Bioinspired synthesis of thermally stable and mechanically strong nanocomposite coatings

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Abstract

An innovative biomimetic method has been developed to synthesize layered nanocomposite coatings using silica and sugar-derived carbon to mimic the formation of a natural seashell structure. The layered nanocomposites are fabricated through alternate coatings of condensed silica and sugar. Sugar-derived carbon is a cost-effective material as well as environmentally friendly. Pyrolysis of sugar will form polycyclic aromatic carbon sheets, i.e., carbon black. The resulting final nanocomposite coatings can survive temperatures of more than 1150 °C and potentially up to 1650 °C. These coatings have strong mechanical properties, with hardness of more than 11 GPa and elastic modulus of 120 GPa, which are 80% greater than those of pure silica. The layered coatings have many applications, such as shielding in the form of mechanical barriers, body armor, and space debris shields.

Introduction

The demand for materials with strong thermal and mechanical properties for harsh environments, such as pulsed power facilities e.g., [1], magnetic fusion reactors (tokamaks) [2], and space industry [3], is increasing. Composite materials mimicking natural structures, involving hard inorganic and soft organic layers, have the potential of providing a sufficiently strong interface while providing an effective load transfer [4]. One of the natural structures is a seashell, which consists of alternating inorganic calcite layers and organic protein layers, resulting in a hard and strong layered shell [5]. Previous studies showed that combining brittle minerals and organic molecules into composites can provide outstanding fracture resistance and structural performance [4].

This paper describes a method to synthesize composite layered materials through coating to mimic seashell structures using tetraethyl orthosilicate (TEOS) as the precursor for brittle inorganic material and sugar as the organic precursor. TEOS has been widely used as a crosslinking agent in silicone – polymer systems or as a precursor to silicon dioxide due to the reactivity of the Si-OR bonds [6]. Sugar-derived carbon is a cost-effective way since sugar is

abundantly available and thus economically favorable and environmentally friendly. Sugar is water soluble and compatible with surfactants and their self-assembly with inorganic silica. The addition of sugar creates uniform composite materials that lead to reproducible results [7]. Pyrolysis of sugar will form polycyclic aromatic carbon sheets, i.e., carbon black, which can be used as a catalyst for biodiesel production [8]. Carbon black is known to increase mechanical properties such as tension, compression, hardness and abrasion (e.g., added as reinforcing agent for tires [9]). Literature studies have shown that adding trace amount of carbon in epoxy or silica will increase the modulus and strength significantly [10, 11].

Materials and methods

Tetraethyl orthosilicate (TEOS) was purchased from Sigma Aldrich with > 99% purity. The stock solution was made using 60 mL TEOS + 60 mL ethanol (EtOH) + 5 mL H₂O + 2 mL HCl (0.1 N) and was placed on a hotplate with a temperature of 60 °C for 90 min to initiate hydrolysis and condensation of TEOS to form a silica network [12]. One mL of stock solution was mixed with 1 mL EtOH, 0.07 g H₂O and 0.1 g of 0.1 N HCl to form the final sol–gel solutions for coating silica layers.

The sugar (C&H Confectioners brand), was purchased from a grocery store. The sugar was analysed by

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Cornerstone Analytical Laboratories using ion chromatography with pulsed amperometric detection and identified to be pure sucrose. About 0.111 g of sugar was mixed with 6.408 g EtOH + 20 mL deionized H₂O to form the coating solution for the sugar layer. The sugar solution was filtered using a 0.25 mm pore filter before coating.

The layered composites were coated on approximately 3.5 × 3.5 cm silicon wafers using a KW-4A spin coater. Approximately 20–30 mL sol–gel silica solution or sugar solution was used for each layer. The spin coater is set at 500 revolutions per minute for 18 s. After each coating, the layered composite was either *thermally pre-treated* by being placed on a hotplate with temperature of ~150–200 °C for ~3–5 min or simply left on the spin coater to dry for 30 s to 1 min (i.e., *without thermal pre-treatment*) before coating another layer. The composites always start and end with a silica layer and alternate between silica and sugar coatings. The final composite was then treated in a tube furnace under vacuum environment with a ramp rate of 5 °C/min to 200 °C, holding for 3 h, then continued ramping to 850 °C and held for another 3 h before cooling down.

In this study, four different layered composite materials were prepared for nanoindentation measurements by Bruker TI Premier system using a Berkovich tip: one 1-layer silica without sugar, two 13-layered composites without thermal pre-treatment, and one 13-layered composite with thermal pre-treatment. The loading and unloading time for nanoindentation is 20 s for each indent and dwelling for 5 s in between. In addition, 3-layered silica and 5-layered composite coatings were prepared and analysed by scanning electron microscope (SEM), scanning transmission electron microscope (STEM) using (High-angle annular dark-field) HAADF/STEM imaging

mode with quantitative electron energy loss spectroscopy analysis [13], an infrared microscope, and thermogravimetric analysis.

Results and discussion

TEOS forms amorphous silica nanoparticles after water hydrolysis and ethyl alcohol condensation. Thermal pre-treatment on a hotplate not only removes solvents and solidifies the coatings, but also initiates silica condensation and sugar pre-carbonization through crosslinking to form a stable silica network. Each silica layer after thermal pre-treatment is around 1 mg, whereas the weight of a sugar layer is minimal (a few micrograms or less). During the final high temperature treatment, three major processes occurred within the coatings: (1) Decomposition of TEOS forms amorphous silica layers by breaking the ethyl function groups (the thickness of each silica layer is around 600–700 nm (Fig. 1A)); (2) Pyrolysis of sugar at temperature > 200 °C forms polycyclic aromatic carbon black sheets [8] (the carbon black layer is only 10–20 nm thick (Fig. 1B)); (3) Heat-based polymerization locks in the nanocomposite architecture via chemical crosslinking within individual layers and also between silica and carbon layers. Thermogravimetric analysis (TGA) shows that both decomposition of TEOS and pyrolysis of sugar are complete at temperatures less than 550 °C (Fig. 2A and B), and the nanocomposite is then thermally stable to over 1150 °C (Fig. 2C).

Infrared spectra show chemical crosslinking of Si–O with carbon ring and Si– with carbon ring (Fig. 3). Compared to pure silica coatings, the 5-layered nanocomposite has two peaks in the range of 1250–1700 cm^{−1} which are the characteristic peaks of carbon black. The distinct peak around

Fig. 1 SEM **A** and STEM **B** cross sectional image showing the 5-layered nanocomposite structure with alternate silica and carbon black layers after heating treatment at more than 800 °C. **B** HAADF image and intensity profiles for carbon and silicon show the interfaces

between substrate and coated silica layers on the right and the sugar-derived carbon layer between two silica layers on the left. The thickness of the carbon layer is estimated to be ~10–20 nm based on the spike of carbon signal

Fig. 2 Thermogravimetric analysis (TGA) for sol-gel coatings (A) (prepared by coating directly on TGA pan multiple times and air dried without any thermal treatment before measurement), sucrose powder (B), and 5-layered and 7-layered coatings (C) (without high temperature treatment). A bare silicon wafer is shown for comparison in C. Once the pyrolysis of sugar and decomposition of TEOS

are complete at 300–550 °C (A and B), the composite materials are stable up to 1150 °C. The ramp rate is 5 °C/min under nitrogen environment for all analyses. Note, the small increase in mass at low temperatures (50–250 °C) is due to buoyant effect when heating is conduction dominated instead of radiation dominated at higher temperatures. The error shown is 0.2% uncertainty

Fig. 3 Attenuated total reflectance (ATR) infrared spectra for 3-layered silica composite coatings compared with 5-layered nanocomposite coating (#1 and #2 are two different measurements on the same coating). In 3-layered silica coating there are only two peaks attributed to the Si–O–Si vibration observed over the range of wavenumbers from 750 to 3800 cm^{-1} , indicating the complete removal of

ethanol group from TEOS. In contrast, the 5-layered nanocomposite coatings have two peaks in the range of 1250–1700 cm^{-1} which are attributed to carbon black. There are additional peaks at 1210, 1120, 975–875 cm^{-1} which are consistent with vibrations of Si- or Si–O- attached to phenyl groups [14], indicating crosslinking between silica and carbon black

940 cm^{-1} and enhanced shoulder around 1210 cm^{-1} for the 5-layered coating is consistent with oxygen bridging silicon and a carbon ring [14]. Similarly, the distinct peak around 1120 cm^{-1} is consistent with vibration of Si- attached to phenyl groups [14]. Chemical crosslinking between silica

and carbon leads to the enhanced mechanical properties. The thermal pre-treatment was expected to play an important role in solidification of the composite coatings while initiating crosslinking. To test the effect of thermal pre-treatment,

Table 1 Nanoindentation results for silicon wafer, pure silica layer, and three 13-layered nanocomposites

n-# of measurements	Max load (mN)	Hardness (GPa)	Reduced modulus (GPa)	Displacement (nm)
Silicon wafer substrate				
n=11	1	9.5 ± 0.22	120.7 ± 2.73	~65
n=8	3	10.4 ± 0.21	118.2 ± 1.69	~122
n=10	5	10.4 ± 0.25	113.8 ± 1.08	~165
n=6	8	10.5 ± 0.10	121.7 ± 1.24	~208
n=2	10	11.3 ± 0.03	118.3 ± 1.39	~230
Pure one silica layer on substrate (#34-1)				
n=15	0.5	5.0 ± 0.27	62.4 ± 4.07	~60
n=7	1	6.3 ± 0.16	68.2 ± 1.12	~80–85
n=9	3	7.2 ± 0.29	78.9 ± 2.94	~150
n=22	5	6.9 ± 0.39	84.1 ± 2.82	~200
n=23	8	7.2 ± 0.25	89.7 ± 1.86	~250
n=22	10	7.5 ± 0.43	93.3 ± 3.24	~280
13-layered nanocomposite with no heating inbetween (#56_TF)				
n=12	3	9.1 ± 0.36	78.5 ± 1.79	~143
13-layered nanocomposite with no heating inbetween (#57_TF)				
n=9	3	9.1 ± 0.36	82.7 ± 1.79	~139
n=6	3	9.3 ± 0.16	83.3 ± 1.36	~137
n=14	5	9.3 ± 0.25	88.4 ± 1.42	~181.5
n=15	12	9.3 ± 0.08	98.1 ± 0.96	~280
13-layered nanocomposite with thermal pretreatment (#58_TF)				
n=4	3	11.0 ± 0.20	126.8 ± 2.10	~117
n=4	12	11.6 ± 0.74	128.4 ± 4.77	~251
n=3	12	11.1 ± 0.18	123.2 ± 2.13	~253

nanocomposites with and without thermal pre-treatment were prepared and tested (Table 1).

Obtaining mechanical properties of thin, layered coatings is known to be challenging through the nanoindentation method. To benchmark nanoindentation results, blank silicon substrates and pure silica layers without sugar were also measured by nanoindentation using various maximum peak forces, from 0.5 to 10 mN, leading to displacements from 60 to 280 nm (Table 1). For a silicon substrate, the hardness and reduced modulus are consistent with different loads except at a high load of 10 mN. The hardness is around 9.5 to 10.5 GPa and the reduced modulus is around 120 GPa (Table 1). For a 600–700 nm thick silica layer without sugar, both hardness and modulus increase with higher loads due to interference of the underlying substrate (Table 1). The influence of a substrate is typically negligible if the displacement is less than 10% of the thickness of the coatings e.g., [15, 16]. Therefore, the values at 0.5 mN and 1 mN are mostly representative of the properties of the silica layer with minimal interference of the underlying substrate. The hardness of the silica layer is between 5 and 6 GPa, and reduced modulus is 60–70 GPa (Table 1), consistent with the modulus value for fused quartz in the literature (i.e., 63.1–69 GPa) [17, 18].

For two 13-layered nanocomposites without thermal pre-treatment, indentation measurements with maximum load of 3, 5 and 12 mN were conducted. Both samples yield similar and consistent results with displacements from 140 to 280 nm (Table 1). Regardless of the displacement depths, the hardness of these layered nanocomposites is greater than 9 GPa and the modulus is greater than 80 GPa. The consistent results with different displacement depths show minimal substrate interference on the hardness and modulus. Compared to pure silica without sugar layers, the hardness of layered nanocomposites is enhanced by 50% from 6 to 9 GPa whereas the modulus also increases from less than 70 GPa to over 80 GPa.

For the 13-layered nanocomposite with thermal pre-treatment, the nanoindentation measurements with 3 and 12 mN loading produced consistent results with hardness greater than 11 GPa and reduced modulus more than 120 GPa, greater than those without thermal pre-treatment and even the silicon substrate (Table 1). The hardness and modulus are enhanced by more than 80% compared to silica coatings without sugar. The results demonstrate that thermal pre-treatment is necessary to form the most robust coatings. Without this step, the hardness and modulus of the nanocomposite is less enhanced.

The reduced modulus for the 13-layered thermally pre-treated nanocomposite is more than 120 GPa, which significantly outperforms literature studies using a similar layer-by-layer assembly technique to synthesize composite material. The greatest moduli reported in literature range from 9 GPa up to 60 GPa [19, 20] for montmorillonite clay and polymeric matrix interlayer composite. These moduli are less than that of natural seashell (~ 70 GPa) [21].

Current debris shields used on pulsed power facilities involve multiple layers of materials such as lithium, beryllium, aluminium, Kapton®, and Spectra® (ultra-high molecular weight polystyrene). Beryllium is the best shield material in terms of thermal stability and mechanical properties. However, the use of lithium or beryllium introduces major environmental safety and health (ES&H) concerns for post-recovery and cleaning due to their respective reactivity and toxicity. Kapton and Spectra have strong mechanical properties, but poor thermal stability with peak service temperatures of ~ 250 °C and ~ 120 °C, respectively. The nanocomposites synthesized using common material silica and sugar have comparable hardness and modulus to the best of the currently used materials without ES&H concerns.

Conclusions

Stable layered composite materials were synthesized by coating alternate inorganic and organic layers using TEOS and sugar as the silica and carbon precursors. After thermal pre-treatment and high temperature calcination, chemical crosslinking between silica and carbon layers enhanced the mechanical properties by more than 80% in hardness and modulus compared with coatings without sugar. The nanocomposite coatings are thermally stable potentially up to 1650 °C and outperform current shield materials without ES&H concerns. This coating technology is agile and flexible, in that coatings on various substrates can be substituted with different compatible coating materials. These robust coatings have broad applications in magnetic fusion reactors, body armor, and space debris mitigation.

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Data availability The datasets generated and analysed during the reported study are available from the corresponding author on a reasonable request.

Declarations

Conflict of interest G.X, H.F., C.M. and J.S. are co-inventors on patent applications on nanocomposite coatings and methods of making.

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