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Literature Review of Polymer Derived Ceramics

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Polymer Derived Ceramics (PDCs), also known as preceramic polymers, are valuable coating agents that are used to produce surface barriers on substrates such as stainless steel. These barriers protect against a multitude of environmental threats, and have been used since their research and development in 1977[2]. This paper seeks to review and demonstrate the remarkable properties and versatility that PDCs have to offer, while also giving a brief overview of the processing techniques used today.

Introduction

Each year money is lost due to physical erosion and chemical corrosion of stainless steel. Physical erosion can take many forms like blowing sand and job required impacts. Chemical corrosion is more complex and encompasses a vast number of mechanisms such as oxidation, destruction by acidic or basic agents, and reaction with salt water. Further complicating the issue is the range of temperatures the stainless steel is subjected to, from around 4 Kelvin to hold liquid helium to hundreds of degrees Celsius in industrial processes.

The application of surface coatings onto stainless steel can help extend lifetimes and prevent these losses. Each different coating is used to counter specific sets of hazards, and obviously no single coating can stop all forms of attack. This paper will focus on the use of ceramics to protect stainless steel. Ceramics are typically hard, brittle, chemically inert, and thermally and electrically insulating. They have exceptionally high melting points. Thus a thin layer can be used to coat stainless steel to prevent against moderate physical impact, oxidation, acids and bases, and electrical environments over a wide range of temperature. To this end this paper mainly discusses the mechanical strength, oxidation protection, and corrosion defense properties of ceramic coatings.

Ceramics are not easily applied to stainless steel. It was only fairly recently in the 1970's that Yajima et al. managed to develop an effective coating process[2]. Generally, this process begins with dissolving a precursor polymer into an alcohol or other common solvent. From there the liquid is coated onto a stainless steel substrate, heated to crosslink the polymer and evaporate the alcohol, and heated further – close to and exceeding 1000 °C – to evaporate all liquids and organics within the coating and create a tough ceramic barrier. Applying the liquid solution to a substrate can be done with many methods, including spin coating and dip coating. The final step of extreme heating is known as pyrolysis, and can be done with various techniques other than simple heating including irradiation with ions or lasers.

After their development, further challenges had to be overcome before successful application and commercialization. The loss of the liquids and organics from the coating create extreme volume shrinkage, which can cause cracks to form, severely weakening the integrity of the coating. A common work around to prevent this is to add what is known as a filler to the coating, with the intention being that the filler would compensate for any gaps or cracks generated in the pyrolysis process. Fillers that simply fill in voids are called passive, and can be ceramic powders or metallic oxide powders. Fillers that react with and absorb gas are called active fillers. Popular examples of active fillers are elemental metal powders, such as aluminum or titanium, which react with extreme heat and an environment of nitrogen or oxygen to form nitrides and oxides. By adding the correct amount of filler, it is possible to reduce the volume shrinkage to zero and greatly diminish the chances of cracks forming in the coating.

Composition

The choice of precursor polymer determines the type of ceramic produced. Silicon carbide is known for its excellent hardness and stability and is used in cutting tools, car parts, and bulletproof vests. To create a coating of it, typically a polycarbosilane (PCS) solution can be used, and the volume loss countered by adding filler powders[3]. Generally, the initial composition provides the chemical building blocks for the coating, and the final composition is fine-tuned by the processing parameters. For example, typically polysiloxanes can be used to produce silicon dioxide, polysilanes for silicon nitride, and oxycarbide and polysilazanes for silicon carbonitride, although they are not strictly limited to these products[4]. Günthner et al. developed a coating of silicon dioxide using perhydropolysilazane (PHPS) by pyrolyzing in ambient air, and using the same precursor, the authors were able to create a layer of silicon nitride by pyrolyzing the coating while under a nitrogen environment[5].

Finally, the extent to which the coating has been converted to a hard ceramic is controlled by the temperature and time. It is not always desirable or practical to create a coating that is entirely ceramic, as this may increase the amount of volume shrinkage and induce cracking, or the substrate may not be able to withstand such temperatures, or the time required is too long. Commonly X-Ray Diffraction (XRD) is used to take measurements of the composition of the coating and decide on appropriate heating procedures.

These are only a few of the possible choices for precursor. Combined with the great variety of processing parameters, such as atmosphere, temperature, time, filler, and dilution, the composition of the final ceramic can be easily adjusted to fit the creator's needs.

Fillers

Many different fillers can be used to compensate for the volume loss that takes place during the cure and pyrolysis or to mix with the coating and introduce additional properties. Passive fillers are chosen to easily mix into polymer solution and to not react with the precursor or the atmosphere, and thus commonly take the powdered form of oxides, nitrides, carbides, or other ceramics. Typical volume concentrations range from ten to forty percent by volume.

Active fillers are selected to react with the atmosphere and absorb gasses to expand and fill the void spaces. This allows the designer to use less filler and change the properties of the filler by using a different gas environment. Typical active fillers are elemental metal powders that react to form oxides or nitrides, such as aluminum, boron, iron, titanium, and chromium[6]. Since these fillers will grow a layer of oxide over time, attrition milling is commonly performed to grind away the oxide. A smaller average particle size will increase the rate of absorption of gas and reduce the filler that is covered by absorbed gasses, which increases the total gas absorption. Attrition milling will also help to break the powders down into smaller particles.

The effects of fillers are not limited to filling in the voids. Lower amounts can provide stability to the coating, increasing the hardness, smoothness, and adhesion. Too much can have the opposite effects. Xiao et al. added varying amounts of aluminum powder to a polysilazane they called PSN1[7]. The SEM images in Figure 1 illustrate the changes to the surface roughness of the coating that the aluminum can make. In the first image of just the polymer, the coating is very rough and broken up into separate islands. In the second image, which is the polymer with 10 vol% aluminum powder, the surface is much smoother. In the third image, which is the polymer with 40 vol% aluminum powder, the surface is somewhat rough and large growths can be seen in the blown up sub section.

The aluminum also changes the hardness and elastic modulus as shown in Figure 2. Increasing the aluminum content brings them both closer to elemental aluminum's natural values, which decreases the strength of the coating. The effects of filler content can be difficult to predict and depend on various chemical and mechanical properties. Generally, greater than 50 vol% cause significant adhesion issues, and the coating will crack or peel[7].

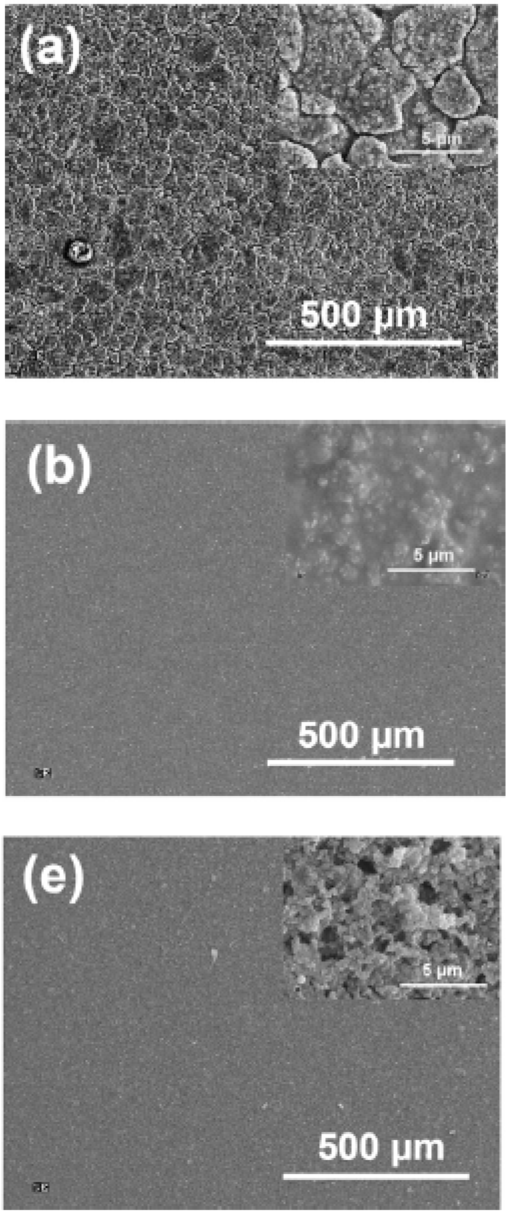

Figure 1[7]. SEM images of (a) PSN1, (b) PSN1 and 10 vol% Al, (e) PSN1 and 40 vol% Al.

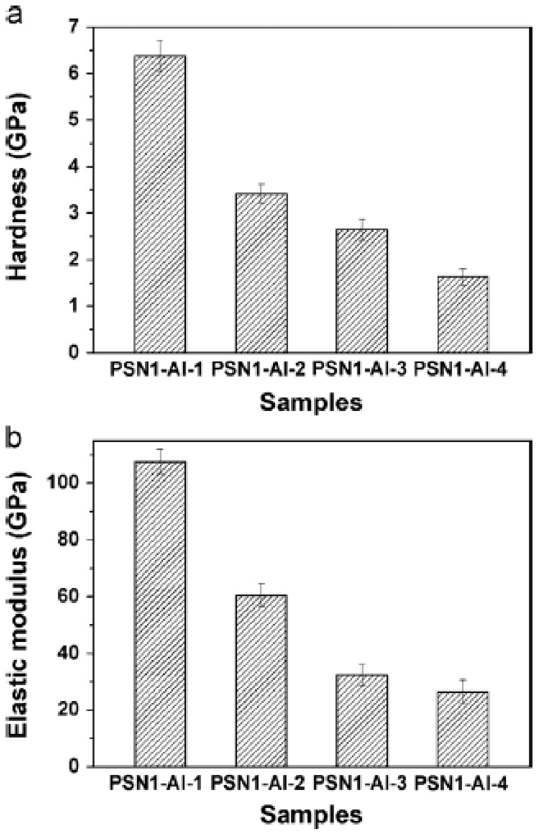

Figure 2[7]. Measurements of hardness and elastic modulus of samples of 304 stainless steel coated with PSN1 mixed with varying amounts of Al powder, where PSN1-Al-1 indicates 10 vol% Al, PSN1-Al-2 indicates 20 vol% Al, PSN1-Al-3 indicates 30 vol% Al, and PSN1-Al-2 indicates 40 vol% Al.

Cure and Pyrolysis Procedure

After coating the substrate, the first cure takes place anywhere from 80 °C to 200 °C, depending on the precursor. Its purpose is to remove the volatile alcohols and some of the organic groups of the polymer to solidify it, and to cross-link the coating. Authors vary in their procedures between pausing at this temperature for several minutes to a couple hours[8] to constantly ramping up to the desired pyrolysis temperature[6].

Figure 3 shows that the heating steps are discrete and vary based on the polymer. Crosslinking is generally accomplished at 100 – 200 °C, pyrolysis takes place anywhere from 450 °C to 1500 °C, and at

1200 °C to 1600 °C crystals nucleate and the coating has been fully converted to ceramic[9].

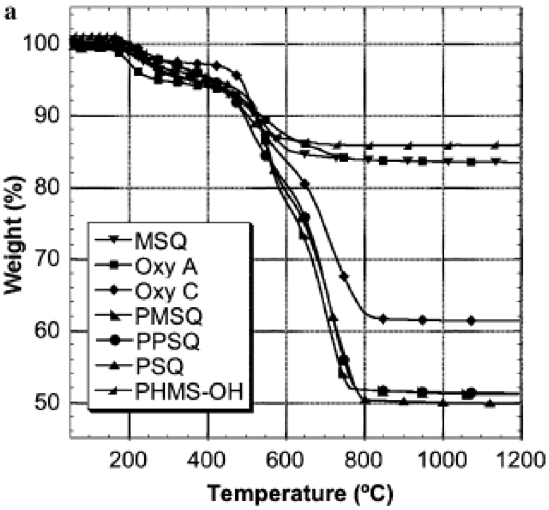

Figure 3[6]. A graph of the temperature dependence of weight percentage of several different polymers. All polymers were heated at a constant 1 °C / min ramp from room temperature to 1200 °C. MSQ is methylsilsesquioxane, Oxy A and Oxy C are different varieties of oxycarbide, PMSQ is phenylmethylsilsesquioxane, PPSQ is phenylpropylsilsesquioxane, PSQ is phenylsilsesquioxane, and PHMS-OH is poly(hydridomethylsiloxane) (PHMS) with OH groups substituted for the H groups.

With other polymers, different weight loss curves are generated. In Figure 4 varieties of the polymers polycarbosilazane and polysilazane, referred to by the authors as ABSE and PHPS, respectively, were studied using TGA. These polymers have completely crosslinked at about 200 °C for PHPS and 300 °C for ABSE with insignificant mass change for both nitrogen and air. Between 200 and 700 °C for PHPS and 300 and 800 °C for the ABSE the polymers give up a lot of their organics, such as ammonia, methane, SiH species, and hydrogen. This causes large amounts of mass loss in the ABSE and in the PHPS in a nitrogen atmosphere; however, it causes mass gain in the PHPS in air due to the oxidation of free silicon and the replacement of bonded nitrogen by oxygen. Above these temperatures, the main change is the coating morphing into a more compact structure[5].

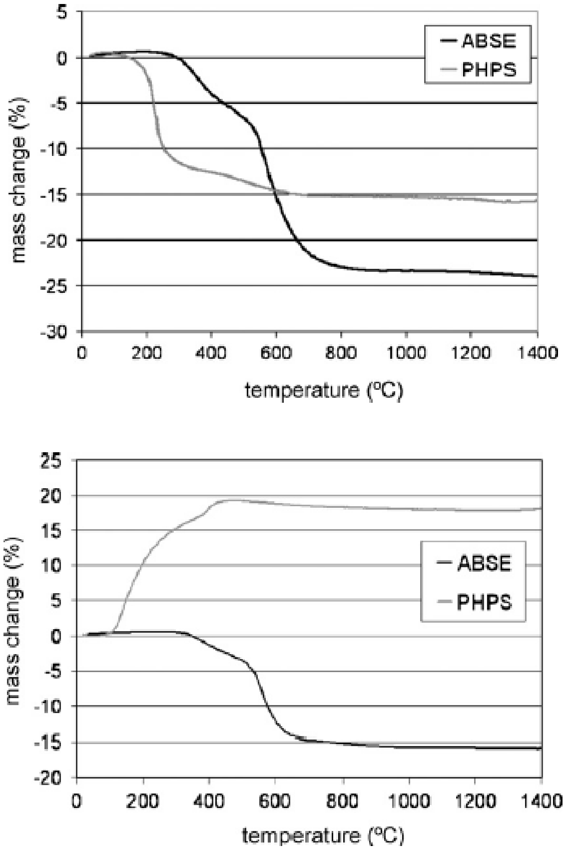

Figure 4[5]. Graphs of mass change dependent on temperature for two different polymers ABSE and PHPS. The top graph is data taken while heating was performed in a nitrogen atmosphere and the bottom graph is data taken while heating was performed in air.

Each polymer undergoes different mass change curves, and minimum temperatures and times required for full conversion to a ceramic can vary widely. Thus, one technique for tuning the performance of a coating is to heat to a preferred temperature. Another option is to change the composition of the heating atmosphere to encourage or discourage chemical reactions.

To analyze the elements of the final coating and thus to see what extent the precursor has been converted to ceramic XRD can be used. Figure 5 shows XRD patterns of PHMS and titanium disilicide that was heated in 200 °C intervals up to 1600 °C in air[10]. At lower temperatures, the composite is mainly titanium disilicide, silicon, and anatase. As the temperature increases the peaks change and the final product shows very strong signals of cristobalite and rutile, with some small amounts of silicon remaining. This can assist in deciding what final temperature to end pyrolysis at, because a coating that has been fully converted to ceramic may not be desirable, and the extremely high temperatures may not be practical.

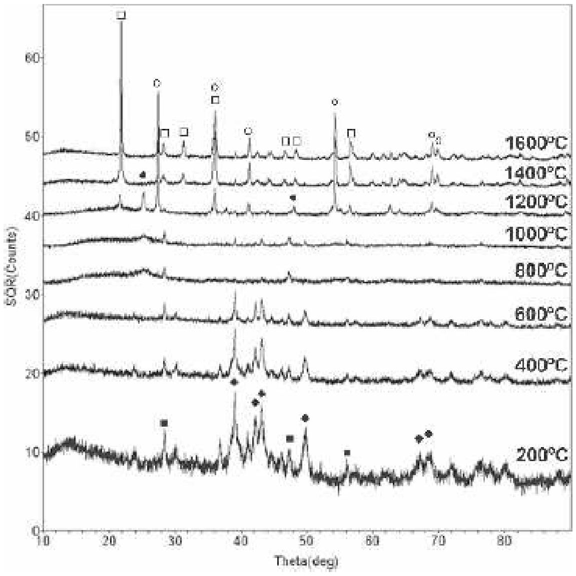

Figure 5[10]. XRD of a PHMS and titanium disilicide composite that was heated and then measured at 200 °C intervals. The shapes above the peaks indicate the composition of the peak. A diamond is titanium disilicide, a filled in square is silicon, a filled in circle is anatase, an empty square is cristobalite, and an empty circle is rutile.

Alternative Curing Procedures

There exist alternative ways to transition the precursor to a final ceramic product. One of these ways is using laser pyrolysis[4]. Colombo et al. deposited a coating of PCS and then irradiated it with a pulsed laser for a total energy of 0.4 to 1 Joule per square millimeter. The result was a ceramic coating of SiC that was very similar to a PCS coating that had been heated to 1000 to 1200 °C. However, the authors estimated that the PCS film had a transmittance of about 93%, and thus about 20 to 30% of the laser energy had been absorbed by their Si substrate and caused significant damage. This transmittance level was brought down to about 80% by coating the film with a layer of carbon or mixing graphite particles into the film, which mostly mitigated the problem.

The advantages of this technique are that the pyrolysis can be done at room temperature, and even if done in air or low vacuum, the coatings are not oxidized. However, the potential damage to the substrate must be taken into consideration.

Bombardment with ions can also work as the final step in manufacturing the coating[11]. Pivin et al. deposited various polymer precursors and irradiated them with carbon or gold ions. This had the effect of cleaving the hydrogen bonds of the precursors, which allows new crosslinking. Though this is thought to be the primary mechanisms, additional lesser processes help to convert the precursors into their corresponding ceramics. Furthermore, the authors noted several differences between their coatings and coatings obtained by heating, such as a higher retention of free carbon in the unheated coatings. This caused a decrease in density from about 2.45 to 2.1 grams per cubic centimeter. However, this also caused an increase in hardness.

Protection

Since the methods of attack on stainless steel are numerous, there are many ways to test the quality of protection afforded by a ceramic coating. One of the most important is oxidation resistance. This is easily done by heating the ceramic to a high temperature, such as 1000 °C, and exposing it to air or pure oxygen. This accelerates the oxidation and allows similar results to a long term test at normal temperatures to take place in a short amount of time, such as an hour instead of a thousand hours. Among other techniques, SEM images can be taken to qualify the oxidation resistance, and depth profiles can show the level of oxygen penetration.

In Figure 6 part of a stainless steel sheet was coated with PHPS and then, in atmosphere, heated to 1000 °C and held there for an hour. This resulted in a very rough oxidized surface on the uncoated stainless steel, whereas the area coated with a ceramic layer is smooth and mostly unaffected[5].

Figure 7 had the same heating procedure on the same stainless steel substrate but heated for 10 hours in air with PHPS or ABSE. The level of oxygen penetration is quantified with depth profile measurements made with glow discharge optical emission spectroscopy (GDOES). At 1000 °C the oxide layer of PHPS is about half that of ABSE and one tenth that of uncoated stainless steel, which has grown to be about 4.5 μm thick. The oxidation protection qualities of the PHPS are shown to be superior to those of ABSE and clearly better than uncoated stainless steel. This is partially because PHPS has significant quantities of free silicon, which when exposed to high temperatures and air made a barrier of silicon dioxide, which is one of the greatest oxygen barriers known. Additionally, the authors noted the absorption of oxygen created a self-healing effect where defects were repaired or grown over by forming additional silicon dioxide[5].

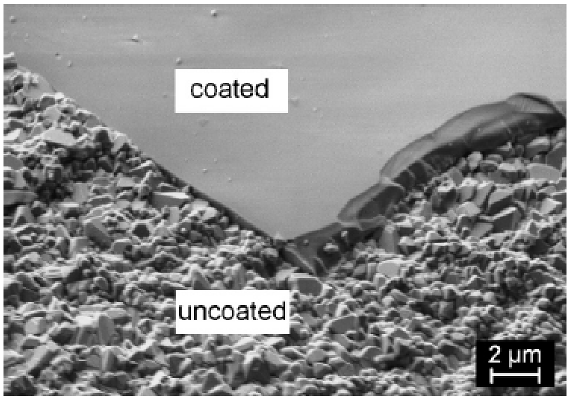

Figure 6[5]. SEM image of stainless steel partially coated with PHPS and heated to 1000 °C in air and held there for 1 hour.

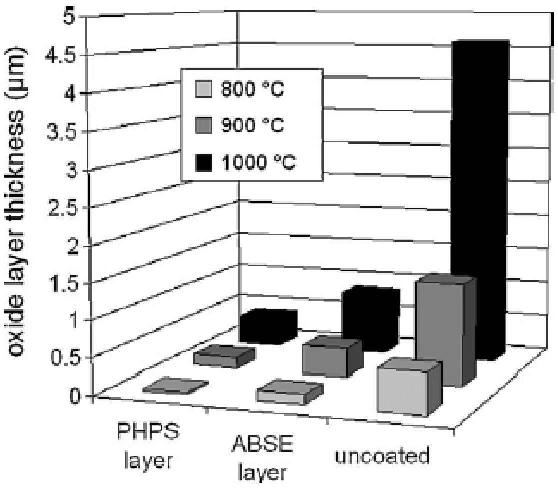

Figure 7[5]. Thicknesses of oxide layer created after heating stainless steel coated with PHPS, ABSE, and uncoated for 10 hours in air.

Conclusion

Coating stainless steel with ceramics imbues the finished product with the exterior properties of the ceramic, such as chemical inertness, resistance to oxidation, and high hardness. This greatly extends the lifetime of the product. Ceramics are susceptible to cracking caused by their volume shrinkage when they are heated, but this can be mitigated with volume loss compensating fillers or alternative curing methods that do not use heat, such as irradiation with ions or light. The transition of the polymer precursor to ceramic takes place in discrete stages at different temperatures, and the interactions between polymer, filler, and pyrolysis conditions make the performance of the final coating very tunable but difficult to predict.

References

2. Yajima et al. "Development of a Silicon Carbide Fibre with High Tensile Strength." Nature 261.5562 (1976): 683-85.

3. Xie et al. "Active Filler (Aluminum–Aluminum Nitride) Controlled Polycarbosilane Pyrolysis."

Journal of Inorganic and Organometallic Polymers and Materials 16.1 (2006): 69-81.

4. Colombo, Paolo. "Silicon Carbide Films by Laser Pyrolysis of Polycarbosilane." Journal of the American Ceramic Society 84.1 (2001): 224-26.

5. Günthner et al. "Particle-Filled PHPS Silazane-Based Coatings on Steel." International Journal of Applied Ceramic Technology 6.3 (2009): 373-80.

6. Torrey et al. "Composite Polymer Derived Ceramic System for Oxidizing Environments." Journal of Materials Science 41.14 (2006): 4617-622.

7. Xiao et al. "Fabrication of Ceramic Coatings from Polysilazane/aluminum: Effect of Aluminum Content on Chemical Composition, Microstructure, and Mechanical Properties." Ceramics International 40.1 (2014): 745-52.

8. Colombo et al. "Multifunctional Advanced Ceramics from Preceramic Polymers and Nano-sized Active Fillers." Journal of the European Ceramic Society 33.3 (2013): 453-69.

9. Colombo et al. "Polymer-Derived Ceramics: 40 Years of Research and Innovation in Advanced Ceramics." Journal of the American Ceramic Society (2010): 1805-837.

10. Torrey, Jessica D., and Rajendra K. Bordia. "Phase and Microstructural Evolution in Polymer-derived Composite Systems and Coatings." Journal of Materials Research J. Mater. Res. 22.07 (2007): 1959-966.

11. Pivin et al. "Comparison of Ion Irradiation Effects in Silicon-Based Preceramic Thin Films." Journal of the American Ceramic Society 83.4 (2000): 713-20.