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Fabrication of ceramic coatings from polysilazane/aluminum: Effect of aluminum content on chemical composition, microstructure, and mechanical properties

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Abstract

Ceramic coatings with a thickness range of 1.5–5.5 μm were successfully prepared with polysilazane (PSN1) as a precursor and aluminum (Al) powder as an active filler. The effect of Al content on chemical composition, microstructure, and mechanical properties of the coatings was investigated. Chemical composition analysis revealed that Al powder was completely converted into Al_2OC and AlN phases during the ceramization process, accompanied by volume expansion. Ceramic coatings derived from less Al powder containing PSN1/Al showed more compacted surface morphology and continuous microstructure. The surface hardness and elastic modulus of ceramic coatings decreased with the increase of the volume fraction of Al from 10% to 40% (Al/PSN1, v/v). The maximum surface hardness and elastic modulus of coatings were 6.38 GPa and 107.66 GPa, respectively.

Keywords: C. Mechanical property; Polysilazane; Aluminum powder; Coatings; Microstructure

1. Introduction

In the past two decades, ceramics and ceramic composites have been successfully and conveniently fabricated by the well-known polymer-derived ceramics (PDCs) route, which has drawn intensive attention due to several advantages over traditional ceramic processing methods, including lower fabrication temperature, compositional homogeneity in the final products, the ability to use polymer-process techniques for processing complex-shaped components and the capability of property tailoring via composition design or thermal treatment parameters adjusting [1–5]. The PDCs route has a great variety of potential applications in the fabrication of bulk ceramics [6,7], ceramic composites [8,9], fibers [10,11], joining material [12], porous materials [13–15], micro electro-mechanical systems [16,17], protective coatings [18–25], and other materials [26]. Among them, preparation of protective coatings from preceramic polymers has been one of the most promising areas.

However, the coatings obtained from PDCs route generally suffer from formation of cracks, unwanted porosity, or even delamination due to large shrinkage of the polymer during cross-linking and pyrolysis process [4,27,28]. How to prepare crack-free and dense ceramic coatings is still a great challenge for the PDCs method. Many researchers reported that the addition of suitable amount of passive or active inorganic filler to the precursor could alleviate these problems [3,28,29]. Passive fillers cannot react with the matrix, and simply dilute the preceramic polymer, thereby reducing the shrinkage of the component upon ceramization and eliminating the occurrence of macrodefects. By contrast, active fillers such as metallic or intermetallic compounds do not only dilute the preceramic polymer, but also react with gaseous byproducts, the heating atmosphere, or the ceramic residue, which brings about volume expansion available to compensate for the shrinkage and thus enables the fabrication of low-porosity and crack-free ceramic coatings.

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Aluminum (Al) powder is commonly used as an active filler due to its high activity and high temperature resistance of formed products. Wang et al. [30] prepared high infrared emissivity coatings with good thermal stability using Al powder as an expansion agent and poly(hydridomethylsiloxane) (PHMS) as polymer precursor. The high infrared emissive property was attributed to the complete conversion of Al into Al_2O_3 and PHMS into SiO_2 at low temperature, as well as the high emissivity enhanced filler agent HW (mixture powders based on SiC). Yang et al. [31] demonstrated the fabrication of dense SiC coatings from the mixture of polycarbosilane and Al powder. However, to our knowledge, research about ceramic coatings based on polysilazane/Al has not been reported. Moreover, the effect of microstructure and composition of coatings derived from preceramic polymer/Al on mechanical properties was not investigated.

In this paper, crack-free ceramic coatings were successfully fabricated using polysilazane (PSN1) as a preceramic polymer and Al powder as an active filler. The influence of the volume of Al powder on the composition, microstructure, and mechanical properties of the coating was studied.

2. Experimental

2.1. Materials

The liquid polysilazane (PSN1, –[SiNH(CHåCH$_2$)]$_x$–[NHSiNH(CH$_3$)]$_y$–, Mn = 600–1000) was synthesized according to the reported method [32]. Al powder with a particle size of 3–5 μm was obtained from Beijing Dekedaojin Co. Ltd. (Beijing, China). Xylene was purchased from Beijing Chemical Works (Beijing, China) and distilled with calcium hydride prior to use. Dicumyl peroxide (DCP) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China) and purified by standard process. Flat stainless steel (AISI 304, thickness: 1 mm) was purchased from Guangdong Zhuyou Stainless Steel Co. Ltd. (Chaozhou, China). Before applying coatings, the stainless steel sheets with dimensions of $10 \times 10\ mm^2$ were washed with acetone, ethanol, and distilled water by ultrasonic treatment respectively, and then dried in nitrogen.

2.2. Preparation of coatings

A slurry dip process was used to prepare the coating. 10–40 vol% Al powder and 0.5 wt% DCP were added to the PSN1 and the mixture was diluted using xylene (solvent) to suit for the dip process. After stirring for 30 min, the slurry was then ball milled for 4 h. The detailed formulations of the slurry are listed in Table 1. The pretreated 304 stainless steel substrates were dip-coated with a hoisting apparatus at a withdrawal rate of 5 mm/s. The coated substrates were heated at 170 °C for 2 h in the oven to allow cross-linking. The cured coatings were pyrolyzed in the tubular furnace under nitrogen atmosphere. The samples were heated at 1 °C/min to 450 °C and held for 1 h, and then the coatings were performed up to 800 °C with heating rate of 5 °C/min and holding time of 1 h under flowing nitrogen, and then temperature decreased to the room temperature at the rate of 5 °C/min.

Table 1
The detailed formulations of the slurry.

Sample	Filler	Solvent	V(Al)/V (PSN1) (%)	V(PSN1+Al)/ V(xylene)	Viscosity (C_p)
PSN1/Al-1	Al	Xylene	10	2:5	1.04
PSN1/Al-2	Al	Xylene	20	2:5	2.07
PSN1/Al-3	Al	Xylene	30	2:5	3.11
PSN1/Al-4	Al	Xylene	40	2:5	5.18

The solvent of the residue slurry was firstly removed by distillation, then cured and pyrolyzed in the same procedure with the heat treatment of the coatings. The obtained powders were used for the relative characterization.

2.3. Characterization methods

Thermal gravimetric analyses (TGA) were carried out on a SII EXSTAR TG/DTA6300 instrument in nitrogen atmosphere at a heating rate of 10 °C/min.

The viscosity was measured on a Brookfield HADV-II viscometer at 25 °C.

Fourier transform infrared (FT-IR) spectra were obtained from a Bruker Tensor-27 FTIR spectrometer in the wavenumber range of 4000–400 cm^{-1}.

X-ray diffraction (XRD) measurements were carried out on a Rigaku D/M4X 2500 diffractometer with Cu-Kα radiation.

X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific (East Grinstead, UK) using 300 W Al-Kα radiations.

The surface and cross section morphologies of the coatings were observed using Hitachi S-4800 scanning electron microscopy (SEM).

The hardness and Young's modulus of the coating were measured by MTS XP Nano-indentation with a Berkovich diamond indenter. The measurements were performed five times with a contact depth ranging from 50 to 300 nm.

3. Results and discussion

3.1. Ceramic yields of cross-linked PSN1 and PSN1/Al

Several criteria need to be considered when selecting a preceramic polymer for the specific application. The first is that the polymer must have a high ceramic yield upon pyrolysis. High ceramic yield polymers are easier to densify and have lower tendency to form cracks and unwanted pores when applied in coatings [4]. Therefore, the ceramic yields of cross-linked PSN1 with different content of Al expansion agent were characterized by TGA measurement. The results of TGA analyses in nitrogen are given in Fig. 1. It can be seen that the ceramic yield of the cross-linked samples was clearly enhanced with increasing of Al content. The ceramic yield of the cross-linked PSN1 without Al was only 72.9% at 800 °C, whereas the ceramic yields of the cross-linked PSN1 with 10–40 vol% Al powder ware up to 77.8%,