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A two-component preceramic polymer system for structured coatings on metals

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ABSTRACT

A liquid polysiloxane system consisting of a polymethoxymethylsiloxan and a hydroxy-terminated linear polysiloxane was used as preceramic polymer coatings on stainless steel. Interface reactions between the polymer derived ceramic matrix and the steel substrate were evaluated during and after pyrolysis with X-ray diffraction analysis and energy dispersive X-ray analysis. The system was loaded with different fillers and the rheological behaviour was investigated with respect to the coating thickness evolution by dip coating processing. Interface reactions with the steel components such as carbide formation and spinel formation were detected in the filler-free system and shear thinning was found to be a useful tool for coating thickness adjustment.

1. Introduction

Coatings are of immense interest to improve an existing material's durability, to extend its area of application by improvement of surface properties, or to open up potentially new applications by adding functionality to its surface. Among numerous established coating processes such as atmospheric plasma spraying, electron-beam physical vapor deposition, RF sputtering or chemical vapor deposition the use of preceramic polymers became a matter of intensive research over the last decade or so. An overview dealing with preceramic polymer processing and properties for the generation of ceramic coatings for a great variety of (potential) applications is given in [1]. Advantages of preceramic polymers are based on the use of cost efficient manufacturing routes from polymer processing technologies such as dip coating or spray coating, low conversion temperatures in a desired atmosphere, tailoring of the microstructure and resulting properties as a function of composition and thermal treatment parameters [2–6]. The processing protocol for the manufacturing of polymer derived ceramics (PDC) form preceramic polymers includes the following steps: mixing/dissolving in a solvent, introduction of particulate fillers (optional), shaping and thermal conversion. While filler-free polymer derived ceramics show linear shrinkage of up to 30% due to the density increase from polymer density (~1–1.2 $g\,cm^{-3}$) to the density of the resulting composite ceramic (2.0 to 3.0 $g\,cm^{-3}$), shrinkage can be minimized by the use of fillers. Typical filler load is in the range from 20 to 50 vol.%. *Inert* filler powders which do not react are e.g. Al_2O_3, SiC, B_4C, and Si_3N_4, while *reactive* fillers like Ti, Cr, Mo, B, $MoSi_2$, etc., may react with the solid and gaseous decomposition products of the polymer precursor to form carbides, oxides, or nitrides. More details of preceramic polymer synthesis, processing, properties and applications can be found in [7]. Recent work in the field of PDC coatings is related to the use of inert and active fillers for applications like antibacterial surface functionalization, oxidation protection, or for the tailoring of the specific surface area [8–18].

In this paper a polymethoxymethylsiloxane was the base preceramic polymer. It was used without and with silicon nitride fillers (Si_3N_4), and stainless steel was coated with an optimized slurry. Pyrolysis was performed between 400 °C and 1000 °C in argon atmosphere. Characterization was carried out with respect to the phase formation in the interface between the coating and the steel substrate and surface structures were imaged.

2. Experimental details

A polymethoxymethylsiloxane, MSE-100 (Wacker Silicone AG, Munich, Germany) and a hydroxy-terminated linear dimethylpolysiloxane, DMS-S12 (Gelest Inc. Morrisville, PA, USA) were used as the preceramic polymer system. Both liquid components were mixed in a glass beaker with a weight fraction of MSE-100 $M_{MSE} = (m_{MSE}/(m_{MSE} + m_{DMS})$ of 0.7. As a room temperature crosslinking catalyst [bis(2-ethylhexanoate)tin] dissolved in 50 wt.% dimethylpolysiloxane (SNB-1101, Gelest Inc. Morrisville, PA, USA) was added. The amount of the catalyst was 1–2 wt.% related to the tin metal. The amount of catalyst as well as the process temperature influences the crosslinking time significantly. A *liquid–solid* transition time of about 35 min was measured for a catalyst concentration of 1.0 wt.% and room temperature. Crosslinking is driven by a two-step mechanism. In the first step

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condensation of silanole groups from the DMS-S12 occurs in the presence of the tin catalyst. This results in the formation of water within the mixture, and no phase separation was observed. Once the water is formed it undergoes diffusion to the methoxy groups of MSE-100 and methanolysis takes place resulting in the formation of siloxane bonds and monomeric reaction products such as methanol. The crosslinking mechanism is described more in detail in [19].

In one set of experiments the liquid samples were used for a dip coating procedure, and in another set of experiments the samples were modified by addition of particulate fillers. Si_3N_4 powder, SiC powder and Al_2O_3 powder were used. The particle size d_{50} of the fillers was measured to be 580 nm, 530 nm and 13 nm, respectively. The resulting filler amount was 5 vol.%, and the fillers were introduced by vigorous stirring with a magnetic stirrer. A processing scheme is shown in Fig. 1.

For proper crosslinking of MSE-100 preceramic polymer water addition is necessary. Since MSE-100 is immiscible with water, hydroxyl terminated polymethylsiloxane (DMS-S12) was added. When a catalyst is added condensation starts with DMS-S12 under the increase in polymer chain length and the release of water. This water actually methanolyses the methoxygroups of MSE-100 and the consecutive step is the formation of siloxane bonds. This process leads to a liquid–solid-transformation and increases the degree of crosslinking of MSE-100 [19]. As a consequence, a small amount of non-reacted water and methanol remain in the sample, and they were removed by a drying procedure at 120 °C for 12 h in a drying furnace.

Catalyst-free, Si_3N_4 containing samples were characterized with respect to their rheological behaviour. Viscosity measurements of the samples were carried out with a rotational rheometer Rheotest 2 (Rheotest Medingen GmbH, Germany) at 25 °C with shear rates ranging from 1 to 1000 s^{-1}.

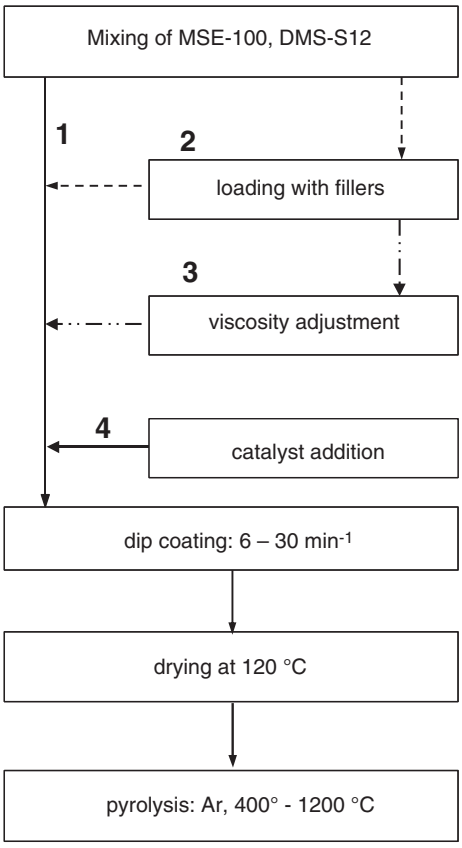

Fig. 1. Processing scheme of metal coating with preceramic polymers; route 1 — coating with a filler-free preceramic polymer system; route 2 — coating with a particle filled slurry (low load); and route 3 — coating with a particle filled slurry (high load, >5 vol.% fillers).

The thermal transformation behaviour of crosslinked and dryed samples was investigated by thermal analysis (TGA) with a simultaneously operating thermobalance STA 409A (Netzsch GmbH, Selb, Germany).

About 50 mg of sample was placed in an alumina crucible and heated to 1000 °C in argon atmosphere with a heating rate of 10 K/min.

Dip coating was carried out with a linear drive (Isel Automation AG, Germany) equipped with a sample holder and a variable withdrawal speed. The metal to be coated was stainless steel (# 1.4301 according to DIN EN 10027-2). The withdrawal speed was varied from 6 mm min^{-1} to 30 mm min^{-1}. After dip coating the samples were dried at 110 °C overnight and pyrolyzed at 1000 °C in argon atmosphere with an Ar flow rate of 0.5 l min^{-1}. Another set of samples was pyrolyzed in argon within the heating chamber of an X-ray diffractometer. The diffractometer used was a Bruker Advance D8 (Bruker AXS, Karlsruhe, Germany) equipped with a high-temperature heating chamber (mri physikalische geraete GmbH, Karlsruhe, Germany). Diffraction spectra for X-ray powder diffraction analysis (XRD) were recorded in 100 °C steps from room temperature to 1050 °C in a flowing argon atmosphere (5 l min^{-1}). XRD measurements were performed with the grazing incidence method, and as a cover window in the high-temperature chamber a capton foil was used. The diffractometer was operated with a tube current of 40 mA and a tube voltage of 40 kV, and Cu-K_α radiation was used. Light microscopy (LM) was carried out for surface structure analysis and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) was used for surface structure analysis as well, and for elemental analysis at the interface between the polymer derived ceramic coating and the metal. The EDX line scan was carried out using a FEI "Quanta 200" (FEI, Hillsboro, OR, USA). The voltage and magnification were set to 10 kV and 3000×, respectively while measuring.

Thermodynamic calculations were carried out with the software package HSC Chemistry 4.1 thermodynamics and data package (Outokumpu Research Oy, Pori, Finland) in order to get information on possible phases and phase stability during thermal treatment and reaction between PDC components and the steel substrate.

3. Results and discussion

3.1. Interface formation and resulting phases

The filler-free system was evaluated with respect to reactions between the PDC coating and the substrate material at elevated temperatures. Because of the elemental composition of the PDC matrix consisting of silicon (Si), carbon (C) and oxygen (O) after pyrolysis and the stainless steel with Fe (71 wt.%), Cr (20 wt.%) and Ni (8 wt.%) as main and Si (0.2 wt.%) and C (0.1 wt.%) as additional component diffusion and/or phase formation was expected during thermal treatment. In Fig. 2 EDX relative element concentration profiles are shown for C, O, Ni, Si and Fe. The interface region is approximately 1.5 μm in width. This is mostly indicated by oxygen and silicon. Both profiles show a slight increase from the left side up to the interface and steeply decrease within a distance of 1.0 to 1.5 μm. The decrease in the C concentration, however, is less pronounced from the PDC matrix (left) to the substrate (right), and no significant differences have been found between the interface region and the PDC matrix. The intensity of the Fe and Ni signals increases within the interface region. The small slope of the C signal found after the 4-μm position indicates a reaction between the carbon and the components of the steel.

In order to figure out if there is a formation of phases resulting from reactions between components of the PDC matrix and the