COMPOSITE SOL-GEL ALUMINA CERAMIC/SILOXANE COATINGS

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF APPLIED SCIENCE
in
THE FACULTY OF GRADUATE STUDIES

DEPARTMENT OF METALS AND MATERIALS ENGINEERING

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THE UNIVERSITY OF BRITISH COLUMBIA
June 2004

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Title of Thesis: Composite Sol-Gel Alumina Ceramic/Siloxane Coatings

Degree: Master of Applied Science Year: 2004

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ABSTRACT

This thesis relates to the novel, relatively low temperature process (160-300°C) for preparation of chemically bonded composite sol-gel (CB-CSG) coatings. This “warm” temperature process (160-300°C) overcomes some drawbacks of the conventional composite sol-gel process, in particular minimization of stresses due to differential thermal expansion coefficient between the coating and the substrate. The biggest contribution of this research involves use of siloxane bond coat between the CB-CSG coating and the mild steel substrate, which relaxes residual stress in the coating, as well as protects the substrate from damage (corrosion) during the chemical bonding process. A method of multi-gun spraying to uniformly distribute the phosphates throughout the coating during the chemical bonding process is also an original contribution of this Thesis. The resulting coatings are free of surface cracks, have medium hardness (6.0GPa), moderate adhesion (42.0MPa) and good scratch resistance (17.0kgf). Electrochemical analysis shows that the multi-layer coating composed of the siloxane bond coat and the CB-CSG “top coat” forms a physical barrier against wet corrosion.
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Nomenclature

Abbreviations

ASMC  alumina reinforced siloxane matrix composite
BC  bond coat
CB  chemically bond
CB-CSG  chemically bonded composite sol-gel
CR  curvature radius or radius of curvature
CSG  composite sol-gel
CTE  coefficient of thermal expansion
CPC  ceramic/polymer composite
DI water  de-ionized water
DSI  depth sensing indentation
FEA  finite element analysis
FGBC  functionally graded bond coat
MAP  mono aluminum phosphate
MMT  montmorillonite
MPS  methylphenylsiloxane
MS  mild steel
PA  phosphoric acid
PCSG  phosphated composite sol-gel
PMMA  poly (methylmethacrylate)
PMPS  poly(methylphenylsiloxane)
PVD   physical vapor deposition
Ref.  reference
SAMC  siloxane modified alumina matrix composite
SEM   scanning electron microscope
SG    sol-gel
SS    stainless steel
TBC   thermal barrier coating
UTS   ultimate tensile strength
Vs.   versus
XRD   x-ray diffraction

Latin Symbols

$a$  contact radius ($\mu$m)
$A, B$  empirical correction factors in sonic wave for modulus determination
$b$  scratch width ($\mu$m)
$d$  density of sample ($g/cm^3$)
$D_s$  density of substrate ($g/cm^3$)
$D_{s-c}$  average density of coating and substrate ($g/cm^3$)
$E$  Young’s modulus (GPa)
$E_I$  elastic modulus of CB-CSG coating (GPa)
\( E_2 \) elastic modulus of substrate (GPa)
\( E_3 \) average elastic modulus (GPa)
\( E_0 \) Young's modulus of fully dense coating (GPa)
\( E_C \) Young's modulus of coating (GPa)
\( E_{cb} \) elastic modulus of CB-CSG coating (GPa)
\( E_d \) dynamic Yong's modulus (GPa)
\( E_p \) elastic modulus of siloxane (GPa)
\( E_s \) elastic modulus of substrate (GPa)
\( f \) effective friction coefficient
\( F_N \) normal load (N)
\( F_t \) transverse force (N)
\( G \) shear modulus (GPa)
\( G_c \) average shear modulus of coating (GPa)
\( G_{d-c} \) average shear modulus of coating and substrate (GPa)
\( h_1, h_2 \) thickness of coating and substrate respectively (\( \mu \)m)
\( h_c, h_p \) thickness of CB-CSG layer and siloxane respectively (\( \mu \)m)
\( H \) Vickers hardness (GPa)
\( h_c \) thickness of CB-CSG layer (\( \mu \)m)
\( h_p \) thickness of siloxane (\( \mu \)m)
\( i_{cor}^0, i_{cor} \) corrosion current densities of the bare and coated substrates respectively (A/m\(^2\))
\( K_c \) interface toughness (MPa. M\(^{1/2}\))
\( K_{IIc} \) Interface fracture toughness (shear) (MPa. m\(^{1/2}\))
\( k \) constant of hydrolysis, molar ratio of hydrolysis

\( L \) dimension (m)

\( m \) mass (g)

\( n \) number of samples

\( N \) resonant frequency (Hz)

\( P \) protection efficiency (%)

\( P_c \) porosity of coating (%)

\( r \) the radius of curvature (\( \mu \)m)

\( r_i \) the radius of indent (\( \mu \)m)

\( R_i \) radius of annular crack (\( \mu \)m)

\( R_a \) the average surface roughness of substrate (\( \mu \)m)

\( R_c \) the radius of curvature with coating (\( \mu \)m)

\( R_s \) the radius of curvature without coating (\( \mu \)m)

\( S_h \) scratch hardness (GPa)

\( t \) thickness (\( \mu \)m)

\( T_c \) thickness of coating (\( \mu \)m)

\( T_{s-c} \) total thickness of coating and substrate (\( \mu \)m)

\( T_s \) thickness of substrate (\( \mu \)m)

\( w \) width (\( \mu \)m)

\( Y \) yield strength (MPa)
GREEK SYMBOLS

α  constant of porosity
δ  deflection (μm)
κ  difference of curvature with and without coating (μm)
σ  thermal expansion mismatch stress (MPa)
Σ  elastic modulus ratio
ν  average Poisson's ration of coating and substrate
ν1  Poisson's ratio of substrate
ν2  Poisson's ratio of CB-CSG coating
νc  Poisson's ratio of coating
νs  Poisson's ratio of substrate
**Acknowledgements**

I would like to express my sincere gratitude to my supervisor Dr. Tom Troczynski (Professor of Ceramics, UBC), group leader Dr. Quanzu Yang, and other colleagues. Many thanks to Dr. Howard Hawthorne for his suggestions on my thesis. I would like to acknowledge the experimental help from Dr. Yongsong Xie and Dr. Zhaolin Tang.

I would also like to acknowledge the financial support of the National Science and Engineering Research Council of Canada, NCE-Auto21, and Datec Coating Corporation. The National Research Council of Canada is acknowledged for the experimental and equipment support.
CHAPTER 1: INTRODUCTION

The processing and characterization of ceramic coatings are important issues in this research. For example, the space-shuttle Columbia disaster happened on February 1, 2003. It is believed that the left wing of the shuttle was scratched by a piece of foam that fell from the external tank during launch, which destroyed the heat-resistant ceramic coating on the outer body and allowed the surface temperature to exceed its critical value upon re-entry. If the coating failure was an interfacial failure, it could be labeled as a manufacturing problem. If the coating failure was a cohesive failure, however, it could be asserted to be a problem related to coating design or to the coating material itself.

In this research, a novel sol-gel processing method was developed to produce a composite sol-gel coating at “warm” temperatures (100-300°C). The average hardness of the coating is ~6.0 GPa, the average adhesion strength is ~42.0 MPa, and the average scratch critical force is ~17.0 kgf. The “warm” temperature process successfully produces coatings free of surface cracks. Aluminum phosphate is used as the binding phase in the sol-gel coating. To obtain suitable strength, it is necessary to homogeneously distribute the phosphate throughout the coating through a method of multi-gun spraying. A siloxane bond coat was developed to reduce the residual stresses due to the differential thermal expansion of the ceramic coating and steel substrate, which decreases the deformation of the substrate. Another merit of this research is that it provides a method to produce a multi-layer ceramic/siloxane coating on mild steel (MS) without coating buckling.
1.1 Introduction to Sol-Gel

A sol is a dispersion of solid particles (~0.1-1 μm) in a liquid where only Brownian motion suspends the particles. A gel is a state in which the liquid phase is dispersed in the solid and vice-versa, yielding a solid network containing liquid components. The sol-gel coating process usually consists of four steps: (1) The desired colloidal particles are dispersed in a liquid to form a sol. (2) The sol is deposited to produce coatings on the substrates by spraying, dipping or spinning. (3) The particles in the sol are polymerized through the removal of the stabilizing components, which produces a gel. (4) The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating [1-4].

There are two distinct reactions in the sol-gel process: hydrolysis of alcohol groups and condensation of the resulting hydroxyl groups. For instance, the isomorphous γ-AlOOH precursor exists as the un-hydrolyzed species [Al(OH)₂]₆⁺ below pH 3, and can be hydrolyzed extensively with increasing pH [1]:

\[
[Al(OH)₂]₆⁺ + kH₂O \rightarrow [Al(OH)ₖ(OH)_{₆-k}]^{(3-k)⁺} + kH₃O⁺ \quad (1.1.1)
\]

\[
kH₃O⁺ + kOH^- \rightarrow 2kH₂O \quad (1.1.2)
\]

where \( k \) is defined as the molar ratio of hydrolysis.
It is generally agreed that the preferred condensation sites are those that maximize interactions between lone pair electrons on a bound hydroxide ligand on one aluminum species with a proton on a water-molecule bound to another aluminum species [1]. For example, two singly-hydrolyzed monomers (k=1) condense to a dimer via an olation reaction [1]:

$$2[Al(H_2O)_6^{3+} - H^+ \rightarrow Al(H_2O)_5OH^{2+}] - 2H_2O \rightarrow Al_2(OH)_2(H_2O)_8^{4+} \quad (1.1.3)$$

However, the condensation mechanism of aluminum isopropoxide is more complex than the above description, and the hydrolysis of the aluminum alkoxides is not very well understood [1].

### 1.2 Advantages of the Composite Sol-Gel Technique

Some non-hydrated fillers can be added into the sol-gel slurry to decrease the shrinkage strain during gelation, producing what is called a composite sol-gel (CSG). The composite sol-gel is a kind of “ceramic paint”, and adheres easily to various metallic substrates like mild steel, stainless steel, aluminum, nickel, and copper. The mono aluminum phosphate can be used as the binder in this paint. It forms a chemical bond with almost everything that can stand the processing temperature [3]. Because the phosphate is used as a chemical bonding phase, a “chemically bonded composite sol-gel” (CB-CSG) coating is produced.
The material in the gel state can be easily shaped into complex geometries, e.g. tube and wheel, by simple air-spraying, dipping or spinning. Another advantage is that high purity products can be produced. Because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent, and hydrolyzed into a sol and subsequently a gel, the composition is highly controllable. It can be sintered at low temperatures, usually around 400-700°C. Generally, the composite sol-gel technique provides a simple, inexpensive, and effective method of producing high quality coatings [5].

1.3 Limitations of Sol-Gel Techniques

There are some limitations to the sol-gel technique, e.g. weak bonding, porosity. In particular, the coating thickness is limited since the mismatch of the coefficient of thermal expansion (CTE) increases with temperature. Higher temperature processing or service often generates stresses that increase with coating thickness. When the residual stresses exceed the adhesion strength, the coating will break up. Particularly, the residual stresses in complex geometric locations, e.g. edges and corners, are more severe than those in a flat shape, which also limits wide application of the sol-gel technique.

Aqueous sol-gel processing typically proceeds in an acidic environment of pH = 2-4, which can corrode mild steel. A conventional way to address this issue is to coat the substrate with zinc or iron phosphate. However, the resulting thin (less than a few microns) and usually micro-porous phosphate films are unstable at the elevated process
temperature (>400°C) needed for chemical bonding. This can lead to the creation of additional interfacial porosity, and which allows access of corrosive species to the steel surface. Such a coating system does not provide long-term corrosion protection for the mild steel.

Therefore, a non-porous and thermally stable "bond-coat" of alumina reinforced siloxane matrix composite (ASMC) film has been developed in this work to coat the mild steel surface. This should protect the substrate during CB-CSG processing at temperatures between 100-400°C as well as providing a siloxane membrane for corrosion protection in storage and service [5]. In other words, when the siloxane is incorporated, the aqueous sol can be deposited on the surface of mild steel and heat treated at 100-400°C.

In order to overcome the limitations of traditional CB-CSG coatings, e.g. high residual stresses, low wear-resistance, and cracks, a "warm" temperature process has been developed. In this system, a siloxane composite bond coat reduces the residual stresses by grading the thermal expansion.

![Molecular structure of PMPS siloxane](image)

**Fig.1.1. Molecular structure of PMPS siloxane [6]**
1.4 Poly(methylphenylsiloxane)

There are several reasons to choose poly(methylphenylsiloxane), PMPS, as a polymer component in the multilayer coating. PMPS has a relatively high service temperature (nominal: 480°C, Cotronics Inc. US) due to its molecular structure. It is an inorganic polymer with no carbon atoms in the backbone and highly cross-linked chains of alternating silicon and oxygen atoms (Fig.1.1), by means of which it can stand a relatively high temperature [6, 7].

1.5 Objectives

The conventional chemically bonded sol-gel process includes an individual deposition of slurry and phosphate and firing at 400-900°C after each deposition. Therefore, it was difficult for such a process to evenly distribute the phosphate throughout the coating. Moreover, cracks were often observed in the conventional method [5, 8]. Therefore, the first objective was to develop a low-temperature process (160-300°C) for the production of a crack-free coating with phosphate distributed homogeneously throughout.

It was difficult to deposit the aqueous slurry on mild steel without buckling of the coating [9]. The second objective was thus to develop a siloxane bond coat for the mild
steel substrate to prevent this buckling. The third objective was to characterize the CB-
CSG coating and its siloxane bond coat through indentation tests, scratch tests, adhesion
tests, and electrochemical analysis.

Since the thin steel substrate often suffers deformation due to residual stresses, it
was believed that the siloxane bond coat could reduce these by grading the thermal
expansion. Therefore, the fourth objective was to gather evidence as to whether or not the
siloxane bond coat reduces the residual stresses due to the differential thermal expansion
of coating and substrate.
CHAPTER 2: LITERATURE REVIEW

2.1 Composite Sol-Gel Ceramic Coatings

The sol-gel process has been successful in the production of hard, erosion resistant and corrosion resistant ceramic coatings and structural ceramics (e.g. Al₂O₃, ZrO₂) [1-5]. However, the sol-gel films have tended to crack if they are thicker than several microns [3]. Calcined ceramic particulates dispersed in a sol-gel matrix produce a composite sol-gel (CSG) coating. This CSG technique avoids the large shrinkage strain of the sol-gel films following heat treatment and densification [9]. The thicker coatings (up to ~500 μm) do not crack upon drying because the gel phase contains up to about 80vol% of ceramic filler. An added advantage of the chemically bonded composite sol-gel (CB-CSG) is the possibility of controlling its strength by simple chemical reactions [5, 8, 10, 11].

It was believed that the composite sol-gel (CSG) coatings still needed a relatively high temperature, typically in excess of 600°C, to gain enough strength and hardness, and to eliminate the porosity due to structural collapse [5, 10]. For most metallic substrates of interest, including steel, aluminum and magnesium alloys, the maximum curing temperature must be, however, below about 600°C. This problem can be avoided if the diffusional process (e.g. sintering) is replaced with a chemical bonding process [3].
In recent research, a paint-like aqueous sol containing the ceramic oxide precursors and inert fillers has been deposited using a pressurized air-spray gun, followed by phosphating and curing at 400-900°C [8]. This is the composite sol-gel ceramic technique.

This technique includes dispersing fine ceramic powders in sol-gel solution, spraying the paint onto a substrate, and finally firing at 400-900°C [12]. The technique has successfully produced 25-200 μm coatings [4], if phosphoric acid (PA) is used to initiate the formation of a phosphated alumina sol-gel coating by subsequent heat treatment at 400-600°C.

It is generally agreed that the liquid mono aluminum phosphate (MAP) is the best binder, which upon heat treatment is eventually converted to three phases, Berlinite and Cristobalite forms of AlPO₄ or Variscite, Al(H₂PO₄)₃. The average hardness of a CB-CSG coating is about 4.0 GPa [13], while the maximum hardness of CB-CSG coating is reported to be ~HV₁₀g 6.47±1.44 GPa [6]. Sometimes, there were some high hardness in isolated areas (~8.0GPa) on the CB-CSG coatings, usually within smoother and shinier regions [40]. Church and Kuntson impregnated 85wt% PA with low concentrations of some other inorganic chemicals, such as ZrO₂, TiO₂, and Cr₂O₃, into the alumina matrix to obtain 7.0-10.0 GPa hardness [10]. The pull-off adhesion was reported to be ~42 MPa [14]. It is very susceptible to substrate interactions [12, 14], which included mechanical interlocks and chemical bonds at the interface, indicating an opportunity to increase the adhesion further.
The conventional composite sol-gel process is an individual deposition method that involves the polymerization of aluminum isopropoxide through the removal of stabilizing organic components. The coating is dried at 70°C to gel the layer and fired at 400-900°C to pyrolyze the remaining organic components, which forms an amorphous or crystalline layer [4]. The following is a well-established process for producing composite sol-gel alumina coatings [3]:

1. Heat at 550°C to form a thin oxidized film on the sand-blasted MS substrate.
2. Spray a 10-60 μm composite sol-gel alumina layer on the substrate.
3. Heat at 550°C for 20 minutes.
4. Spray composite sol to the desired thickness.
5. Heat at 550°C for 10 minutes.
6. Brush with 85% phosphoric acid.
7. Heat at 250°C for 20 minutes and at 600°C for 20 minutes.

There are some inevitable drawbacks to this process. First, when the phosphoric acid (PA) is over-impregnated on the surface of green CSG. It forms pseudoboehmite or gelatinous boehmite, which has a low strength [3, 4, 12], and produces solid aluminum phosphate at room temperature, which often induces cracking. Second, the phosphate needs to reach the interface and form a chemical bond between the coating and the substrate, but it is difficult for the individually deposited phosphate to penetrate through a CSG layer more than 20 μm thick. Third, the relatively high temperature, 550-600°C,
sometimes affects the properties of the substrate, e.g. Al or Mg. It is probable that phase transformations occur in the substrate. Finally, this process uses chemical reactions at 550-600°C [3]:

\[
\text{Al}_2\text{O}_3 + 2\text{H}_3\text{PO}_4 \rightarrow 2\text{Al}(\text{H}_2\text{PO}_4)_3 + \text{H}_2\text{O} \tag{2.1}
\]

\[
\text{Al}(\text{H}_2\text{PO}_4)_3 \leftrightarrow 2\text{H}_3\text{PO}_4 + \text{AlPO}_4 \tag{2.2}
\]

\[
\text{Al}(\text{H}_2\text{PO}_4)_3 + \text{Al}_2\text{O}_3 \leftrightarrow 3\text{AlPO}_4 + 3\text{H}_2\text{O} \tag{2.3}
\]

These reactions are related to the complicated transformations of various phases, which often generate large mismatches in thermal expansion during cool-down from 550-600°C. Therefore, if the conventional method is followed, cracks are inevitable.

A viable way to produce crack-free coatings is to decrease the process temperature. Unfortunately, there is no report on a “warm” temperature (<250°C) version of the composite sol-gel alumina coating process.

### 2.2 Aqueous Sol-Gel Ceramic Coatings on Steel

Mild steel is very difficult to coat with the acidic aqueous sol-gel slurry due to its easy corrosion during heat treatment in air. The conventional way to try to prevent this is as follows: (1) deposit the sol-gel derived coating on phosphatized (zinc or iron
phosphate) mild steel; (2) heat-treat it in an inert atmosphere; and (3) cover it with epoxy resin after heat treatment during storage and service [15].

This method has some disadvantages: (1) the treatment in inert atmosphere requires complex and expensive equipment [15, 16]; (2) the commonly-used phosphate layer cannot survive beyond 300°C; and (3) the epoxy resin on the surface cannot resist high temperatures and possesses low scratch resistance.

Sometimes the sol-gel coating on MS needs to be heat treated in air, which requires an inhibitor-doped sol, but these inhibitors often decrease the adhesion strength of the coatings [17]. Therefore, to deposit aqueous sol-gel coating on MS, the biggest challenge is to overcome the weak corrosion resistance of MS, and to produce a coating with high adhesion strength and good resistance to buckling.

2.3 Functionally Graded Bond Coat

To address the problem of weak bonding, usually a bond coat (BC) is used to increase the adhesion strength of a coating system. For example, the glue utilized in dental crowns is a good example of a BC, in this case a highly adhesive polymer connecting the top porcelain layer and the tooth substrate. Another example of BC is the zinc phosphate used to bond an aluminosilicate top-layer on an MS substrate [15].
However, in most cases, the variation in composition between the other layers and the BC is always the main reason for a large mismatch in thermal expansion. In other words, the traditional ceramic/metal system commonly suffers failures due to the excessive residual stresses generated during heating and cooling. The residual stresses have a substantial effect on the coating properties, which can give rise to either deformation of the substrate or buckling of the coating [18-21].

Thus, people have tried to use a functionally graded bond coat (FGBC), a BC with a gradual variation of composition, to solve the problem. The first concept of FGBC was proposed to withstand the severe stress of the CTE mismatch in ceramic engines. The unique idea of FGBC was to provide a composite coating, where the coating composition varies gradually from coating to substrate [23].

The literature [21-28] showed that FGBCs could grade the thermal expansion, and thus reduce the residual stresses following cool-down from a high temperature. Therefore, the FGBC has been an indispensable constituent for thick coating systems to reduce the residual stresses [28-33].

A polymer should be an ideal candidate for the bond coat, since polymers have a lot of advantages, e.g. excellent resilience, good adhesion, good corrosion resistance, and fluid-impermeability. Unfortunately, there has not been any report on the sol-gel ceramic/siloxane FGBC, because most polymers begin to degrade above 150°C, while
the conventional sol-gel process temperature is often >400°C. Therefore, there has not been very much research on the polymer/ceramic sol-gel process.

2.4 Chemically Bonded Phosphate Ceramics

It is technologically important to fabricate alumina ceramics at "warm" temperatures (<300°C). The phosphate sol-gel alumina has a low formation temperature of ~150°C, at which the ceramic is likely to be stress-free. Moreover, the phosphate alumina ceramic (Berlinite) has a high compressive strength of ~110 MPa. The mono aluminum phosphate can chemically bond to many materials [34], except some organic polymers.

Kingery first used the phosphoric acid to bond alumina at 250-300°C [35]. Later, mono aluminum phosphate (MAP) hydrates were produced by the reaction between alumina and orthophosphoric acid at 100-150°C. MAP can convert to Berlinite above 150°C as a binding phase [36-38]. A well-crystallized AlPO₄ (Berlinite) was even synthesized at 150°C by reacting boehmite and phosphoric acid [37, 38-42]. The hardness values of Berlinite and Variscite are ~6.5 GPa and ~4.0 GPa respectively [43-46]. It is generally agreed that the liquid mono aluminum phosphate (MAP) is converted to three phases upon heat treatment: Berlinite, Cristobalite forms of AlPO₄, or Variscite, Al(H₂PO₄)₃ [36]. Only the Berlinite was formed when the MAP was cured for 4 days at ~150°C [34-36]. The Berlinite was formed by the following reaction [34]:

14
\[ Al_2O_3 + 2AlH_3(PO_4)_2 \cdot H_2O \rightarrow 4AlPO_4 + 4H_2O \]  

(B.4)

Berlinite is the phase that bonds individual particles and forms the Berlinite-bonded alumina ceramic [34]. The curing time decreases with increasing temperature [40-43]. The monolithic alumina gels can be formed by hydrolysis and condensation of aluminum alkoxide, and the phosphorus acts as the “bridge” in the network of the phosphate ceramic [39].

From the earlier limited research [44-49], it is seen to be possible to produce a well-crystallized composite sol-gel ceramic coating at ~160°C, which has high adhesion strength, high compressive strength, high hardness, and even high modulus.

2.5 Residual Stresses in Multi-layer Coatings

The most suitable method to determine residual stresses is finite element analysis (FEA), which can quantitatively identify the stress distribution in complex multi-layer structures. However, as a so-called “closed-form analytical method,” FEA is limited to case-by-case studies [50-56]. Lattice structure measurement techniques, such as X-ray diffraction, are difficult to implement. A viable stress “indicator” is the curvature radius (CR) of a coating system [13] using the so-called “wafer” method. For example, a “wafer” curvature method has been used to measure the residual stress (140 MPa) in an aluminide bond coat (elastic modulus ≈ 110GPa) [15].
The residual stresses in the CB-CSG coating can be related to the following: (1) the stress due to chemical reactions; (2) phase transformation-induced stress; (3) geometrically induced stress, e.g. at edges and corners; (4) thermal expansion coefficient (CTE) mismatch-induced stress; (5) the external service stress. This research is focused on the CTE mismatch-induced stress.

When the CTE of the substrate is smaller than that of the coating, the coating is in tension. When the CTE of substrate is larger than that of coating, the coating is in a state of compression [8, 32, 57, 58]. The bending moment or the residual stress increases with the increment of coating thickness, and correspondingly the curvature radius (CR) of the coating decreases with the increase of bending force [23, 33]. For the same thickness, the residual stress of a siloxane bond coating should be smaller than that of a 100% CB-CSG coating, since the visco-elastic siloxane relaxes the stresses more easily than brittle ceramics [12].

The curvature radius (CR) can provide a context for analysis of the relationship between the stress and the coating thickness. The salient characteristics are as follows: the bending moment increases with the increment of the coating thickness, and tends to approach a fixed value, while the curvature radius of the coating decreases with monotonic increase of the coating thickness [58].
When the thickness and elastic modulus of the bond coat were much smaller than those of the CB-CSG top layer, the CB-CSG/siloxane could be regarded as a single layer system in order to use the bi-material model for calculating the residual stress. Thus, the thermal mismatch stress \( \sigma^T \) in the coating was calculated according to the equation below (2.5) [32]:

\[
\kappa = \frac{6\xi^2(1+\xi)(1-\nu_2)\sigma^T}{E_2 h_1 [(\sum \xi^2 - 1)^2 + 4 \sum \xi (1+\xi)^2]}
\]  

(2.5)

Where \( \kappa \) is the difference of curvature with and without coating \( \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \) respectively

\( h_1 \) and \( h_2 \) are the thickness of coating and substrate respectively, \( \xi = h_1/h_2 \)

\( E_2 \) and \( \nu_2 \) are substrate elastic modulus and Poisson’s ratio of substrate respectively

\( E_i \) and \( \nu_i \) are CB-CSG elastic modulus and Poisson’s ratio of coating respectively

The deflection \( \delta \) of equation (2.5) is \( \delta = \kappa D^2 / 8 \) [32], where \( D \) is the substrate diameter or length.

Elastic modulus ratio of coating to that of substrate, \( \Sigma = \frac{E_i/(1-\nu_i)}{E_2/(1-\nu_2)} \).

The average elastic modulus \( E_3 \) of the dual layer coating was estimated by,
\[ E_3 = \frac{h_c}{h_c + h_p} E_c + \frac{h_p}{h_c + h_p} E_p \]  

\[ (2.6) \]

$h_c$ and $h_p$ are the thickness of the CB-CSG layer and the siloxane layer respectively

$E_c$ and $E_p$ are the elastic modulus of the CB-CSG layer and the siloxane layer respectively

There have been many debates over the accurate determination of the residual stress in a bilayer system. Equation (2.5) was built upon a "fully elastic" model [32], which is also dependent on the relative thickness $h_1/h_2$ and the relative modulus ratio $\Sigma$. However, this equation can still help in understanding the rationale of the sol-gel process.

2.6 Ceramic/polymer Composite Coatings

Historically, it was believed that polymers and ceramics were irrelevant to each other because polymers were mainly used for low temperature applications while ceramics were often used for high temperature applications because of their intrinsically strong bonds. Consequently, there has not been very much research on the ceramic/polymer composite system, except some studies of low temperature polymer/ceramic composites, since the difference in the processing temperatures of ceramics and polymers is too large.

With the development of high temperature polymers and the low-temperature processing of ceramics, e.g. the chemically bonded sol-gel technique, it is now possible to heat-treat polymers and ceramics together and to develop the ceramic/polymer
composite system, which may promise a combination of the advantages of both polymers and ceramics, e.g. good elasticity and high hardness.

Recently, ceramic/polymer composite (CPC) coatings have evoked intense research interests due to their unique characteristics [60-83], e.g. thermal barriers [66], compliant layers [5, 81], mechanical strength [82], stress tolerance [54], molecular barriers [82] and flame retardant properties [83]. The development of CPC coatings can be tracked back to the research done by Toyota in 1990 [79, 81]. CPCs were commonly a sort of low-load ceramic reinforced polymer matrix composite, where the ceramic was usually montmorillonites (MMTs), and the polymer matrix could be nylon [79], poly(methyl methacrylate) (PMMA) [84], epoxy resin [85], polystyrene [86], polyurethane [87], polyaniline [88], etc. Yeh and coworkers found that the incorporation of MMT into a polyaniline matrix led to an effectively enhanced corrosion resistance of polyaniline after a number of measurements of electrochemical corrosion [89]. Messaddeq et al. dispersed PMMA into a zirconia sol and fired at 200°C for 10 minutes, increasing the lifetime of stainless steel [90].

Masalski and colleagues [91] believed that the CPC coating had to be fired above 400°C to achieve high adhesion strength, and that thus the main drawback of the ceramic/polymer composite was the temperature limitation. The industry always demands high-temperature systems. Unfortunately, there has not been very much research related to the high-temperature (>450°C) co-sintering process of ceramics and polymers. Therefore, it is necessary to do more intensive research exploring this unknown field.
2.7 Adhesion of Coatings

The adhesion is one of the most important issues in sol-gel coating characterization. Unfortunately there is not very much information about the assessment of coating adhesion because the correlation between failure modes and adherence is still poorly understood despite the widespread use of adherence tests. For example, Du et al. [70] reported that they still do not fully understand the different adhesion performance among the sol-gel coatings after peel testing. Sexsmith and Troczynski [92] proposed a model of a peel test to calculate the experimentally determined stress-strain relationship. Lin and Berndt [93] summarized the most widely-used measurements on adhesion: ASTM-C633 or DIN-50160. They agreed that these tests are simple but do not promote any deep understanding of coating performance. Scratch was a practical way to assess coating adhesion [48]. Basically, there are two types of scratch failure, cohesive failure and interfacial failure [50]. Cohesive failure indicates good interfacial adhesion, but interfacial failure is often generated by defects, e.g. pores and cracks, that are created during the processing [51].

Xie and Hawthorne [13, 94] summarized the advantages and disadvantages of the different ways of assessing coating adhesion: pull-off tests, peel tests, four-point bending tests, indentation tests and scratching tests. They attested that micro-cracking could release the thermal stresses, and that the CB-CSG coating interface was strengthened
with increased processing temperature. They also cited that they still did not completely understand the reasons of the measured interfacial toughness and residual stress data trends in their sol-gel coating research [40]. But they believed that the interfacial fracture toughness was a reasonable way to characterize the adhesion of sol-gel coatings.

In pull-off tests, the critical normal load, at which the coating detachment initiates, is often used to determine the adhesion strength of a coating. Generally, it is believed that the use of critical normal load (pull-off) is adequate for a semi-quantitative routine monitoring of the adhesion [50]. However, this is only suitable for comparison between coating systems with close properties. For different coatings, the comparison of coating/substrate adhesion could not be achieved by simply comparing the critical normal load. For example, in pull-off tests, the brittle sol-gel alumina coating often broke up at the interface, but the detachment of the soft siloxane bond coat often occurred in the middle of the coating rather than at the interface. In this case, it was not suitable to use the pull-off adhesion test to compare the CB-CSG coating and the siloxane polymer coating.

Another problem in the understanding of coating adhesion was the lack of reliable models, even though many researchers have proposed a number of models for adhesion bonds, such as chemical bonding [95, 96], diffusion [97-99], mechanical interlocking [100], and residual stresses [81]. When looking at the literature related to the adhesion of sol-gel coatings to metallic substrates, clear relations could not be found, e.g.
substrate roughness, heat-treatment temperature and coating adhesion. This was always due to incomplete information about processing conditions.

For example, Masalski and coauthors [102] reported that the sol-gel Al₂O₃ coating fired at 500°C had a better failure resistance than that fired at 850°C, but they did not give any reason why the higher temperature curing led to a better adhesion. Bergmann [104, 105] believed that the surface roughness of substrate increased the adhesion strength, and the adhesion increased with the increment of preheating temperature of substrate for a given surface roughness. He also observed that alumina and zirconia had poor contact with the substrates when they were sprayed on a smooth (roughness, \(R_a \approx 0.05 \ \mu m\)) stainless steel substrate [106]. According to the work of Richard et al. [109], the residual stresses near the interface decreased with decreasing surface roughness. The adhesion increased linearly with the increment of cold (<100°C) substrate roughness, and the adhesion increased with the increment of substrate temperature, where the best adhesion could be obtained between 300 and 500°C for stainless steel [96]. However, a clear quantification of coating adhesion vs. substrate roughness was not given.

On the other hand, the substrate surface conditions were also important factors contributing to the adhesion strength. The metallic-substrate surfaces in air were covered with a layer of metal oxide. The density and thickness of this metal oxide layer varied depending on the metal-substrate, and on how the surface was treated. For example, phosphoric acid anodizing of steel generated a hard porous iron oxide layer with a thickness of about 50 nm [110, 111]. The iron oxide layer had a significant population of
hydroxyl groups in a humid environment. These surface hydroxyls could participate in the sol-gel condensation reaction to form a chemical linkage, M-O-Fe. This chemical bond formation produced a strong interaction of the sol-gel layer with the MS surface in the initial stage [70]. This research can give an explanation as to the rationale of the individual deposition of conventional sol-gel process. It is possible to form weak bonds between the non-phosphate sol-gel coating and the steel substrate, but these weak bonds can degrade at elevated temperatures and thus yield a decrease in the adhesion strength [70]. Therefore, the question of how to control the substrate-surface conditions was another important issue in sol-gel coating research.

On the whole, it was believed that there was not enough information to promote a deep understanding of the relationship between coating adhesion and sol-gel processing [112-120]. The standard of adhesion is still poorly understood [121-128]. Therefore, in order to understand the abovementioned problems to the necessary extent, further investigation of adhesion is required. The interfacial fracture toughness is a basic parameter of the interface. Therefore, it is a potential candidate for characterization of the adhesion of the sol-gel coating.

2.8 Chloride Corrosion

The following electrochemical equations govern the corrosion of iron in a sodium chloride solution [113]:
The contact of iron with water and oxygen or hydrogen forms a galvanic cell leading to the oxidation of iron. Since iron possesses anodic and cathodic sites, e.g., carbon in the constant electric contact, the only way to inhibit corrosion is to eliminate the contact between the electrolyte and the reactants [113]. The siloxane bond coating suppresses the cathodic reaction by limiting the diffusion of the electrolyte, i.e., oxygen and water, to the substrate. It also blocks the transport of electrons to the iron surface.

In a sodium chloride solution, the chloride is one of the most deleterious factors in terms of steel corrosion. The antagonistic nature of the Cl⁻ ions is due to their ability to absorb on the steel surface, where high current densities are generated at the Cl⁻ adsorption site. Hydrolysis of iron ions from the anodic reaction causes a decrease in pH, which discourages oxide film repair and accelerates attacks. Even in high-purity water, in which the level of Cl⁻ is as low as a few milligrams per liter, the attack of Cl⁻ ions on mild steel results in uniform rather than localized corrosion [113].
2.9 Corrosion Protection by Multi-Layer Coatings

A ceramic coating can reduce corrosion of a metal substrate, since the ceramic material is usually nobler than the metal. Compositions, interfaces, defects, thickness, and structures are the important parameters affecting the corrosion resistance of a coating.

The chemical composition of the coating and the microstructure of the substrate exhibits a direct influence on the electrochemical behavior of the system [129]. The corrosion rate is normally proportional to the corrosion-current density [113]. The corrosion resistance of the multi-layer coatings is significantly different from that of the single-layer coatings [130]. The multi-layer coatings have a much smaller corrosion current density than the mono-layer coatings and the bare MS because in the multi-layer system, the pinholes can be fully blocked by corrosion products, e.g. iron oxides, which prevents further transport of oxygen to the steel substrate [131].

The protection efficiency, $P$ can be represented by:

$$P(\%) = 100 \left( 1 - \frac{i_{\text{cor}}}{i_{\text{cor}}^0} \right)$$  \hspace{1cm} (2.10)

where $i_{\text{cor}}^0$ and $i_{\text{cor}}$ denote corrosion current densities of the bare and coated substrates respectively [126].
Coating defects act as pathways that allow the corrosive species to reach the interface [132]. The pores and micro-cracks provide a direct path for corrosive species and lead to rapid localized galvanic corrosion of the metal substrate [132, 133]. The corrosion current of the sol-gel coatings decreases to $\sim 10^{-4}$ times that of the mild steel substrates with the presence of homogeneous macro-pores [134].

The ceramic particles incorporated into the methylphenylsiloxane (MPS) hybrid coating enhance the corrosion resistance of steel: the corrosion resistance increases with increasing coating thickness, and acts as a physical barrier, which effectively separates the anode from the cathode [5, 126]. The corrosion-resistance of the interface is increased with the incorporation of the polymer component, a fact attributed to the formation of chemical bonding at the interface [126].

The polymer bond coat not only improves the adhesion, but also increases the corrosion resistance of the system [136]. The corrosion protection of the bond coat increased with increasing coating thickness [137].

In summary, it is believed that the multi-layer coating forms a better barrier against wet corrosion than the single-layer coating. The polymer bond coat can increase the corrosion resistance of the coating system, in addition to improving bond strength and decreasing residual stresses in the system, this supports the original objective of this thesis.
CHAPTER 3: EXPERIMENTAL PROCEDURE

3.1 Substrate Preparation

AISI 1010 mild steel was used as a substrate. The substrates (3.8x3.8 cm) were sandblasted by 70-80 psi air pressure using 220 grit brown fused-alumina particles, resulting in a surface roughness of 0.5-5 μm. The average surface roughness ($R_a$) was measured by a Wyko® optical interference surface profiler (Veeco Instruments Inc., USA).

3.2 Deposition of Coatings

The original alumina sol was prepared by adding 306 g (1.5 mol) aluminum isopropoxide ($\text{Al(iOCH(CH}_3)_2)_3$, 98%, Aldrich) to 3L hot (85°C) distilled water. 1M nitric acid was used to adjust the pH of the sol to 3. The mixture was stirred vigorously for 16 hours at 85°C. The excess solvent was slowly evaporated from the sol until its molarity was 1.5 M. 42 g calcined $\alpha$-alumina (0.3-0.5 μm, A16SG Alcoa Industrial Chemicals, USA) was added to 100 mL of the original sol as the filler. The sol was ball-milled for 24 hours to break apart particle aggregates and to ensure uniformity of the solution before the spraying of the coating.
The sol was sprayed on the mild steel substrate, followed by the spraying of mono aluminum phosphate (MAP) and methylphenylsiloxane (MPS, Dureaseal 1529H Cotronics Corp., USA). The MAP and MPS were deposited by using two spray-guns in a back-draft booth. Subsequently, the sol was deposited again followed by the impregnation of 25wt% mono aluminum phosphate (MAP), curing at 121°C for 4 hours, and finally baking at 300°C for 30 minutes.

A two-gun method is used to distribute the MAP throughout the coating. It consists of one gun spraying the sol and another gun lightly spraying 25wt% MAP occasionally. It is believed that this is the only way to distribute phosphate throughout the CB-CSG coating when the coating is thicker than 20µm.

Fig.3.1. Schematic representations of three basic multi-layer structures
Three variants of this basic process were used to produce coating types A to C, as shown in Fig.3.1. Group A was the dual-layer system containing the siloxane bond coat and the CB-CSG top coat on the MS substrate. Group B was a tri-layer system, containing a CB-CSG primer, a siloxane bond coat and a CB-CSG top coat. Group C was a mono-layer CB-CSG coating on the MS substrate. The MS substrates used in the mono-layer Group C were heated to 500°C to oxidize their surfaces so that they could be treated with aqueous slurry afterward. The samples were kept in a glass container with a desiccant to prevent contamination.

3.3 Low Temperature Process

This process uses low-temperature curing to produce a CB-CSG alumina coating free of surface cracks, including 1 day of curing at 121°C and 5 days of curing at 160°C. After the 1 day of curing at 121°C, the MAP reacts with hydrated alumina and forms AlPO₄. Chemical bonding occurs when the AlPO₄ is converted to Berlite as the bonding agent after 5 days of curing at 160°C. The residual phosphate was washed away with warm (45°C) water. The following is the detailed procedure for this low-temperature process:

1. Heat at 550°C to form a thin oxidized film on the sand-blasted mild steel.
2. Spray sol and 25% MAP with two guns to the desired thickness.
3. Cure at 160°C for 1 day.
4. Spray 50% MAP onto the coating surface.

5. Cure at 160°C for 5 days.

6. Wash away the residual phosphate with water at 45°C.

This low temperature process includes a multi-gun spraying technique to distribute the phosphate throughout the coating and prevent cracks. It can produce the same coatings as the conventional method (referred to pp.10). In this low temperature process, mono aluminum phosphate reacts preferentially with the small, reactive particles, e.g. γ-hydrated alumina, during the 160°C curing, and provides a bonding phase for the coarser filler particles, e.g. α-alumina. This coating is gradually consolidated without generation of strains during the 5 days of curing at 160°C.

3.4 Scratch Tests

The scratching critical force at which a coating fails was used to represent its scratch resistance. All measurements are performed on a Romulus IV apparatus (Quad Group, USA) at a changing vertical load of 0-45 kg and a 2.0 cm distance. The coating moved at a constant rate of travel (0.04 mm/s) and the force increased at a constant rate of loading (0.1 kg/s) until the coating failed. A sensor near the scratch tip detected the acoustic signals from the coating fracture and confirmed the critical force values.
In this research, a hemispherical diamond tip with a radius of 533 μm was used. The scratch tests were conducted on the finely polished coating surfaces. The surface of the coating was polished to a roughness of less than 1 μm with 2400 grit sandpaper.

Scratch hardness \( S_h \) is defined by the following equation:

\[
S_h = \frac{8F_N}{\pi b^2}
\]  

where \( F_N \) is the normal load and \( b \) is the scratch width \([40]\), which is the distance between the scratch ridges. \( \frac{\pi b^2}{8} \) is the projected load bearing area based on the assumption that the coating behaves perfectly plastically and the load is carried only by the front half of the spherical tip. Four samples per group were used to determine the average critical force and the average scratch hardness.

3.5 Indentation Hardness Measurements

The average hardness of 30 samples was measured by a micro-hardness tester (Micromet 3, Tech-met, ON, Canada) using a Vickers indenter at a load of 300 g and a duration of 15 seconds.

A nano-indentation system (Fisherscope H100, Germany) was used to measure the elastic modulus of the coating. Normal load on the Berkovich indenter was ranged
from 0.4 to 10 mN in 25 equal increments at a rate of one per second, and then held at the peak load for another 50 seconds.

The 5 mm thick substrates were used to prevent the indenter from affecting the deformation of the coating system, because there was always a plastic zone under the indent field. The depth of this plastic zone was ~1.5 times the indent diagonal-length. Each successive indent was isolated at a distance of ~1 mm to avoid overlapping of plastic zone onto neighboring indents.

A Rockwell C hardness tester (Buehler Inc., USA) was used to determine the coating's interfacial fracture toughness. Each sample (Group C) was cut into three coupons for measurement of the interfacial fracture toughness.

The Rockwell C indenter was a spherical diamond with a 0.2 mm tip radius. The test procedure was conducted according to ASTM standard E18-02. As the high-load indenter (150 kgf) was applied on the coating and caused the plastic deformation of the underlying substrate, the severe deformation of the substrate forced the coating to be displaced radially and induced a compressive radial stress in the coating which decreased with the increase in distance from the indenter. The critical crack extension force was determined by measuring the size of the detachment area [13, 40, 48]. The measured crack size was the average of three indentations. The calculation of interfacial fracture toughness was performed according to the method of Ref. [13].
3.5 Adhesion Tests

The adhesion strength of the coatings to the steel substrate was tested by a pull-off test, ASTM standard C-633-79. Five samples per group were tested to determine the average tensile strength. The coatings were glued to two identical rods by a 3M 2214 regular epoxy adhesive.

The adhesion measurements were made using an Instron universal testing machine (Instron Corp. USA) with 4,450 kg load cell at a cross-head speed of 1 mm/minute. The maximum force at which the two rods were separated was determined (see Fig.3.2). After the test, the cross-sections of the fractures were observed by SEM.

Fig.3.2. Setting of the pull-off tests
3.6 Air Permeability Measurements

The average air permeability was measured by a “Vacuperm” permeability tester (University of Missouri-Rolla, USA). The coatings were deposited onto the porous tiles, with a permeability of ~5.0 millidarcys. The average value of five samples was taken as the air permeability of the coating.

In the permeability tester, it pumps the air into the chamber and then forces the air to permeate the coating. A sensor simultaneously detects the pressure in the chamber and sends it to a computer. The computer calculates the permeability of the samples by a model between the pressure and the time.

3.7 “Wafer” Curvature Radius Measurements

200-300 μm thick 316 stainless steel was used as the substrate. All the samples were cooled down from the 300°C firing before the radius of the surface curvature was measured.

The first group of samples (Group C) included bare substrate, 10μm, 20 μm, 30μm, 40μm, 60 μm, 80 μm, and 100 μm thick CB-CSG coatings respectively. Another six Group A coatings contained a 30 μm CB-CSG top coat and different thickness values for the siloxane primer, e.g. 0 μm, 5 μm, 8μm, 10 μm, 15 μm, and 20 μm respectively,
and each sample was measured 4 times at different locations. There was approximately ±2 \( \mu \)m deviation of the thickness measurement for each sample.

An interferometric surface imaging system (WYKO NT-2000, Veeco Instruments Inc. USA) was used to measure the radius of curvature of the bare substrates and the coatings. Each measurement was focused on a 3.7×4.8 mm area. The final curvature radius \( R_n \) of each area was the average of absolute \( R_x \) and \( R_y \); therefore, the radius of curvature of each sample was calculated by,

\[
r = \frac{1}{n} \sum_{n=1}^{4} |R_n|
\]

(3.1)

The radius of curvature of each sample was taken as the average value of four measurements. The highest and lowest values were not included.

3.8 Microscopy and XRD

The preparation of the samples used for SEM observations comprised sectioning with a diamond saw, vacuum mounting with a low-viscosity resin (Industrial Formulators, Inc. Canada), followed by polishing with 50-1200 grit sandpaper, 5, 1, and 0.5 \( \mu \)m diamond slurries, and silk cloth on the grooved metal platens. The samples were polished to a flatness <0.1 \( \mu \)m with nano-size colloidal silica.
For the fracture observation samples, the coupons were cut vertically from the substrate towards the coating with a high-speed saw to obtain a V-groove close to the coating. The sample was placed in liquid nitrogen for approximately 1 minute, and then broken immediately after being taken out. 600 and 1,200 grit sandpaper and 1 μm diamond paste were used to polish the faces normal to the fracture plane of samples. The moving direction of the polishing wheel was from coating to substrate, to prevent cracks from propagating due to the external load while polishing. The epoxy mounting also could have protected the cracks from deformation to some extent. The samples for the crack observations were prepared in the same way.

The specimens were carbon coated (~20 angstrom) for BSE (backscattering electron) detection of the cross-sectional morphology coupled with EDX (Energy Dispersed X-ray). The cross-sections of the siloxane layer sputtered by gold were detected at a high magnification by SE (secondary electron) with a Hitachi S-2300 SEM instrument at a working voltage of ~20.0 kV.

A coating thickness gauge (Positector 6000, DeFelsko Corp., NY, USA) was used to measure the thickness of the sol-gel coatings. All the coating thicknesses were confirmed by the measurements from the SEM images of their cross-sections.

X-ray diffraction (XRD) was performed on an X-ray generator platform (Philips PW 1830). The surface morphology of the coatings was observed by a Nikon EPIPHOT 300 optical microscope. The alumina volume percentages of five samples per group were
assessed by an image analyzer (Clemex version PE™ 3.5, Clemex Technologies Inc., Canada).

3.9 Potentiodynamic Evaluations of the Coatings

All Potentiodynamic evaluations were carried out by a Solartron 1286 potentiostat (Solartron Group Companies, UK) using the Windows™ XP operating system in conjunction with a Dell™ PIII PC. The Potentiodynamic evaluations were conducted as follows:

- A piece of copper wire was welded onto the back surface of the substrate.
- The exposed surface of the copper wire and the edges of the samples were stamped with epoxy.
- The cut edges and epoxy crevices were sealed with a waterproof TEFLON® tape and an acetone diluted stop-off lacquer (50% Microstop, Pyramid Plastics, Inc), which was a insulating and waterproof paint, in order to prevent galvanic actions along the edges and defects between the epoxy and the coatings.
- The sample was fixed in a quartz glass tube whose end was sealed by waterproof tape. A 0.7×0.7 mm section within the center of each sample was exposed to solution during the testing and faced with the luggin capillary as close as possible.
- Nitrogen (+10 psi) was connected to drive off the oxygen in the water, and the electrolyte was magnetically stirred while the experiment was running.
CHAPTER 4: RESULTS AND DISCUSSION

4.1 Coating Structures

4.1.1 Group A Structure

Figure 4.1.1 shows a typical dual-layer microstructure of the Group A coating. The coating is comprised of a siloxane bond coat and a CB-CSG top coat, where the CB-CSG top-layer is well anchored to the siloxane bond coat.

![Fig.4.1.1 SEM image of dual-layer coating](image)

The $\alpha$-$\text{Al}_2\text{O}_3$ particles or the CSG aggregates penetrated into the siloxane primer and acted as reinforcing phases. These reinforcing phases form mechanical interlocks between the siloxane and the CSG. In Fig.4.1.2, there was a siloxane/$\text{Al}_2\text{O}_3$ composite area in the siloxane bond coat near the top coat. Some of the CB-CSG aggregates even
penetrated into the bottom of the siloxane bond coat, forming a CB-CSG/siloxane composite primer. Actually, the siloxane film is in a discontinuous state at some locations. This might be why the Group A coating had a higher adhesion strength (~10.0 MPa) than that of the 100% siloxane (4-7.0 MPa).

Since the poly(methylphenylsiloxane) (PMPS) does not adhere well to ceramics, it was necessary to simultaneously spray the monomer MPS and the CSG sol before curing them together. This process allows the alumina particles to penetrate into the siloxane matrix and to form good anchoring points.

Fig.4.1.2 Ceramic/polymer composite layer between bond-coat and top-coat.
Therefore, the siloxane composite layer could be considered as a functionally graded bond coat with a graded composition from top coat to bond coat, reducing the thermal expansion mismatch among the different coating layers.

4.1.2 Group B Structure

Figure 4.1.3 is a SEM picture of the tri-layer microstructure of the Group B coating, consisting of a ~5 μm siloxane layer interleaved with a 30-40 μm CB-CSG top coat and a 10-20 μm CB-CSG primer, resulting in a sandwich structure coating. Figure 4.1.4 is a higher magnification of Fig.4.1.3; in some places, the siloxane bond coat presents a discontinuous siloxane film. The purpose of developing the tri-layer Group B coating was to increase the strength of the bond coat.

Fig.4.1.3. CB-CSG/siloxane /CB-CSG tri-layer structural coating (Group B)
Fig. 4.1.4 Tri-layer Coating structure

The stiff CB-CSG layer is to absorb external loads and protect the soft siloxane under-layer in service. The siloxane under-layer in turn prevents the spread of cracks into other layers and relaxes the stress to the substrate. Some cracks originate at the coating/substrate interface and develop through the coating, hurting its adhesion properties. Therefore, the siloxane bond-coat can also act as a crack inhibitor, thereby possibly increasing the fracture resistance of the coating.
4.1.3 Group C Structures

Figure 4.1.5 shows a mono-layer CB-CSG coating on an oxidized mild steel substrate. There is no crack observed through the cross-section. Figure 4.1.6 is a
phosphorus mapping by EDX, and shows evidence of the uniform phosphate distribution throughout the coating achieved via the two-gun preparation method.

In most cases, such phosphorus mappings by EDX show that the phosphorus concentration gradually increases from the interface to the surface. The surface has the highest concentration of phosphate, and the interface has the lowest concentration. The final step of the process has traditionally been to deposit a large volume of phosphate on the coating surface, and this is the reason why the surface usually has the highest concentration of phosphorus. This phenomenon also shows that the phosphate cannot penetrate through the thick CB-CSG layer, and thus that only two-gun spraying can distribute phosphate evenly throughout the coating.
4.2 Cracks and Air Permeability

4.2.1 Cracks in Coatings

The conventional composite sol-gel method involves multi-step spraying and individually firing at 550-600°C, which often generates cracks, e.g. shrinkage cracks, phosphate cracks and thermal expansion-mismatch cracks.

Fig.4.2.1 Drying-shrinkage cracks
Drying shrinkage often induces cracks when the water evaporation occurs too quickly. The shrinkage cracks are often of small size and invisible to the eye (Fig. 4.2.1), and can be easily obscured by polishing with 1200 grit sandpaper. Freeze-drying is also a viable way to decrease the shrinkage strain and avoid shrinkage cracks.

Fig. 4.2.2 Web-like phosphate cracks

To increase the hardness and adhesion of the sol-gel coating, it is necessary to impregnate enough phosphate. However, brushing of 85% phosphoric acid onto the green-body of composite sol-gel alumina often generates the phosphate cracks even at room temperature. Figure 4.2.2 is an example of "phosphate cracks". The phosphate cracks often appear in a web-like shape on the coating surface.
Essentially, phosphate cracks are generated by the chemical reactions of the phosphoric acid and the hydrate alumina. When the phosphoric acid (PA) is over-impregnated on the surface of green body, it forms pseudoboehmite or gelatinous boehmite, which has a low strength (referred to pp.10). The gelatinous boehmite reacts with the residual phosphoric acid (PA), as shown in equation (4.2.1).

\[
H_3PO_4 + AlOOH \Rightarrow AlPO_4 \downarrow + 2H_2O
\]  

(4.2.1)

Fig.4.2.3 The cracks due to the mismatch of CTE
This reaction produces solid aluminum phosphate at room temperature, which often induces strains in the green network. When the stresses accompanying the strains exceed the strength of the green network, they will induce phosphate cracks. Usage of mono aluminum phosphate (MAP) can decrease the probability of producing phosphate cracks by means of retarding the chemical reactions at room temperature, since MAP is less chemically active than PA.

When the green sol-gel is deposited with 85% phosphoric acid, the phosphoric acid will react with alumina to form MAP. When fired at 550-600°C, the MAP will quickly convert to Berlinite, Cristobalite or other phases, which causes volume changes over a short time. When the coating is cooled down, the differential thermal expansion of the different phases will generate mismatch cracks.

Fig.4.2.4 The surface crack-free coating after 4 days of curing at 160°C
On the other hand, the differential thermal expansion of the sol-gel coating and the metallic substrate also induces strains in the conventional sol-gel process, which lead to large cracks visible to the eye. Figure 4.2.3 is a heavily phosphatized coating. The coating surface induces cracks due to the brushing of 85% PA and CTE mismatch. This kind of cracking is the biggest challenge in the traditional chemically bonded sol-gel process. The CTE mismatch cracks are very difficult to prevent, since the thermal expansion differences are inevitable with changing temperature.

Fig.4.2.5 The high magnification of surface crack-free coating
One viable way to prevent the phosphate cracks and the CTE-mismatch cracks is to decrease the processing temperature. Curing at 160°C for 5 days allows some stress relaxation and produces crack-free coatings. This low temperature curing allows the MAP to gradually transform to Berlineite without inducing large strains. After the phase transformation is completed, the coating is almost stress-free. This was evidenced by "Wafer" experiment, which will be discussed in chapter 4.5. After long-term curing, the coating obtains a strength that allows it to be fired again at a higher temperature (>300°C) and cooled down without generation of cracks. Fig.4.2.4 shows a surface crack-free coating after 5 days of curing at 160°C. There are no cracks even at the corners and the edges. Fig.4.2.5 is a higher magnification of the surface crack-free coating by the low temperature process. It is reasonable that low temperature (160°C) curing reduces the possibility of cracking due to differential thermal expansion.

4.2.2 Air-Permeability

Table.4.2.1 shows that the CB-CSG coating is air permeable at a thickness of ~40 μm. The air permeability of traditional CB-CSG coatings is higher than that of low temperature CB-CSG coatings, implying that the low temperature curing produces fewer defects, e.g. pores, cracks and fissures, than the traditional sol-gel method. The air permeability after curing at 160°C is ~0.23 millidarcy, indicating that the sol-gel coating is relatively dense.
<table>
<thead>
<tr>
<th>Air Permeability (milidarcy)</th>
<th>Traditional</th>
<th>New</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300-500°C firing</td>
<td>160°C curing</td>
</tr>
<tr>
<td>Dual-layer Group A</td>
<td>NM</td>
<td>Non-detectable</td>
</tr>
<tr>
<td>Tri-layer Group B</td>
<td>NM</td>
<td>Non-detectable</td>
</tr>
<tr>
<td>Mono-layer Group C (40 μm)</td>
<td>0.45 (0.08)</td>
<td>0.23 (0.03)</td>
</tr>
</tbody>
</table>

*Values in parentheses show the standard deviation
*NM: not measured

Generally, the air permeability of CB-CSG coatings decreases with increasing thickness. The air-permeability of the siloxane incorporated CB-CSG multi-layer coating is non-detectable (Table 4.2.1). Plausibly, the hermetic monomer sealed the voids of the gel-network during spraying and prevented the substrate from contacting corrosive species such as oxygen, and the polymer islands decreased the number of CB-CSG channels after the polymerization of methylphenylsiloxane (MPS). When these islands connect together and form a continuous layer, it is difficult for the oxygen to contact the substrate in the multi-layer coating system. The corrosion protection of the multi-layer coating will be discussed in chapter 4.7.
4.3 Contact Measurements

4.3.1 Hardness of CB-CSG Ceramic

The average hardness of the CB-CSG surface was measured as 6.24 GPa, close to the hardness of Berlinite. This could be explained by the processing, where, after the final coating step (spraying of 50wt% MAP onto the CB-CSG surface), the mono aluminum phosphate (MAP) formed a chemical bond with the CSG and gradually transformed to Berlinite or Cristobalite during curing at 160°C for 5 days (referred to pp.14).

Figure 4.3.1 is an indentation trace on the top surface of a Group A coating, the hardness of which was measured as 6.05 GPa. Similarly, the hardness of the top surface of the Group C coating (Fig.4.3.2) was 6.26 GPa. The CB-CSG coating (Group C) is believed to be a Berlinite-bonded alumina network; however, there are some micro-pores, channels for the evaporation of water, on the surface of the CB-CSG coating, causing the measured hardness to be lower than that of Berlinite.

The hardness of Berlinite is ~6.5 GPa, and the average hardness of the Group C coating is ~6.24 GPa, homogeneously distributed across the coating surface. Therefore, it is believed that the Berlinite AlPO₄ is distributed homogeneously across the surface of the CB-CSG coating. It was accepted that only the Berlinite was formed after the MAP
was cured at ~150°C for 4 days, where the mono aluminum phosphate hydrate reacted with alumina at ~150°C and formed Berlinite by the following reaction [34]:

\[ Al_2O_3 + 2AlH_3(PO_4)\_2 \cdot H_2O \rightarrow 4AlPO_4 + 4H_2O \] (4.3.1)

Fig.4.3.1. SEM indentation trace of CB-CSG surface, Vickers indent 300g load

Berlinite is the phase that bonds individual alumina particles and forms the berlinite-bonded alumina ceramic. However, in this research, a well-crystallized AlPO₄ network was not found by XRD. It is believed that only the vitreous Berlinite (hardness 6.5 GPa) was formed on the surface and inside the coating [65].

The cross-sectional hardness measurements were conducted on samples mounted within a 25.0mm diameter cast epoxy-resin block, which could prevent the error caused
by the coating thickness. Additionally, the 40-100 μm CB-CSG coating decreased the
influence of coating thickness to a tolerable extent, since, in thin films, the cross-sectional
hardness was affected by the substrate. Figure 4.3.3 shows an image of the mono-layer
Group C coating. A hardness of 6.0 GPa was measured at the interface, providing further
evidence of phosphate distribution to the interface by the multi-gun spray technique.
From observation of Fig.4.3.3, the Berlineite phase formed at the interface without
generating a crack along the interface. In Fig.4.3.4, the indentation was conducted right
on the interface between coating and substrate, but crack onset did not occur at the apexes
of the indent contour, demonstrating the high adhesion strength of the CB-CSG coating.
However, as seen in Fig.4.3.5, there may have been an interfacial crack induced along the
interface, which was obscured by the elastic siloxane. The hardness of siloxane was
measured at 0.12 GPa.

Fig.4.3.2 SEM indentation trace on CB-CSG surface, 300g load
For some samples, the cross-sectional hardness of the CB-CSG coating was between 3.0-6.0GPa, i.e. between that of Variscite and Berlineite, indicating that the bonding agent could be a mixture of the two. Occasionally, however, some of the 3.0GPa values could have been related to the heterogeneity of micro-structure, i.e. porosity or agglomeration of γ-alumina or Variscite, even though the 45°C water washes away most of the Variscite and hydrated γ-alumina on the surface. It is believed that long-term curing would eventually convert the rest of the Variscite to Berlineite.

![SEM indentation trace of CB-CSG ceramic coating](image)

**Fig.4.3.3. The SEM indentation trace of CB-CSG ceramic coating, Vickers indent 300 g load, Group C**

In some extreme results, a surface hardness of ~10.0 GPa was observed, which might have been caused by the hard aggregation of alpha alumina and strong ligands of chemical bonds, or possibly by well-crystallized Berlineite or Cristobalite (referred to
It is possible to form a network with the combination of Berlinite binders and \( \alpha \)-alumina fillers, which have an average hardness over 10 GPa. Therefore, the relationship between the control of impregnating chemicals and the hardness of the coating needs further research.

4.3.4 The SEM indentation trace of CB-CSG ceramic coating, Vickers indent 300 g load, Group C

4.3.5 Indentation trace of substrate-polymer-coating cross section, indented at 300 g load, Group A
4.3.2 Interfacial Fracture Toughness

The interfacial fracture toughness is a basic material parameter of the interface. The higher the interfacial fracture toughness, the higher the adhesion strength of the coating. Therefore, it is believed that the interfacial fracture toughness is a reasonable indicator of coating adhesion and that its measurement is a good way to quantitatively assess the interface.

When a high-load Rockwell C indenter is applied to a coating surface, the coating experiences interfacial cracks between coating and substrate \( r=a \). The interfacial cracks spread radially toward a critical point where the energy release rate was unable to propagate the cracks. The value for interfacial fracture toughness was identified with the value of energy release at which the cracks arrested, as schematically depicted in Fig.4.3.6, showing a model of the detachment by a high load axisymmetric indenter. The detachment occurs as follows: (1) the interfacial crack front is forced to advance and to break up the coating by displacement of the substrate; (2) the detachment occurs with an unbuckled annular plate of coating, which remains intact; (3) the annular plate of coating buckles.
The Rockwell C indentation could induce some radial cracks in the coating that were not caused by displacement of the substrate. Optical image analysis avoids the obscuring of micro-cracks due to gold sputtering or carbon coating for SEM sample preparation, and therefore an optical microscope was used instead of SEM. Figure 4.3.7
depicts the trait of the interface between CB-CSG coating and substrate where the radial cracks resulted from the tensile hoop stresses when the coating was displaced radially. The detached coating adjacent to the indentation was carefully discerned through the use of image analysis software (Clemex version PE™ 3.5, Clemex Technologies Inc., Canada), with which the contact radius \( (a) \) and the radius of the indentation-induced annular cracks \( (R_i) \) were measured, as shown in Fig.4.3.7 and Fig.4.3.8.

Fig.4.3.7. Optical images of typical coating detachment after Rockwell C indentation

Fig.4.3.8 Detachment area of Fig.4.3.7 by image analysis
Since the delamination is due to mode II (shear) interface cracking only, the interfacial fracture toughness is presented by $K_{ijc}$. The models and calculation of interfacial fracture toughness are taken from the literature [13].

**Fig.4.3.9. A plot of substrate surface roughness and interfacial fracture toughness**

Figure 4.3.9 shows a plot of interfacial surface roughness and interfacial fracture toughness, where the interfacial fracture toughness increased with the surface roughness of the substrate; the rougher the substrate surface, the higher the adhesion strength. However, after the surface roughness reached a value higher than 4 μm, the interfacial fracture toughness tended to become stable at 3.5-4.0 MPa.m$^{1/2}$. Therefore, the optimum surface roughness of the substrate should be ~4.0-5.0 μm, at which the coating possessed a good capability to withstand shatter or to absorb impact energy. The sand-blasted steel substrate resulted in a higher interfacial fracture toughness than the grinded steel.
substrate [13]. However, the model of the interfacial fracture toughness was based upon the “fully-elastic model” [13]. The drawback of using optical image analysis to measure the radius of annular cracks is that it depends on the experience and skills of the operator. As seen in Fig. 4.3.9, typical data scatter for the $K_{\text{IC}}$ is $0.5-0.7\text{MPa.m}^{1/2}$ or up to 30% of the average.

4.3.3 Nano Indentation and Sonic Wave Modulus

Table 4.3.1 lists the average hardness and elastic modulus of the CB-CSG top coat and the siloxane bond coat, measured by a depth-sensing indentation. The hardness and elastic modulus of siloxane were much lower than those of the CB-CSG ceramic. These values will be used to determine residual stresses in a later chapter. The Poisson’s ratio of CB-CSG was 0.25 as measured by sonic waves (see Appendix I).

From Table 4.3.1, the dynamic Young’s modulus of the coating as measured by acoustic method (sonic waves) was ~225 GPa, which seemed remarkably different from that measured by the nano-indenter. It is probable that the acoustic method neglected the presence of defects, e.g. cracks and pores, and was averaged via the vibrational frequency of the coatings containing 80wt% $\alpha$-alumina (elastic modulus: ~370 GPa). On the other hand, the surface defects, e.g. open-pores and surface fissures, affected the values of the indentation method, so the values measured by acoustic methods were often higher than those measured by indentation.
Table 4.3.1. The average values of hardness and elastic modulus measured by nano-indenter

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness (GPa)</th>
<th>(\frac{E}{1-\nu^2}) (GPa)</th>
<th>Elastic Modulus by Sonic Wave (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siloxane Bond Coat</td>
<td>0.12 (0.05)</td>
<td>5.0 (0.4)</td>
<td>NM</td>
</tr>
<tr>
<td>CB-CSG Top Coat</td>
<td>7.65 (2.7)</td>
<td>122.0 (30.0)</td>
<td>225.45 (40.0)</td>
</tr>
</tbody>
</table>

*Values in parentheses show the standard deviation
*NM: not measured
4.4 Scratch Resistance

4.4.1 Critical Scratching Force for Coatings

As measured by parallel scratching, the average critical force values for Groups A, B, and C were 4.7 kg, 10.3 kg and 17.0 kg respectively (Table 4.4.1). These values depend on the volume percentage of reinforcement in the siloxane, referred to chapter 4.6.

Table 4.4.1 Scratch resistance of various coating structures

<table>
<thead>
<tr>
<th>Groups</th>
<th>Structure</th>
<th>Critical Force (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group A</td>
<td>Dual-layer</td>
<td>4.7 (0.5)</td>
</tr>
<tr>
<td>Group B</td>
<td>Tri-layer</td>
<td>10.3 (1.0)</td>
</tr>
<tr>
<td>Group C</td>
<td>Mono-layer</td>
<td>17.0 (1.4)</td>
</tr>
</tbody>
</table>

* Values in parentheses show the standard deviation

The image analysis showed that the percentage of reinforcement in the siloxane was ~10vol% and ~25vol% in dual-layer Group A and tri-layer Group B respectively. The critical force increased with the increment of coating thickness. Tri-layer Group B had a CB-CSG primer ~5-10 μm thicker than that of dual-layer Group A. Therefore, tri-layer Group B had a higher critical force than dual-layer Group A. Although mono-layer Group C did not have the polymer constituent referred to Fig.4.4.1 (a), it possessed the highest scratch resistance.
As shown in Fig.4.4.1 (b), the distance traveled by the stylus under an increasing load (0-45 kg) at the onset of coating failure was ~0.82 cm. This result also was verified by the assessment of effective friction, which was defined as the transverse force ($F_t$, diamond drag force) divided by the normal force ($F_n$).

\[
f = \frac{Transverse}{Normal} \times 100 = \frac{F_t}{F_n} \times 100 \text{ (no unit)} \tag{4.4.1}
\]

Fig.4.4.1. (a) Optical micrograph of a scratch groove (at 100X); (b) curves of normal force, acoustics, effective friction and distance;
At a magnification of 100X, the scratching artifacts of the coating were clearly discerned. An abrupt change in the effective friction, in Fig.4.4.1 (b), signaled the coating failure, which is thought to be caused by one of the following critical events: (1) the CB-CSG is torn from the substrate; (2) the substrate fails and the diamond dislodges substrate material; (3) the adhesive strength of the coating is exceeded.

In the case shown in Fig.4.4.1 (b), the acoustic signal recording indicates that the surface of the CB-CSG coating cracked initially at 0.18 cm and the critical force at the onset of CB-CSG surface spallation was ~2.5 kg.

---

Fig.4.4.2. The scratch critical force vs. coating thickness (for mono-layer Group C CB-CSG coating)
The scratch critical force at which the coating fails increases with an increase in coating thickness: the thicker the coating, the higher the critical force. Figure 4.4.2 shows the critical force vs. the coating thickness. When coating thickness was below 60 μm, the critical force tended to increase with the coating thickness. However, the average residual stresses in the CB-CSG coating also increased with increasing coating thickness (e.g. compare Fig.4.5.1 in Chapter 4.5). Therefore, after a certain thickness, the critical force begins to decrease with increasing coating thickness.

When the coating is being scratched, the stresses include the residual stress from processing and the bending stress from scratching. From Fig. 4.4.2, it is apparent that: (1) when the thickness of the Group C coatings was below 20 μm, the stresses could be considered to be negligible. The critical force increased almost linearly with increasing coating thickness; (2) in the 20-60 μm thickness range, the effects of the stresses could not be ignored, the rate of change of the critical force with thickness decreased due to the stresses; (3) after 60 μm, the critical force decreased with further increase in coating thickness because of the residual stresses. However, if the residual stress were relaxed, the critical force would likely continue to increase with increasing of the coating thickness. Stress relaxation will be discussed in chapter 4.5.

Generally, the CB-CSG mono-layer coatings had good scratch resistance when their thickness was below 100 μm.
4.4.2 Scratch Hardness of Coatings

There are two types of scratch failure: cohesive failure and interfacial failure. The form of cohesive failure is usually partial cone cracking or conformal cracking. Partial cone cracking often occurs around the perimeter of the trailing edge of the scratch tip. Conformal cracking forms in front of the moving indenter at the leading edge rather than at the trailing edge. Figure 4.4.1 (a) shows the onset of some conformal cracking at the leading edge of the scratch. This kind of cracking is often due to the cohesive properties of the coating network.

Fig.4.4.3. Optical micro-graph of scratching made on CB-CSG coating, 100X, scratch moving direction from right to left
Interfacial failure often presents as a chipping of the coating in front of the scratch tip, which is related to failure at the interface. This type of failure develops with increasing scratch load. Not all of the chipping is directly correlated with the interface; some failures related to the pores or micro-cracks can also be considered to be interfacial.

Interfacial failures often manifest as a ring crack in the coating and lead to chipping, which is essentially the kinking of a delamination crack back into and through the coating, as schematically shown in Fig.4.4.4. Generally, interfacial failure is the likely cause when a chipping event is observed.

![Schematic of cohesive failure and interfacial failure](image)

Fig.4.4.4. schematic of cohesive failure and interfacial failure

For example, in-situ observation of Fig.4.4.3, which was a CB-CSG coating produced by the conventional method, indicated that the obvious chipping event dominated the scratching procedure, and no cone cracks or conformal cracks appeared.
In consequence of this observation, the defects at the interface, e.g. fissures and flaws, could not be considered negligible. Interfacial failure dominated the whole scratching procedure, even under a low load. In other words, no cone cracks were found at the trailing edge or at the scratching head. Therefore, interfacial failure is the dominant mode.

Interfacial failures are due to the defects, e.g. pores and cracks, which are often generated during high temperature processing. For example, the higher the process temperature, the faster the water evaporation and the greater the porosity. Therefore, low temperature curing is an effective way to prevent interfacial failure.

The scratch hardness was independent of the surface roughness of the coating. Literature [13] shows the linear trend of the scratch-hardness values across the specimen obtained from the experimental data. The scratch hardness is between 5.5-6.0 GPa, and it is a little lower than that measured by Vickers indentation because the scratch hardness measurement includes the effects of porosity.

Even though there was some hardness variation across the coating, it still reflected the homogeneous distribution of hardness over the coating surface and thus the homogeneous distribution of the chemical bonds.
4.5 Thermal Residual Stresses

The steel substrate is always subject to residual compression in a ceramic coating/metal system following cool-down from a high temperature, and as a result suffers deformation. One purpose of using the siloxane bond coat (BC) is to decrease the effect of the residual stress to the substrate. In this chapter, the residual stress was estimated by a “wafer” curvature method. This approach revealed whether or not the siloxane bond coat could relax the residual stresses due to visco-elastic deformation of the BC.

It is hypothesized that the incorporation of siloxane relaxed the interfacial differential thermal contraction stress during cooling from process temperature through the visco-elastic deformation of the siloxane. When a coating/substrate composite is at an elevated temperature and cooled down to room temperature, the mismatch of thermal expansion coefficient between the coating and the substrate results in the residual stress. The direction of warping is always the same: the coating warps towards the substrate, which indicates that the thermal expansion coefficient of the CB-CSG coating is lower than that of the steel substrate.

The plots in Fig. 4.5.1 show that the bending moment increased with increasing coating thickness. The original data are listed in the Appendix II. In this result, the
Curvature radius decreased as coating thickness increased, indicating that the average stress increased with increasing coating thickness.

![Graph showing CB-CSG thickness vs. radius of curvature](image)

**Fig. 4.5.1 The CB-CSG thickness vs. the radius of curvature**

Figure 4.5.2 is a typical interferometric result for the 60 µm thick Group C coating without siloxane bond coat, where the average curvature radius is 1.35 m. Figure 4.5.3 is the result for the bare substrate, where the measured curvature radius is 17.24 m. Figure 4.5.4 is the result for Group A, i.e. for the 60 µm thickness top coat and the 5-10 µm siloxane BC. The average curvature radius in Fig. 4.5.4 is 14.47 m, much larger than that of a CB-CSG coating of the same thickness.
Fig. 4.5.2. A typical interferometric result from a *Group C* coating (r=1.35m)
Fig. 4.5.3 A typical interferometric result from a bare substrate (r=17.24m)

Considering that the CB-CSG Poisson’s ratio is 0.25 and that the Young’s modulus of siloxane as measured by a depth-sensing indentation was 5.0 GPa, the calculated average residual stress for the Group C coating in Fig. 4.5.2 is calculated using
equation (2.5) to be \(-8.0\) MPa, and that for the Group A coating in Fig.4.5.4 is \(0.30\) MPa.

Fig.4.5.4 30\(\mu\)m CB-CSG coating, containing 5-10\(\mu\)m siloxane bond coat (r=14.47m)

The residual stress for the Group A coating system was much lower than that for the Group C system, indicating that the incorporation of siloxane substantially decreased the thermally induced stress. The siloxane bond coat significantly decreases the thermal
stress between the CB-CSG and the substrate. The siloxane $BC$ acts as a compliant layer, which relaxes the stress caused by the thermal expansion coefficient mismatch. The siloxane bond coat thus significantly decreases deformation of the substrate.

![Graph showing the thickness of siloxane bond coat vs. the curvature radius](image)

**Fig.4.5.5 The thickness of siloxane bond coat vs. the curvature radius**

The trend of the experimental results in Fig.4.5.5 showed that, for the Group A coating, the curvature radius rapidly increased when the siloxane thickness was below ~10 $\mu$m. At a thickness higher than 10 $\mu$m, the $CR$ stabilized at 14-15 m, which appeared to indicate that the 10 $\mu$m siloxane $BC$ was enough to relax the residual stresses. It thus seems unnecessary to increase the siloxane thickness beyond 10 $\mu$m.
It is not easy to control the thickness of the bond-coat by hand-spraying when its thickness is below 10 μm, in particular below 5 μm. The bond coat was often discontinuous when it was thinner than 10 μm, since the surface roughness of the substrate was around 5 μm. At a thickness greater than 10 μm, however, the bond coat became a continuous layer, and the residual stress and the curvature radius tended to be stable.

Therefore, the compliant bond coat can release the energy of thermal stress, accommodate the bending severity of the coating or substrate, and decrease the deformation of the substrate. A plausible analysis shows that the natural warp of the substrate during firing does not greatly affect the final curvature radius of the coating. Since the steel substrates are isotropic, the heat treatment and ambient cooling can also be made homogeneous, showing implicitly that the warping and deformation of the substrate can be neglected during the heat treatment.

It can therefore be concluded that the siloxane primer decreases the thermal stress to which the substrate is subjected. The siloxane \( BC \) acts as a compliant layer, grading the thermal expansion coefficient mismatch by releasing the energy and relaxing the stresses.
4.6 Adhesion

4.6.1 Group A Adhesion

Figure 4.6.1 gives a schematic of the fracture mechanisms of the coatings in Groups A to C.

Fig.4.6.1. Schematics of fracture mechanisms in different coating structures
In dual-layer Group A, the CB-CSG ceramic layer generally provides the wear resistance, and the siloxane bond coat is able to undergo visco-elastic deformation in service. The average bonding strength of Group A is \(~10.0\) MPa (10\% alumina), a higher adhesion strength than that of 100\% siloxane.

Figure 4.6.2 is an SEM image of a Group A coating after an adhesion test, as schematically depicted in Fig.4.6.1 (a). It shows that break-up seemed to occur at the interface between the bond coat and the substrate. It appears, from Fig.4.6.3, that the siloxane adhesion to the substrate was stronger than that of the CB-CSG to the siloxane; but under the optical microscope, in Fig.4.6.4, it was found that the fracture occurred inside the siloxane bond coat and not at the interface between the CB-CSG and the siloxane. Figure 4.6.5 indicates that the ultimate tensile strength of siloxane is lower than its adhesion strength, because the adhesion of siloxane is comprised of two components, mechanical interlocks and polymeric adhesion.

![Fracture surface of Group A after an adhesion strength test](image-url)
Fig. 4.6.3. Appearance of the fracture surface generated in adhesion test

Fig. 4.6.4. An appearance of fracture surface after a pull-off adhesion test
4.6.2 Group B Adhesion

The tri-layer Group B (25% alumina) had an average ultimate tensile strength for the siloxane bond coat of ~13.0 MPa. The bonding of the CB-CSG primer to the sandblasted mild steel consisted of mechanical interlocks and chemical bonds provided by the aluminum phosphates.

Figure 4.6.6 shows the fracture of a tri-layer Group B coating, which started at the weakest point of the bond coat and ended at the outer surface of the top coat, where the fracture was contained within the top coat by the bond coat, referred to Fig.4.6.1 (b). The weakest point of BC strength is usually the area of lowest alumina concentration. Spurious cracks, generated by the pulling force, were sometimes found to occur in the CB-CSG top coat, but they were unlikely to penetrate into the sub-layer unless they occurred in those areas where the siloxane was thinnest. Figure 4.6.7 shows a crack that was prevented from developing into the primer by the bond coat.
Fig. 4.6.6. SEM image of Group B fracture surface after an adhesion strength test

Fig. 4.6.7 A crack was constrained within one layer by the siloxane BC
The tri-layer Group B coatings had a higher yield strength than that of the dual-layer Group A coatings because the strength of the bond coat appears to be dependent on the volume percentage of alumina, increasing with volume percentage of alumina. Compared with Group A, Group B had a higher percentage of alumina, giving it a higher strength. However, the adhesion of Group A was as low as 10.0 MPa, indicating that the strength of 100% siloxane was lower than 10.0 MPa.

Fig.4.6.8. SEM image of Group C fracture surface after an adhesion strength test

4.6.3 Group C Adhesion

Figure 4.6.8 shows a brittle fracture in adhesion test for a mono-layer CB-CSG coating (Group C), as schematically depicted in Fig.4.6.1 (c). The fracture occurred at the interface and developed along the coating, indicating that the tensile strength of CB-CSG is higher than the strength of its adhesion to the substrate. The average adhesion strength of Group C was measured as 42.0 MPa. The adhesion strength increased with increasing volume percentage of siloxane [5].
In some cases, an adhesion strength as high as \(~70.0\) MPa for Group C was observed. There are several factors that affect the measurement of pull-off adhesion strength: (1) the adhesion is limited by the strength of the epoxy glue used \(~70.0\) MPa; (2) the effect of pores in the brittle CB-CSG coatings is sensitive to the alignment of the applied force; (3) the prevalence of crack propagation in brittle CB-CSG coatings reduces the critical force of detachment; (4) the adhesion strength is dependent on the surface roughness of the substrate. Hence, the actual adhesion might be higher than the pull-off results for a certain coating/substrate combination, since the adhesion strength could be detrimentally affected by the above defects.
4.7 Potentiodynamic Evaluations of Sol-Gel Alumina Coatings

It was anticipated that the composite multi-layered coating would improve the corrosion resistance of the metallic substrate due to: (i) the statistical possibility of the number of through-coating defects (e.g. pores, cracks) decreasing with increasing coating thickness; (ii) the decrease in the opportunity for through-pore formation, due to the mechanical penetration or anchorage of different layers; (iii) the partial filling of ceramic pores by the polymer during curing.

The results of the electrochemical evaluation, Fig.4.7.1, revealed that the multi-layer coatings formed an effective physical barrier against wet corrosion. There was a siloxane layer in dual-layer Group A and in tri-layer Group B, which increased the ohmic resistance of the whole system, and decreased the corrosion rate significantly. Tri-layer Group B had a lower corrosion current density (2-3×10⁻⁷ A/m²) than dual-layer Group A (5-7×10⁻⁶ A/m²), because the Group B coating was thicker (~10 μm) than the Group A coating for the same thickness of siloxane bond coat and CB-CSG top layers. The corrosion currents of the coated mild steel were around one order of magnitude smaller than those of the bare mild steel. Mono-layer Group C had a higher corrosion current (~10⁻⁶ A/m²) and a smaller corrosion resistance than Groups A and B because there were more permeable channels in the mono-layer Group C coating, associated with physicochemical changes in both the siloxane and CB-CSG material - e.g. shrinkage.
water vapor, and organics-burnout during the curing in both the siloxane and the CB-CSG material.

Fig. 4.7.1. Polarization curves of the CSG/siloxane coating (Group A-C) on the mild steel substrates compared with that of the bare mild steel (pH=5, DI H₂O)

Fig. 4.7.1 shows that the dual-layer Group A coating formed an effective physical barrier against wet corrosion. The shape of the polarization curve of the coated substrates was not very different from that of bare substrate: there were not passivation regions present, which implies that the coating indeed provided a physical barrier for blocking the electrochemical corrosion process, but that the electrochemical behavior of the substrate also affected the trend of polarization at this thickness.

By plotting the potential versus the logarithm of the current for the various thicknesses of CSG/siloxane bond coatings, the relationship between current density and coating thickness was determined for a Group A coating system including a 5-10 μm
siloxane bond coat, and a 10-100 μm CB-CSG coating [5]. The corrosion current density decreased with increasing thickness, and was constant at \( \sim 10^{-9} \text{ A/cm}^2 \) for the coatings thicker than \( \sim 50 \mu \text{m} \) [5]. This might be because the limited number of through-pores had been fully blocked by corrosion products, preventing further transport of oxygen to the steel substrate when the thickness of CB-CSG was over 50 μm.

Table 4.7.1 Corrosion protection efficiency of different structure coatings

<table>
<thead>
<tr>
<th>Structure</th>
<th>Group A</th>
<th>Group B</th>
<th>Group C</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI H(_2)O</td>
<td>97%</td>
<td>99%</td>
<td>92%</td>
</tr>
<tr>
<td>1wt% NaCl</td>
<td>94%</td>
<td>96%</td>
<td>84%</td>
</tr>
</tbody>
</table>

The corrosion current densities were obtained from the intersection of the anodic and cathodic Tafel lines for DI water and 1wt% NaCl solution. The corrosion protection efficiency of the Group A coating in DI H\(_2\)O was calculated to be \( \sim \)97% according to equation (2.10). The corrosion efficiency was 94% in 1wt% NaCl solution (pH=5). Table 4.7.1 shows the corrosion protection efficiency of the other groups in both the DI H\(_2\)O and the 1wt% NaCl solution.

The CB-CSG/siloxane bond coating had a better corrosion protection efficiency than the traditional non-siloxane CB-CSG coating in DI H\(_2\)O because the insulating siloxane decreased the permeability of the coating to liquid corrosive medium.
In NaCl solution, the siloxane bond coat offers better corrosion resistance, since the PMPS has two advantages in terms of corrosion resistance to cathode ions, e.g. OH\(^-\) or Cl\(^-\): (1) The hydrophobic nature of the PMPS repels water molecules being absorbed onto its surface. (2) The siloxane component separates the metallic substrate from the corrosive solution, i.e. because of the polymer barrier there is no anodic reaction caused by hydrolysis of iron ions and changing of localized pH values.
CHAPTER 5: CONCLUSIONS

5.1 Summary of Coating Properties

A "warm" temperature (160-300°C) process has been developed to produce CB-CSG coatings free of surface cracks. It overcomes the drawbacks of the traditional process for producing chemically bonded composite sol-gel coatings, e.g. cracks, low thickness, low hardness, and poor phosphate distribution. The use of mono aluminum phosphate leads to fewer phosphate cracks than the use of phosphoric acid. The low temperature (160°C) curing alleviates the problems associated with the thermal expansion coefficient mismatch. A multi-gun spray technique was developed to distribute the phosphate homogeneously throughout the coating. The technique results in a crack-free chemically bonded composite sol-gel (CB-CSG) alumina coating with medium hardness (6.0 GPa), moderate adhesion (42.0 MPa) and good scratch-resistance (17.0 kgf).

The novel siloxane/ceramic functionally gradient multilayer structural coatings were successfully fabricated using multi-gun deposition methods. It is believed that multi-gun spraying is critical for the process, as it allows the deposition of an aqueous sol onto mild steel without risk of coating buckling and interfacial corrosion. The multi-gun spraying method disperses the CSG particles throughout the siloxane and the phosphate throughout the CSG, which significantly increases the mechanical performance of the coating and distributes uniformly the phosphate bonds throughout the ceramic coating.
The resulting siloxane/CB-CSG multilayer coatings were found to be uniform, adhesive, and relatively dense.

Three groups of coatings (A, B, C) were processed. For the Group A and B coatings, the thermally stable siloxane-based “bond coat” film was deposited onto the mild steel to protect the metal surface during the CB-CSG processing. The CB-CSG “top coat” protected the siloxane-based bond coat (and the metallic substrate) from wear damage. The siloxane-based bond coat provided corrosion resistance and damage tolerance through its low permeability, its good adhesion, and its elasticity.

5.2 Summary of Adhesion

The adhesion of the coatings was dependent on the siloxane/alumina composite strength in the multi-layer structure. During processing of the coatings, the alpha alumina particles were mixed into the siloxane, which increased the strength of the whole coating system. The traditional mono-layer Group C (40µm) had a 42.0 MPa adhesion strength, a 17.0 kg scratch critical force, and a ~0.2 milidarcy permeability to air.

The adhesion strength of the coatings increased with the surface roughness of the substrate: the rougher the substrate surface, the higher the adhesion strength. However, after the surface roughness reached a value higher than 4 µm, the rate of increase of interfacial fracture toughness tended to become stable at 3.5-4.0MPa.m^{1/2}. Therefore, the
optimum surface roughness of the substrate is ~4.0 μm. The sand-blasted stainless steel substrate resulted in a higher fracture toughness than the grinded stainless steel substrate.

5.3 Summary of Contact Measurements

The average hardness of the mono-layer CB-CSG ceramic coatings was 6.0 GPa. The mono aluminum phosphate (MAP) formed chemical bonds with the CSG and converted to berlinite or cristobalite after 5 days of curing at 160°C.

The average scratch critical force values for Groups A, B, and C were 4.7 kg, 10.3 kg and 17.0 kg respectively, and these values were dependent on the volume percentage of siloxane. The scratch critical force increased with increasing coating thickness: the thicker the coating, the higher the critical force. When the thickness was below 20 μm, the stresses were considered to be negligible. The critical force increased almost linearly with increasing coating thickness. For thickness values from 20-60 μm, the effects of the residual stresses could not be ignored, as the rate of increase of scratch critical force vs. thickness decreased due to the contribution of the residual stresses. After 60 μm, the critical force decreased with increasing coating thickness due to the effect of these stresses.

The interfacial scratch failures were due to defects, e.g. pores and cracks, which are often generated by the high temperature processing. Therefore, low temperature
curing is an effective way to prevent interfacial failure. The CB-CSG mono-layer Group C coating generally had good scratch resistance when its thickness was less than 100 μm.

5.4 Summary of Residual Stress and Potentiodynamic Evaluations

An important merit of this work is the use of the inorganic (siloxane) polymer bond coat (primer) at the interface between the metallic substrate and the ceramic coating. It is believed that such a coating system has been proposed and explored for the first time in this work.

The “Wafer” experiments to determine the curvature radius show that the siloxane primer can significantly decrease the thermally induced stress in the CB-CSG coating. The siloxane primer can be used as a compliant layer, which relaxes the stress caused by the thermal expansion coefficient mismatch. The siloxane bond coat can also increase the bond strength of the coating by decreasing the number of coating defects.

The potentiodynamic and permeability experiments showed that the CB-CSG ceramic coatings with siloxane significantly decreased ceramic porosity and increased corrosion resistance of the mild steel substrates. The corrosion current density of the CB-CSG coating decreased with increasing overall coating thickness (>100μm), and finally tended to stabilize at ~10^{-9} A/cm². The influence of the substrate decreased with increasing coating thickness. The corrosion protection efficiency of the traditional CB-CSG is ~92%. Multilayer coatings form effective physical barriers to enhance corrosion
protection of the mild steel substrate. In particular, the incorporation of siloxane increases the corrosion resistance of coated mild steel in 1wt% NaCl solution. A summary of the coating characteristics for Groups A to C is given in Table 5.1.

5.5 Conclusions

A “warm” temperature process (160-300°C) has been developed to modify the traditional sol-gel coating process. It overcomes the drawbacks of the traditional process for producing composite sol-gel coatings, e.g. cracks, low thickness, low hardness, and poor phosphate distribution. A multi-gun spraying technique was developed to more effectively distribute the phosphate throughout the coating. The new process employs low temperature curing (160°C), which results in a sol-gel alumina coating free of surface cracks with a medium hardness (6.0 GPa), a moderate adhesion (42.0 MPa) and good scratch resistance (17.0 kgf). This process can be used to produce relatively thick (40-300 μm) coatings. The air permeability of the CB-CSG coating is ~0.5 milidarcy at a thickness of 40.0 μm. This research also explains why CB-CSG coatings have medium hardness and good scratch resistance.

Another merit of this research is the use of polymeric siloxane as the bond coat for CB-CSG coatings, which acts to relax the residual stress between the CB-CSG coating and the steel substrate, and therefore decreases substrate deformation. The siloxane and the aqueous sol were deposited onto the mild steel through a multi-gun
spraying technique, which successfully prevented the coating from buckling on the non-oxidized mild steel substrate during the heat treatment at temperatures up to 300°C.

Table 5.1. The summary of characteristics of various coatings

<table>
<thead>
<tr>
<th>Properties</th>
<th>Group A</th>
<th>Group B</th>
<th>Group C</th>
<th>Siloxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating Structure</td>
<td>Dual-layer</td>
<td>Tri-layer</td>
<td>Mono-layer</td>
<td>NM</td>
</tr>
<tr>
<td>Adhesion strength (MPa)</td>
<td>13.0</td>
<td>18.0</td>
<td>42.0</td>
<td>&lt;10MPa</td>
</tr>
<tr>
<td>Scratch Critical Force (kg)</td>
<td>4.7</td>
<td>10.3</td>
<td>17.0</td>
<td>NM</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>N/A</td>
<td>N/A</td>
<td>6.24</td>
<td>0.12</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>N/A</td>
<td>N/A</td>
<td>0.25</td>
<td>0.35</td>
</tr>
<tr>
<td>Air Permeability (milidarcys)</td>
<td>Non-detectable</td>
<td>Non-detectable</td>
<td>~0.2</td>
<td>impermeable</td>
</tr>
<tr>
<td>Residual Stress at 40μm (MPa)</td>
<td>&lt;1.0</td>
<td>N/A</td>
<td>~8.0</td>
<td>0</td>
</tr>
<tr>
<td>Interface Fracture Toughness</td>
<td>N/A</td>
<td>N/A</td>
<td>3.5</td>
<td>NM</td>
</tr>
<tr>
<td>(MPa.m$^{1/2}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elastic Modulus (Sonic, GPa)</td>
<td>N/A</td>
<td>N/A</td>
<td>225.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Protection Efficiency (DI H$_2$O)</td>
<td>97%</td>
<td>99%</td>
<td>92%</td>
<td>NM</td>
</tr>
<tr>
<td>Protection Efficiency (1% NaCl)</td>
<td>94%</td>
<td>96%</td>
<td>84%</td>
<td>NM</td>
</tr>
</tbody>
</table>

*NM: not measured
CHAPTER 6: FUTURE WORK

One merit of this work was the development of a "warm" temperature process for producing a crack-free composite sol-gel alumina coating, which includes a multi-gun spraying technique to distribute phosphate throughout the coating. Future work should therefore focus on developing a further understanding of the issues related to the "warm" temperature process, to increase the adhesion, hardness and scratch resistance of the coatings. The following subjects should be addressed:

1. Adjusting the "warm" temperature process to homogeneously distribute the phosphate through the coating.
2. Modifying the "warm" temperature process to form a well-crystallized phosphate alumina coating.
3. Increasing the adhesion and the hardness of the coatings up to 70 MPa and 10 GPa respectively.
4. Modeling the behavior of the CB-CSG coating at high temperatures.

Another contribution of this work is the development of inorganic polymer bond coat for residual stress relaxation and corrosion protection. However, there are some uncertainties in the production of the siloxane bond coat. Since the adhesion of the siloxane bond coat is dependent on mechanical interlocking, the mechanical anchoring is
stronger and thus the adhesion strength of the bond coat is higher at points where there is greater penetration of alumina particles.

Therefore, future work should also include further study of the adhesion of the siloxane bond coat to metals and ceramics, the effects of secondary particulate phases dispersed in the siloxane bond coat, the characteristics of the viscoelastic deformation of the bond coat, the effects of chemical modifications of the bond coat on its performance in residual stress relaxation, and the modeling of the stress relaxation due to the bond coat.
References:


Appendix I  Determination of Young’s modulus by Sonic Waves

An ultrasonic wave tester (GrindoSonic MK5 “Industrial” Instrument, J.W.Lemmens, Inc., MO, USA) is used to measure the elastic modulus and Poisson’s ratio according to ASTM C-1259-04.

The dynamic Young’s modulus can be obtained from [117-119]:

\[ E_d = \frac{10^{-7}}{981} \times 4L^2N^2d \]  

(I-1)

where \( E_d \) = modulus of sample (GPa)
\( L \) = dimension of sample (cm)
\( N \) = resonant frequency (Hz)
\( d \) = density of sample (g/cm\(^3\))

For rectangular shape substrate, shear modulus can be calculated from [120, 121]:

\[ G = \frac{4LmN^2}{wt} \times \left[ B/(1 + A) \right] \]  

(I-2)

where \( L \) = dimension of sample, \( t \) = thickness, \( w \) = width, \( m \) = mass, \( N \) = resonant frequency, \( A \), \( B \) = empirical correction factors dependent on \( w \) and \( t \).

Poisson’s ratio can be calculated by:

\[ \nu_c = \frac{E_c}{2G_c} - 1 \]  

(I-3)

where:
\( \nu_c \) = Poisson's ratio of coating
\( E_c \) = Young's modulus of coating
\( G_c \) = shear modulus of coating

Considering that there are some pores in the coating, the corroborated equation can be used as [122]:

\[
E = E_0 (1 - \alpha P_c)
\]

where \( E \) is the Young's modulus of porous coating, \( E_0 \) represents the modulus of fully dense coating, \( P_c \) is the volume fraction porosity. For perfectly spherical holes the constant (\( \alpha \)) is the following function of coating Poisson's ratio \( \nu_c \) [122]:

\[
\alpha = \frac{3(9 + 5\nu_c)(1 - \nu_c)}{2(7 - 5\nu_c)}
\]

The following method includes testing of uncoated substrates as a reference from which the effect of the coating may be obtained and the coating's modulus can be calculated [123, 124]:

1. Measure the bare substrate's density \( D_s \) and thickness \( T_s \)
2. Measure the coated substrate's density \( D_{s-c} \) and thickness \( T_{s-c} \). Coating's density (\( D \)) can be calculated by:
\[ D_{s-c} = \frac{T_s}{T_{s-c}} D_s + \frac{T}{T_{s-c}} D \]

3. Input substrate’s Poisson’s ratio.

4. Measure the bare substrate’s Young’s Modulus \( E_{d-s} \) by 90° flexural mode.

5. Input initial coated substrate’s Poisson’s ratio \( \nu_l \).

6. Measure the coated substrate’s Young’s Modulus \( E_{d-c} \) by 90° flexural mode.

7. Measure the coated substrate’s shear Modulus \( G_{d-c} \).

8. Calculate the coated substrate’s Poisson’s ratio \( \nu \):

\[ \nu = \frac{E}{2G} - 1 \]

9. If \( \frac{\nu - \nu_l}{\nu} < 0.02\% \) then \( \nu_l = \nu \) go to step 7.

10. Calculate the coating’s modulus \( E_C \) by:

\[ E_C = \left( \frac{T_s}{T_{s-c}} \right) E_{d-s} + \left( \frac{T_{s-c} - T_s}{T_{s-c}} \right) E_d \]

11. Calculate the coating’s shear modulus \( G_C \) by:

\[ G_C = \frac{T_s}{T_{s-c}} G_{d-s} + \frac{T_{s-c} - T_s}{T_{s-c}} G_d \]

12. Calculate the coating’s Poisson’s ratio \( \nu_C \):

\[ \nu_C = \frac{E_C}{2G_C} - 1 \]

13. Checked by the equation:
\[
\frac{N'}{N_0} = \left[ 1 + \alpha_c \cdot \frac{E_c}{E_s} - 1 \right] \left[ 1 + \alpha_c \cdot \frac{D_c}{D_s} - 1 \right], \text{ where } N' \text{: resonant frequency of coated substrate,}
\]

\[\alpha_c = \frac{T_{s-c} - T_s}{T_{s-c}}, \text{ } E_c: \text{ coating's elastic modulus, } E_s: \text{ substrate's elastic modulus, } D_c: \text{ coating's density, } D_s: \text{ substrate's density.} \]

16. Final \( \nu_C, E_C \) and \( G_C \) obtained.

**Note:** this method shows the satisfactory results only when the thickness of substrate is below 400\( \mu \)m and coating thickness is above 40\( \mu \)m [125].
Appendix II Original Data of the Radius of Curvature vs. Thickness

Table II.1 CB-CSG thickness vs. curvature radius for Group C

| Group C          | X (m)  | Y (m)  | (|X| + |Y|)/2 (m) | Average (m) |
|------------------|--------|--------|--------------|-------------|
| Bare substrate   | 18.62  | 15.86  | 17.24        | 16.5 (0.63) |
|                  | 18.32  | 15.14  | 16.73        |             |
|                  | 16.23  | 15.29  | 15.76        |             |
|                  | 15.82  | 16.72  | 16.27        |             |
| 10±2μm CB-CSG    | 9.82   | 11.44  | 14.63        | 13.6 (0.95) |
|                  | 10.89  | 16.25  | 13.57        |             |
|                  | 14.11  | 10.57  | 12.34        |             |
|                  | 14.93  | 12.79  | 13.86        |             |
| 20±2μm CB-CSG    | 12.16  | 9.82   | 8.99         | 8.5 (0.55)  |
|                  | 3.99   | -19.48 | 7.74         |             |
|                  | 2.69   | 18.20  | 8.45         |             |
|                  | 12.62  | 11.04  | 8.82         |             |
| 30±2 μm CB-CSG   | 5.69   | 0.66   | 3.18         | 3.35 (0.31) |
|                  | 3.26   | 3.02   | 3.14         |             |
|                  | 2.29   | 4.84   | 3.81         |             |
|                  | -3.26  | 3.30   | 3.28         |             |
| 40±2 μm CB-CSG   | -2.07  | 3.95   | 3.01         | 2.21 (0.58) |
|                  | 2.09   | 4.03   | 2.06         |             |
|                  | -0.75  | 3.53   | 2.14         |             |
|                  | 1.48   | 1.79   | 1.64         |             |
| 60±2μm CB-CSG    | 2.15   | 1.61   | 1.88         | 1.51 (0.39) |
|                  | 3.01   | 1.22   | 1.22         |             |
|                  | 1.74   | 0.50   | 1.12         |             |
|                  | 2.43   | 1.17   | 1.80         |             |
| 80±2μm CB-CSG    | 1.76   | 2.12   | 1.94         | 1.49 (0.51) |
|                  | 0.57   | 1.50   | 1.04         |             |
|                  | 2.12   | 1.69   | 1.91         |             |
|                  | 1.10   | 1.02   | 1.06         |             |
| 100±5 μm CB-CSG  | 0.73   | 2.64   | 1.69         | 1.47 (0.35) |
|                  | 1.48   | 1.45   | 1.47         |             |
|                  | 0.67   | 1.27   | 0.97         |             |
|                  | 1.50   | 2.09   | 1.73         |             |

*Values in parentheses show the standard deviation
Table II.2 Siloxane Thickness vs. Curvature Radius for Group A

| Group A            | X (m)  | Y (m)  | (|X|+|Y|)/2 (m) | Average(m) |
|--------------------|--------|--------|---------------|------------|
| 0 µm siloxane      | 6.51   | -0.45  | 3.48          | 3.5 (0.92) |
|                    | -8.26  | -0.63  | 4.45          |            |
|                    | -3.82  | -0.73  | 2.28          |            |
|                    | -3.29  | 4.48   | 3.89          |            |
| 5±2 µm siloxane    | 9.46   | 11.63  | 12.38         | 12.7 (0.99)|
|                    | 21.25  | 6.21   | 13.73         |            |
|                    | 13.06  | 13.40  | 13.23         |            |
|                    | 8.72   | -14.20 | 11.46         |            |
| 8±2 µm siloxane    | 13.80  | 11.60  | 12.70         | 13.5 (0.63)|
|                    | 20.30  | 7.10   | 13.70         |            |
|                    | 15.40  | 11.40  | 13.40         |            |
|                    | -14.13 | 14.27  | 14.20         |            |
| 10±2 µm siloxane   | 11.76  | 13.20  | 13.48         | 14.3 (1.29)|
|                    | 14.00  | 15.22  | 14.61         |            |
|                    | 21.20  | 0.75   | 15.98         |            |
|                    | 17.06  | -13.20 | 13.13         |            |
| 15±2 µm siloxane   | -11.11 | -18.81 | 14.96         | 14.4 (1.49)|
|                    | -11.61 | -19.99 | 15.80         |            |
|                    | -12.87 | 16.21  | 14.54         |            |
|                    | -10.18 | 14.42  | 12.30         |            |
| 20±2 µm siloxane   | 21.98  | 7.78   | 14.88         | 14.9 (1.76)|
|                    | 16.25  | 9.57   | 12.91         |            |
|                    | 20.81  | 8.41   | 14.61         |            |
|                    | 17.26  | 17.14  | 17.20         |            |

*Values in parentheses show the standard deviation