identified PHPS as very suitable coating system for the protection of steel against oxidation and corrosion.[7] PHPS is produced by ammonolysis of dichlorosilane SiH_2Cl_2 and contains no organic groups (Fig. 2). Due to the large number of Si–H bonds the PHPS is highly reactive especially with hydroxyl groups.[23]
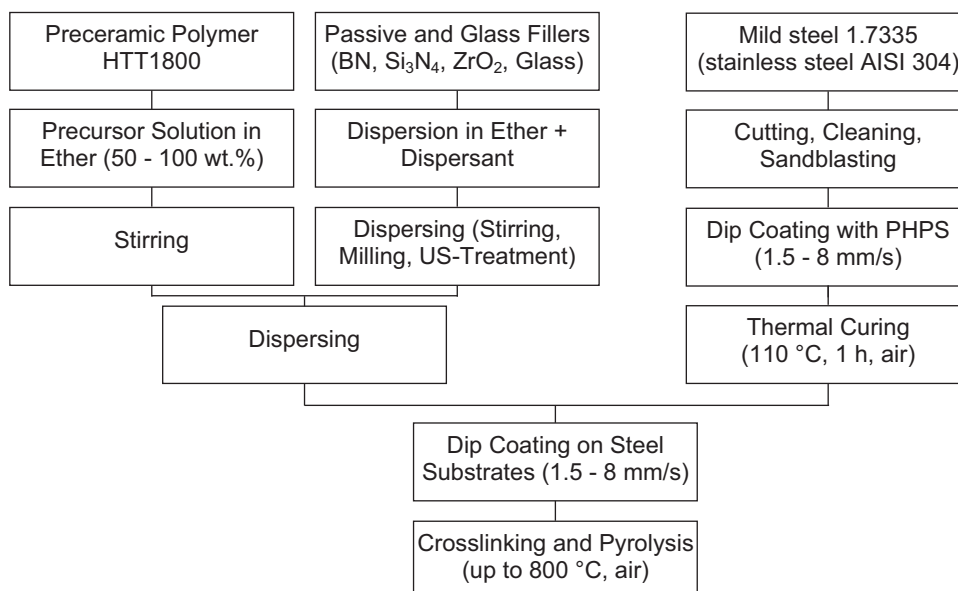
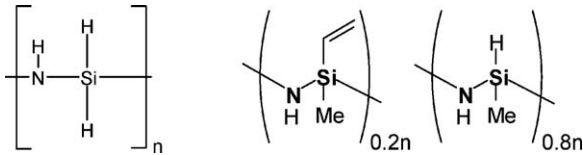Fig. 1. Processing flow chart for coating systems.

Fig. 2. Basic structure unit of the PHPS (left) and HTT1800 (right) precursors.
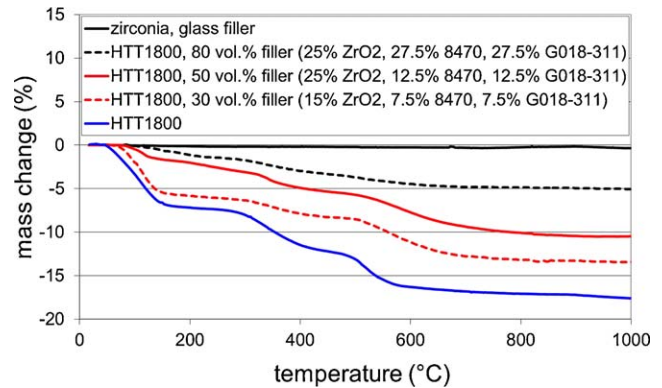

Fig. 3. TG analysis of filler powders (ZrO_2 + glass 8470 + glass G018-311), different HTT1800/filler/dispersant composites and pure HTT1800 in air with a heating rate of 3 K/min.

The liquid HTT1800 polysilazane is synthesized by co-ammonolysis of dichloro-methylvinylsilane and dichloro-methylsilane (Fig. 2). It can be crosslinked by heating to 180–200 °C or – at lower temperatures – by adding a free radical initiator, such as dicumylperoxide (DCP).[22] In this work, HTT1800 was used with 3 wt.% DCP.

Ceramic (BN, Si_3N_4, ZrO_2) and glass (Schott 8470, 8472, G018-198, G018-311) filled polysilazane-based coatings were produced according to the processing scheme shown in Fig. 1. The coating quality was evaluated by visual and light microscopic investigations. The focus was mainly on the homogeneity, adhesion and failure of the coatings.

PHPS-based composite coatings could not be applied by the dip-coating technique, since the viscosity of the coating slurry is too low (PHPS only available as 20 wt.% solution). The BN- and Si_3N_4-filled glass/ceramic coatings were inhomogeneous, porous and not protective, because the coatings segregated into a glass and a nitride rich phase. Furthermore, composite coatings with the glass powders 8472 and G018-198 as fillers were not uniform, since the glass particles settled rapidly in the suspension. The reason for this lies in the high density and particle size of the glass powders (see Table 2).

The best composite coatings could be achieved with HTT1800 as precursor and ZrO_2, glass 8470 and glass G018-311 as fillers. In order to adjust the coating properties over a wide range between an enamel and a ceramic like system, the filler content (zirconia + glass systems) in the resulting ceramic coatings was varied from 30 up to 80 vol.%. The coating slurries are well dispersed after stirring and ultrasonic agitation (each 30 min).

The pyrolysis behavior of the pure glass and zirconia powders, different HTT1800/ZrO_2/glass/dispersant mixtures and the HTT1800 polysilazane were characterized by TGA measurements. The results of the TG analyses in air are given in Fig. 3.

As shown in Fig. 3, the conversion of the HTT1800 polymer into an amorphous SiCNO–ceramic takes place in three steps. In the first step up to about 130 °C, a significant mass loss is detected due to the evaporation of mono- and oligomeric species. Afterwards, the cross-linking of the precursor leading to an unmeltable polymer occurs. During the third step between 300 and 700 °C mainly NH_3, CH_4, CO_2 and H_2O are removed. The ceramic yield after thermal treatment at 1000 °C in air is 82 wt.%. The results are in good agreement to findings of Bahloul et al.,[24] who investigated the thermal decomposition of a polysilazane in different atmospheres.

As expected, the pure zirconia and glass powders show no significant mass change up to 1000 °C in air.

The pyrolysis behavior of the HTT1800/ZrO_2/glass/dispersant mixtures lies in between the TGA curva-

tures of the pure HTT1800 and the zirconia/glass powders. From the behavior of three different composite mixtures can be concluded, that the ceramic yield of the composites increases with the filler content. At temperatures higher than 700 °C no significant mass change can be detected. Furthermore, the results indicate that no interactions between the HTT1800 polysilazane and the zirconia/glass powders take place so that the fillers can be assumed as passive fillers.

3.2. Pre-treatment and bond coat on mild steel substrates

As mentioned in the experimental procedure, mainly mild steel (13CrMo4) and – for comparative studies – also stainless steel (AISI 304) plates were used as substrate materials. Mild steel was investigated, because it is commonly used in harsh environments like in waste incineration plants and for applications in the chemical industry, where it is strongly attacked by corrosion and oxidation. For mild steel the α to γ phase transformation, which is associated with a high volume change, takes places at about 723 °C.[25] Since this transformation often leads to the formation of cracks or to the delamination of the coatings, the pyrolysis of the composite coatings was conducted at 700 °C. Furthermore, – as discussed in the last chapter – the main polymer to ceramic conversion of the HTT1800 system by separation of gases is completed after a thermal treatment up to 700 °C.

In order to achieve well adherent and homogeneous coatings without failures, a pre-treatment of the substrate material is very important. The influence of different sandblast parameters, cleaning procedures and bond coatings was examined.

In the original state, the mild steel was partially corroded and a porous oxide layer was present. To remove this low adherent oxide layer and other contaminations, the steel samples were sandblasted. Furthermore, this treatment leads to a roughening of the surface, so that the adhesion of coatings can be improved.

In Fig. 4a the surface of a mild steel sample, which was sandblasted with corundum particles (d_{50}: 110 μm, pressure: 3 bar) is displayed. This treatment results in a rough and sharp-edged surface with an average surface roughness R_z of 8 μm. How-
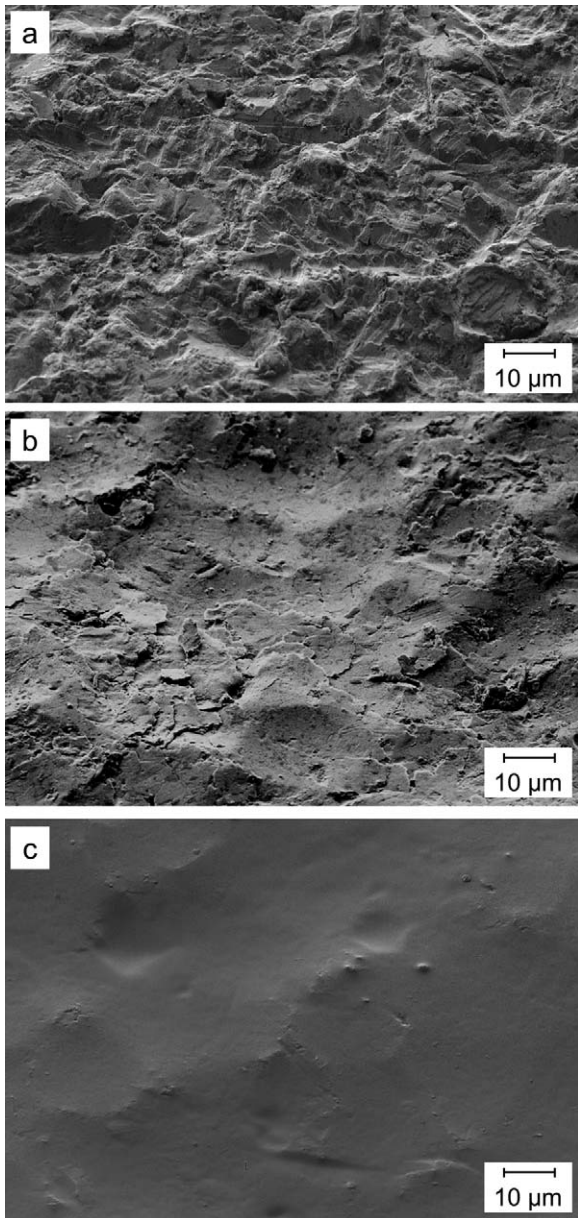
Fig. 4. Scanning electron micrographs (SEM) of different pre-treated mild steel samples; (a) sandblasted with corundum; (b) sandblasted with glass beads; (c) sandblasted with glass beads, coated with PHPS and cured at 300 °C, 1 h, air.

Fig. 5. Scanning electron micrograph of a composite coating (50 vol.% HTT1800, 25 vol.% ZrO_2, 12.5 vol.% glass 8470, 12.5 vol.% glass G018-311) on pre-treated mild steel; pyrolyzed at 700 °C, 1 h, air.

pyrolysis step, the mild steel substrate is strongly oxidized and therefore, the composite coatings fail at the interface.

To overcome this problem, PHPS was tested as a bond coating (Fig. 4c). It can be seen from Fig. 4c, that the sandblasted steel surface (glass beads) is uniformly wetted and covered by the about 1 μm thick PHPS coating.

On mild steel substrates, an oxide layer with adsorbed water is present in air. Polysilazanes react with hydroxyl groups of the substrate surface by the following simplified reactions[24]:

$$Fe–OH + \equiv Si–NH–Si\equiv \ \rightarrow \ \equiv Fe–O–Si\equiv + H_2N–Si\equiv \qquad (1)$$

$$Fe–OH + H_2N–Si\equiv \ \rightarrow \ \equiv Fe–O–Si\equiv + NH_3 \qquad (2)$$

We conclude that direct chemical metal–O–Si bonds between the steel and the precursor-based coatings are formed. Thus, the adhesion of the precursor layers on metals is very strong.[7,13,14]

Furthermore, the oxidation of mild steel during pyrolysis in air up to 700 °C can be prevented by the thin PHPS-based coatings. Previous investigations already showed that the polysilazane PHPS is very suitable for the protection of steel against oxidation.[7] This is due to the formation of a SiON-based ceramic at relatively low temperatures and the high ceramic yield of the PHPS system in air, resulting in a very dense and passivating barrier coating. As can be seen in Fig. 5, this combined pre-treatment (sand blasting with glass beads, ultrasonic cleaning in acetone, PHPS bond coat) is well suited to achieve well adherent composite top coatings on mild steel.

3.3. Composite top coatings

The polysilazane-based glass/ceramic top coatings were processed as described above. For this purpose HTT1800 was used as precursor and ZrO_2, glass 8470 and glass G018-311 as fillers. The coating slurries are well dispersed after stirring and ultrasonic agitation (each 30 min). Uniform composite coatings were obtained by the dip-coating method. According to Landau and Levich,[27] the coating thickness primarily depends on the withdrawal speed, the viscosity and the density of the slurry.

In Fig. 6a, a SEM micrograph of a HTT1800/glass composite coating on stainless steel is presented. As can be seen from

ever, the sharp borders and peaks could initiate the formation of cracks in the composite coatings.

As can be seen in Fig. 4b, a more uniform and compacted surface is achieved by the sandblasting with glass beads (d_{50}: 90 μm, pressure: 3 bar). The average surface roughness R_z is decreased to a value of about 4 μm. This treatment also removes the surface oxide layers. Well adherent and homogeneous composite coatings could be applied on such pre-treated mild steel samples. However, after pyrolysis in air, the coatings delaminated from the substrate.

As is known from the literature, a thermal treatment in air at temperatures higher than about 550 °C leads to the formation of a fast growing and poorly adherent oxide scale on the mild steel.[26] Since the glass/ceramic coatings are porous during the
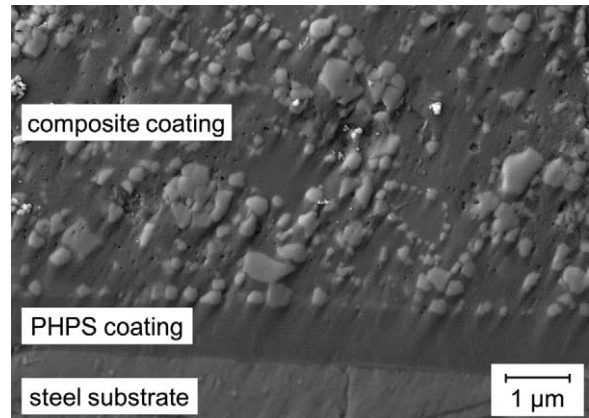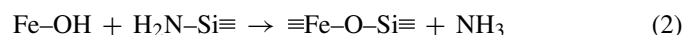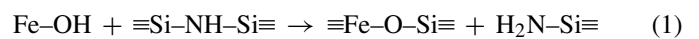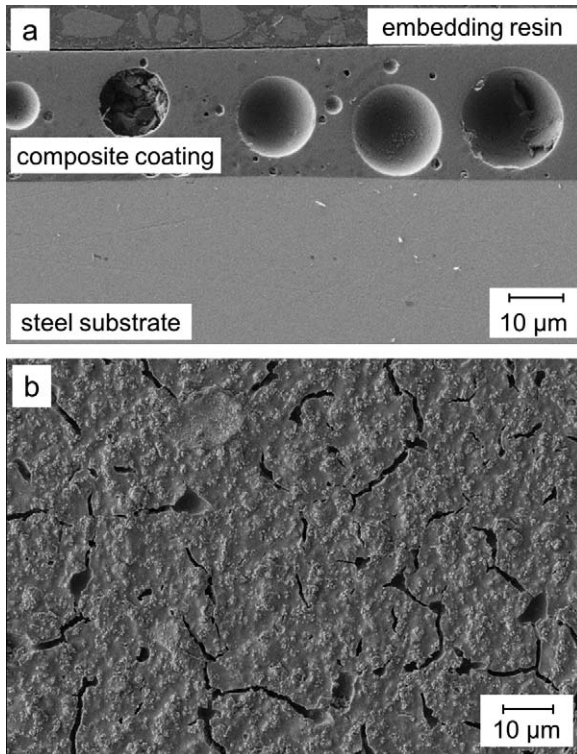
Fig. 6. Scanning electron micrographs of composite coatings on mild steel, each pyrolyzed at 700 °C for 1 h in air; (a) 30 vol.% HTT1800, 35 vol.% glass 8470, 35 vol.% glass G018-311; (b) 70 vol.% HTT1800, 15 vol.% ZrO₂, 7.5 vol.% glass 8470, 7.5 vol.% glass G018-311.

Fig. 7. Scanning electron micrograph of a glass/ceramic coating (20 vol.% HTT1800, 25 vol.% ZrO₂, 27.5 vol.% glass 8470, 27.5 vol.% glass G018-311) on mild steel; pyrolyzed at 700 °C, 1 h, air.

the cross-section, the softening of the glass additives, which occurs at temperatures higher than 570 °C (see Table 2), leads to a homogeneous glass/ceramic matrix. The shape and geometry of the glass particles is no longer present. Furthermore, the glass and HTT1800-derived phases cannot be distinguished. However, the approximately 25 μm thick composite coatings exhibit very big closed pores. This problem is already known from the processing of enamels, where the formation of pores in general cannot be completely avoided. The pores result from the release of gases, which are generated from the conversion of the polysilazane HTT1800 and from the decomposition of the dispersant and/or from other organic species in the glass additives. Since the diameter of the pores lies in the range of the coating thickness, such coatings do not possess environmental barrier properties.

One way to reduce the porosity and the pore size of the coatings is to enable the escape of the gases. This can be done by a skeletal construction of the coatings. Hence, zirconia was added as passive filler and as a refractory constituent. Furthermore, zirconia is characterized by its high temperature stability, good mechanical properties and very low thermal conductivity. In order to adjust the coating properties in a wide range between an enamel and a ceramic like system, the zirconia and glass filler content in the ceramic coatings was varied from 30 up to 80 vol.%. A composite coating with a high content of the polysilazane HTT1800 is shown in Fig. 6b.

The high volume shrinkage of the precursor leads to the formation of cracks and pores in the 10 μm thick coatings. Thus, the
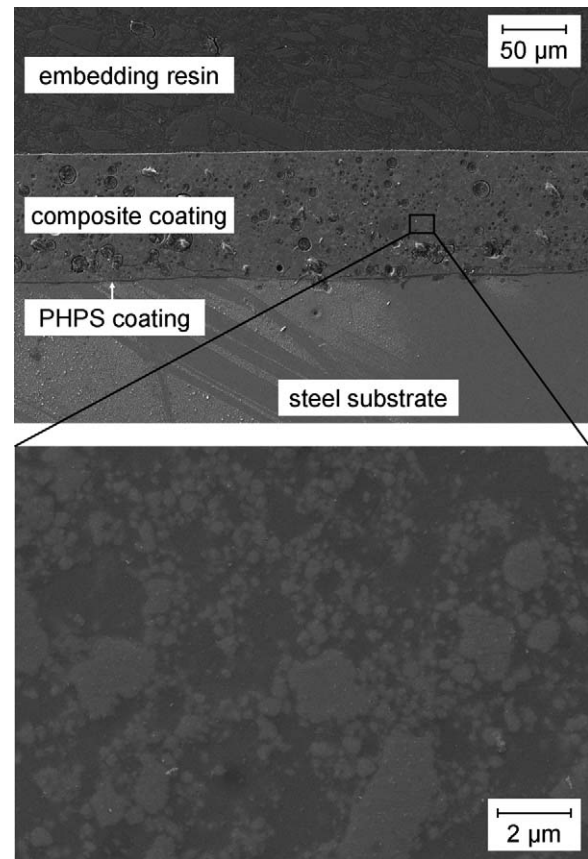
volume fraction of the polysilazane resin was reduced. A composite coating with a HTT1800 content of 50 vol.% has already been shown in Fig. 5. For this composition, crackfree composite coatings up to 15 μm can be applied.

Composite coatings with a polysilazane content between 20 and 40 vol.% were also investigated. In Fig. 7, SEM micrographs of such a glass/ceramic coating on mild steel are presented (20 vol.% HTT 1800).

As can be seen from the cross sections, the composite coating is dense, uniform, well adherent and the ZrO₂ particles are distributed homogeneously in the matrix. The about 1 μm thick PHPS bond coat is also visible. The composite coatings contain some small closed pores with a diameter up to 10 μm. Furthermore, no cracks or delamination can be detected both within and at the interface of the approximately 100 μm thick coating. As discussed in the introduction, the critical coating thickness of polymer derived ceramic composite coatings is about 20 μm.[12–14,17] These results on the new glass/ceramic polysilazane-based coatings show, that the critical coating thickness can be clearly increased by the addition of suitable glass and ceramic fillers.

The phase composition and microstructure of the coatings was also investigated by X-ray diffraction studies (see Fig. 8). The glass filled polysilazane-based coatings are fully amorphous after a pyrolysis in air at 700 °C. For the glass and zirconia filled
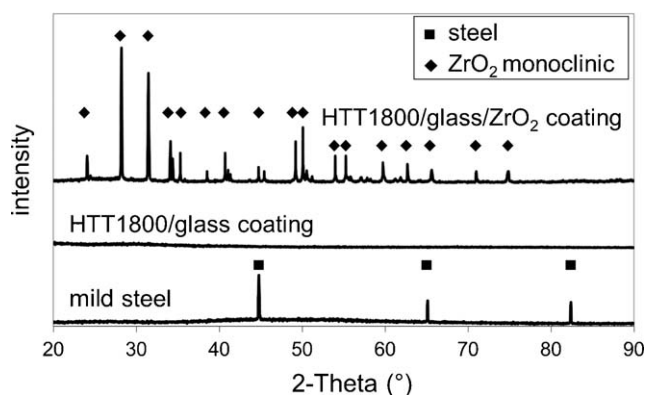
Fig. 8. X-ray diffraction patterns of mild steel, HTT1800/glass coating and HTT1800/glass/ZrO_2 coating on mild steel; coatings pyrolyzed at 700 °C, 1 h, air.

coatings, only the crystalline phase of monoclinic ZrO_2 can be detected. The results of the XRD-measurements also exhibit, that the coated mild steel substrates are not oxidized under the used pyrolysis conditions.

It can be concluded form the SEM and XRD studies, that no reactions take place between the polysilazane HTT1800 and the filler materials. By the addition of glass and zirconia fillers a near-net shape polymer–ceramic conversion with a reduction in the volume shrinkage and a decrease in the porosity can be achieved. The optimized composite coatings consist of two phases, where the monoclinic zirconia particles are distributed in an amorphous matrix.

3.4. Cyclic oxidation behavior of the coating system

In order to investigate the environmental protection ability of the coatings, cyclic oxidation tests were conducted in air. Since thermal stresses are often a problem for ceramic coatings on metals, cyclic oxidation tests at 700 °C with heating and cooling rates of 10 K/min and holding times of 30 min at 700 °C as well as at room temperature were performed. After three consecutive cycles no spalling, defects, or cracks are visible both at the surface and at the interface of the optimized coating systems (see Fig. 9).

The reason for this very good behavior at thermal loads originates from the tailored thermal expansion coefficients of the composite coating systems. The thermal expansion coefficients of the fillers and the substrate are given in Table 2. For polymer derived SiCN(O)–ceramics the thermal expansion coefficient is in the range of $3–4 \times 10^{-6}$/K.[10] Based on these data, the thermal expansion coefficient of the coating system can be approximated according to the rule of mixture.[28] The calculated value is about 9×10^{-6}/K which is close to the coefficient of the mild steel substrate ($11–13.5 \times 10^{-6}$/K). Due to this, the thermal stresses are reduced. The existence of pores is also postulated as a benefit, since the thermal shock resistance of the coatings may also be improved by a homogeneous porosity. The reason for this behavior is that the porosity leads to a reduction of the modulus of the coatings and therefore to a decrease of the magnitude of the residual stresses under thermal cycling.[29]
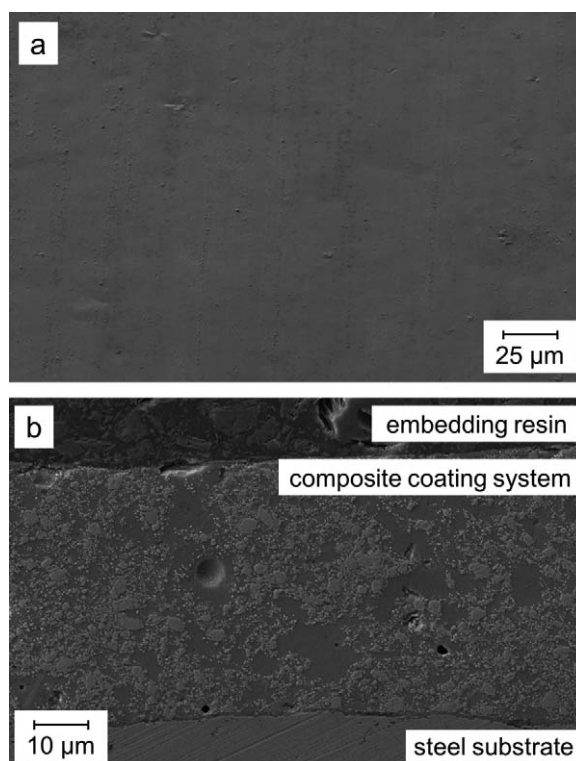

Fig. 9. Scanning electron micrograph of a coating system (bond coat: PHPS; top coat: 20 vol.% HTT1800, 25 vol.% ZrO_2, 27.5 vol.% glass 8470, 27.5 vol.% glass G018-311) on mild steel after cyclic oxidation test (3×700 °C); (a) top view; (b) cross section.

Furthermore, no oxidation of the mild steel substrate can be detected after the cyclic tests (see Fig. 9b). The composite coating system with a thickness of about 50 μm is well adherent and crackfree. This indicates that the coating system acts as a very good barrier against oxidation.

Further work will be done on the study of other filler systems and on the investigation of the environmental barrier properties of the composite coatings, especially their oxidation and corrosion behavior under extreme conditions such as in combustion environments or in molten salts.

4. Conclusion

In this work, a double layer polysilazane-based environmental barrier coating system for steel was developed. For this, different polysilazane systems, ceramic fillers and glass additives were selected and investigated as coating materials. A processing route which includes pre-treatment of the steel substrates, preparation of the coating slurry, application of the bond coat and the composite top coat by dip-coating and thermal treatment in air was studied.

The investigations show that the pre-treatment as well as the application of a PHPS bond coat on mild steel substrates are very important to achieve well adherent composite coatings. Due to the reactivity of the PHPS polysilazane, direct chemical bonds between the mild steel substrates and the PHPS are formed. Therefore the PHPS-based bond coat increases the adhesion of

the composite top coatings and further acts as diffusion barrier against oxidation during the pyrolysis step of the coating system.

The best composite top coatings could be achieved with HTT1800 polysilazane, filled with zirconia as passive filler and the glass systems 8470 and G018-311 as sealing agents. After a thermal treatment in air at 700 °C, uniform, dense and crack-free composite coatings on mild steel were achieved.

The critical coating thickness of the coating systems can be increased up to 100 μm, if the polysilazane and filler systems, their volume fractions and the processing parameters are tailored and optimized. Microstructural analysis by SEM and XRD investigated that the ZrO_2 particles are homogeneously dispersed in the amorphous matrix. Cyclic oxidation tests showed that the coating system protects mild steel against oxidation up to 700 °C.

The results confirm that the combination of PDCs with tailored fillers and glass systems enable the processing of thick, dense and crack-free composite coating systems. Furthermore, the double coatings can be processed in air at relatively low temperatures, leading to an efficient process. These coatings are suitable as protective coatings at medium temperatures, e.g. for exhaust systems, waste incineration plants, metal or glass casting and for applications in the chemical industry.

Acknowledgements

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