

Mechanical properties of polymer-derived ceramic composite coatings on steel

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Abstract

Polymer-derived ceramics have shown promise as a novel way to process low-dimensional ceramics such as fibers and coatings. A polymer-derived ceramic composite coating on steel as a barrier to oxidation and carburization has been developed using poly(hydridomethylsiloxane) as the matrix and titanium disilicide as the filler. Processing parameters have been optimized and coatings of $\sim 18 \mu\text{m}$ thick and a density of 2.57 g/cm^3 have been produced. This paper presents the results of mechanical testing of the coating and the coating–steel interface. The hardness of the coating after pyrolysis to 800°C was determined to be $4.8 \pm 1.0 \text{ GPa}$ and the modulus in the range of $49\text{--}54 \text{ GPa}$. The tensile strength of the coating was 1.9 GPa and the ultimate shear strength of the interface was found to be 2.35 GPa .

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1. Introduction

The processing of ceramics and ceramic composites from polymeric precursors has garnered attention due to several advantages it offers over traditional methods of ceramic processing, including lower pyrolysis temperature and the ability to use polymeric processing techniques, such as dip coating and injection molding.^{1,2} The most promising area for the application of these materials has been in low-dimensional products such as coatings.^{3–5} The focus of this research is to implement the novel processing of preceramic polymers to develop a ceramic composite coating on stainless steel as barrier to oxidation and carburization. The anticipated application is for industrial use in steam methane reforming (SMR) reaction chambers, where steel is exposed to steam and methane gas at temperatures of $\sim 800^\circ\text{C}$. This environment creates surface embrittlement of the steel and reaction products can flake off, contaminating the reaction chamber.

Many preceramic polymers are now on the market (precursors to carbides, nitrides, and oxides are readily available) and these are typically combined with an inert or reactive filler and pyrolyzed under argon or nitrogen atmospheres.⁶ Since the coating that will be made requires oxidation resistance, a polysiloxane polymer pyrolyzed in air will be employed in this study with a reactive binary metal as a filler. Previous work has identified a suitable polymer-expansion agent system, optimized processing parameters, and characterized the compositional and microstructural evolution of the coatings as a function of pyrolysis temperature.^{7–9} This paper will focus on the mechanical characterization of these coatings including hardness, elastic modulus, ultimate tensile strength, and interfacial shear strength.

In order to characterize the mechanical properties of this brittle composite coating on a ductile metal substrate, several techniques were surveyed. Nanoindentation accompanied with atomic force microscopy, as outlined by Oliver and Pharr, proved to be ideal for measuring the hardness and elastic modulus of the coatings as a function of position across the coating–steel interface.^{10,11} Sandwich geometry techniques, double cantilever and Brazil nut, were used for determination of interfacial properties between the coating and steel.^{12,13} In both cases, the inability to create a sufficient precrack and the failure of the epoxy used to sandwich the coating yielded poor results. Instead,

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a tensile strain method developed by Agrawal and Raj was employed.^{14,15} This method can be used directly for thin brittle coatings on ductile substrates. As a tensile strain is applied to a coated substrate, the metal deforms plastically while the ceramic coating deforms elastically. The stress state and distribution are determined by the properties of the metal–ceramic interface. When the tensile stress in the coating reaches the fracture stress of the film, cracks form transverse to the load direction, and the crack density increases as the strain on the system increases. From observation of these cracks and the strains at which they occur, the ultimate shear strength of the coating/steel interface and the tensile strength of the coating can be determined.¹⁴ Results of this study and further work needed to apply this technique to thick composite coatings will be discussed.

2. Materials and experimental techniques

Poly(hydridomethylsiloxane) (PHMS) (Gelest, Inc., Malta, NY, USA) was used as the matrix preceramic polymer, and titanium disilicide, in submicron particle size (Accumet Materials, Briarcliff Manor, NY, USA), was employed as the expansion agent based on previous studies.^{7,8} Coatings were processed using a slurry dip coating method as follows: TiSi_2 expansion agent is attrition milled for 5 h, in isopropanol, washed with isopropanol, and then dried at 100 °C. 30-vol.% expansion agent is added to the PHMS. The slurry must be diluted to a viscosity of 15 cP using *n*-octane. Half of the required *n*-octane is added to the slurry which is then ball milled for 4 h. The remaining *n*-octane is used to dissolve the catalyst: 0.05% by weight (to PHMS) of ruthenium carbonyl catalyst, $\text{Ru}_3\text{CO}_{12}$. After ball milling, the catalyst is added to the slurry and stirred to mix. Type 316 stainless steel substrates are polished with 600 grit SiC paper, cleaned, and dried. Dip coating is performed using a Universal Testing Machine (Instron 4505, Instron Corporation, Norwood, MA, USA) with a constant withdrawal rate of 50 cm/min. The coated substrates are heated at 2 °C/min to 150 °C and held for 2 h in humid air to crosslink the polymer. They are then heated at 2 °C/min in dry flowing air to 800 °C, held for 2 h, and cooled at 2 °C/min.

Nanoindentation, to determine the hardness and elastic modulus of the coatings, was performed at Pacific Northwest National Laboratory, Richland, WA, USA, using a Hysitron TriboScope with a standard Berkovich indenter in conjunction with an atomic force microscope (Nanoscope III AFM, Veeco Metrology Inc., Tuscon, AZ, USA).¹⁰ Both top and cross-sectional views were examined on samples pyrolyzed at 600 and 800 °C. Cross-sectional samples were mounted in epoxy, sectioned, and polished to a 0.05 μm finish. Single indentation load-displacement responses were measured across the coating–steel interface using a 1000 μN load. Indents normal to the coating surface were made using loads ranging from 25–300 μN in the 800 °C sample and 25–100 μN in the coatings pyrolyzed at 600 °C.

The elastic modulus of the coatings was also determined using an impulse excitation technique.¹⁶ PHMS/ TiSi_2 slurry was dip-coated onto one face of substrates of dimensions

1.4 mm \times 5 mm \times 30 mm and pyrolyzed to 800 °C. The exact dimensions and the mass of each substrate were measured both before and after coating and the elastic modulus measurement was performed both before and after coating using ultrasonic resonance (GrindoSonic Mk4-1, J.W. Lemmens N.V., Belgium). The out-of-plane flexural vibration mode was investigated by placing the substrate on two rubber supports spaced at the flexural node lines 0.224 L from each end of the substrate.¹⁶ The microphone was held on one of these nodes and the out-of-plane impulse point was lightly tapped using a 0.5 mm diameter ceramic sphere attached to a plastic rod to create the vibration. The modulus of the coating was calculated by comparing the modulus of the steel substrate to that of the composite beam, as defined by Chandra and Clynne.¹⁷

Samples were prepared for interfacial strain testing by coating one face of 10 mm \times 30 mm 316 stainless steel substrates and pyrolyzing to 800 °C.^{14,15} After pyrolysis the edges of the substrate were polished to remove any excess ceramic. Substrates were loaded in tension at a constant crosshead velocity of 0.5 mm/min to the desired strain state using an Instron testing machine. Coatings were strained to 5, 7.5, 10, 15, and 20%. A scanning electron microscope was used to measure crack spacing in the coatings.

3. Results and discussion

Previously published physical and microstructural analysis of the coatings shows that they are $\sim 18 \mu\text{m}$ thick with a density of 2.57 g/cm³.⁹ The volume fraction of porosity after pyrolysis to 800 °C was estimated to be 0.10. The coating consists of TiSi_2 , anatase, and amorphous Si–O–C, with <3% residual carbon. A diffusion reaction layer of Fe and Cr oxide is visible at the interface, indicating good bonding of the coating to the steel substrate.⁸

Hardness and elastic modulus were measured using nanoindentation and atomic force microscopy (AFM) for samples at various pyrolysis temperatures. Scans were made across the coating/steel interface for samples pyrolyzed at 600 and 800 °C, placing indents at 2 μm intervals. Fig. 1 shows an example of the plots that were obtained for the 800 °C sample. Hardness was much higher in the steel than in the coating for the 600 °C sample, averaging $4.2 \pm 0.85 \text{ GPa}$ in the steel and dropping to an average of $2.5 \pm 0.45 \text{ GPa}$ in the coating (Fig. 2). Data points greater than 12 μm from the interface were excluded in the averages, as these were approaching the edge of the coating and had the potential to be artificially low. In the 800 °C sample, there was little change from the steel to the coating, averaging $4.8 \pm 1.0 \text{ GPa}$, other than some very high values close to the interface (Fig. 3). This could be an artifact of the oxide diffusion layer between the steel and the coating. The measured hardness of the coating, especially close to the interface for the 800 °C sample, is most likely affected by the interphase between the coating and substrate. This could account for the high hardness near the interface.

Elastic modulus follows a similar trend in that the value measured for the 600 °C sample is less than that for the 800 °C sample, from an average of $39 \pm 7.2 \text{ GPa}$ to one of $54 \pm 8.1 \text{ GPa}$

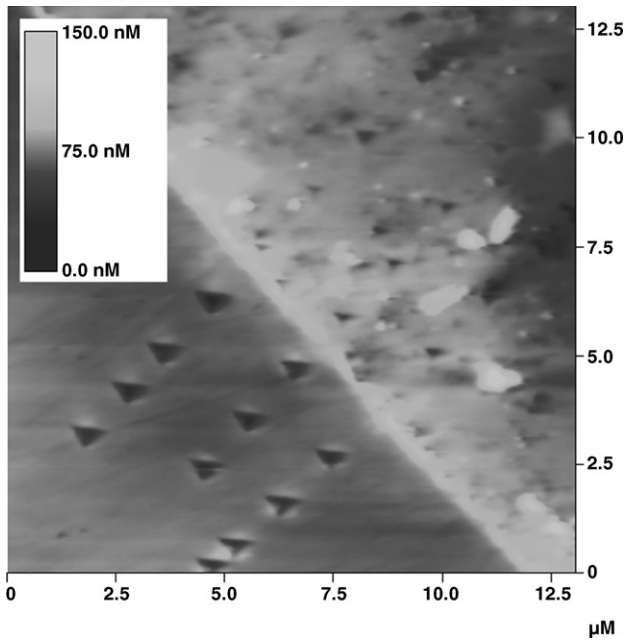


Fig. 1. Atomic force microscopy (AFM) image of nanoindentations across the interface of a coating pyrolyzed at 800 °C on a steel substrate.

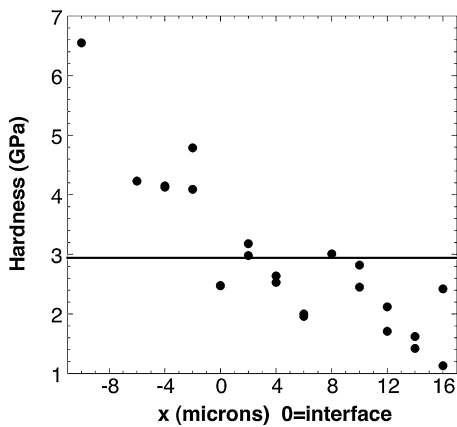


Fig. 2. Hardness as a function of position across the coating/steel interface for a sample pyrolyzed at 600 °C. Negative position represents the steel, zero the interface, and positive the coating.

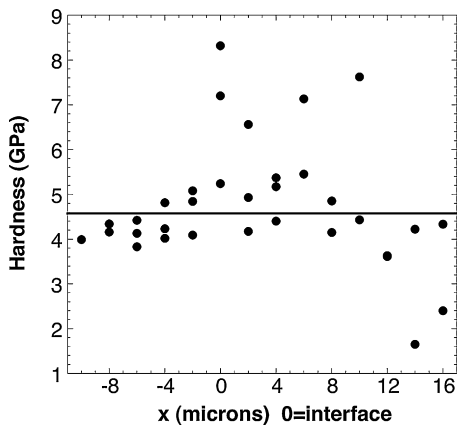


Fig. 3. Hardness as a function of position across the coating/steel interface for a sample pyrolyzed at 800 °C. Negative position represents the steel, zero the interface, and positive the coating.

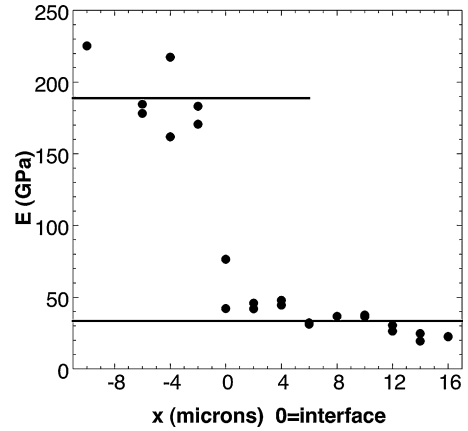


Fig. 4. Elastic modulus as a function of position across the coating/steel interface for a sample pyrolyzed at 600 °C. Negative position represents the steel, zero the interface, and positive the coating.

(Figs. 4 and 5). A marked drop in modulus can be seen across the interface in both samples. This is to be expected, as 316 stainless steel is a hard steel with a published modulus of 190 GPa.¹⁸ The coating has been shown to consist mainly of amorphous SiO₂ and TiO₂, and contain some amount of porosity on a fine scale in the matrix polymer-derived ceramic; it would, therefore, be expected to have a modulus lower than that of the fully dense amorphous phases (modulus ~70 GPa).

Hardness and elastic modulus were also measured from the top surface of the coating for samples pyrolyzed at 600 and 800 °C (Figs. 6 and 7). Although, a trend can be seen towards a decrease in both properties as a function of indenter depth, there is a large amount of scatter in both data sets. This can be attributed to the surface roughness of the coatings. The surface roughness is roughly the size of the filler particles, 0.1–1.0 μm diameter. This is on the order of, if not greater than, the size of the nanoindenter itself, causing the large amount of scatter. Hardness was also tested via Vickers microindentation. These values were also inconsistent, however, due to substrate effects. For future measurements of a similar kind, cross-sectional nanoindentation appears to be the best method for obtaining repeatable data for hardness and modulus.

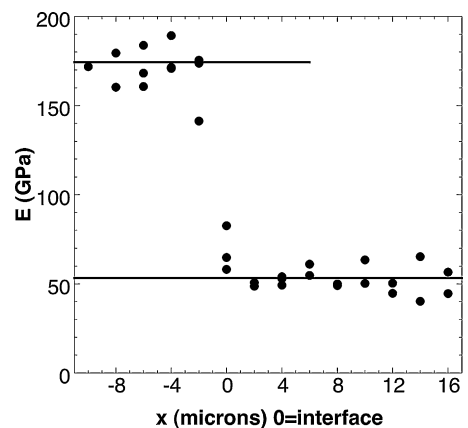


Fig. 5. Elastic modulus as a function of position across the coating/steel interface for a sample pyrolyzed at 800 °C. Negative position represents the steel, zero the interface, and positive the coating.

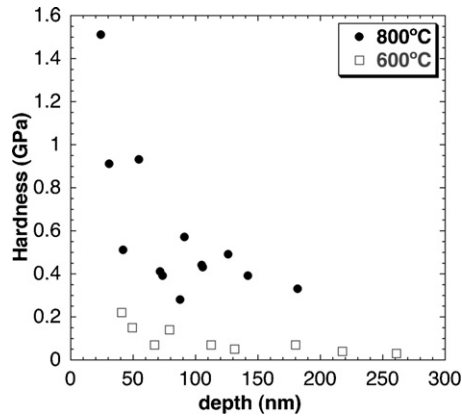


Fig. 6. Hardness as a function of indentation depth for samples pyrolyzed at 600 and 800 °C.

Elastic modulus was also determined using impulse excitation.¹⁶ The modulus of the bare steel was determined to be 204 ± 6.1 GPa; the substrates were then coated and a modulus of 198 ± 6.3 GPa was obtained for the composite beam. Using the relationship derived by Chandra and Clyne, the composite coating pyrolyzed at 800 °C was found to have an elastic modulus of 49 ± 3.9 GPa.¹⁷ This is in very close agreement with the value obtained by nanoindentation of the coating/steel cross-section (54 ± 8.1 GPa).

A strain test developed by Agrawal and Raj was used to test the coating–steel interface because of the ability to directly test coated specimens without the introduction of external materials, such as epoxy, which are needed for sandwich geometries such as the double cantilever beam.^{14,15} Coatings pyrolyzed to 800 °C were placed in tension to strains of 5, 7.5, 10, 15, and 20%. SEM was used to analyze the crack spacing in each of the tested samples (Figs. 8 and 9). No cracks were present in the 5% strain sample, crack density increased from 7.5% strain to 15% strain, and at 20% strain the coating had begun to spall. It is interesting to note that the coating fails not by delamination at the interface, but through debonding within the coating.

The crack spacing distributions for strains of 7.5, 10, and 15% are presented in Fig. 10. These values were used to calculate the tensile strength of the film and the ultimate shear strength of the

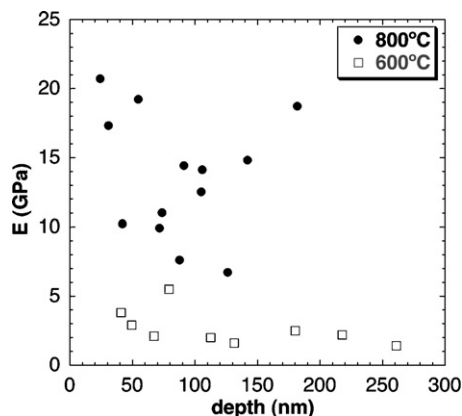


Fig. 7. Elastic modulus as a function of indentation depth for samples pyrolyzed at 600 and 800 °C.

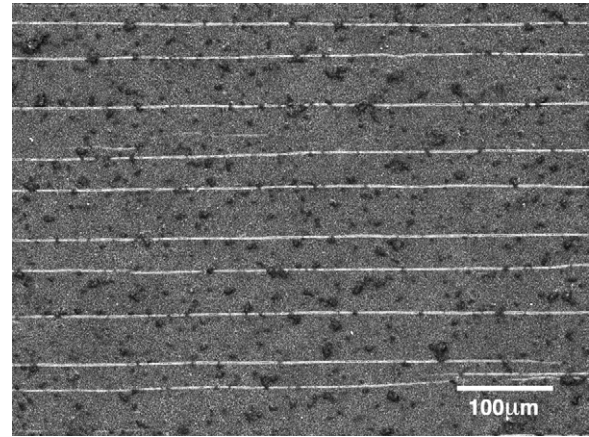


Fig. 8. Micrograph of a coating pyrolyzed at 800 °C and strained in tension to an engineering strain of 7.5%. Cracks are clearly visible with a median crack spacing of 46.7 μm.

coating/steel interface using Eqs. (1) and (2), respectively.^{14,15}

$$\hat{\sigma} = \varepsilon_f E \quad (1)$$

$$\hat{\tau} = \frac{\pi \delta}{\lambda_{\max}} \hat{\sigma} \quad (2)$$

The following elastic modulus and coating thickness values were used for the coatings: $E = 50$ GPa and $\delta = 18$ μm. The strain at failure, ε_f was taken to be 7.5%, as this is the strain at which cracks first appeared; the maximum crack spacing, λ_{\max} , was determined to be 45 μm based on the crack spacing at 10 and 15% strains. The tensile strength of the film can then be calculated to be 3.75 GPa, and the ultimate shear strength of the interface to be 4.7 GPa. A detailed analysis of the error associated with this technique is presented in ref. 15, and the uncertainty is found to be less than 20%. This study shows that it is possible to apply this technique to thick composite coatings. However, several issues need to be addressed before this analysis can be applied directly to thick coatings, as evident from the high values reported for both tensile strength in the film and interfacial shear strength. One important effect is that for

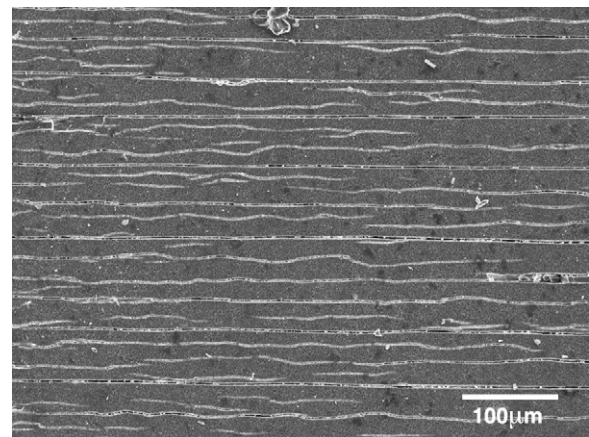


Fig. 9. Micrograph of a coating pyrolyzed at 800 °C and strained in tension to an engineering strain of 15%. Cracks are clearly visible with a median crack spacing of 17.5 μm.

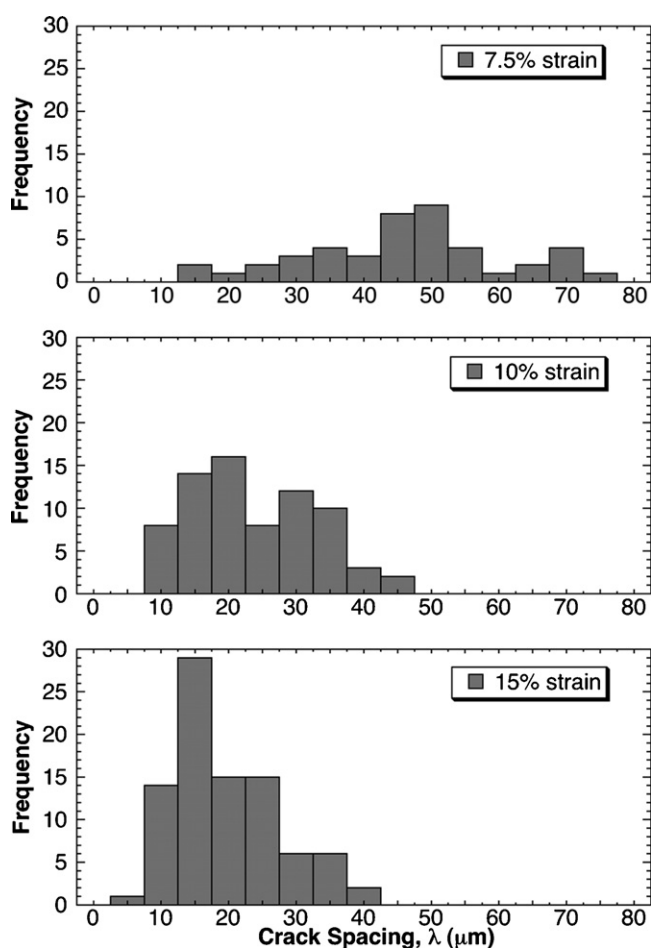


Fig. 10. Distributions of crack spacing, λ , in composite coatings tested to tensile strains of 7.5, 10, and 15%.

thin coatings, the tensile stress in the coating is assumed to be constant across the thickness. This will not be a good assumption for thick coatings. As a first approximation, it is assumed that the in-plane tensile stress in the coating is zero at the free surface and linearly increases to a peak value at the interface. With this assumption, an average coating stress which is half of the maximum stress is obtained. Using this assumption, the tensile strength of the coating is calculated to be 1.9 GPa and the shear strength of the interface 2.35 GPa. More accurate analysis is needed to properly adapt this test to thick coatings. The experimental results in this study have shown that transverse cracks form in a manner similar to thin coatings.

4. Conclusions

Mechanical properties were determined for amorphous composite ceramic coatings on stainless steel. The hardness of the coating after pyrolysis to 800 °C was determined to be 4.8 ± 1.0 GPa and the modulus in the range of 49–54 GPa. The ultimate shear strength of the composite coating/steel interface was found to be 2.35 GPa and the tensile strength of the coating was 1.9 GPa. It has also been shown that periodic transverse

cracks form in thick brittle coatings on ductile substrates in the tensile strain test.

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References

- Greil, P., Near net shape manufacturing of polymer-derived ceramics. *J. Eur. Ceram. Soc.*, 1998, **18**, 1905–1914.
- Walter, S., Suttor, D., Erny, T., Hahn, B. and Greil, P., Injection moulding of polysiloxane/filler mixtures for oxycarbide ceramic composites. *J. Eur. Ceram. Soc.*, 1996, **16**, 387–393.
- Bill, J. and Heimann, D., Polymer-derived ceramic coatings on C/C-SiC composites. *J. Eur. Ceram. Soc.*, 1996, **16**, 1115–1120.
- Abe, Y., Kagayama, K., Takamura, N., Gunji, T., Yoshihara, T. and Takahashi, N., Preparation and properties of polysilsesquioxanes. Function and characterization of coating agents and films. *J. Non-Cryst. Solids*, 2000, **261**, 39–51.
- Blum, Y. D. and Macqueen, B., Modifications of hydrosiloxane polymers for coatings applications. *Surf. Coat. Int. Part B: Coat. Trans.*, 2001, **84**(B1), 27–33.
- Greil, P., Active-filler-controlled pyrolysis of preceramic polymers. *J. Amer. Ceram. Soc.*, 1995, **78**(4), 835–848.
- Torrey, J. D., Bordia, R. K., Henager Jr., C. H., Blum, Y., Shin, Y. and Samuels, W. D., Composite polymer-derived ceramic system for oxidizing environments. *J. Mater. Sci.*, 2006, **41**, 4617–4622.
- Torrey, J. D. and Bordia, R. K., Polymer-derived ceramic composite coatings: processing and characterization of coatings on steel. Accepted for publication in *J. Amer. Ceram. Soc.*, 2007.
- Torrey, J. D. and Bordia, R. K., Phase and microstructural evolution in polymer-derived ceramic composite systems and coatings. *J. Mater. Res.*, 2007, **22**(7), 1959–1966.
- Oliver, W. C. and Pharr, G. M., Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology. *J. Mater. Res.*, 2004, **19**(1).
- Scharf, T. W., Deng, H. and Barnard, J. A., Mechanical and fracture toughness studies of amorphous SiC-N hard coatings using nanoindentation. *J. Vac. Sci. Technol., A*, 1997, **15**(3), 963–967.
- Kanninen, M. F., An augmented double cantilever beam model for studying crack propagation and arrest. *Int. J. Fract.*, 1973, **9**(1), 83–92.
- Atkinson, C., Smelser, R. E. and Sanchez, J., Combined mode fracture via the cracked Brazilian disk test. *Int. J. Fract.*, 1982, **18**(4), 279–291.
- Agrawal, D. C. and Raj, R., Measurement of the ultimate shear strength of a metal–ceramic interface. *Acta Metal.*, 1989, **37**, 1265–1270.
- Agrawal, D. C. and Raj, R., Ultimate shear strengths of copper-silica and nickel-silica interfaces. *Mater. Sci. Eng.*, 1990, **A126**, 125–131.
- ASTM E 1876, Standard test method for dynamic Young's modulus, shear modulus, and Poisson's ration by impulse excitation of vibration. *ASTM Test Method E1876*. ASTM Book of Standards 03.01, 2001.
- Chandra, L. and Clyne, T. W., Use of an ultrasonic resonance technique to measure the in-plane Young's modulus of thin diamond films deposited by a DC plasma jet. *J. Mater. Sci. Lett.*, 1993, **12**(3), 191–195.
- Website Matweb: Material Property Database: AISI Type 316 Stainless Steel, Annealed Plate: <http://www.matweb.com/>, 2006.