# PROCESS ENGINEERING OF THICK DIELECTRIC FILMS BY CHEMICALLY BONDED COMPOSITE SOL-GEL

by

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#### **ABSTRACT**

This research explores new processing methods to decrease residual stress in ceramic films on metallic substrates, and thus to prevent large-scale cracking in the films. The system of particular concern is alumina-based ceramic coating on aluminum alloy, wherein coefficient of thermal expansion (CTE) of the ceramic is about 3x smaller than that of the alloy. The specific goal was to achieve relatively thick (~0.2mm) and substantially low density of cracks in dielectric films of alumina-based ceramic on aluminum alloy AA5052, by Chemically Bonded Composite Sol-Gel (CB-CSG) process. The principal strategies undertaken in the materials process engineering involved: (i) multi-layer film deposition - to introduce the intermediate steps of stress relaxation; (ii) composite sol-gel slurries with bimodal particle size distribution - to decrease the overall process temperature, and to decrease film strain during thermal treatment as well as to increase the density and stability of the slurries; (iii) chemical bonding of the film through phosphating – to further decrease the process temperature to the level of 300°C; and (iv) introduction of organic-phase (citric acid) derived bond coats at the interface between the AA5052 substrate and the ceramic coating to achieve residual stress relaxation through viscoelastic deformation of the bond coat.

The coatings were processed through spray deposition of consecutive ~40  $\mu$ m thick layers, heat-treated at 300°C for 10 min after each deposition. Two size fractions of alumina powders (average size of 0.5  $\mu$ m of "fine" and 3  $\mu$ m of "coarse") were used in formulation of the Composite Sol-Gel (CSG) slurry, and the fine/coarse particle content was optimized based on slurry viscosity and stability, as well as properties of the final coating. The coatings were characterized for microstructure, residual stresses and dielectric strength, as a function of the process parameters. The most important finding of this work is that it is possible to deposit thick ceramic films on aluminum alloy substrates, if all four processing strategies listed above are implemented simultaneously. In particular, the citric acid – derived organoceramic bond coats seem to play an important role in relaxing residual stresses resulting from differential thermal contraction and expansion.

It is concluded that the viscoelastically deforming organo-ceramic bond coat helps to relax residual stresses in the coating layers due to differential thermal contraction/expansion, and thus allows deposition of films of up to 200  $\mu$ m thickness. Dielectric strength of the CB-CSG alumina coated AA5052 aluminum reached a maximum of 15±1 kV/mm for the first layer, and subsequently decreased to 10.5±1 kV/mm. It is believed that this decrease in the dielectric strength after the first layer is caused by increased density of cracks in the coating, as evidenced by decrease of the residual stress in the coatings.

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# List of Greek Symbols

- k Thermal conductivity  $(W/m \cdot K)$
- $\sigma$  Strength (MPa)
- $\alpha$  Coefficient of Thermal Expansion, CTE, (K<sup>-1</sup>)
- ε Strain (no unit)
- v Poisson's ratio (no unit)
- $\sigma_x$  Stress in direction of x-axis (MPa)
- v Velocity of a settling particle (mm/s)
- $\eta$  Viscosity (Pa.s)
- $\rho_1$  Density of a solid (g/cc)
- $\rho_2$  Density of fluid (g/cc)
- $\tau$  Relaxation time (sec)

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## List of Roman Symbols

- $R_2$  Thermal shock resistance parameter (W/m)
- *E* Young's modulus (MPa)
- $h_0$  Thickness of substrate (µm)
- $I_0$  Stiffness (N/m)
- $z_0$  Point of the neutral axis ( $\mu$ m)
- *M* Bending moment (Nm)
- $\overline{E}$  Average Young's modulus (MPa)
- E(z) Young's modulus at position z (GPa)
- *d* Lattice spacing (Å)
- $D_a$  Apparent density (g/cc)
- $W_d$  Weight of a sample in air (g)
- $W_s$  Water-soaked weight of a specimen (g)
- $W_i$  Weight of a sample immersed in water (g)
- $R_a$  Average roughness (µm)
- |z| Distance measured from the mean line in measuring roughness (mm)
- *L* Sample length in the x-direction (mm)
- $K_{\varepsilon}$  Strain constant (no unit)
- *D* Displacement of a drive shaft (=0.05mm)
- *t* Sample thickness (mm)
- *l* Length of span (= 40mm)
- *F* Force on a sphere (N)
- a Radius of a particle ( $\mu$ m)

- g Gravity acceleration  $(9.8 \text{ m/s}^2)$
- $V_{\rm p}$  Volume fraction
- V<sub>B</sub> Breakdown voltage

# List of Abbreviations

CTE	Coefficient of Thermal Expansion
AA5052	Aluminum Alloy 5052
CA	Citric Acid
CSG	Composite Sol-Gel
CB-CSG	Chemically Bonded Composite Sol-Gel
TDF	Thick Dielectric Film
NMR	Nuclear Magnetic Resonance
XRD	X-ray Diffraction
DS	Dielectric Strength
DT-TGA	Differential Thermal-Thermo Gravimetric Analyzer
DMTA	Dynamic Mechanical Thermal Analyzer
DMA	Dynamic Thermal Analyzer
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
CAD	Citric Acid-Derivative

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#### CHAPTER 1 INTRODUCTION

Ceramic coatings have a variety of applications, such as electrical and thermal insulation [1.1-1.4], corrosion and wear protection [1.5,1.6], and many other functions, such as catalysis or gas sensors [1.7]. The factors which affect electrical properties of ceramic coatings for electrical insulation include the band gap, but also engineering properties such as thickness and microstructure. When a ceramic coating (i.e.,  $Al_2O_3$ ,  $CTE = -8 \times 10^{-6}/^{\circ}C$ ) on a metal (i.e., AA5052, CTE= $\sim 24 \times 10^{-6}$ /°C) is considered, heat treatment temperature is a significant factor to be taken into account because of typically large thermal expansion mismatch between ceramic coatings and metals. Upon cooling, a metallic substrate will typically contract significantly more than the deposited ceramic layer, resulting in tensile stresses in the metal and compressive stresses in the ceramic layer [1.8-1.10]. This thermal mismatch limits processing and frequently induces failure of the coatings. For example, Olding et. al [1.11] studied alumina-alumina composite sol-gel coatings on steel for electrical insulation. They have found it very difficult to coat such a ceramic composite on steel with >100 µm thick coat without delamination due to micro cracking and thermal mismatch triggered macro-cracking. However, according to their research  $[1.11] > 100 \mu m$  thick ceramic coating has been required for the coating breakdown voltage above 2kV. It is therefore a processing challenge to overcome the above disadvantages, to be able to deposit thick ceramic coatings on metals without failure of coatings. This challenge is undertaken as one of the principal objectives of the present work.

In order to address the effects of a large difference in CTE between the ceramic coating and a metallic substrate, an alternative coating processing methods should be

considered. For example, polymers can be applied to a ceramic-metal interface as a bond coat to mitigate stresses at the interface [1.12,1.13]. The viscoelastically deforming polymeric bond coat provides the means of relaxing stresses in the ceramic-metal interface during cooling. Kozuka *et.al* [1.12] reported that a sol-gel derived silica and titania coatings with an organic polymer (polyvinylpyrrolidone and polyvinylacetamide) bond coat, deposited on silicon by spin-coating, could be fabricated crack-free. Lower heat treatment temperatures also reduce the thermal expansion mismatch stresses [1.14]. This is difficult to achieve if the coating is to be sintered. In this respect, sol-gel processing substantially allows to reduce the temperature and thus reduce the residual stresses. This aspect is also explored in the present work.

In the current work we study (and attempt to solve) the processing limitations for thick ceramic coatings on metals through innovative use of "bond coats", the intermediate layers between the metallic substrate and the ceramic "top coat". Citric acid (CA) has been used as a precursor for the organo-ceramic bond coat. The Chemically Bonded Composite Sol-Gel (CB-CSG) and gradual deposition method has been used to lower the heat treatment temperatures for coatings. All three approaches (i.e. (i) introduction of the bond coat, (ii) decrease of process temperature through use of CB-CSG, and (iii) gradual (multilayer) deposition method, were aimed at decreasing residual stress in the ceramic coating such that relatively thick films (>0.2mm) can be deposited without spallation on light metals such as aluminum alloys (AA5052).

Although CA is a widely used dispersant for alumina suspension [1.15-1.18], it

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transforms to an amorphous, poorly defined organic phase at elevated temperatures, and is believed to provide polymeric (viscoelastic) behavior [1.19]. The CB-CSG method requires firing temperatures as low as ~300 °C [1.20]. The CB-CSG method has been developed using chemical reaction between sol-derived nano-alumina (, i.e. <0.05µm particles derived from low-temperature, i.e. 300°C, thermal decomposition of aluminum hydroxide) and phosphoric acid. This chemical reaction (refer to Section 2.1.4.1) provides bonding between alumina particles (0.5-3µm) and metal substrate when used in coating by forming aluminum phosphates in the coating and in the interface in the CB-CSG process [1.21].

The current process engineering study explores the combined use of CB-CSG with a CA-derived bond coat as an innovative technique to deposit thick dielectric films (TDF) on metallic substrates with large difference in CTE between them (alumina:  $8 \times 10^{-6/\circ}$ C, AA5052:  $24 \times 10^{-6/\circ}$ C), to insulate heating elements (i.e., carbon based electrical resistive films) from the base metal substrate. Phosphate-bonded alumina and aluminum alloy (AA5052) are used in the current work as the ceramic coating and the metal substrate, respectively. Phosphate-bonded alumina has a potential for application as an electrical insulation film resistant to voltages up to 2kV, providing the thickness of the coatings is >200 µm, Fig.1.1 [1.22]. The resistive film must be insulated from the metal substrate to pass the standard safety test (2kV for 3 sec). Alumina is a promising insulation material for the heating elements, e.g. in common appliances such as kettles, due to its relatively high thermal conductivity (30 W/mK) and high dielectric strength (10-16 kV/mm) [1.23]. Aluminum alloy, AA5052, is also preferable because of its low density (2.68 g/cc) and excellent thermal conductivity (138 W/mK) [1.24]. It has been reported by Datec Coating Corp., supporting this research, that

such 3kW heating element system can boil 1 liter of water in 2 min. Table1-1 compares the currently used metallic substrates for heating elements. Even though CTE of AA5052  $(24 \times 10^{-6})^{\circ}$ C) is much larger than that of stainless steel (SS,  $10 \times 10^{-6})^{\circ}$ C), the heating efficiency (i.e. low losses due to high thermal conductivity) of AA5052 presents a great advantage. Therefore, it is worthwhile to develop a process in which the alumina coating is deposited on AA5052 to provide sufficient electrical resistance films.



Fig.1-1 High efficiency heater and its application for water boiling

**Table 1-1** Comparison of a current stainless steel (430) and proposed aluminum alloy (5052) metal substrate for heating elements [1.24].

Property	Stainless Steel (430)	Aluminum alloy (5052)
Density (g/cc)	7.7	2.68
Thermal Conductivity (W/m·K)	20	138
Coefficient of Thermal Expansion :CTE (×10 <sup>-6</sup> /°C)	10	23.75
Melting Point (°C)	1425-1510	600
Yield strength (MPa)	310	90-255

#### CHAPTER 2 LITERATURE REVIEW

#### 2.1 Ceramic Coating Processing

The thickness of ceramic coatings depends on the intended applications, e.g optical coatings are generally thin (sub-micron), while electrically insulating coatings usually have to be relatively thick (> 100  $\mu$ m) to achieve sufficient dielectric strength [2.1-2.2]. In the current study, we investigated thick (>200  $\mu$ m) alumina coatings proposed as electrically insulating films for heating elements. Processing of the thick coatings for the heating element was studied via the Chemically Bonded Composite Sol-Gel (CB-CSG) technique which can provide much thicker films than a conventional sol-gel technique [1.5]. The sol-gel technique has been one of the most promising processes since it does not require complicated equipment and high temperature heat treatment (< 500 °C) [2.3-2.8].

#### 2.1.1 Sol-Gel Processing

The sol-gel technique can use a water-based process or an alcohol-based process, a through solution of metal salt or metal alkoxide, respectively [2.9]. The first step in the water-based process is to form a sol by hydrolysis of the metal ions, M:

$$M^{n+} + nH_2O \rightarrow M(OH)_n + nH^+$$
(2.1-1)

Gelation of the sol is achieved by either dehydration or an increase in pH. During the gelation by the dehydration, the energy barrier to gelation is reduced by the increase in the concentration of electrolyte in the diffuse layer around the individual particles. Increase in pH reduces the magnitude of positive surface charge on the sol particles, leading to the reduction of repulsive forces between particles and lowering the height of the energy barrier

[2.10], leading to gelation.

In the preparation of alumina sols, various aluminum compounds can be used, such as aluminum iso-propoxide (Al(OC<sub>3</sub>H<sub>7</sub>)), aluminum butoxide (Al(OC<sub>4</sub>H<sub>9</sub>)<sub>3</sub>) and boehmite (AlOOH)) [2.11]. In particular, alumina sol from boehmite can be formed via hydrolysis and condensation of Al<sup>3+</sup> ions in water at pH>3 as follows [2.12];

$$Al(O)-OH + H-OH \rightarrow Al(OH)_3$$
 (2.1-2)

$$[Al(H_2O)_6]^{3+} + h H_2O \rightarrow [Al(OH)_h(H_2O)_{6-h}]^{(3-h)+} + h H_3O^+$$
(2.1-3a)

$$h \operatorname{H}_{3}\operatorname{O}^{+} + h \operatorname{OH}^{-} \to 2h\operatorname{H}_{2}\operatorname{O}$$
(2.1-3b)

where *h* indicates the molar ratio of hydrolysis. For *h*>2.46, rapid precipitation of condensed, amorphous, or weakly crystalline hydrated alumina phases occurs. The most common crystalline phase in the reaction, Eq.2.1-3a is pseudoboehmite,  $\gamma$ -Al(OH)<sub>3</sub> [2.12]. When  $\gamma$ -Al(OH)<sub>3</sub> is dispersed in water, a polymerized structure forms;

$$Al(OH)_{3} + H \cdot OH \rightarrow [Al(OH)_{3} (OH)]^{-} + H^{+} \Leftrightarrow$$

$$[Al(OH)_{3} - OH]^{-} + H^{+} + [Al(OH)_{3} - OH]^{-} \rightarrow [(OH)_{3}Al - O - Al(OH)_{3}]^{2-} + H_{3}O^{+} \qquad (2.1-4)$$

Fig 2.1-1 illustrates the surface of water-based alumina for varying pH. For pH<9,  $H^+$  is adsorbed on the surface, creating an effective positive charge, [O-Al-O-H-H]<sup>+</sup>. At pH>9,  $H^+$  desorbs from the surface of the aluminum oxide in water, creating an effective negative charge on the surface [2.13-2.16].



Fig.2.1-1 Reaction of the hydrated surface of alumina with H<sub>3</sub>O+ or OH.[2.13,2.14]

#### 2.1.2 Composite Sol-Gel

The sol-gel process technique provides many advantages over conventional ceramic processes, including high purity raw materials (i.e., >99.5 %) and low heat treatment temperatures (i.e.< 500 °C) [2.17-2.21]. However, it has a significant drawback, namely the large processing shrinkage (>90 %), resulting in cracks [2.17-2.22]. A composite sol-gel technique has been recently proposed to avoid the disadvantage of the large shrinkage of a sol-gel that causes cracks in thick coatings on metallic substrates [2.23-2.25]. The composite sol-gel is fabricated by dispersing ceramic powders, fibers, or whiskers as a second phase into the sol. The patent by Barrow *et al.* [2.23] has disclosed ceramic coatings of thicker than 100  $\mu$ m on selected substrates using a composite sol-gel technology. The composite sol-gel coatings did not crack during drying because of the high weight percentage of the filler in the slurry. Murrell [2.26] also reported that coating thickness with the sol alone is limited to less than 10  $\mu$ m without cracks, while >25  $\mu$ m can be coated by composite sol-gel. In the case of

alumina, the 20 wt% alumina sol with the dispersed alumina powder is suggested for a coating thickness of >25  $\mu$ m [2.26]. Figure 2.1-2 presents the schematic of the formation of a 3D network of alumina as the filler and alumina sol upon drying.



**Fig.2.1-2** Schematic of sol particles gluing coated particles into a coherent 3 dimensional structure [2.26].

 $\alpha$ -Alumina is a favorable filler to make the composite sol-gel with alumina sol because the alumina precursor transforms to the same chemical compositions as the  $\alpha$ alumina at elevated temperatures, i.e. AlO(OH)  $\rightarrow \gamma$ -Al<sub>2</sub>O<sub>3</sub> (at 450 °C)  $\rightarrow \delta$ -Al<sub>2</sub>O<sub>3</sub> (at 600 °C)  $\rightarrow \theta$ -Al<sub>2</sub>O<sub>3</sub> (at 800-1000 °C)  $\rightarrow \alpha$ -Al<sub>2</sub>O<sub>3</sub> (at >1200 °C) [2.27,2.28]. The alumina composite sol forms the three dimensional network structure by connecting the adsorbed sols, resulting in a relatively low surface area (~3 m<sup>2</sup>/g) material during the gelation [2.26]. By having such a low surface area, packing density of particles is increased allowing increases the thickness of a single coating deposition. However, no research for SG or CSG thick (100200µm) alumina coating on aluminum has been reported.

### 2.1.3 Packing of Particles

In order to minimize the void volume, different particle sizes should be mixed as shown in Fig.2.1-3, also known in ceramic processing science as "grading" [2.29].



Fig.2.1-3 Packing of spheres of different sizes; (a) theoretical packing and (b) practical packing [2.29]

"Smaller particles introduced and distributed in the interstices of packed larger particles will reduce the porosity and pore size. Large particles added to finer particles displace fines and pores and reduce the porosity [2.29]." Very high densities may be obtained using this principle, e.g. McGeary [2.30] experimentally achieved a packing density of ~95% for a quaternary system of vibrated steel spheres while obtained a packing density of ~70% for a binary system. Figure 2.1-4 plots the porosity of two component mixtures of tabular aluminas [2.31].



**Fig.2.1-4** Calculated and experimental total porosity for vibrated, two-component mixtures of tabular alumina fines (-200+325 mesh) and three different coarse fractions [2.31].

Blending of different particle sizes (i.e. grading) to achieve high packing density is common in formulating coarse-grained refractories. The commonly used batch for high density packing is approximately 60-65 wt.% coarse particles and 35-40 wt.% fine particles. Another study of packing density by Hugill and Rees [2.29] provides ternary diagram using silica particles of three distinctive sizes, Fig.2.1-5. According to their diagram, the most suitable mixture ratio for the highest density of the silica bulk ( $\sim 1.74$  g/cc) is 45% coarse, 10% medium, and 45% fine particles. These results were applied in the current study for the fabrication of coatings with as high packing density as possible.



**Fig.2.1-5** Apparent density graded and fired mixtures of silica rock. The solid circle indicates the highest density of silica ( $\sim$ 1.74 g/cc) [2.29].

#### 2.1.4 Chemically Bonded Composite Sol-Gel (CB-CSG)

Ceramics made by sol-gel are usually sintered at temperatures >500°C to achieve appropriate mechanical strength and density. However, such a high temperature limits the use of ceramic coatings on some metallic substrates whose melting temperatures are low, such as aluminum and magnesium. If the properties of a ceramic coating obtained by high temperature sintering can be obtained by low sintering temperature synthesis, it will serve as an impetus to the improvement of ceramic coatings. This can be obtained by introducing chemical species to ceramic composite sols, inducing a chemical reaction between the chemical species and ceramics at as low temperature as 300°C. This process is known as a Chemically Bonded Composite Sol-Gel (CB-CSG). The chemical used in the current study for alumina composite sols is phosphoric acid, commonly used for processing of monoaluminum phosphate  $(Al(H_2PO_4)_3)$  and aluminum phosphate  $(AlPO_4)$  [1.2,2.32-2.39]. The chemical bonding via phosphating on sol-gel derived oxides (alumina,  $Al_2O_3$ ) or hydrated oxide (aluminum hydroxide, Al(OH)<sub>3</sub>) provides denser and harder ceramics than ordinary composite gel derived ceramics, after heat treatment at temperatures as low as 300°C [2.36,2.37].

Previous studies [2.32-2.39] indicate that the phosphates can reduce porosity by playing a role as an amorphous binder, and form a chemical reaction with alumina, lowering the firing temperature to ~300°C, resulting in strength comparable to that of ceramics made at conventional (high) sintering temperatures >1000°C. Thus, strong and dense ceramics can be produced through the chemical reaction between alumina and phosphates. This reaction depends on the ratio of Al:P and temperature. The product, aluminum meta phosphate

(Al(PO<sub>3</sub>)<sub>3</sub>), is favored by high phosphate-loading conditions (Al/P<1) whereas aluminum orthophosphates (AlPO<sub>4</sub>) are favored by low phosphate loading conditions (Al/P≥1) [2.33]. The reaction of alumina or hydrated alumina with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) is exothermic and produces mono-aluminum phosphate (Al(H<sub>2</sub>PO<sub>4</sub>)<sub>3</sub>) as an amorphous binder at low temperature (<500°C) [2.40]:

:

$$Al_2O_3 + 6H_3PO_4 \rightarrow 2Al(H_2PO_4)_3 + 3H_2O$$
 (2.1-1)

$$Al(OH)_3 + H_3PO_4 \rightarrow amorphous phase$$
 (2.1-2)

Mono-aluminum phosphate produces AlPO<sub>4</sub> and AlPO<sub>4</sub>. H<sub>3</sub>PO<sub>4</sub> when heated as well:

$$Al(H_2PO_4)_3 \rightarrow AlPO_4 \cdot H_3PO_4 + H_3PO_4$$
(2.1-3)

$$Al(H_2PO_4)_3 \rightarrow AlPO_4 + 2 H_3PO_4 \qquad (2.1-4)$$

In order to have a complete reaction, e.g. dehydration and the formation of stable aluminum phosphate, a heating temperature above 500°C is required [2.40]. Figure 2.1-6 illustrates schematically bonding between the phosphates, alumina and alumina sol. Reaction according to Eq.2.1-2 takes place on the surface of alumina particles and Eq.2.1-3 and Eq.2.1-4 in the solution.



Alumina sol- reacted with phosphates

**Fig.2.1-6** Schematic of interactions between alumina particles or alumina sols and phosphates in a CB-CSG system [2.33].

#### **2.1.4.1** Transformation of Phosphates

The chemical bonding reaction depends on the ratio of Al:P, the reaction temperature, and the reactant's surface area. AlPO<sub>4</sub> has attractive properties, e.g. stability up to ~1800°C [2.34]. AlPO<sub>4</sub> is the final product of the reaction between alumina (anhydrous or hydrated alumina) and orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>). Bothe *et al.* [2.34-2.35] studied the reactions between phosphoric acid and different aluminas (anhydrous alumina and hydrated alumina) for varying temperatures and surface areas. According to their research, AlPO<sub>4</sub>·H<sub>2</sub>O forms at 113-133°C when alumina reacts with phosphoric acid, for a molar ratio of Al/P=1:1. Dehydration of AlPO<sub>4</sub>-H<sub>2</sub>O to get AlPO<sub>4</sub> is nearly complete at about 170°C. Hydrated alumina,  $\gamma$ -boehmite and gibbsite, produce berlinite (equivalent to quartz structure) while anhydrous alumina produce cristobalite.

Bothe *et al.* [2.35] studied the chemical bonding reactions for anhydrous and hydrated alumina. According to their results, in the case of anhydrous alumina, the heat released during the reaction increases for a high initial surface area and high concentration of phosphates. On the other hand, for the hydrated alumina, although the boehmite is finer and more crystalline than gibbsite (0.5  $\mu$ m particle size), the heat released in the boehmite during the reaction was lower than that for the gibbsite (e.g., boehmite: ~32 J/mol and gibbsite: ~40 J/mol). This was explained by the higher solubility of gibbsite than that of boehmite [2.35]. For both anhydrous and hydrated alumina, the heat released increases with high temperature and concentration of phosphoric acid. Formation of type A (tridymite), B (berlinite), and C (cristobalite) phosphates depends on the temperature and the ratio of Al/P. Type A is favored by high concentration (Al:P=1:6-12) and high temperature. Type C and B are formed with

the ratio of 1:3 and 1:1 of Al:P, respectively [2.33-2.35]:

$$<140^{\circ}C >200^{\circ}C$$
  
Al<sub>2</sub>O<sub>3</sub>+H<sub>3</sub>PO<sub>4</sub>  $\longrightarrow$  AlPO<sub>4</sub>+1/2 Al<sub>2</sub>O<sub>3</sub> +3/2H<sub>2</sub>O  $\longrightarrow$  AlPO<sub>4</sub>(-B,-C)+ 1/2 Al<sub>2</sub>O<sub>3</sub> (2.1-5)

$$450-600^{\circ}\text{C} \qquad 650-800^{\circ}\text{C}, -3/2 \text{ H}_2\text{O}$$
  
10 Al<sub>2</sub>O<sub>3</sub>(<1µm)+H<sub>3</sub>PO<sub>4</sub>  $\rightarrow$  amorphous phase  $\rightarrow$  AlPO<sub>4</sub>(-B,-C) + 19/2 Al<sub>2</sub>O<sub>3</sub> (2.1-6)

 $500^{\circ}\text{C}, 3 \text{ H}_{2}\text{O} \qquad 800^{\circ}\text{C}$ Al(OH)<sub>3</sub> + H<sub>3</sub>PO<sub>4</sub>  $\longrightarrow$  1/2 AlPO<sub>4</sub>-B + 1/6 Al(PO<sub>3</sub>)<sub>3</sub>-B +1/6 Al<sub>2</sub>O<sub>3</sub>  $\longrightarrow$ 

$$1/2 \text{ AlPO}_4 - A + 1/6 \text{ Al}(PO_3)_3 - A + 1/6 \text{ Al}_2O_3$$
 (2.1-7)

$$200^{\circ}\text{C}, -2 \text{ H}_2\text{O} \qquad 500^{\circ}\text{C}, -\text{H}_2\text{O}$$
  
Al(OH)<sub>3</sub> + H<sub>3</sub>PO<sub>4</sub>  $\longrightarrow$  1/3Al(H<sub>2</sub>PO<sub>4</sub>)<sub>3</sub> +1/3 Al<sub>2</sub>O<sub>3</sub>  $\longrightarrow$  1/3 Al(PO<sub>3</sub>)<sub>3</sub>-B +1/3 Al<sub>2</sub>O<sub>3</sub>

 $\begin{array}{ccc} 800^{\circ}\text{C} & 1200^{\circ}\text{C} \\ \longrightarrow 1/3 \text{ Al}(\text{PO}_3)_3\text{-A} + 1/3 \text{ Al}_2\text{O}_3 \longrightarrow 1/3 \text{ Al}\text{PO}_4\text{-C} + 1/3 \text{ Al}_2\text{O}_3 + 1/3\text{P}_2\text{O}_5 \end{array} (2.1\text{-}8)$ 

#### 2.2 Citric Acid in Ceramic Processing

Ceramic powders dispersed in liquids are normally unstable due to Van der Waals attraction forces, resulting in large (>10 um) agglomerates, and fast sedimentation of the clusters. Although a certain amount of agglomeration may be advantageous in deposition of thick ceramic coatings [2.41], excessive agglomeration may cause undesirable viscosity change of the slurry. Controlling viscosity of alumina slurry for spray coating in this study is a significant processing factor. The viscosity of the slurry can be controlled by adding a stabilizing dispersant into the slurry, such as citric acid. Organic dispersants are widely used

to control the surface charge for stability of suspensions in aqueous systems [2.42-46, 2.48-50]. The quality of the colloid is usually determined by its state of dispersion. 'In aqueous colloidal processing of alumina powders, control of the suspension properties is usually achieved by adjustment of the repulsive double layer forces either by (i) protonation or deprotonation of the surface hydroxyl (-OH) group, thereby creating a surface charge; (ii) addition of specific adsorbing organic or inorganic oligo- or polyelectrolytes [2.44].' The key factor to achieve optimized coating properties with an alumina composite sol is the ability to stabilize the alumina slurry and to control its viscosity during spraying. This can be achieved by adding citric acid (CA) as a dispersant to the slurry [2.41].

#### 2.2.1 Citric Acid

The p $K_a$  (i.e. acid dissociation constant; the lower the p $K_a$  the more acidic the solution) of citric acid CA (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>), Fig.2.2-1a, at the ionic strength (*I*=0.1) is between 3 and 6 [2.44]. CA adsorbs on alumina in an acidic environment (pH<7) and desorbs in an alkaline region [2.45]. CA may have somewhat different structure depending on the pH of the solution, e.g. the form of citric acid in the neutral and base solution, and tricarballylic acid in acid solution, Fig.2.2-1 [2.44].

At room temperature, CA is a white crystalline powder. It can exist either in an anhydrous form ( $C_6H_8O_7$ ), or as a monohydrate ( $C_6H_8O_7$ ·H<sub>2</sub>O) that contains one water molecule for every acid molecule. The anhydrous form crystallizes from hot water, while the monohydrate forms when CA crystallizes from cold water. The monohydrate dissolves readily in water. It can also be converted to the anhydrous form by heating it above 74°C





Fig.2.2-1 Structural formula of (a) citric acid and (b) tricarballylic acid [2.44].

### 2.2.2 Role of Citric Acid in Aqueous Alumina Suspensions

CA is widely used as a dispersant for aqueous alumina suspensions [2.43-2.45,2.48]; adsorption of CA on particle surface causes an increase of double layer repulsion [2.44]. The hydroxyl group at the interface between alumina and water can be exchanged for a carboxylate group which might change the surface charge [2.52,2.53]. According to the ligand exchange model, the adsorption of the CA onto the surface of alumina particles can be drawn as in Fig.2.2-2. Citric acid has three functional groups of carboxylic acid sites. These carboxylic acid sites can be dissociated (i.e., COO<sup>-</sup> at pH>3) or not be dissociated (i.e., COOH at pH<3) depending on the solvent conditions of pH [2.49].



**Fig.2.2-2** Schematic of hydroxyl group on the surface of alumina sol exchange for carboxyl group in a citric acid containing aqueous suspension system.

The adsorption of the ions in the oxide-solution by the ligand exchange does not influence the surface charge because it is a simple exchange of -OH group for -COO. A change of the surface charge occurs only when an additional carboxylate group that is not coordinated to the surface is present in the molecule. Two carboxylate groups coordinate to the same Lewis base center, or  $-OH_2^+$  group is exchanged instead of a hydroxyl group [2.44]. It is believed that the surface charge of the dispersed alumina particles does not change because a pH of the alumina slurry is ~4.7. [2.43,2.44]. Usually, the amount of the CA in an aqueous system is small (< ~0.2 wt%) since it influences the viscosity of a slurry. When the amount of citric acid in a suspension is increased, the isoelectric point (IEP) of the suspension is changed (i.e., IEP is at pH=7 with 0.1 wt% citric acid and at pH=3.4 with 0.4 wt% citric acid) [2.44]. A larger concentration of the CA than desirable (i.e., > 0.15 wt% at

3<pH<7) in the suspension causes the reduction and, finally, disappearance of the repulsive double-layer and then agglomeration of the dispersed particles [2.44]. Therefore, it is important to control the concentration of the CA in a suspension for an appropriate viscosity of the suspension.

#### 2.2.3 NMR for Testing Materials

Nuclear magnetic resonance (NMR) spectroscopy has long been a primary characterization technique for liquid samples. NMR involves the interaction of the nuclear magnetic dipole with magnetic fields. These interactions provide detailed information on the atomic environment. The frequency or the magnetic field is swept to obtain a resonance. The information in such a resonant spectrum includes line position, often related to the chemical shift. This information can then be interpreted to give insight into the local atomic environment of those atoms responsible for the resonance [2.54]. The table of <sup>13</sup>C NMR absorptions of major functional groups is attached in Table A-3 in the Appendix [2.55].

The chemical shift (expressed in ppm) and spin-spin couplings of such nuclei as <sup>1</sup>H and <sup>13</sup>C are used routinely to analyze the chemical composition of organic compounds [2.54]. A material is placed in a magnetic field (i.e., 1 to 20 T). The magnetic dipole of certain nuclei, such as hydrogen or carbon, will tend to line up with the magnetic field. These nuclei will precess, or rotate, at a particular frequency that is dependent on the nuclide and the magnetic field strength. Adding energy in the form of radiowaves at this specific resonance frequency will cause the nucleus to be pushed out of alignment with the magnetic field. The nucleus, after some short period of time, will then fall back into alignment with the magnetic
field and emit a radiowave in the process. The emitted radiowaves are monitored, and plotted as a function of field frequency (ppm). [2.54].

## 2.3 Dielectric Properties of Ceramics

### 2.3.1 Ceramic Insulators

Ceramic materials contribute to the crucial functions of a variety of electronics including packaging devices, sensors, memory storage, and communication devices. The major use of electronic ceramics includes capacitor dielectrics, thick film components, and ceramic substrates [1.1,2.56-2.58]. Most ceramic materials are classified as electrical insulators, i.e. with the energy band gap >7 eV. A good dielectric insulator should have resistance to breakdown under high voltages and it should not draw appreciable power from the circuit. It also must have reasonable physical stability, and none of its characteristics should vary much over a wide temperature range [2.58]. The advantages of using ceramics as electrical insulators are their capability for high-temperature operation without significant degradation in chemical, mechanical, or dielectric properties.

Ceramic materials have a wide range of thermal conductivities (1-300 W/m K) [1.1], depending both on the composition, microstructure and structural defects in the material. The highest thermal conduction has dense and single phase oxide such as BeO, or non oxide such as AlN and SiC. The presence of complex oxides such as MgO-Al<sub>2</sub>O<sub>3</sub> and MgO-SiO<sub>2</sub> and microstructural features such as pores, cracks, and second phases, generally lowers the thermal conductivity, Table 2.3-1 [1.1].

Materials	BeO	MgO	Al <sub>2</sub> O <sub>3</sub>	MgO-Al <sub>2</sub> O <sub>3</sub>	MgO-SiO <sub>2</sub>	AlN	SiC
Conductivity (W/m·K at 100°C)	210	36	30	15	5.3	250	100

 Table 2.3-1
 Thermal conductivity of single and complex oxides [1.1].

For an electrical ceramic insulator such as alumina, degradation of the properties upon heating is controlled by thermal conductivity (30 W/m·K at 100°C ), tensile strength (300 MPa at 25°C), the coefficient of thermal expansion ( $8.3 \times 10^{-6}$ / °C at 25-1000°C), elastic modulus (400 GPa) [2.59,2.60]. These properties control the thermal shock resistance, which is an important parameter when choosing a ceramic insulator for applications in which temperature change may be severe, such as heaters, resistor cores and thick-film substrates. The thermal shock resistance parameter,  $R_2$  (applicable for low thermal conductivity materials, for example ceramics), may be defined as;

$$R_2 = \frac{k\sigma}{\alpha E} \tag{2.3-1}$$

where k is a thermal conductivity (W/m·K),  $\sigma$  strength (MPa),  $\alpha$  coefficient of thermal expansion (K<sup>-1</sup>), and E Young's modulus (GPa) [2.60,2.61].

Alumina (96-99 wt.%) is currently one of the most widely used ceramic materials for electrical insulators. It has demonstrated superior properties such as high dielectric strength (10-16 kV/mm), high hardness (Vicker's hardness 1600), high mechanical strength (300 MPa), and relatively high thermal shock resistance, as shown in Table 2.3-2 [1.3, 2.59, 2.60].

Material	at 100 °C	at 400 °C	at 1000 °C
Al <sub>2</sub> O <sub>3</sub>	2.7	1.1	0.6
MgO	1.98	0.9	0.5
Mullite	1.1	0.8	0.8
ZrO <sub>2</sub>	0.3	0.3	0.3
Porcelain	0.5	0.1	0.5

**Table 2.3-2** Thermal shock resistance (W/m) for ceramic materials [2.60]

#### 2.3.2 Dielectric Strength

"Dielectric strength is a measure of the maximum voltage gradient that can be impressed across the dielectric without physical degradation of its insulating properties, leading to breakdown [1.1]." The dielectric strength of electrically insulating materials can be influenced by their intrinsic properties (i.e., the lower dielectric constant, preferably  $\ll$  30, the better dielectric), geometry (i.e., the thicker the better) and flaws (i.e., the lower amount of the cracks, pores, and second phases the better), but also by the measurement conditions (i.e., less humidity the better) [1.1]. Buchanan [1.1] classified a material whose dielectric strength is grater than 5 kV/mm at room temperature as good insulator. In that sense, alumina is one of the best candidates because it has low dielectric constant ( $\sim$  8.2-10.2) and high dielectric strength ( $\sim$ 10-16 kV/mm) [1.1]. Aluminum phosphate (AIPO<sub>4</sub>, berlinite) is also considered as a good dielectric material due to its low dielectric constant value of  $\sim$ 4.5-6 at between 10kHz-1MHz [2.62,61] so it presumably improves the dielectric properties of alumina coatings when contained. According to those results [2.61,2.62], H<sub>2</sub>O contents in AlPO<sub>4</sub> also increase the dielectric constant because hydroxyl group (OH<sup>-</sup>) is randomly occupied in sites and associated with P, forming P-OH. However, in the current study, it is believed that the amount of aluminum phosphate formed by reaction between phosphoric acid and alumina sources (both sols and fillers) during heat treatment is too small (~2 wt %) affects the alumina coatings.

For gases, the breakdown happens due to collision of electrons with gaseous atoms leading to further ionization. For liquids, breakdown is caused by dielectric heating and ionization processes by mobile ions in the liquid. For solids, breakdown can be explained by several possible mechanisms: intrinsic, thermal, ionization, and electromechanical breakdown [1.1]. In addition to the environmental factors, microstructural defects (i.e., impurities and pores) and a local increase of temperature (i.e. local hot spots), influence dielectric strength. Increase in the level of impurities, temperature and porosity decreases dielectric strength [2.64].

Dielectric strength of alumina has been intensively studied as a function of various different additives (i.e., polymers, SiO<sub>2</sub>, and Mg) in the alumina matrix [2.65-2.68] or as an additive in other oxide materials (i.e., SiO<sub>2</sub>) [2.64], and for the various forms for pure alumina [2.69-2.71]. Olding *et al.* [2.67] investigated dielectric properties of alumina and alumina/silica sol-gel composite coatings. They found it difficult to deposit coatings thicker than 100 $\mu$ m without cracks when using small particle sizes (~0.3  $\mu$ m) alone and in a mixture with large particles (~3.6  $\mu$ m). However, they suggested that a using mixture of large (~ 3.6

 $\mu$ m) and small (~ 0.3  $\mu$ m) alumina particles allowed deposition of thick films (>100  $\mu$ m), with high breakdown voltages over 3000V<sub>AC</sub>. García-Cerda *et al.* [2.64] also investigated the dielectric strength with respect to the effects of alumina doped (1 wt.%) into sol-gel derived silica films (0.25-0.4  $\mu$ m) on a silicon substrate at ~ up to 200°C. They found that alumina-doped silica films have higher dielectric breakdown strength (~250 V/mm) than that of pure silica film (~ 6 V/mm).

The dielectric breakdown in solids can be classified as intrinsic, ionization, thermal, and electrochemical [1.1,2.72]. Intrinsic breakdown (by electrons released from an electrode, knocking down other electrons and leading to avalanche breakdown) occurs rarely because the high electric field ( $\sim 10^6 - 10^7$  V/cm) is required. Ionization breakdown occurs in inhomogeneous dielectrics through the partial discharges resulting in the pores or cracks in the ceramic. The ionization of gases inside of the pores occurs when the ceramic is subject to a high enough electric field, resulting in the local generation of heat in the ceramic. This local heat causes a temperature gradient and eventually an increase in the conduction of electrons followed by locally generated thermal stresses. Thermal breakdown is generally caused by the local heating when the heat conduction rate from the electrode is faster than heat dissipation out of the ceramics. Thermal breakdown depends on the thermal conductivity and geometry of an electrode [1.1,2.72].

## 2.4 Residual Stresses in Ceramic Coatings

Thermal expansion mismatch of two joined materials leads to thermal stresses if the system temperature changes. A body uniformly heated to increase its temperature by  $\Delta T$ 

expands, the strain described by a second-order tensor ( $\varepsilon_{ij}$ ). The connecting property is called the linear coefficient of thermal expansion,  $\alpha_{ij}$ , i.e.

$$\varepsilon_{ij} = \alpha_{ij} \,\Delta T \tag{2.4.1}$$

A polycrystalline ceramic consists of a random array of single crystals. If these crystals are non-cubic and the temperature is changed, each crystal will attempt to strain differently from its neighbors. Therefore, adjacent crystals will push or pull on each other, creating local residual strains in the material. These strains are termed residual because they exist even in the absence of the applied stresses. In some cases, this effect can give rise to local micro-cracking. Indeed, this may happen as the material is first cooled after high temperature fabrication. As a reference, fracture strain for polycrystalline ceramic is typically less than 0.001 (0.1%) [2.73-2.76].

The CB-CSG coatings studied in the present work are made of several, e.g. five, layers of alumina. Thermal expansion of each alumina layer, which is newly deposited on a previous layer, may differ from the previous coating layer due to the presence of cracks and pores introduced during the heat treatment. The development of stresses in such multi-layer coatings may be described by the "rod" model in Fig.2.4-1 [2.76]. The rods have different coefficient of thermal expansion,  $\alpha_1, \alpha_2$ , and  $\alpha_3$  ( $\alpha_1 > \alpha_2 > \alpha_3$ ) and different Young's moduli,  $E_1$ ,  $E_2$ , and  $E_3$ . Assume that the structure is initially in equilibrium and is then cooled. If the overall strain induced in the structure by the cooling is  $\varepsilon$ , it is clear that the rods will be subject to residual stresses, as rod 1 would prefer to shrink more than rods 2 and 3. Thus, rod 1 will end up in uniaxial tension and rod 3 in uniaxial compression. The net value of  $\varepsilon$  will be determined by a force balance. Assuming the materials are linear-elastic, the stresses in the rods are  $E_1(\alpha_1 \Delta T \cdot \varepsilon)$ ,  $E_2(\alpha_2 \Delta T \cdot \varepsilon)$ , and  $E_3(\alpha_3 \Delta T \cdot \varepsilon)$ , and by using a force balance, the average coefficient of thermal expansion,  $\varepsilon = \alpha \Delta T$ , where [2.76]:

$$\alpha = \frac{E_1 \alpha_1 + E_2 \alpha_2 + E_3 \alpha_3}{E_1 + E_2 + E_3}$$
(2.4.2)



**Fig.2.4-1** Model for the expansion of (a) three rods with different coefficients of thermal expansion [2.74] and (b) alumina CB-CSG multi-coating layers with viscoelastic organic bond coat, as in the present study.

If the Young's moduli values of the rods (or coating layers) are the same, the average thermal expansion becomes  $\alpha = (\alpha_1 + \alpha_2 + \alpha_3)/3$ . Microcracks lower the thermal expansion in non-cubic polycrystalline materials where there is the significant thermal expansion anisotropy. For example, if the tensile stresses in rod 1 become so high that failure occurs, the stress in this rod is released. The equilibrium is now defined by rods 2 and 3, so  $\alpha = (\alpha_2 + \alpha_3)/2$ . Let's consider  $\alpha_1 = 4, \alpha_2 = 3$ , and  $\alpha_3 = 2$  as assumed in the rod model. In the initial equilibrium average thermal expansion becomes 3. If rod 1 fails due to the stresses, new thermal expansion becomes 2.5. Thus, the overall coefficient of thermal expansion is reduced [2.76].

Accordingly, microcracking in the multilayered ceramic coatings can reduce their thermal expansion (contraction) and stiffness, and relax the residual stresses.

This rod model can be further adapted to the current study by including a CA-derived viscoelastic bond coat, Fig.2.4-1b, represented by a spring-dashpot model [2.78]. If the strain is maintained constant the stress changes with time [2.78] :

$$E(t) = \frac{\sigma(t)}{\varepsilon_0} \tag{2.4-3}$$

where E(t) is the relaxation modulus,  $\sigma(t)$  is stress, and  $\varepsilon_0$  the constant strain. Newton's law, Eq.(2.4-4a), is the equation of motion for a model with a simple linear viscous behavior and integration, Eq.(2.4-4a) for constant stress  $\sigma_0$ , yields Eq.(2.4-4b).

$$\sigma = \eta \frac{d\varepsilon}{dt} \tag{2.4-4a}$$

$$\varepsilon(t) = \frac{\sigma_0}{\eta} t \tag{2.4-4b}$$

where  $\eta$  is the material viscosity. By using Maxwell model [2.79], viscoelastic behavior of a material can be expressed through the combination of Hooke's law (first term on the right side) and Newton's law (second term on the right side):

$$\frac{d\varepsilon}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$
(2.4-5)

where  $\eta = \tau E$ , where  $\tau$  is the proportionality constant between *E* and  $\eta$ , which is known as relaxation time of element. For constant strain application,  $d\epsilon/dt = 0$  and Eq. (2.4-5) can be transformed as follows:

$$\frac{d\sigma}{\sigma} = d\ln\sigma = -\frac{dt}{\tau} \tag{2.4-6a}$$

$$\ln \sigma(t) = \ln \sigma_0 - \frac{t}{\tau} \tag{2.4-6b}$$

Exponentiation and division by  $\varepsilon_0$  produces

$$\frac{\sigma(t)}{\varepsilon_0} = \frac{\sigma_0}{\varepsilon_0} e^{-t/\tau}$$
(2.4-6c)

Where  $\sigma(t)/\varepsilon_0 = E(t)$  and  $\sigma_0/\varepsilon_0 = E$ , so Eq.(2.4-6c) becomes

$$E(t) = Ee^{-t/\tau}$$
 (2.4-6d)

From Eq.(2.4-6d), it is clear that stress relaxation, E(t), is controlled by viscosity of a material (through  $\eta = \tau E$ ).

## 2.4.1 Mitigation of Residual Stresses in Coatings

The strategies to reduce the residual stress in coatings include graded compositions and porosity [2.80-2.82] and inclusion of bond coat at the interface [2.83-2.85] between the ceramic layer and metal substrate. The above methods are widely used in the thermal barrier coatings (TBC) because the magnitude of stresses in the coatings depends on the process temperature, on the coefficient of thermal expansion, and on the Young's modulus of the deposited materials and metal substrates [2.86]. Portinha *et al* [2.81] reported an improvement in the thermal shock resistance of  $ZrO_2$ - $Y_2O_3$  coating by grading the porosity (from ~10% in the first layer to ~17% in the top layer) and by using a bond coat (NiCoCrAlY); the gradient coating layers decrease thermal conductivity during processing and applications [2.80,2.81]. Ilavsky *et al* [2.86] also investigated the effect of yttriastabilized zirconia (YSZ) dispersed in metal (stainless-steel and NiCrAl) as a cermet bond coat, on thermal expansion, by two different spraying methods such as atmospheric plasma spraying (APS) and high velocity oxygen fuel (HVOF) spraying. They found that the thermal expansion via both methods was decreased with the increasing YSZ in the metal (i.e., CTE of  $16.4 \times 10^{-6}$ /°C for 100% NiCrAl and  $12.9 \times 10^{-6}$ /°C for 50% NiCrAl) as shown in Fig.2.4-2. Kozuka *et al* [2.85] reported use of organic polymers as a bond coat, in the system of sol-gel-derived titania coating on silica glass, with poly-vinylpyrrolidone (PVP) bond coat. The critical thickness for the coating was 0.2 µm without PVP, and increased up to 2 µm when PVP was added in the sol at a mole ratio of PVP to titania of 0.5.



Fig.2.4-2 Thermal expansion of (a) stainless-steel-based and (b) NiCrAl-based materials [2.86]

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## 2.4.2 Determination of Residual Stress in Coating Systems

There are the several methods to evaluate residual stresses in coatings, such as hole drilling, layer removal, and curvature measurement. Each technique has its own limitations depending on shape and coating material properties. In the current study, the alumina coated aluminum is subject to the residual stresses caused by thermal mismatch and it is therefore of interest to compare the residual stresses measured by curvature and X-ray diffraction (XRD). The effect of residual stresses on dielectric strength of coatings was also investigated.

## 2.4.2.1 Determination of Residual Stress by Curvature Method

Residual stress determination by curvature is a common method and it is a nondestructive technique. This technique determines the average through-thickness stresses. Based on the knowledge of the average Young's modulus, curvatures, stiffness, bending moment, and geometry of the coated metal, residual stresses can be calculated [2.87]. The curvature origin may be illustrated through the process illustrated in Fig.2.4-3. As a coating system, including metal substrate coated by ceramic, experiences differential shrinkage (on cooling) or expansion in heating, the system bends (as well known for the bi-metal switches) and residual stresses develop in the ceramic and metal, as represented schematically in Fig.2.4-3 [2.80,2.88]. The bending curvature may be used to determine the level of residual stresses.

Consider a homogeneous metal substrate in the shape of a beam with thickness  $h_0$ , stiffness  $I_0$ , Young's modulus  $\bar{E}_0$ , and the point of the neutral axis  $z_0$  where the strain is zero, Fig.2.4-4. For the simple case,  $z_0 = h_0/2$  and  $I_0 = \bar{E}_0 h_0^3/12$ , A state of equibiaxial stress exist in



**Fig.2.4-3** Behavior of a ceramic coated metal substrate in thermal cycling. (a) stress-free initial stage at elevated temperature,  $T_1$ , (b) ceramic coated substrate experiences differential shrinkage after cooling to temperature,  $T_2 < T_1$ . (c) Bending is allowed to balance the stresses in ceramic coating and a metal substrate [2.88]

the plate when the length and width of the beam are significantly higher (i.e.,  $>\times 100$ ) than its thickness which is considered in the current study. Thus, biaxial beam stiffness can then be written as

$$I_{bi} = \frac{I_0}{(1-\nu)} = \frac{h_0^3 \overline{E}_0}{12(1-\nu)}$$
(2.4-9)

where *v* is Poisson's ratio.



Fig.2.4-4 Profile of a coating structure [2.87]

When a coating layer of thickness  $\Delta h$  is deposited on the substrate of thickness  $h_0$ , new average Young's modulus  $\bar{E}_1$  of the coated substrate can be determined. The total thickness of the beam becomes  $h_1=h_0+\Delta h$  as shown in Fig.2.4-4. The stiffness of the new coated beam,  $I_1$  can be obtained experimentally by four-point bending test using following equation [2.87];

$$I_1 = \frac{M}{k} \tag{2.4-10}$$

where M is bending moment and k curvature. From the difference between the bending stiffness  $\Delta I = I_1 - I_0$ , average Young's modulus E of the added layer of thickness  $\Delta h$  can be derived in the thin film,  $(\Delta h \ll h_0)$  as follows [2.87]:

$$E = \frac{\Delta I}{\Delta h} \left( h_0 - z_0 + \frac{\Delta h}{2} \right)^{-2} \tag{2.4-11}$$

Once the Young's modulus of the added layer is evaluated, the new average Young's modulus  $\overline{E}$  and new position of neutral axis  $z_{N1}$  of the beam of total thickness  $h_1$  can be obtained as follows [2.87]:

$$\overline{E}_1 = \frac{\Delta h E + h_0 \overline{E}_0}{h_1} \tag{2.4-12}$$

$$z_{N1} = \frac{h_0 \overline{E}_0 z_0 + \Delta h \overline{E} \left(h_0 + \frac{\Delta h}{2}\right)}{h_1 \overline{E}_1}$$
(2.4-13)

When the second layer of thickness  $\Delta h$  is deposited on the first coated layer, calculation of the new average Young's modulus  $\vec{E}_2$  and neutral axis  $z_{N2}$  with thickness  $h_2$  is followed as described above.

In order to use the above procedure for stress determination, the curvature of the coated beam has to be evaluated before and after processing at a given temperature (i.e.  $300^{\circ}$ C). The variation of curvature,  $\Delta k$ , is enough to provide an internal stress distribution in the beam due to strain mismatch between the substrate and the coating. Knowing  $I_1$ ,  $h_0$ , v,  $z_{N1}$ ,  $\bar{E}$ , and E(z), the average stress in the added layer at the given temperature can be

obtained as follows [2.87]:

$$\Delta\sigma(z) = E(z)(z - z_{N1})\Delta k - \frac{\Delta h E(z)\sigma_0}{h_1\overline{E}_1}$$
(2.4-14a)

$$\sigma_{0} = I_{1} \frac{\Delta k}{\Delta h} \left( h_{0} - \dot{z}_{N1} + \frac{\Delta h}{2} \right)^{-1}$$
(2.4-14b)

where E(z) is the Young's modulus at position z.

## 2.4.2.2 Determination of Residual Stress by X-ray Diffraction

Determination of residual stresses by XRD technique is a non-destructive method and may be used complementary to other methods (i.e., curvature measurement) [2.89-2.97]. When materials are deformed elastically, lattice spacing changes corresponding to the magnitude of the stress applied, which causes the shift of the Bragg diffraction peaks. By knowing the shift of diffraction peaks and Young's modulus of the material, stresses can be determined by X-ray diffraction [2.89-2.96].

There are two different XRD techniques for evaluation of residual stresses in coatings. One is the ' $\theta$  -2 $\theta$ ' method and the other is the ' $Sin^2\psi$ ' method. For better quantitative measurement, the  $Sin^2\psi$  method is commonly used due to the uncertainty of lattice spacing of unstressed material,  $d_0$  [2.97]. However, in the current study, we used the ' $\theta$  -2 $\theta$ ' due to the possibility of observation of strain change with coating deposition, wherein  $d_0$  is observed by measuring ground gel-cast alumina reference material.

Consider a ceramic coated on a metal, with a difference in coefficient of thermal

expansion (CTE) between a ceramic ( $a_C$ ) and metal ( $a_M$ ), where  $a_C < a_M$ . When this coated metal is heat treated, biaxial or triaxial stress systems will develop [2.95]. The structure of the ceramic coating system, as used in the current work, is subjected to a biaxial stress (i.e.,  $t_C \ll t_M$ , where  $t_C$  and  $t_M$  is the thickness of a coating and metal substrate, respectively) [2.93]. The stress,  $\sigma_z$ , in the normal direction (z axis) at the free surface is always zero. Thus, biaxial stresses were considered in the XRD stress measurement.

Consider a portion of the surface of a stressed material, Fig.2.4-5. Stresses,  $\sigma_x$  and  $\sigma_y$ , are parallel to the surface and  $\sigma_z$  is zero. However, strain  $\varepsilon_z$  normal to the surface has a finite value, as follows [2.95];

$$\varepsilon_z = -v(\varepsilon_x + \varepsilon_y) = -\frac{v}{E}(\sigma_x + \sigma_y)$$
(2.4-15)

where  $\varepsilon_x$ ,  $\varepsilon_y$ , and  $\varepsilon_z$  is a strain in the direction of x, y and z, respectively, and v is Poisson's ratio and E is a Young's modulus of stressed body. The value of  $\varepsilon_z$  can be found by measuring the lattice spacing d under stress and  $d_0$  at the stress-free state of planes parallel to the surface and given by [2.95]:

$$\varepsilon_z = \frac{d - d_0}{d_0} \tag{2.4-16}$$

From the Eqs.(2.4-15) and (2.4-16) and considering that  $\sigma_x = \sigma_y = \sigma_c$ , the value of the residual stress parallel to the free surface can be obtained as follows [2.95,2.97]:

$$\frac{d-d_0}{d_0} = -\frac{v}{E}(\sigma_x + \sigma_y) \tag{2.4-17a}$$

$$\sigma_{c} = -\frac{E}{2\nu} \frac{d - d_{0}}{d_{0}}$$
(2.4-17b)



**Fig.2.4-5** Directions of stress and strain ( $\sigma_x$  and  $\sigma_y$  parallel to the surface and  $\sigma_z$  normal to the surface) at the surface of a stressed material.

The magnitude of the stresses determined by the XRD method may be different from that measured by the curvature method because penetration depth of X-ray is very shallow (i.e.,  $< -5 \ \mu$ m) and hence the stress measured by XRD is the surface stress. However, the trend of the stresses determined by XRD methods agrees well with the curvature method. Kesler *et al* [2.93] compared residual stresses of Mo coatings on steel by XRD and curvature measurements, Fig.2.4-6. The stress values measured by XRD showed lower values than those measured by curvature measurement due to the nature of the two measurement techniques. The values from XRD can be further reduced due to surface roughness effects causing lower penetration of X-rays, while the curvature measures the average stress in an added layer [2.93].



**Fig.2.4-6** Comparison of stresses of Mo coatings on steel measured by (a) X-ray diffraction and (b) curvature measurement [2.93]

## CHAPTER 3 SCOPE AND OBJECTIVES

## 3.1 Scope of the Investigation

This study focuses on innovative approaches to deposit  $> 200 \text{ }\mu\text{m}$  thick phosphatebonded alumina coatings on aluminum substrates, for the application as electrically insulating thick films. The key feature of the work is development of novel ceramic processing methodology for thick ceramic films on metallic substrates with substantially larger coefficient of thermal expansion. The following four processing approaches are undertaken to minimize the effects of the relatively large thermal expansion / contraction mismatch between alumina and aluminum alloy (AA5052) for the process of thick dielectric films while avoiding coating failure: (i) the use of the composite sol-gel (CSG) for the thick dielectric ceramic coatings (ii) the relatively low processing temperature of 300°C by using the novel chemically bonded composite sol-gel (CB-CSG) with chemical reaction between phosphoric acid and alumina; (ii) reduction of thermal stresses through the use of novel citric acid - derived organic (viscoelastic) bond coats, and (iii) multilayer (graded) coating deposition. The deposited films are characterized for the microstructural features, residual stress (through bending and XRD methods) and dielectric strength. It was discovered that segregation of CA/alumina sol nano-composite during the coating heat treatment process to the interface between the coating and the substrate allows forming in-situ nano-composite organo-ceramic bond coat (after partial pyrolysis of CA during the heat treatment). The effects of precursor preparation (alumina, sol, and CA) and coating thickness buildup on residual stress development and dielectric properties of the coating were investigated in terms of the coating thickness.

#### **3.2 Objectives**

The principal objective is to study and develop novel ceramic coating processing techniques to decrease residual stresses in thick ceramic films on metals. In particular, materials with relatively large difference in coefficient of thermal expansion (CTE) between the two phases are of interest, such as alumina and AA5052.

In order to reach the above broad goal, the following processing objectives and techniques were explored, with the specific tasks defined for each objective:

- Objective: to reduce shrinkage of ceramic films on metallic substrates; to address this objective, the Composite Sol-Gel (CSG) technique was used for coating slurry preparation. The objective was to overcome the basic disadvantage of the conventional sol-gel technology, such as high shrinkage (up to ~95 vol.%) causing micro-cracking and thick coating failure. CSG can reduce the shrinkage to ~75 vol.%
- Objective: to reduce process temperature; to achieve this, CB-CSG technique for ceramic bond formation was developed. The chemical reaction between phosphoric acid and alumina sol provides ceramic bond in the coating at process temperatures of 300°C, and the chemical reaction between phosphoric acid and metallic substrate provides adhesion of the coating to the substrate; the relatively low processing temperature of 300°C allows for lowering thermal strain and reduction of residual stresses.
- Objective: to reduce stress buildup during deposition of thick films: addressed by multi-layer coating deposition. The objective to achieve a thick, low density of cracked coating, and to prevent delamination of the ceramic coatings, requires that the

deposition process is step-wise; in this work it was necessary to deposit multiple layers, ~40  $\mu$ m thick each, including the heat treatment cycle after each layer deposition, to obtain an overall coating thickness of >200  $\mu$ m. The system characteristics, in particular residual stress, are monitored after depositing each consecutive layer of coating.

Objective: to relax thermal stresses in coating through provision for viscoelastic flow at interface; to achieve this objective, organo-ceramic bond coats were introduced. In order to decrease the effect of the difference in CTE between the alumina and AA5052, causing unacceptably large residual stresses in the >200 µm thick coatings, citric acid / alumina sol composite is utilized as a bond coat for the mitigation of the stresses by viscoelastic relaxation at the interface.

The process development objectives listed above are augmented by characterization of the coating-substrate systems processed at various conditions. Residual stresses were monitored using a curvature method and the results were compared to a X-ray diffraction (XRD) method. As the applied aspect of this work contemplates use of the thick coatings as electrical insulators for heating elements, the objective is also to characterize the coatings for electrical properties, in particular breakdown voltage and dielectric strength.

## CHAPTER 4 EXPERIMENTAL METHODOLOGY

## 4.1 Processing of Alumina Composite Sol-Gel

## 4.1.1 Alumina Composite Sols

Boehmite (AlOOH, SOL-2PK, Condea, Germany) was used as a precursor for the alumina sols and citric acid (CA, 99.7%,  $C_6H_6O_7$ , anhydrous, FisherScientific, USA) was used as a dispersant and a bond coat precursor. Compositions of the composite sol are given in Table 4.1-1. 0.1 wt.% of CA in the total contents of the coating solution was dissolved in 150ml of distilled water, and alumina sol precursors (1.5M) were added into the distilled water and mixed at pH= 4. In order to obtain a homogeneous dispersion, the solution was ultrasonicated (with Ultrasonic Disruptor Probe, Horiba, USA) at room temperature for 10 min. The most suitable ratio of the total amount of alumina powders dispersed to the gel derived alumina sols was previously found to be 86:14 [4.1].

Table 4.1-1	Preparation	of the alumina	composite sol	slurry l	by the	concentration	of	fine
alumina par	ticles, ~0.5 μm	n, in coarse alur	nina particles, ~	-3 μm				

		Ratio of Fine to Coarse Alumina Particles				
	-	30:70	35:65	40:60	45:55	50:50
$H_2O$ (Distilled) (g)		150	150	150	150	150
Citric Acid	(g)	0.234	0.234	0.234	0.234	0.234
AlOOH (g)		13.5	13.5	13.5	13.5	13.5
$Al_2O_3(g)$	0.5 μm	21.15	24.68	28.2	31.73	35.25
	3 µm	49.35	45.82	42.3	38.775	35.25
Description	1	A30	A35	A40	A45	A50

In the current study, two different particle sizes of alumina powders (A16-SG, ~0.5  $\mu$ m, and P662B, ~3  $\mu$ m, Alcoa, USA) were dispersed in the alumina sol for the fabrication of the composite sols with varying the ratio of fine to coarse particles (30:70, 35:65, 40:60, 45:55, 50:50; referred to as mix A30, A35, A40, A45, and A50, respectively), Table 4.1-1. Ball-milling (~140 rpm) for 12h, 24h, and 48h was conducted for optimizing the homogeneous alumina composite sols. Table 4.1-1 summarizes the sample preparations with the amount of each material.

## 4.1.2 Characterization of Alumina Composite Sols

Particle size distribution was analyzed by a particle size distribution analyzer using a light scattering method (Horiba CAPA-700, USA). The composite sols of each concentration were diluted and put into a test tube provided along with the analyzer. The test tube was placed with a reference (i.e. distilled water) in position and was centrifuged at 960 rpm for  $\sim$ 30 min. In addition to the particle size distribution, the specific surface area (m<sup>2</sup>/g) of particles in the composite sols of each concentration was calculated by assuming spherical shape of particles of known density (i.e. 3.96 g/cc for alumina).

A water absorption method (generally called 'Archimedes Method') was used to measure the density of the alumina composite sol-gel. Due to the difficulty of direct measurement of coating porosity on aluminum alloy (i.e. due to coating separation in water during vacuuming), the density of gel-cast CSG alumina was considered as representative of that of the alumina coating, i.e. by neglecting kinetic effects during spray coating. Alumina composite sols were gel-casted in a tray until they completely dried in air and were subsequently fired at 300°C for ~10min followed by the phosphating (refer to Section 4.2.3). Thereafter, the samples were set in water and placed in a vacuum chamber. Water absorption was completed by the vacuuming, at pressure of ~10 mmHg. Then all the samples were weighed for the calculation of the density as follows;

$$D_a = \frac{W_a}{W_s - W_i} \times \rho_{water} \tag{4.3-1}$$

where  $D_a$  is the apparent density,  $W_a$  the weight of a sample in the air,  $W_s$  the water-soaked weight of the sample, and  $W_i$  the weight of the sample immersed in water. The weight of the samples in air (" $W_a$ ") was pre-conducted prior to water absorption.

A viscometer (Model DV-II, Brookfield, USA) was used to measure the viscosity change of the alumina composite sols with time. The alumina CSG slurry was placed in the viscometer right after taking the slurry out of the ball-milling device. Time interval between taking out and measuring the viscosity of the slurry was approximately 2 min. Data were sequentially collected at 10 second intervals for 1h with a total of 360 data points. The minimum reading sensitivity is 20 cp for the current equipment setting (i.e. 50 rpm, spindle #5).

#### 4.1.3 Thermal Behavior of CA

Citric acid was used as a dispersant for both alumina composite sol-gel and bond coat formation. According to the literature [4.2], the melting point of the CA is  $\sim$ 150°C and it decomposes at  $\sim$ 170°C. In order to verify this thermal behavior of CA, a Differential

Thermal-Thermo Gravimetric Analyzer (DT-TGA, SETARAM TG96, France) was utilized. About 30 mg of CA was placed in an alumina crucible and heated up to 500°C in a vacuum at heating rate of 10°C/min.

In order to simulate the physical behavior of CA in the alumina coating during heat treatment, porous sintered alumina with ~60 vol % of porosity (i.e. alumina slurry with a particle size of 3 µm was cast into a rectangle mold, dried, and then heat treated at 1200°C for >10 hours) was impregnated with CA. In the model experiment, the sintered alumina was placed on CA (solid) in a Petri-dish, so the only bottom side of the alumina contacted the CA. Then the Petri-dish was heat-treated up to 300°C to observe the pattern of CA melting and wetting the alumina. Scanning electron microscopy (SEM, Hitachi S-3000N, Japan) and Energy Dispersive X-ray analysis (EDX, Hitachi S-3000N, Japan) were used to analyze the morphology and chemical composition of such CA containing alumina.

## 4.2 Processing of CB-CSG Coatings for Thick Dielectric Films

The CB-CSG coating process in the present study consists of (i) preparation of composite sols (as described above) and surface preparation (sand-blasting) of AA5052 substrates; (ii) coating deposition (by spraying); (iii) specimen heat-treatment at 300°C; (iv) specimen impregnation with diluted phosphoric acid (by spraying) to achieve chemically bonded composite sol-gel, and (v) heat-treatment again at 300°C. These steps produced a single coating layer of the thickness of ~40  $\mu$ m. Therefore to reach the total thickness of ~200  $\mu$ m, the process (steps ii-v) was repeated five times. The steps of heat-treatment and phosphating were conducted in sequence after each coating layer deposition. The following

sections explain the above steps in detail.

## 4.2.1 Surface Preparation of AA5052 Substrate

Sand-blasting of AA5052 substrates was conducted as a surface preparation prior to the coating deposition, to promote interlocking between substrates and the ceramics deposited. AA5052 was cut into 55mm×10mm as required for the test of Young's modulus and residual stress through curvature measurements. The substrate was sand-blasted (Cyclone, blasting system, USA) with a pressure of ~90 psi, using silica grit size of 60. Figure 4.2-1 compares the cross-sectional images of the non-surface treated and a sand blasted aluminum substrate. In the case of the non-sand blasted substrate, the aluminum



Fig.4.2-1 Cross sectional SEM images for (a) non-sand blasted (b) sand blasted AA5052 substrate.

substrate has an even surface, resulting in the failure of a coating deposition due to the absence of the interlocking between the coating and the substrate. On the other hand, a rough surface is observed in the sand-blasted aluminum substrate, improving the initial

bonding of the coating through mechanical interlocking. The roughness of a sand blasted substrate was measured by using a Form Talysurf Series 2 (Talyor Hobson LTD., England), Fig.4.2-2. The method of a center-line average  $R_{a}$ , was used and defined as follows [4.3]:

$$R_{a} = \frac{1}{L} \int_{0}^{L} |z| dx$$
 (4.2-1)

where z is measured from the mean line and L the profile sample length in the x-direction.



**Fig.4.2-2** Profilometer of the sand blasted aluminum substrate used in this work and schematic of determination of roughness value, Ra, using a mean line [4.3]. The average roughness,  $R_a$  of the substrate shown above is 5.87 µm.

#### 4.2.2 Spray Coating

Spray coating for the composite sol-gel (CSG) coating was conducted on one side of the AA5052 substrates. The sand blasted AA5052 substrates were placed on a flat board and sprayed (Delta Air Spray Gun, Graco Inc., USA) with alumina composite sols at a pressure of ~25 psi, as shown in Fig.4.2-3. For the best coating surface finish, the slurry must reach proper viscosity range of 200cp-400cp. If viscosity is too low, sprayed slurry flows along the surface of the substrate. If the viscosity is too high, the slurry is not sprayed properly and the

spray gun is plugged. A maximum film thickness of 40-50 µm without coating failure (i.e. cracks causing coating separation during coating process) was achieved by single deposition. The coated substrate was then dried in air followed by the heat-treatment at 300°C for 10min. Then, phosphating is required for chemical bonding and hardening (details are in the following section below). The processes can be repeated to achieve desired coating thickness. In the current study, 5 multi-layers were deposited in the same manner.



Fig.4.2-3 Spray coating setup. Spraying has been repeated 5 times until the desired thickness of coating (>200  $\mu$ m) is reached.

## 4.2.3 Chemical Bonding of the Coatings by Phosphating

20 wt% diluted phosphoric acid ( $H_3PO_4$ , 85%, Fisher Scientific, USA) was applied on top of the CSG coated AA5052 via spray with a pressure of ~25 psi. The phosphoric acid penetrated into the coating pores during drying, and generating a chemical bonding via reaction between alumina and phosphoric acid during heat treatment, Fig.4.2-4.



Fig.4.2-4 Schematic of the Chemically Bonded Composite Sol-Gel [2.33]

Phosphating improves the interfacial adhesion by forming an aluminum phosphate between aluminum substrates and phosphoric acid according to following reaction [4.4]:

$$2Al + 6 H_3PO_4 \rightarrow 2Al(H_2PO_4)_3 + 3H_2 \uparrow$$

$$(4.2-1)$$

As shown in Eq.(4.2-1), hydrogen gas can be generated during phosphoric acid application onto the alumina coated surface. It may cause coating failure by delamination of layers with excess amount of phosphate during processing, so control of the amount of phosphate must be carefully conducted. Thus, phosphating is one of the most significant steps of the process and great deal of care must be taken to execute it properly. If phosphating is applied directly onto AA5052 prior to CSG coatings, thin aluminum phosphate film formed by the chemical reaction between phosphoric acid and AA5052 would be damaged by hydrogen, resulting in the decrease in the adhesion of CSG to AA5052. This is the reason why post phosphating of

CSG coatings was executed in the current study.

In order to determine the most suitable concentration of phosphating in the current work, different concentrations (i.e. 0.5, 1, 1.5, and 2 wt.%) of diluted phosphoric acid were added into the pre-prepared composite alumina sols. Those composite sols were then poured ("gel-cast") in a circular aluminum tray and completely air-dried for several days. The 2 wt.% of phosphoric acid-contained alumina composite gels demonstrated no cracking even if it had a large shrinkage (i.e., ~40 vol.%), while cracks occurred in all other concentrations. However, the problem of controlling the amount of phosphating during the spray processing of the coatings still remains a challenge of the current study.

## 4.2.4 Heat Treatment

A heat treatment of the CB-CSG alumina coatings is necessary to thermally activate the processes of sol decomposition and chemical bonding (phosphating) reactions to cure the coating and to increase the coating adhesion. After deposition of CSG alumina and drying, the alumina coated AA5052 were heat-treated in air at 300 °C (at the heating rate of ~10 °C/min) for 10min and then slowly cooled (<1°/min) to room temperature. After phosphating (described in Section 4.2.3), the specimens were then heat-treated at the same conditions for the chemical bonding. These steps were repeated until the desired coating thickness was obtained. In the current study, 5 layers were deposited and thus 10 heat treatments were executed.

# 4.3 Characterization of CB-CSG Coatings for Thick Dielectric Films4.3.1 Dielectric Strength Measurements

The Sentry 20 AC/DC Hipot Tester (QuadTech, Inc., USA) was used to measure the breakdown voltage, up to 5 kV-AC and 6 kV-DC. A copper flat-end rod electrode with 3 mm diameter was utilized in contacting to a coating surface, Figure 4.3-1. The voltage was applied for at least 3 seconds according to safety standard, at 5 points per coating sample (typically one point in the center and 4 points in the adjacent corners were selected). The smallest and the greatest values were discarded (the smallest value of a breakdown voltage may significantly affect material's dielectric property in real cases. However, in the current study, no large differences between the smallest and second-smallest values were observed. The values measured at each point are present in the appendix, Table A-4). Dielectric strength (DS, kV/mm) is defined as  $DS=V_B/t$ , where  $V_B$  is the breakdown voltage and t the thickness of the sample.



Fig.4.3-1 Setup of the hipot tester for the breakdown voltage measurement.

## 4.3.2 Curvature Measurements

'Talysurf profilometer and 3D surface mapping (Taylor Hobson LTD, England) were utilized to measure the curvature before and after each heat treatment. This device has a stylus at the end of an arm scanning across the surface of the sample, Fig.4.3-2. A side of sand-blasted AA5052 before coating was faced down on the station and the initial curvature of the AA5052 was measured by probing the surface three times with 0.5 mm span in each line and the averaged curvature for each AA5052 was computed. After each alumina coating deposition on such AA5052 and the heat treatment, the same side (opposite side or noncoated side) of the coated samples as the surface previously measured was being probed with the same condition, and then the change in the curvature before and after coating and heat treatment was observed. This process was repeated after each deposition until the whole coating process was completed.



Fig.4.3-2 Sample location in Talysurf Profilomer.

## 4.3.3 Residual Stress Determination by X-ray Diffraction

X-ray diffraction (MultiFlex X-Ray Diffractometer, Rigaku Co., Japan) was utilized to obtain the residual stresses of the surface of the coatings for validation of residual stresses measured by curvature measurement. By knowing the strain changes of the surface of the coatings as well as Young's modulus and Poisson's ratio of a coating material, residual stresses of the surface of each deposited coating layer can be calculated as described in Eqs.(2.4-15) through (2.4-17). In order to observe the strain changes of the surface of the coated layers, it is necessary to measure the lattice spacing of an unstressed material, which was the gel-cast alumina in the current study. This gel-cast alumina was heat-treated at 300°C followed by phosphating by dipping into the 20 % diluted phosphoric acid and heat treated at 300 °C for ~10 min, ground into powder, and scanned for XRD reference data. Strain for each subsequent coating layer was measured and compared with the reference data. After completion of the measurements, the software (MDI Jade 7, Materials Data, Inc, USA) automatically calculates a lattice spacing of each sample at a certain angle,  $2\theta$ . Intensity of the beam was 40 kV with 20 mA and 2-theta (2 $\theta$ ) was set up from 20 to 80 degrees with a speed of 2 degrees/min.

## 4.3.4 Young's Modulus Measurement of Alumina CB-CSG Coatings

Average Young's modulus,  $\bar{E}$ , of the alumina coated AA5052 at room temperature and an elevated temperature up to 300 °C was measured by 'Dynamic Mechanical Thermal Analyzer (DMTA V, Rheometric Scientific, USA), Fig.4.3-3, which is based on the 3-point bending theory. 'This unit examines viscoelastic or elastic materials according to temperature and frequency dependent behavior. A small strain (deformation) is imposed on the material by applying a stress. The amount of strain resulting from the applied stress leads to information about the modulus of the materials [4.5].' All measurements were repeated three times with different coating samples and then average data were obtained.

Specific dimensions of the specimen were required to fit in the device (i.e., 55 mm in length and ~6.5 mm in width for a typical beam). The strain  $\varepsilon$  (based on specimen geometry) of the specimen was obtained by using Eq. 4.3-1a and 4.3-1b. This strain was used as a



**Fig.4.3-3** Sample location in Dynamic Mechanical Thermal Analyzer, DMTA for a stiffness and Young's modulus measurements for beam samples.

parameter in the operating software and stresses exerted in the specimen were observed through Eqs. 4.3-2a and 4.3-2b [4.7]. The average Young's modulus ( $\sigma/\epsilon$ ) of the specimen was then obtained using the formulas (Eqs.4.3-1 and 4.3-2);

$$\varepsilon = K_{\varepsilon} \cdot D \tag{4.3-1a}$$

$$K_{\varepsilon} = \frac{3t}{l^2} \tag{4.3-1b}$$

where  $\varepsilon$  is the strain of the sample,  $K_{\varepsilon}$  the strain constant for a given geometry, and D the displacement of the drive shaft (=0.05 mm), t is the total sample thickness (substrate+coating) and l is the length of span (= 40 mm).

$$\sigma = K_{\sigma} \times F \tag{4.3-2a}$$

$$K_{\sigma} = \frac{3l}{wt^2} G_c \tag{4.3-2b}$$

where  $\sigma$  is the stress (MPa),  $K_{\sigma}$  the stress constant, w the width of a specimen (mm), F is the force necessary to produce the sample displacement D (measured through the load cell), and  $G_c$  the gravitational constant (9.8 m/s<sup>2</sup>).

In order to measure the Young's modulus of the coated specimens at room temperature, the strain of the sample was defined (by the user based on the geometry of the specimen using Eq. 4.3-1) and entered into a software program as a test parameter; a load is automatically applied to the specimen to reach the specified strain of the specimen which was manually defined in the beginning. Then this applied force was used for calculating stresses exerted to the coated specimen. In addition, average Young's modulus of the specimens at elevated temperature up to 300 °C was also observed. For the observation of the change in the mechanical behavior of the specimens during the heat treatment (including heating and cooling), a temperature of the DMTA was held at 300°C for 30 min. Table 4.3-1 provides examples of the data used in this measurement. A complete set of data for all samples is included in the Appendix Table A-1.

For the verification of the measurement mentioned above, the change in Young's modulus of coated samples at various temperatures (including heating up to 300 °C and cooling to room temperature) in terms of time, DMA (Q800, TA Instruments, USA) has been used, Fig.4.3-4. DMA is the same as dynamic mechanical thermal analyzer (DMTA) but an alternative name. 3-point bending theory is also utilized throughout the test. Geometry of all samples is required to be a beam (~55 mm X 10 mm). Those beam specimens are supported at both ends and a force is applied in the middle. The amplitude (10  $\mu$ m) of the beams for the displacement is set up for the constant strain of the sample, and then the magnitude of the force,~ 1N, is applied to the beams.

Coating layers	Total Thickness (mm, substrate + coating)	Width (mm)	Strain ( <i>ɛ</i> )
AA5052 (Substrate)	1.56	6.32	0.000293
1 <sup>st</sup>	1.6	6.45	0.000300
2 <sup>nd</sup>	1.65	6.48	0.000309
3 <sup>rd</sup>	1.69	6.5	0.000317
4 <sup>th</sup>	1.75	6.5	0.000328
5 <sup>th</sup>	1.81	6.55	0.000339

**Table 4.3-1** Example of sample geometries and strain used to obtain the Young's modulusby using Dynamic Mechanical Thermal Analyzer, DMTA


Fig.4.3-4 DMA for measuring average Young's modulus at various temperatures in 3-point bending.

Temperature was ramped to 300°C at 10°C/min, and held for 30 min to simulate the coating heat treatment process. The change of the Young's modulus on cooling was also measured. Then resultant stress/strain provides the average Young's modulus ( $\sigma/\varepsilon$ ) of the beams as follows.

$$\sigma = \frac{3 \cdot F \cdot L}{w \cdot t^2} \tag{4.3-3a}$$

$$\varepsilon = \frac{6 \cdot \delta \cdot t}{2 \cdot L^2 \cdot \left[1 + \frac{6}{10} \cdot (1 + v) \cdot \left(\frac{t}{L}\right)^2\right]}$$
(4.3-3b)

where  $\sigma$  is the stress (MPa),  $\varepsilon$  the strain, F the applied force (N),  $\delta$  the amplitude of deformation ( $\mu$ m), L the half sample length (span, mm), t the sample thickness (mm), w the

sample width (mm), and v the Poison's ratio.

The Average Young's modulus (coating + substrate),  $\vec{E}$ , for the coated AA5052 samples of any given thickness at room temperature, was used to evaluate average residual stresses in coatings by combining Young's modulus of added layer, E (~10 GPa, by micro-indentation method), curvature change before and after heat-treatment as well as geometry of coated aluminum. The calculation was previously described in Eqs.(2.4-10) through (2.4-14) in Chapter 3 and their results will be detailed in Chapter 6.

## CHAPTER 5 STUDY OF ALUMINA COMPOSITE SOL-GEL FOR THICK DIELECTRIC FILMS

### 5.1 Characterization of Alumina Composite Sol

The coating process included two different types of alumina particles (~0.5  $\mu$ m and ~3  $\mu$ m average size) as fillers. It was therefore necessary to define the most suitable composition of the coatings. In this chapter, characterization of composite sols and composite gel-cast samples are discussed. CSG viscosity, particle size distribution, and settling characteristics were investigated, and morphology and density were observed for alumina gel-cast.

## 5.1.1 Viscosity of Alumina Composite Sols with Various Concentrations of Fine Alumina Particles

The viscosity of the alumina composite sols with 5 different concentrations (A30, A35, A40, A45, and A50) of the fine alumina particles, ~0.5  $\mu$ m, was compared for various ball-milling times, and plotted as a function of aging times, for up to 60min. Figure 5.1-1 shows the viscosity of the alumina composite sols with various concentrations (A30-A50) after 12 hr ball-milling. There is significant difference between A50 and other samples. A50 exhibits initially higher viscosity than others and also shows rapid viscosity change up to ~ 600 cp within 60 min, due to the overall higher surface area of the larger amount of fine alumina particles in this sample. This large viscosity change over such a short period of time indicates that this mixture will not be sprayable since the suitable range of viscosity for spray-coating is 200-400 cp. Even though this range of viscosity lasts ~10 min for A50, this fast viscosity change may provide wide size distribution of the as-sprayed CSG droplets (i.e., from below 1 $\mu$ m to tens of micrometers), which results in uneven coating surface during

spraying. Therefore, A50 with 12h ball-milling was not suitable for the coating processing. Other concentrations of A30-A40 show significantly lower viscosity than the most suitable viscosity of 200-400cp for spray coatings in the current work although the viscosity of A45 has slightly increased after 50 min.



Fig.5.1-1 Viscosity of alumina composite sols ball-milled for 12 hours. The concentration in the legend box stands for the amount of fine alumina particles ( $\sim 0.5 \mu m$ ) in the mixtures with coarse ones ( $\sim 3 \mu m$ ).

The viscosity change observed for the slurries is related to the settling rate of alumina particles in the sol suspension. Settling velocity of the particles depends on the size of particle and the viscosity of a suspension. That is, unless the particles dispersed are small enough to be held in suspension by Brownian motion they will undergo settling. The particle settling velocity is given by [5.24].

$$v = \frac{2(\rho_1 - \rho_2)g_a a^2}{9\eta}$$
(5.1-1)

where *a* is the radius of a particle,  $\eta$  viscosity of a medium,  $\rho_1$  and  $\rho_2$  the densities of the particle and fluid, respectively, and  $g_a$  is the gravitational constant. Eq. (5.1-1) is often used to measure particle size by determining the rate of particle settling [5.24].

The presence of the large agglomerated particles leads to undesirable particle separation effects caused by fast sedimentation [5.14]. As a result, a spindle measures viscosity of the alumina sol suspension rather than whole composite slurry. Thus the slurry with high contents of larger particles (i.e., < A50) shows lower viscosity than that with low contents of larger particles (i.e. A50).

Figure 5.1-2 compares the viscosity change for all samples, versus time, after 24 hr ball-milling. According to the preliminary results, horizontal doted lines at the ~200-400 cp represent viscosity of the spray-able range for the best coating result (of the composite sols i.e., ~10  $\mu$ m thickness in one direction pass without solution flow along the edges of the substrate as well as a fast gelation of ~10-20 min after spray). The rapid viscosity change of A50 is observed until ~1000 cp in 20min and it increases gradually. In other words, during the measurement of the viscosity, the slurry becomes gelatinous and a gelatinous speed is

dramatically increased at a certain time due to the hydrolysis and condensation mechanism of the sol-gel. This fast gelation causes the dramatic increase in the shear stress (because of a little liquid flow, lowering a speed of spindle) of the surface of the spindle which results in an increase in the viscosity. After this fast gelation period, its gelation speed is slowly decreased causing gradual increase in the viscosity. The viscosity of 200-400 cp in A50 remains only for ~5min. On the other hand, A40 and A45 show the slow increase of viscosity which is suitable for spray coating. A30 and A35 exhibit viscosity less than 100 cp which is not sufficient for the spray coating due to the frequent flow of solutions along the surface during spraying. Regarding the most suitable viscosity of 200-400 cp and the time taken to reach the viscosity of 200 cp, A40 has been determined as the best candidate for spray coatings in the current work.



**Fig.5.1-2** Viscosity of alumina composite sols ball-milled for 24 hours. Dot lines show the range of the viscosity (~200-400 cp) suitable for spray coatings.

Figure 5.1-3 illustrates the viscosity change for all samples as a function of time, after 48h ball-milling. The viscosities of the A45 and A50 rapidly increase due to the result of breaking down agglomerated alumina particles during the ball-milling. A40 demonstrates a gradual viscosity increase without abrupt change. Although A40 shows gradual change in viscosity, the spray-able time range is much shorter (e.g. ~10min) than that after 24 h ball-milling (e.g., ~30min). A30 and A35 still show a low viscosity until 50min aging and it shows the suitability for spraying viscosity, 200-400 cp, after 50 min.



**Fig.5.1-3** Viscosity of alumina composite sol ball-milled for 48 hours. Dot lines show the range of the viscosity (200-400 cp) suitable for spray coatings. The concentration of A40 offers longest work time while A45 and A50 are beyond the workable range. A30 and A35 are below the viscosity range suitable for spray coatings.

As a result of these observations it is determined that higher concentration of fine particles (from A30 to A50) in the slurry and longer ball-milling time increases the slurry viscosity. Initially, ball-milling breaks down particles, and thus increases specific surface area. Second (later) part of ball milling is to mix the slurry homogeneously to achieve a stable suspension [5.27]. According to the above observations, supported by previously reported relationship between the viscosity and the surface area [5.14,5.24,5.26], the slurry with 24h ball-milling has been selected for further experiments. Figure 5.1-4 demonstrates the change of the specific surface area (determined by particle size analyzer (CAPA-700, Horiba, Ltd. Japan)) and the viscosity of CSG (alumina particles dispersed in the alumina sols) by varying the concentration of fine alumina particles.



Fig.5.1-4 Viscosity and specific surface area of 24h ball-milled mixed CSG with varying concentration of the fine particles.

The higher surface area correlates well with higher viscosity, for all types of samples. Based on these results, A40 with 24h ball-milling time has been selected for further research on CB-CSG spray coatings.

### 5.1.2 Particle Size Distribution in Alumina CSG

Figure 5.1-5 shows the particle size distribution of as received fine (~0.5 µm) and coarse (~3 µm) alumina particles, as determined by Horiba Particle Size analyzer (refer to Section 4.1.2). The bars indicate the frequency (or wt%) of each particle size range and the lines shows the cumulative frequency. The majority of particles (~80 %) are  $\leq 1 \mu m$  while the minority of particles (~20 %) is >1  $\mu$ m. Figures 5.1-6 show the particle size distribution for the 24h ball-milled alumina composite sols with varying concentration of the fine particles. It is observed that the particle size distributions are gradually wider with increasing concentration of fine particles. For example, the range of the particle size distribution for both A30 and A35 is from 0.2 µm to 3 µm, Fig.5.1-6a,b, from 0.2 µm to 5 µm for A40 and A45, Fig.5.1-6c,d, and from 0.2 µm to 6µm for A50, Fig.5.1-6e, respectively. It is observed that the cumulative frequency of sub-micron sizes is < 40 % for A30 and A35 while the frequency of the sub-micron sizes of > 40 % occurs in > A40-A50. The maximum particle size of alumina composite sols increases with the concentration of fine particles, likely due to agglomeration of fine particles during ball-milling. However, the agglomerated particles do not significantly influence the viscosity.



**Fig.5.1-5** Particle size distribution of 24h ball-milled alumina composite sols with single particle size fraction: (a) fine alumina particles and (b) coarse alumina particles (submicron range in the inset).



**Fig.5.1-6** Particle size distribution of the alumina composite sols with varying concentrations of the fine particles, after 24h ball-milling. (a) A30, (b) A35, (c) A40, (d) A45, and (e) A50.



Fig.5.1-6 (continued)



Fig.5.1-6 (continued)

Table 5.1-1 summarizes the particle size distribution measurements for the alumina composite sols as well as the specific surface area. The specific surface area slightly increases for A30 and A35, and significantly increases (by about 7 %) from A35 to A40.

Table 5.1-1	Summary of	particle	size	distribution	of the	alumina	composite	sols	after	24h
ball-milling.										

Concentration of Fine Alumina, wt%	Specific Surface Area, m²/g	Standard Deviation, µm	Diameter in Median, μm	Minimum/Maximum Particle Size, μm
P662B alone	0.785	1.57	2.17	2/4
A30	1.914	0.54	1.23	0.2/3
A35	1.916	0.59	1.23	0.2/3
A40	2.056	0.81	1.13	0.2/5
A45	2.066	1.01	1.14	0.2/5
A50	2.076	1.24	1.17	0.2/6
A16 alone	3.782	0.64	0.44	0.2/3

No significant effect of the concentration of fine particles on the viscosity was observed for A30 and A35 whilst the remarkable increase in the specific surface area for A40 appears to leading to viscosity change (e.g., from <40 cps to  $\sim$  200 cps in the first 20 min after ball milling) leading to the best performance of this suspension in the current spray coating.

### 5.1.3 Settling of Alumina Particles in the Composite Sol

Settling rate of particles dispersed in a suspension is a simple method for evaluating the degree of dispersion, or stabilization of suspension [5.23]. The agglomerated and coarser particles settle faster while fine particles in stable slurries settle slower and produce densely packed cake. According to Eq.(5.1-1), settling depends on the size of particle and the viscosity of a medium. Figure 5.1-7 shows the calculated settling velocity of alumina particles dispersed in the alumina sol, according to Eq.(5.1-1). For the evaluation of settling



**Fig.5.1-7** Prediction of the velocity of settling alumina particles in the alumina sol suspension in terms of the radius of the particles.

particles in the current study, the viscosity of the fluid (i.e., alumina sol suspension) used was 15 cp [4.1], density of the particles and fluid, 3.96 g/cc and 1 g/cc, and gravity constant 9.81 m/s<sup>2</sup>. According to Eq.(5.1-1), the velocity increases with the radius of the particles. It is observed that the sedimentation velocity of the fine particles, ~0.5  $\mu$ m, is approximately 35 times slower than that of the coarse ones at ~3  $\mu$ m. Thus, higher concentration of fine particles leads to higher viscosity of CSG due to slower particle settling. To confirm these predictions, the settling patterns for particles in alumina composite sol were observed.

Figure 5.1-8 shows the settlement pattern of the as-received fine and coarse alumina particles after ball-milling for 12h and 24h. No settling of fine particles was observed (left 2 samples in all Fig.5.1-8) while the coarse particles (right 2 samples) substantially settled, i.e. the settling height increased up to 6 times within 12 hrs, in agreement with Eq.(5.1-1). The rate of the sedimentation for the fine and coarse alumina samples is plotted as a function of time, for ball-milling time of 12 h and 24 h, in Fig.5.1-9. It is observed that, regardless of the ball-milling time, settling only happens for the coarse particles. The settling rate of coarser particles decreases continuously, i.e., from 0.18 to 0.12 mm/min or from 3 to 2  $\mu$ m/sec, in the first 3 hours of test, possibly due to increased concentration and interaction between the particles. Assuming that the initial settling rate of about 3  $\mu$ m/sec is indicative of the actual size of settling agglomerate, Figure 5.1-7 may be used to estimate the average radius of the settling particles. It is read that the radius is close to 2  $\mu$ m, i.e. diameter close to 4  $\mu$ m, indicating low degree of agglomeration of the nominally 3 $\mu$ m large particles in the suspension.

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(a)

(b)



(c)



**Fig.5.1-8** Settling patterns for fine (~0.5  $\mu$ m) and coarse (~3  $\mu$ m) alumina particles in alumina sol suspension with a ball-milling of (a) 0 min (b) 30 min (c) 5h, and (d) 12h. Left 2 cylinders represent fine alumina particles (with 12h and 24h ball-milling, respectively) while right 2cylinders represent coarse alumina particles (with 12h and 24h ball-milling, respectively) in all pictures (a-d).



**Fig.5.1-9** The rate of settlement of two different alumina particles,  $\sim 0.5 \ \mu m$  and  $\sim 3 \ \mu m$  in alumina suspension of viscosity of 10-20 cp. Slurries were ball-milled for 12 h and 24 h.

Figure 5.1-10 exhibits the settlement pattern of the alumina composite sols with varying concentrations of fine particles (i.e. samples A30 to A50) after 12 h ball-milling, for up to 24 hrs of sedimentation time. The sample A50 shows settlement distance <1% of the original height. Although the sedimentation is also observed for A40 and A45, those samples show less settling distance and lower settling rate than A30 and A35. However, in order to have stable slurries for spray, the slurries with no sedimentation are required. Thus, the settling results suggest that more extensive ball-milling is needed for better dispersion of the alumina particles in the sol suspension. Figure 5.1-11 plots the settling rate as a function of (a) time and (b) concentration of fine alumina particles, based on Fig.5.1-10. In Fig.5.1-11a,





(b)



(c)

(d)

**Fig.5.1-10** Settlement of alumina composite sol after 12h ball-milling. Pictures were taken (a) right after ball-milling, (b) after 1hr, (c) 12hrs, and (d) 24hrs after ball milling stop. The samples are A30, A35, A40, A45, and A50 from left to right in each picture. Vertical arrows in (d) indicate the magnitude of separation of the alumina sol and alumina particles.

fast settling is observed during the first 30 min and then slower thereafter. Figure 5.1-11b shows the settling speed in terms of the concentrations of fine particles added. It is shown that the higher concentration of coarse particles the higher the settling rate. In particular, A30 and A35 whose median particle size is > 3  $\mu$ m demonstrate faster settling than all others whose particle sizes is  $< 3 \mu m$ . It is also shown that the difference of the settling rate is up to 6 times depending on concentration of fine particles. It seems that ball-milling for 12h is not sufficient for the spray coatings. Thus, 24 h ball-milling was undertaken for all the samples. Settling of particles dispersed in alumina sol after 24 h ball-milling is illustrated in Fig.5.1-12. No significant settling is observed for all concentrations except for minor settling observed in < A40 at 24 h monitoring. By comparing the previous results in Fig.5.1-10, the current result shows that the longer ball-milling time improves stabilization of the suspensions, and thus less sedimentation of particles. It is believed that this slower rate of sedimentation was related to a degree of homogeneity of the fine particles dispersed as a result of ball-milling. For the case of A30 and A35, the particle settling is still observed. This result suggests that longer ball-milling is required for a homogeneous dispersion and particle breakdown.

Based on Fig.5.1-12, the rate of settling of mixed particles was plotted in Fig.5.1-13. Settling happened only for A30 and A35 and their settling rates decreased by as much as ~2 times as compared to those 12 hr ball-milled, Fig.5.1-12a. Faster settlement was observed in the first ~90 min. in both concentrations of A30 and A35, and slowed down afterwards. The settling tests agree with Stokes' Law, Eq. (5.1-1), i.e. fine particles-containing-slurry settle



ball-milling as a function of (a) time and (b) concentrations of fine alumina particles.



**Fig.5.1-12** Settlement pattern of mixed alumina particles after 24h ball-milling. Pictures were taken (a) right after ball-milling, (b) after 1h, (c) after 12h and (d) after 24h from the ball milling stop. The samples are A30, A35, A40, A45, and A50 from the left in each picture. Vertical arrows in (d) indicate the separation of the alumina sols and particles. Measurable settling was observed in A30 and A35 only.

slower. It is concluded that higher viscosity and slower settling rate has been observed for higher concentration of fine particles with longer ball-milling time due to the better homogeneity and higher surface area of solids in suspension. Thus, the most suitable mixing ratio of the fine particles to coarse particles used for the current study was determined to be 40 to 60 and appropriate ball-milling time is 24 hrs. Accordingly such alumina composite sols have been gel-cast and characterized for morphology and density.



Fig.5.1-13 Rate of settlement of alumina CSG suspensions after 24 h ball-milling.

### 5.2 Characterization of Alumina Composite Sol-Gel

# 5.2.1 Morphology of Alumina Composite Sol-Gel with Various Concentration of Fine Size Alumina Particles

The objective of this part of the work is to determine how different size alumina particles affect CSG morphology, in particular the ability to decrease the porosity of the final CB-CSG coating for the thick dielectric films. Subsequently, the best microstructure, consisting of the smallest pores and the least amount of pores, was chosen as a candidate for further investigation of spray coating process, including CA-derived interfacial bond coat formation.

Figure 5.2-1 shows the microstructures of a fracture surface of dry-pressed pellets of as-received (a) 100 % coarse alumina particles (~3  $\mu$ m) and (b) 100 % fine alumina particles (~0.5  $\mu$ m), pelletized by a pressure of ~ 63 MPa (1 ton load on 1.4 cm diameter pellet). This test is a simple demonstration of how such different particles alone pack under the same conditions. Plate-like particles are observed in Fig.5.2-1a, which randomly contact each other, through edge-edge, edge-surface, and surface-surface contact points. Thus, many large voids (i.e., resulting in overall porosity of ~55 %) are observed. The fine particles, Fig.5.2-1b, pack much better, resulting in an overall porosity of ~45 % for the pellet.

Figure 5.2-2 shows the fracture surfaces of gel-cast of alumina composite sols (CSG) with various concentrations of the fine and coarse alumina particles (A30 to A50) and heat treated at 300 °C for 20 min. Sol-gel derived alumina is observed in voids between the crystalline alumina particles. The presence of this sol-gel derived alumina is due to the low temperature heat-treatment of alumina sol at 300 °C. It is well known that the first





**Fig.5.2-1** Fracture surfaces of pelletized alumina samples. (a) 100% coarse alumina particles,  $\sim$ 3 µm and (b) 100% fine alumina particles,  $\sim$ 0.5 µm.



**Fig.5.2-2** Microstructures of alumina CSG with the concentrations of (a) A30, (b) A35, (c) A40, (d) A45, and (e) A50 of fine alumina particles ( $\sim 0.5 \mu m$ ) in gel-cast samples (all in the same magnification of 3k).

crystalline phase appearing during heat treatment of the sol is a rhombohedral alumina (i.e.,  $\gamma$ -alumina), at ~450 °C [5.11-5.13]. XRD data for the currently used alumina sol with varying temperature from 200-500 °C are shown in Fig.5.2-3. It is observed that all peaks are broadened after heat treatment at 300 °C. Also, no significant phase change is observed up to 300 °C while the phase change (formation of  $\gamma$ -alumina) is observed after 400 °C. Solgel derived alumina is well distributed throughout the alumina gel cast, Fig.5.2-2. It is therefore expected that the sol-gel derived alumina acts as a binder for the crystalline  $\alpha$ -alumina particles and it is the first to react with the phosphoric acid during the chemical bonding process [2.33]. However, large fraction of voids are still observed in A30 and A35 as well as agglomerations; less voids and agglomerations are found for A40, and in particular for A45 and A50 (refer to Section 5.2.2 below for detailed data of density measurement for all these samples).



Fig. 5.2-3 XRD spectra of alumina sol after heat treatment at 200-500°C

# 5.2.2 Effect of the Specific Surface Area on Density and Viscosity of Alumina Composite Sol-Gel

The density of gel-cast CSG samples is plotted in Fig.5.2-4. For the CSG containing only the coarse alumina particles (~3  $\mu$ m), the re-separation due to particles settling down during gel-casting is too fast and therefore, the density was not measured. However, the density of CSG with only fine (~0.5  $\mu$ m) alumina particles is 2.25 g/cc (i.e. porosity of ~36%) which is close to that of A40 and A45. This density gradually decreases with the increase of coarse particles content in CSG, except for A50 which shows higher density than



**Fig.5.2-4** Density of gel cast CSG including a mixture of two different sizes of alumina powders vs. concentration of the fine alumina particles. The size of the fine and coarse particles is  $\sim 0.5$  and  $\sim 3\mu m$ , respectively.

CSG containing fine particles only. This result somewhat deviates from literature data [2.30] where the highest density in binary system appears for mixture ratio of 35-40 % fine particles to 65-60 % coarse particles. However, this ratio has been obtained for macroscopic systems, i.e. by vibrating steels spheres to fill the voids between larger particles with smaller particles. Gel-casting is very different process, where no external factors (i.e., press or vibration) were applied, and at the same time electrostatic interactions between the fine particles may affect the packing density. The gel-cast CSG density change with the concentrations of fine particles correlates well with the specific surface area ( $m^2/g$ ), as shown in Fig.5.2-5.



Fig.5.2-5 Comparison of density, and specific surface area of CSG as a function of concentration of fine particles.

### 5.3 Summary

Alumina composite sol for spray coatings were investigated in terms of viscosity, particle size distribution, settling rate of particles, density, and morphology. The mixture of two different particle sizes of the alumina composite sol exhibits better properties than single size particles alone, i.e. more stable viscosity and higher density after gel-casting. 12 hour ball-milled composite sols exhibit low viscosity of < 40cp for A30 and A45 while increase in viscosity was observed for A50. 24 hour and 48hr ball-milled composite sols showed higher viscosity than 12 hour ball-milled slurry for all concentrations due to the homogeneity of particle size distributions. A40 after 24 hour ball-milling shows the most suitable viscosity range of 200-400 cps for ~30 min, which is suitable for spray coating. The ratio of coarse to fine particles at this concentration (A40) is close to 60:40 which is declared as the most suitable mixture in this study. Analysis of the particle size distributions indicate that the more fine particles in the suspension the greater is the maximum particle size. This is due to agglomeration of fine particles dispersed in the alumina sols. The presence of submicron particles gradually increases from 37 % to 47 % for the compositions A30, A35, A40, and then it is constant as the concentration of the fine particles increases in A45 and A50. Longer ball-milling time (i.e. 24 hours) provided less settling than a shorter time (i.e. 12 hours), due to increase of the specific surface area of particles in the slurry. The composite sols with higher concentration of fine particles demonstrated relatively higher density than ones with lower concentration of fine particles after gel-casting. The most suitable ratio of the coarse to fine particles in the composite sols has been determined to be 60:40. Accordingly, the most suitable concentration of A40 (40 wt.% of the fine particles) with 24 hours ball-milling has been selected for spray coating to fabricate thick alumina dielectric films on AA5052.

## CHAPTER 6 CB-CSG COATINGS WITH CITRIC ACID-DERIVED BOND COAT

### 6.1 Cross Sectional Morphology of CB-CSG Coatings

Figures 6.1-1 through Fig.6.1-3 show the cross sectional microstructures of the CB-CSG alumina coated AA5052 using the slurry mixture of A40 (composed of 40% of 0.5 µm fine alumina particles and 60% of 3  $\mu$ m coarse alumina particles, in alumina sol, refer to Table 4.1-1 in Section 4.1.1 for further details). The first coating layer, Fig.6.1-1, with the thickness of ~40 µm was homogeneously deposited on AA5052 sandblasted substrate without cracks. It is observed that the "amorphous phase", which was determined to be a composite of alumina sol and the citric acid (CA) residue, appears uniformly throughout the coatings and fills the pores. This phase was also observed along the interface as a  $\sim 1 \mu m$  thin layer. This interfacial film is the key difference between the samples free of CA and samples with CA, and forms a unique organo-ceramic bond coat (BC) in this system. The effect of CA on coatings will be discussed in more detail in section 6.2.2. The 2<sup>nd</sup> layer does not introduce any new features into this system. After the 3<sup>rd</sup> layer is deposited, resulting in  $\sim$ 120 µm total coating thickness, Fig.6.1-2, vertical cracks near the surface and a delaminated-ceramic-metal interface are observed; these structural discontinuities are filled with the amorphous phase (which is later determined to be sol / CA derivative composite, refer to Section 6.2.2). The interfacial BC film thickens to the range of 1-2 µm. The last (5<sup>th</sup>) coating segment deposition, Fig.6.1-3, results in a total coating thickness of ~200 µm. The BC film has further widened up to  $\sim 10 \,\mu\text{m}$ , and more vertical cracks form, but again they are filled with the amorphous phase.





**Fig.6.1-1** SEM images of the 1<sup>st</sup> layer of the A40 coating. (a) overall view, (b) the interface, and (c) the coating volume, respectively.



**Fig.6.1-2** SEM images of the A40 coating after deposition of the 3<sup>rd</sup> layer. (a) overall view, (b) the interface, and (c) the coating volume, respectively.



**Fig.6.1-3** SEM images of the coating after deposition of the  $5^{th}$  layer of the mixture of A40. (a) overall view, (b) the interface, and (c) the coating volume, respectively.

Figures 6.1-1 through Fig.6.1-3 show the development of the morphology of CAderived amorphous phase within the multilayered coatings. The thickness of the amorphous phase at the interface gradually increases with the additional coating layers, reaching up to  $\sim 5\%$  of the total coating thickness. It is clear therefore that the amorphous sol/CA derivative composite phase continuously migrates to the interface during the consecutive steps of the coating processing. Once at the interface, the phase acts as a unique viscoelastic bond coat, helping to relax the residual stresses and thus to indirectly improve the coating microstructure (i.e. preventing thermal cycle cracking, and thus providing higher bonding strength and higher dielectric strength). CA-derived bond coat provided bond strength of up to  $\sim 15$  MPa (observed with the first coating layer deposited) while only 5MPa bond strength was observed for the coating without CA. The unique ability of the CB-CSG system containing CA is the segregation of CA+sol nanocomposite towards microstructural discontinuities, e.g. the interfaces but also cracks which may be forming during heat treatment (thus thermal cycling) of the coating. Such segregation, filling the cracks, in essence heals the cracks and thus strengthens the coating.

This hypothesis for the presence of CA derived amorphous composite phase (including alumina sol nanoparticles) is supported by studying the morphology of the alumina bulk gel-cast CB-CSG impregnated with CA, as illustrated later in Fig.6.2-4.

### 6.2 Effects of Citric Acid on CB-CSG Coatings

The studies of CA-derived organic bond coats for TDFs were prompted by the observation that the addition of CA to the alumina-based CB-CSG slurries increased the coating adhesion on metals to ~15 MPa for coatings up to 200  $\mu$ m thick from ~5 MPa (without CA and a thickness of <50  $\mu$ m). It was subsequently discovered that CA, during heat treatment of the coating, is rejected from the coating volume and thus forms an organic-inorganic composite (i.e. organic phase derived from partial decomposition of CA, and mixed with alumina sol) layer at the interface between the coating and the metal. The structural and chemical characteristics of such "modified CA" remain largely unknown in this work, and therefore will be referred to as CA-Derivative, CAD in short. An additional key observation was that no delamination of the coatings from the metal substrate was observed during processing, even for relatively thick coatings, for the systems including CA. The effect of CA on coatings will be discussed later in the section 6.2.2.

A hypothesis was formulated in the current study that the products of the partial thermal decomposition of CA de-wet the alumina and aluminum phosphates in the coatings, and thus migrate to the interface (and to the top surface of the coating). At the interface, such viscolastically deforming films substantially relax the residual stresses due to thermal expansion/contraction mismatch between the coating and the substrate. The results of research to verify this hypothesis are presented in this chapter.

### **6.2.1** Behavior of Citric Acid at Elevated Temperatures

A Differential Thermal-Thermo Gravimetric Analyzer (DT-TGA, SETARAM TG96, France) was used to investigate the thermal properties of as-received CA and CA admixed to the alumina coatings. Gel-cast alumina, containing 0.1 wt.% citric acid, which was fabricated under the same conditions as the coating slurry A40, was examined instead of using alumina coated aluminum due to the size limitation of the equipment. For example, a crucible for the DT-TGA is designated only for a small amount (~0.5g) of specimen material.

DT-TGA results for the as-received CA, Fig.6.2-1a, are compared with the TGA results for the gel-cast alumina with/without CA, Fig.6.2-1b, and the DTA results for the gelcast alumina with/without CA, Fig.6.2-1c. In Fig.6.2-1a, an endothermic peak without the reduction of mass is observed at 150 °C, indicating melting of CA [2.47]. Upon further heating, mass reduction is observed between ~200 and ~250 °C due to an endothermic reaction of dehydration. Two endothermic peaks are also observed at ~330 °C where the mass reduction is almost completed due to the decomposition of hydroxyl group (-OH) and carboxyl group (-COOH) [2.51]. The products formed by this decomposition at ~330 °C are cis or trans aconitic acid or aconitic anhydride [2.51]. Until this temperature, there is still a small amount (~10 %) of CA present. Thus, the CA-Derivative, CAD, is a complex mix of the products of partial decomposition of CA, and not-decomposed CA. Figure 6.2-1b indicates a continuous weight loss through the entire thermal cycling due to the dehydration of alumina CSG and CA decomposition. A slight difference in the weight loss between CAcontaining and non CA-containing alumina CSG is observed due to the dehydration and decomposition of CA. The heat flow curves of both specimens in Fig.6.2-1c overlap, i.e.


**Fig.6.2-1** DTA-TGA data for (a) as-received CA; (b) alumina CSG with/without CA (TGA only) and (c) alumina CSG with/without CA (DTA only). Heat flow for alumina CSG with/without CA overlaps, resulting in a single curve.

thermal behavior of the alumina CSG with/without CA is essentially the same (or beyond resolution capability of the instrument).

For the investigation of phase changes of CA at elevated temperatures (up to 300°C) with varying hold times at 300°C, X-ray diffraction (XRD) spectra and Nuclear Magnetic Resonance (NMR, Avance 300 Spectrometer, Bruker Biospin Co., USA) have been utilized. In the XRD spectra, Fig.6.2-2a,b, it is seen that as- received CA is crystalline and it becomes amorphous at 170-300°C, although broad peaks at  $2\theta = \sim 20$  and  $\sim 35$  deg are still present at 170°C and 200°C. No peak at  $2\theta = \sim 35$  is observed after heat treatment at 300°C for 10-30 min while the peak at  $2\theta = \sim 20$  with a low intensity is still present.

Figure 6.2-3 shows the result of the NMR test for citric acid heat-treated at 300°C for ~10 min in air, resulting in CAD, and they are compared with the spectra of as-received CA. In Fig.6.2-3a, the main peaks appear at 70-80 and 170-180 ppm. Each peak indicates methyl group, C-C, and >C=O, respectively. After heat treatment at 300°C for ~10 min, new peaks are formed at 10-20 ppm and 120-140 ppm indicative of alkyl groups, i.e., methyl group, - CH<sub>3</sub> or C-H, and an olefinic carbon species, C=C, respectively [2.51,2.55] while the peak at 75 ppm disappeared. The peak at 170-180 ppm is still present, indicative of a functional group such as >C=O< group [2.51,2.55]. This result agrees well with a study of the NMR of CA [2.51], and indicates that CA is to some extent still present in CAD after a heat treatment at 300°C up to 30 minutes, although the decomposition of CA has been suggested to start at ~170°C [2.47]. Heat-treated CA (white as-received) appeared light brown and viscous at ~150°C. It turned into dark brown above 170°C and later gradually black CAD up to 300°C,







(b)

**Fig.6.2-2** XRD spectra of CA at elevated temperatures; (a) as-received and (b) after holding at elevated temperature up to 300°C with varying hold time at 300°C from 10 to 30 min.



**Fig.6.2-3** <sup>13</sup>C NMR spectra of CA (a) as-received, (b) heat-treated at 300 °C and (c) the reference from the literature [ 2.51].

and was of a solid consistency. It is anticipated that this amorphous black residue, termed in this work "CA Derivative" CAD plays a significant role in the formation of the interfacial bond-coat. The color change indicates the gradual (or partial) decomposition of CA, with the remains including complex organic material CAD with multiple functional groups such as - $CH_3$ , C=O, and C=C, as seen in the NMR spectra.

### 6.2.2 Role of Citric Acid in CB-CSG Coatings

For better understanding of the effect of CA on the coatings during the heat treatment up to 300°C and CAD formation, porous (~50%) model sintered alumina have been studied before and after impregnation with a large excess of CA (approximately ~5 wt% of CA in the impregnated samples). Figure 6.2-4 shows the comparison between fracture surfaces of asreceived (a,b) and CA-impregnated (c,d) porous alumina after the heat treatment at 300°C. It is clearly observed that alumina particles are aggregated into relatively large (~3  $\mu$ m) clusters and pores between particles, Fig.6.2-4b. However, in Fig.6.1-4d which is also a magnification of Fig.6.2-4c, a continuous amorphous film between particles as well as pores is observed, which is the CAD residue (after heat treatment).



**Fig.6.2-4** Comparison of the fracture morphologies of as-received (a,b) and (c,d) CA-impregnated porous alumina specimens ( $\sim$ 3µm,  $\sim$ 50 % porosity) followed by heat treatment at 300°C.

EDX analysis, Fig.6.2-5, supports the hypothesis of the presence of the CAD residue after 300°C heat treatment. Peaks for 100 % of alumina are observed in Fig.6.2-5a while there is a new peak representing 28 at% carbon in Fig.6.2-5b (reliability of determination of the amount of carbon by EDX is however low since carbon is one of the lightest materials EDX can detect. However, the ratio of other elements remains constant). This EDX result agrees well with DT-TGA and NMR confirming the presence of the residue CAD in the heat treated alumina samples.



Fig.6.2-5 EDX analysis of (a) the as-received and (b) CA-impregnated model porous alumina specimens.

The key phenomenon controlling the in-situ formation of the organic CAD-based bond coat is the transfer of the CA from within the coating volume, to the coating/metal interface (and coating surface), with simultaneous decomposition of CA during the heat treatment. It is believed that the migration of molten CA through the pores of the specimen during heat treatment above ~200°C (wherein the migrating viscous CAD liquid carries also fine alumina sol particles) may be caused by the change (increase) of the wetting angle of CA-derived organic residue on alumina, due to increase of the interfacial energy  $\Gamma$  (at CAalumina interface).

As the wetting angle  $\theta$  is controlled through the well known equation, i.e.

$$\cos(\theta) = \{\Gamma(sv) - \Gamma(sl)\} / \Gamma(lv)$$
(6.2-1)

where  $\theta$  is the wetting angle,  $\Gamma(sv)$  the interfacial energy between solid and vapor,  $\Gamma(sl)$ between solid and liquid, and  $\Gamma(lv)$  between liquid and vapor.  $\Gamma(sv)$  is expected to remain constant during the heat treatment, whereas decomposition of CA is expected to increase the  $\Gamma$  (sl) and  $\Gamma$  (lv), thus decrease  $\cos(\theta)$  and increase of the wetting angle  $\theta$ . The resulting dynamic de-wetting process aids in repelling of the organic phase from within the fine pores of coarse alumina particles network, towards the coarser pores, cracks, interface and free surface of the coating (similar phenomenon is sometimes observed in experiments with mixed metal powders, wherein poor wettability of the liquid component on the solid powder results in repulsion of the liquid from the mix [6.1]). The organic phase exuded from the volume of the coating may also carry with it the finest fraction of the coating particles, i.e. the alumina-sol (AlOOH) nano-particles. The wetting of alumina sol by molten CA is expected to be better than alumina due to the hydroxylated surface of the sol particles (this is confirmed later in this Chapter), and thus de-wetting driven separation of CA and AlOOH is more difficult than separation of CA and Al<sub>2</sub>O<sub>3</sub>. Effectively, the interfacial film of a nanocomposite of CAD mixed with alumina sol particles forms the interfacial bond coat. This hypothesis is further verified below.

Figure 6.2-6 compares the cross sections of CA-free and CA containing CB-CSG alumina coated aluminum. Figure 6.2-6a illustrates the typical coating morphology of the CB-CSG alumina, with voids between coarse alumina particles (~  $40\pm5$  vol%, obtained by water absorption), and the alumina sol-derived phase filling the pores and binding the particles together [6.2,6.3]. The ~0.1 wt% CA containing CB-CSG alumina coating, Fig.6.2-6b, shows slightly less pores (~ $35\pm5$  vol%) and amorphous phase at the interface between the coating and the AA5052 substrate.

EDX analysis of this interfacial film, Fig.6.2-7, indicates the presence of C, O, Al, and small amount of P (hydrogen is not "seen" by EDX), suggesting that the film is composed of alumina (sol-derived), organic residue (CAD), and trace amount of phosphate. Atomic ratio of aluminum to oxygen is 1:2=0.5 in alumina sol (AlOOH) and 1:1.5=0.67 in calcined alumina (Al<sub>2</sub>O<sub>3</sub>). The Al/O ratio determined for the Bond Coat (BC) layer, refer to Fig.6.2-6, is about 1/2.6=0.38, suggesting that part of the oxygen resides in CAD. Although hydrogen is not detectable by EDX, its amount in CAD is expected to be rather small, compare Fig.6.2-1, 2. As BC microstructure does not indicate presence of any calcined alumina (these >0.5µm particles would be visible under SEM), it is reasonable to assume that BC includes AlOOH, with atomic ratio of aluminum to oxygen of 0.5, and CAD. Neglecting the content of hydrogen and phosphorous, the BC is therefore composed of approximately 10 at% of Al, 20 at% of O (in AlOOH), and 6at% of O and 64 at% of C in CAD. This would translate into approximate composition of the BC of 40 wt% of boehmite sol (perhaps partially decomposed sol) and 60 wt% of CAD, both phases having poor crystallinity.

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(a)



**Fig.6.2-6** Comparison of alumina coated aluminum (a) without CA and (b) with CA. ~40 vol% porosity is observed in (a) while ~ 35 vol% porosity is observed in (b) due to filling effect of CA. Porosity was measured by water absorption.



**Fig.6.2-7** EDX analysis, by (a) peaks and (b) quantification, of the Bond Coat layer between the CB-CSG coating and aluminum (the system includes additionally hydrogen, which is not detected by EDX).

To further investigate the above hypothesis, wetting angle of molten CA at 150°C on the surface of sintered alumina was measured to be ~135°, Fig.6.2-8a while the wetting angle of the CA on gel-cast alumina sol sample was ~70°, Fig.6.2-8b. The wettability of CA on alumina sols and a sintered alumina has also been investigated at elevated temperatures up to ~300°C. The initial CA (i.e. as dissolved in water in 1:1 by wt.%) shows the wetting angle of ~10°. As the temperature increases to 150°C, molten CA contracts (wetting angle increases) and it is pushed out from the surface of the alumina while it bubbles due to the dehydration. Above 170°C CA color progressively changes to dark brown, indicating the decomposition of CA as previously discussed in Section 6.2.1, while the wetting angle increases towards 135°.





**Fig.6.2-8** Investigation of wettibility of CA melted at ~150°C on (a) a sintered alumina and (b) sol-gel derived alumina.

## 6.2.3 Stress Mitigation for CB-CSG Coated Aluminum

It has been assumed that the bond coat (BC) consisting of alumina sol and a CAD increased thermal shock resistance of the coatings on AA5052 by relaxing stresses during the process, in terms of successfully made thick alumina coatings on AA5052. In order to verify this assumption, it was hypothesized that the sol+CAD bond coat may behave viscoelastically, and thus provides relax the differential means to thermal expansion/contraction stress. In order to evaluate this hypothesis, three different types of coated beam specimens were tested for the pattern of strain recovery in three point bending of 1) alumina coatings with and 2) without CA on aluminum alloy substrate, as well as 3) an as-received Al alloy substrate alone as a reference sample. The procedure was as follows: constant force of 18N was applied for 1h to each specimen and then removed; strain recovery was then observed and compared for each beam, Fig.6.2-9

Both the AA5052 alloy substrate and the ceramic coating (Al<sub>2</sub>O<sub>3</sub>-based CB-CSG) can be considered as elastic materials at room temperature, while CAD/alumina sol is expected to behave as a viscoelastic material. If this is true, the AA5052 substrate only and the substrate with CA-free coating should recover to zero-strain immediately after stress removal, whereas the CA-containing coated sample should exhibit non-zero recovery strain, decreasing gradually with time.

Figure 6.2-9a illustrates essentially identical behavior for the substrate only, and the substrate with the ceramic coating free of CA. Strain recovery for AA5052 substrate only and CA-free CB-CSG coated AA5052 seemed to be time dependent. The strain of the



**Fig.6.2-9** Profiles of strain recovery after removal of the constant force of 18N, applied to AA5052 substrate, and the substrate with alumina coatings with/without citric acid. The force was removed after holding for 60 min. CA in the legend refers to citric acid. (a) overview, (b) magnified between 70 and 120 min, and (c) log scale of (b)

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AA5052 substrate at the applied force removal point was about 0.0027  $\mu$ m and it gradually decreased to the constant strain of about 0.0018 µm. The difference between these strains is however within the strain resolution of DMA, so it can not be considered as significant. The CA-free CB-CSG coated AA5052 showed the strain of about 0.0045 µm at the applied force removal point and it decreased to about 0.0025 µm. The difference between the strains was big enough to be considered as significant, presumably due to slow crack growth in the coating. The behavior of the CA-containing CB-CSG coated AA5052 also showed time dependent strain recovery. Its strain at the applied force removal point was about 0.0083 µm and it reached the constant strain of about 0.0060 µm after 120 min. However, this CAcontaining CB-CSG showed the highest strain at the end of the constant force application period, and it also showed the highest residual strain after the force removal. This is presumably due to the combination of progressive cracking in the coating, and deformation of CAD interface. While the AA5052 substrate recovered essentially all strain upon removal of the applied stress, and the sample CB-SCG coated without CA also showed the same trend (98% recovery), CA-containing CB-CSG coated specimen recovers only 92 % of its original deformation. These observations are not sufficient to claim that CAD+sol behaves viscoelastically at the interface between CB-CSG coatings and AA5052 substrate. Observation of the coating's retention on various samples, Fig.A-5 in the Appendix, suggests a strong effect of CA on mitigation of residual stress. Further research on viscoelastic properties for CAD+sol is suggested for the future work.

The log-log plots in Fig.6.2-9c indicate strain recovery patterns for the three types of specimens by assuming the following equation [2.79];

$$\varepsilon(t) = \varepsilon_0 e^{-\frac{t}{\tau}} \tag{6.2-2}$$

From the above equation, it can be understood that the higher relaxation time,  $\tau$ , the lower the strain changes. For example, each slope of the sample indicates the value of the 'loge/ $\tau$ (or 0.434/ $\tau$ )' by taking the log function in Eq.(6.2-2). For each slope, one can obtain the relaxation time, $\tau$ , for each sample as follows;  $\tau$ =0.891 for the CA containing sample,  $\tau$ = 0.427 for the CA free sample, and  $\tau$ =0.270 for AA5052 alone. This result shows that the CA containing sample has the highest value of  $\tau$ , showing the longest stress relaxation time. It is also observed that rather higher  $\tau$  is obtained in the CA free sample than AA5052 alone. It is presumably due to the defects in the coatings (i.e., porosity and cracks). Therefore, CA containing sample in Fig.6.2-9c describes sufficiently well viscoelastic behavior of these samples [2.79]

Viscoelastic materials can be characterized in terms of relaxation modulus, defined by the following equation [2.79].

$$E(t) = E \cdot e^{-\frac{t}{\tau}} \tag{6.2-3}$$

The comparison of the modulus of alumina coated AA5052 (with/without CA) and AA5052 substrate alone was studied at sinusoidal force of 40 MPa applied for 1h in order to verify the above demonstrated viscoelastic effect of CAD on coatings (refer to Section 4.3.4 for the details of procedure and calculation of the modulus). Fig.6.2-10a summarizes the results of this test in linear axis system and Fig.6.2-10b in log-log scale. It is observed that the relaxation modulus of as-received AA5052 substrate decreases during the first period of loading time, ~30 min and then it remains approximately constant. The decrease in modulus

of AA5052 at constant stress loading may be related to relaxation of residual stresses introduced during forming and machining of the alloy (refer to the Appendix Fig.A-1). The relaxation modulus of CB-CSG alumina coated AA5052 without the CA also decreases during the test with a similar rate and time constant as un-coated specimen. The effects of the CA are weak as behavior of the AA5052 substrate dominates behavior of the whole coating systems as it is much thicker than coating (~1600  $\mu$ m vs ~80  $\mu$ m).

At t=0, the moduli of the three specimens are 64 GPa, 59 GPa and 58 GPa respectively. The lower value of relaxation modulus of CB-CSG alumina-only-coated AA5052 at t=0 is due to lower Young's modulus of the alumina coating (10 GPa, obtained by indentation method, refer to Section 4.3.4). Similarly, relaxation modulus for the CAcontaining coated AA5052 at times is even lower than one with no CA containing coating, due to the stress relaxation by CAD in the alumina/Al interface. In terms of the relaxation time,  $\tau$ , the lowest  $\tau$  (=31.000) is obtained in the CA containing sample while the relaxation times for the AA5052 only and the CA free sample are 60.278 and 43.838, respectively. This result agrees well with that obtained from Fig.9.2-9c which showed the highest  $\tau$  in the CA containing sample. According to the above result, it can be concluded that the CA plays an important role as a stress relaxation during coating processing.

These results may also be compared with calculations of the moduli, assuming the lower value of Young's modulus for additional layers, and of the CAD bond coat. According to Eq.(2.4-12), if the modulus of the substrate of thickness  $h_0$  is  $E_0$ , and a layer of coating thickness,  $\Delta h$ , is added (with modulus E), the modulus of composite specimen is now



(b)

Fig.6.2-10 Relaxation moduli of CA containing CB-CSG alumina coated AA5052, compared with as received AA5052 and conventional (CA-free) CB-CSG alumina coatings on AA5052. Thickness of the coatings was ~100  $\mu$ m. (a) linear axis scale and (b) log-log scale.

 $\bar{E}_1 = (\Delta h \cdot E + h_0 \cdot E_0)/h_1$ , where  $h_1 = h_0 + \Delta h$ . Using the specific geometry of the test samples (i.e.  $\Delta h = 40 \ \mu m$  and  $h_0 = 1600 \ \mu m$ ) and average Young's modulus of alumina coated AA5052 (i.e.  $\bar{E}_1 = 58 \ \text{GPa}$ ), one can calculate the Young's modulus of the added coating layer, *E*.

Using the procedure outlined above, the calculation of *E* of the added layer of CB-CSG coating produces a negative value of about -180 GPa, indicating  $\bar{E}_1 < E_0$  (and considering  $h_1 = \Delta h + h_0 \approx h_0$  due to  $h_0 >> \Delta h$ ). It means that the CB-CSG alumina coating with CAD bond coat does not contribute to the increase in the stiffness of the system. This is believed to be yet another evidence that the CAD intermediate layer (bond coat) relaxes the interfacial stress during specimen deformation (this effect will be discussed in more details in Section 6.3.2).

## 6.3 Determination of Residual Stresses in CB-CSG Alumina Coated Aluminum alloy (AA5052)

Residual stress in the coating/substrate system produces curvature changes of the coated substrate. In the current research, it was expected that residual stresses in thick multi-layered CB-CSG alumina films on aluminum alloy is due to the relatively large thermal expansion mismatch (i.e. alumina:  $8 \times 10^{-6/\circ}$ C, believed unchanged due to inclusion of about ~2 wt% of phosphates in the chemical bonding process, and AA5052,  $24 \times 10^{-6/\circ}$ C, believed to be unmodified by the minor alloying elements in AA5052). Monitoring of residual stress as a function of process parameters, in particular coating thickness and presence of CAD, allows optimizing the deposition process. In order to determine the residual stress value, the curvature change of the coated substrate was measured before and after coating deposition and heat treatment.

# 6.3.1 Curvature of CB-CSG Alumina Coated AA5052 Alloy System

Figure 6.3-1 shows the radius of curvature of CB-CSG alumina coated AA5052 for each additional coating layer, as the overall coating thickness is increased. The initial curvature of AA5052 substrate before coating deposition has been measured to be  $2.2 \pm 0.5$ m, presumably due to machining and sand-blasting induced stress (the Appendix Fig.A1).



**Fig.6.3-1** Radius of the curvature of AA5052 aluminum substrate before (i.e. at zero coating thickness) and after deposition of coatings of increasing thickness.

Subsequently, the measurements were repeated after each layer of coating deposition followed by heat treatment at 300°C. It is observed that each additional coating layer alters

the bending of substrate/coating system, i.e. increase in radius of curvature is observed. The radius of the curvature of the substrate with the first coating layer deposited ( $\sim 40 \text{ }\mu\text{m}$ ) increases from 2.2 m to 3.6 m, i.e. the system becomes more flat after the first coating layer deposition. This radius of curvature (3.6m average) remains approximately constant after deposition of the subsequent layers of the coating, although the scatter of results is relatively large. Considering just the average values of the radius of curvature, deposition of the second coating layer (~80 µm in total) decreases the radius, and then it gradually increases again with each additional layer deposition up to 200 µm of the final coating thickness. It appears therefore that cracks, affecting the state of stresses and thus beam curvature, formed in the coatings until the thickness of  $\sim 80 \,\mu m$ . The cracks appear to form in the third layer of the coating, i.e. exceeding 120 µm thickness. The maximum stresses caused by thermal mismatch between the coatings and aluminum substrate might be in the first coating layer. The stresses subsequently relax during follow-up heat treatment after deposition of the second coating layer. The observed change of sample curvature agrees well with the literature, i.e. it has been observed that the curvature can shift from convex to concave during

repeated heat treatment due to the balance of residual stresses [6.4].

#### 6.3.2 Young's Modulus of CB-CSG Alumina Coated AA5052

According to the Eq.(2.4-14), average Young's modulus of the coated specimen is important factor in determination of the residual stress developing in the additional coating layers. Thus, the change in average Young's modulus of the coated sample, with each layer of coating deposition, was determined in Section 2.4.2.1. Figure 6.3-2 shows the comparison of the average Young's modulus for CB-CSG alumina coated AA5052 calculated using Eq.(2.4-12) [2.60] (using the modulus of the coated film determined through indentation to be ~10 GPa) and the modulus experimentally obtained by Dynamic Mechanical Thermal Analyzer (DMTA), as a function of the coating thickness.



**Fig.6.3-2** Average Young's modulus of coated AA5052 aluminum, as determined by calculation and experiment.

The calculated average Young's modulus of the coated AA5052 agrees well with the experimental average Young's modulus until the accumulated coating thickness of 120  $\mu$ m, and subsequently the measured values deviate (decrease) from the calculated ones, reaching difference of ~9 GPa (or ~14 %) for the coating thickness of ~200  $\mu$ m. This difference is attributed to accumulation of defects (i.e., cracking), with coating thickness [6.5,6.6]. It appears therefore that ~80  $\mu$ m is the critical thickness for the coating to start significant cracking due to accumulation of residual stresses.

Figure 6.3-3 compiles the results of measurements of the change of average Young's modulus of as-received AA5052 substrate and coated samples with temperature, when the consecutive layers of coatings are added to the sample (Dynamic Mechanical Analysis was used, as described in Section 4.3.4). As expected, Young's modulus of all samples decreases during heat treatment at up to 300°C, and increases again during cooling. At constant temperature of 300°C, held for 30 min (Fig 6.3-4b-f) an increase in the modulus of coated samples is observed while the modulus of un-coated AA5052 remains constant. This effect is attributed to the progress of chemical bonding process in the coating layers (refer to Section 2.1.4). However, as determined above, the parallel process of coating damage accumulation, i.e. cracking, in coatings thicker than 80 µm counter-balances the effect of the chemical bonding on sample stiffness. This complex interplay of stiffness increase due to chemical bonding, and decrease due to accumulation of microfracture in the coatings cooled to nearroom temperature, determines the final modulus of the coatings. For example, only the first and the second layer coated substrate return to their initial Young's modulus through the entire heating cycle, elasticity as of the AA5052 dominates the system



**Fig.6.3-3** Young's modulus of (a) as-received AA5052 and (b)-(f) CB-CSG alumina coated AA5052 aluminum measured during heating and cooling cycles: (b)  $1^{st}$  layer deposited (c)  $2^{nd}$  layer added (d)  $3^{rd}$  layer added (e)  $4^{th}$  layer added and (f)  $5^{th}$  layer added.

behavior and there are no defects in the coatings. Significant decrease in the modulus during the cycle is found between the 3<sup>rd</sup> and the 4<sup>th</sup> layer, indicating damage to the coatings. This conclusion is supported by analyzing cross-sectional morphology of the coatings in Fig.6.1-1 through Fig.6.1-3.

Heat treatment of the coating/substrate system results in complex and interactive phenomena including chemical bonding, differential thermal expansion/contraction and damage accumulation. During the heat treatment, both the coating and the substrate are free to expand without constraint as the coating (and the interface) has no integrity due to lack of chemical bond within the coating. The chemical bonding process at 300°C provides, however, a bond within the coating, and between the coating and the interface, thus increasing coating stiffness. Upon cooling, differential thermal shrinkage (i.e. larger in the AA5052 substrate than alumina coating) introduces stress which may lead to coating cracking, thus decreasing its stiffness. The process repeats for the consecutive layers of coating deposition. For example, the loss of the Young's modulus for the third layer is ~ 3.6 %, and ~8.9 % for the 4<sup>th</sup> layer, and 8.3 % for the 5<sup>th</sup> layer.

## 6.3.3 Strain Measurement by X-ray Diffraction (XRD)

Figure 6.3-4 shows XRD spectra of the chemically bonded CSG alumina coatings, under the stress-free state (refer to Fig.A-4), Fig.6.2-4a, which is a reference ground gel-cast material, and for the multilayer CB-CSG coated aluminum in the order of 1<sup>st</sup> to 5<sup>th</sup> layer, Fig.6.2-4b-f.



**Fig.6.3-4** XRD peaks of alpha-alumina at (a) stress-free state and (b)~(f) under the stressed state in the order of  $1^{st}$  to  $5^{th}$  layer.

The aluminum substrate peaks are observed for the coated samples until the  $3^{rd}$  layer due to the coating penetration by the incident beam of 40 kV, and by the diffracted signal. It is

observed that the main peak at  $2\theta = 35.24$  has slightly been shifted toward the smaller  $2\theta$ angle until the 3<sup>rd</sup> layer and shifted again toward the larger  $2\theta$  angle thereafter. The shift is indicative of lattice spacing change due to residual stress. Tensile stress increases lattice spacing, so the corresponding x-ray peaks shift to smaller angles [6.7]. This phenomenon is observed in Fig.6.3-5a-b. A different direction in the angle shifts is observed from between the first and second layers and at  $3^{rd}$  layer (~120 µm thick), in agreement with the curvature data in Fig.6.3-1, Section 6.3.1. Figure 6.3-5 shows the strain in terms of relative lattice spacing shift,  $\Delta d/d$ , calculated through  $2\theta$  (degree) angle shifts for the major peaks, as a function of coating thickness, using formula Eq.2.4-16, section 2.4.2.2. The diffraction angle shift reflects the state of stress within the coating, i.e., tension with an angle shift toward smaller values and compression towards larger [6.7]. The angle shift toward smaller values occurs between stress-free state and 1<sup>st</sup> coating layer and it remains until the 2<sup>nd</sup> layer. The angle shifts towards larger values between 2<sup>nd</sup> and 3<sup>rd</sup> layer. The associated strain essentially returns to near-zero values, if the scatter of the results is taken into the account. This indicates stress relaxation, likely through coating cracking, as determined previously. These all explanations can be supported by cross sectional morphologies of coatings in Figs. 6.1-1 through 6.1-3.



Fig.6.3-5 Comparison of (a) strain and (b) angle shift by XRD vs. coating thickness.

## 6.3.4 Average Residual Stresses in the Alumina CB-CSG Coating Layer on Aluminum alloy (AA5052)

Based on the lattice spacing change, the state of stresses can be determined at a certain coating thickness, using Eqs. (2.4-17a,b) in Section 2.4.2.2 The surface of the 1<sup>st</sup> coating layer, ~40  $\mu$ m thick, was in a state of tension. The magnitude of tensile stress decreased with additional coating layer deposition as the previously deposited (underlying) coating layers decrease the difference in CTE between the additional coating and the underlying substrate (of aluminum alloy and the already deposited CB-CSG coatings). The stresses cause bending of the substrate/coating system [6.4]. By knowing the curvature, Young's modulus, and geometry of coated substrates, the residual stress can be obtained according to the bending theory [2.60]. The respective formulas and method of calculation are included in Section 2.4.2.1.

Figure 6.3-6 illustrates the result of the calculations of residual stresses in CB-CSG alumina coated aluminum through the thickness of alumina coating layers. The empirical values of average Young's moduli of AA5052 substrate and coated samples were used as discussed in Section 6.3.2, as well as the calculated average Young's moduli (refer to Section 2.4-12 for the formula). No significant difference in the residual stresses calculated using the above two values of Young's modulus was found throughout the thickness even at the thickness of 200  $\mu$ m, where the difference of 10 GPa of Young's modulus was found, as shown in Fig.6.3-3. Tensile stresses (100-170MPa) were dominant up to the 2<sup>nd</sup> layer of thickness of 80  $\mu$ m (i.e. the radius of the curvature decreases), then they gradually change to approximately constant (about -50MPa) compressive stresses (the radius of the curvature increases). This was previously predicted by the result from the curvature change: the

direction change in the curvature of the alumina coated aluminum happens between the  $2^{nd}$  (80 µm) and  $3^{rd}$  (120 µm) layer. At the thickness of 120 µm and above, the coating has the lowest, constant compressive stress. It is expected that during the heat treatment after the  $3^{rd}$  layer of deposition, cracks form and therefore the stresses are related. Since the CB-CSG alumina coating has a relatively high level of porosity, ~45% and a low Young's modulus (i.e. 10 GPa), it is also reasonable to expect a low value of the residual stresses. The maximum residual stress measured is ~180 MPa in tension in the first layer of thickness ~40 µm, and the minimum stress is ~80 MPa in compression in the 5<sup>th</sup> layer, 200 µm thick.



**Fig.6.3-6** Comparison of residual stress obtained from bending theory, using calculated Young's modulus and experimentally obtained Young's modulus by 3-point bending test for alumina CB-CSG coatings on AA5052.

The residual stresses calculated based on sample bending are compared with those obtained by XRD measurement in Fig.6.3-7. The residual stresses obtained by XRD measurement are indicative of the surface stresses due to the shallow penetration of X-ray. As discussed in Section 6.3.3, strain changes in each coating layer were used to determine the residual stresses. It is observed that the tensile stresses are dominant up to the  $2^{nd}$  layer, 80  $\mu$ m, and change to compressive stresses at the  $3^{rd}$  layer, and then the state of the stress shifts to the tensile stress again. The XRD derived trend is supported by the results of the curvature measurement. The differences may be partially attributed to the specifics of each method: the values obtained through the curvature measurements refer to the average residual stress through the coating layers, while the values by XRD refer to the shift angle (2 $\theta$ ) due to the relatively high scanning speed. The resulting scatter is relatively large, which may lead to a general conclusion that significant stresses are present in coatings thinner than 120  $\mu$ m, and are subsequently relaxed through cracking to near-zero value for thicker coatings.



Fig.6.3-7 Comparison of the residual stresses determined by XRD and curvature methods

### 6.4 Electrical Properties of Alumina CB-CSG Coatings

Thick dielectric films (~200  $\mu$ m), consisting of 5 consecutively deposited layers of CB-CSG alumina, each ~40 $\mu$ m thick in a single deposit, with CA-derived bond coat, have been successfully deposited on AA5052. The microstructures and the thickness of the alumina coatings affect the dielectric strength of coatings, particularly crack and pores [6.8]. Those defects degrade the electrical properties: the more pores or cracks the lower the breakdown voltage. The fabrication of the CB-CSG alumina multi-layered coatings with the dielectric strength of >2000 V<sub>AC</sub> is the applied target for the current study. To determine the dielectric strength, the breakdown voltage of the coatings was measured as a function of

coating thickness. However, as shown above, the thickness of the coatings is also a parameter determining the level of residual stresses, and eventually cracking of thicker coatings. As a result, it is also essential to study the relationship between residual stresses and dielectric strength in terms of coating thickness.

### 6.4.1 Dielectric Strength of CB-CSG Alumina Coatings

### 6.4.1.1 Effect of the shape of an electrode

In order to apply the CB-CSG technology for the manufacture of low cost and high efficiency heating elements, a dielectric breakdown voltage of over  $2000V_{AC}$  is necessary for the ceramic coatings. However, the measured value of the breakdown voltage depends not only on the properties of coating materials but also the geometry of an electrode which directly contacts the surface of the insulating material [6.8]. A sharp-ended electrode generally reads a higher value than a flat-ended one. The tip of the sharp-ended electrode has less contact area to a coating surface, leading to the low probability of discharging by gases (i.e., air) when an electric field is applied. Since it is difficult to fabricate a perfectly even and smooth coating surface, flaws such as cracks and roughness always exist throughout the surface of the coatings. These flaws may introduce unexpected discharge leading to low breakdown voltages. Discharge is the phenomenon of ionization of electrons in an electrode [6.8]. Therefore, the breakdown voltage values will be different depending upon both the shape of the electrode and a part of the coating surface where the electrode is placed. In this study, the effect of the shape of the electrode on the dielectric breakdown voltage of the alumina coated aluminum has been investigated, Fig. 6.4-1. As expected, a higher breakdown voltage is obtained for the sharp-ended electrode, especially for the coating thickness above  $80 \ \mu m$  where more defects (i.e., pores or cracks) are present in the coating. Therefore, it is reasonable to use a flat-ended probe in this study for more accurate (averaged-out over the electrode end) data collection.



**Fig.6.4-1** Comparison of the effect of the shape of the electrode (sharp end vs. flat round end) on the dielectric breakdown voltage of CB-CSG alumina coatings deposited on aluminum.

#### 6.4.1.2 Dielectric Strength of CB-CSG Alumina Coated AA5052

The breakdown voltage and dielectric strength are related through the microstructure and thickness of coating material. The dielectric strength is inversely proportional to the thickness of coatings after certain thickness is reached, even though the breakdown voltage increases with the thickness. This is because the probability of flaws occurring in the coating increases with the coating thickness. We believe that only thermal breakdown and ionization breakdown components operate in the current coatings due to the local heat generation by the electrode and pores or cracks present in the coatings.

Since the dielectric strength is related to the microstructures of material, it is worthwhile plotting the porosity of the coating material to better understand the relation between the dielectric strength and the porosity. Figure 6.4-2 shows open porosity (vol%) of the consecutive CB-CSG alumina coating layers deposited on aluminum, as determined through water absorption. The porosity displays a linear increase with each added layer. The increase in the porosity is mainly caused by the cracks, affecting dielectric strength as coating thickness increases.

Figures 6.4-3 and Fig.6.4-4 show the result of the measurements of breakdown voltage and the dielectric strength of the CB-CSG alumina coated aluminum, respectively. Complete data on the breakdown voltage of the alumina coated AA5052 is included in the Appendix, Table A-4. The breakdown voltage for the coatings of the total thickness of ~200  $\mu$ m is ~2100 V<sub>AC</sub> and the highest dielectric strength of ~15kV/mm is observed at the first layer. The breakdown voltage for the 1<sup>st</sup> layer was higher than that of the two-layered


Fig.6.4-2 Open porosity of the consecutive alumina coating layers.

coating, and the trend continues through layer #5 although at smaller rate. The  $2^{nd}$  layer of thickness of ~80 µm can be considered as a critical thickness regarding dielectric strength. This thickness agrees well with the study by Olding *et.al* [2.67] of a similar system based on alumina-silica dielectric coatings. The dielectric strength, Fig.6.4-4 obtained from the result of the breakdown voltage in Fig.6.4-3, is inversely proportional to the thickness due to the increase in the density of flaws (pores and cracks) with thickness of the coating. For the  $1^{st}$  layer of 40 µm, the dielectric strength is ~15 kV/mm. However, at the  $2^{nd}$  layer of 80 µm, the dielectric strength decreases with thickness and this trend continues in each subsequent layer. The relation between residual stresses (as determined through sample curvature measurements) and the dielectric strength as a function of the coating thickness is plotted in Fig.6.4-5. Residual stresses decrease until the  $4^{th}$  layer is deposited, at overall coating thickness of 160 µm, and slightly increase after this thickness. Similarly, the dielectric



**Fig.6.4-3** Breakdown voltage of the CB-CSG alumina coated aluminum as a function of thickness of the coating. The average thickness of one single deposit is  $\sim 40 \ \mu m$  and the coating is made of 5 layers.



**Fig.6.4-4** Dielectric strength of the CB-CSG alumina coated aluminum with the thickness of the coating.

strength decreases between the thicknesses of 40 and 80  $\mu$ m, and then gradually decreases thereafter. For the 1<sup>st</sup> layer, high values of the residual stresses and dielectric strength are obtained due to no significant density of defects present in the coatings.



**Fig.6.4-5** Relationships between residual stress ( $\blacktriangle$ ) and dielectric strength ( $\blacksquare$ ) with respect to coating thickness.

However, after the 2<sup>nd</sup> layer, the residual stresses decrease along with the dielectric strength due to the increment of the density of cracks and pores. After this thickness, the state of the stresses changes to compression without the significant difference in the dielectric strength. Although the presence of defects is one of the determining factors for the dielectric strength, accumulation of coating layers partially compensate for the loss of dielectric strength due to increasing density of defects.

#### 6.5 Summary

The properties of CB-CSG alumina coated AA5052 alloy have been studied in terms of the process parameters affecting the mechanical and dielectric properties. The citric acid (CA) dispersant combines with the alumina sol component of CSG, partially decomposes during the heat treatment into an amorphous phase starting at ~150°C, and fills the cracks and pores within CB-CSG alumina. It also migrates to the interface between the coating and the substrate. It is hypothesized that the sol/CA derivative containing CB-CSG alumina coatings shows viscoelastic behavior and thus aids in stress relaxation especially in the regions of high density of sol/CA derivative composite, such as an interface.

With the knowledge of geometry, average Young's modulus  $\vec{E}$  of CB-CSG alumina coated AA5052, and the Young's modulus E of the consecutive CB-CSG alumina layers, and the coated sample curvature before and after heat treatment at a given temperature, the residual stress of coated layers was calculated. The residual stresses obtained by the curvature method were compared with those obtained by monitoring lattice parameter change by X-ray diffraction. The values of stresses obtained by each technique were different but similar trend was obtained. The difference may be attributed to the specifics of the measurement methods: the X-ray method determined only the stresses at the surface of the coatings while the curvature method determined the average stresses through the entire thicknesses of the coating. The stress in coating layers was predominantly tensile (especially for thinner coatings) while the substrate is in compression. The maximum stress determined by both methods was found in the 1<sup>st</sup> layer due to the strong effect of thermal mismatch in the coating layer near the substrate. After the 1<sup>st</sup> layer has been deposited and heat treated, this stress continuously decreased. Eventually cracks formed in the thicker coatings and thus the stresses decreased.

The dielectric strength of the CB-CSG alumina coated aluminum decreased with the increase in the coating thickness. The maximum dielectric strength of ~15 kV/mm was observed for the 1<sup>st</sup> coating segment deposition and this value decreased for each subsequent layer. However, the scale of decrease between the 1<sup>st</sup> and 2<sup>nd</sup> layer is different from other layers due to the increase in the density of pores. After this initial thickness, in addition to pores, cracks also form due to the thermal mismatch during processing, further decreasing the dielectric strength.

The relationship between the dielectric strength and the residual stresses in the coating as a function of the thickness of the coatings has also been investigated. The trend of the residual stresses agrees well with the dielectric strength of the CB-CSG alumina coated AA5052 in terms of the coating thickness due to the increase of defect density in the microstructure. The maximum value in the 1<sup>st</sup> layer for both the residual stress and dielectric strength means that there were few defects in the coatings. From the 2<sup>nd</sup> layer deposition, the residual stress decreases, which means that the defects present release the stress, but also the presence of cracks lowers the dielectric strength. Therefore, it is observed that the dielectric strength and the residual stresses in the coatings are related to the microstructures of the coatings.

#### CHAPTER 7 CONCLUSIONS

This thesis concerns novel processes for thick films of ceramics on metal substrates with substantially larger coefficient of thermal expansion. The general objective was to propose and analyze the new processing methods to decrease residual stress in the films and thus to prevent large-scale cracking in the films. The newly developed process was then used to achieve relatively thick (~0.2mm) dielectric films of alumina-based ceramic on aluminum alloy AA5052, by Chemically Bonded Composite Sol-Gel (CB-CSG) process. This study of the CB-CSG alumina coated AA5052 aluminum system proposed and evaluated novel processing methods to overcome the current limits of deposition of thick ceramic coatings on metallic substrates with large difference in CTE. The principal strategies undertaken in the material process engineering involved: (i) multi-layer film deposition, (ii) composite sol-gel slurries with bi-modal particle size distribution, (iii) chemical bonding of the film through phosphating, and (iv) introduction of organic-phase (citric acid) derived bond coats at the interface between the AA5052 substrate and the ceramic coating.

As a result of development and investigation of the above novel CB-CSG processing techniques thick alumina-based coatings have been successfully deposited on AA5052 substrate and characterized. The thickness of the coatings was approximately 200 $\mu$ m, and they were processed through spray-deposition of consecutive layers, approximately 40  $\mu$ m thick each, heat-treated at 300°C for ~10 min after each deposition. Two size fractions of alumina powders ("fine" of average size 0.5  $\mu$ m and "coarse" of 3  $\mu$ m) were used in formulation of the Composite Sol-Gel (CSG) slurry. The mixing ratio of the fine/coarse particles content was investigated based on slurry viscosity and stability, as well as properties

of the final coating. The coatings were characterized for microstructure, residual stresses and dielectric strength, as a function of the process parameters.

The most important finding of this work is that it is possible to deposit thick ceramic films on aluminum alloy substrates, if all four processing strategies listed above are implemented simultaneously. In particular, the citric acid – derived organo-ceramic bond coats seem to play important role in relaxing residual stresses resulting from differential thermal contraction and expansion. Based on the results of this work, the following specific conclusions are drawn in reference to the four process development categories listed above:

#### (i) composite sol-gel slurries with bi-modal particle size distribution

This was introduced to decrease the overall process temperature, and to decrease film strain during thermal treatment as well as to increase the density and stability of composite sols. The sol-gel based slurry allows to decrease the process temperature to 500°C level, but large shrinkage (up to 90 vol.%) is a significant disadvantage, leading to failure of coatings thicker than about 1 µm. A composite sol-gel (CSG) is introduced to decrease such a high shrinkage by adding ceramic fillers into the sol, providing the composition of a solid body of 86 vol.% of the filler and 14vol% of the sol-derived phase. It was observed that the longer the ball-milling time and the larger the amount of the fine particles the higher the viscosity of the solution. A40 composition with 24 h ball-milling demonstrated the appropriate viscosity required for the spray-deposition of the coatings, which is 200-400 cp. The investigation of CSG slurry stability through observation of the settling patterns supports the importance of ball-milling time in achieving slurry stability. For the same concentration

of fine particles, the longer ball-milling improved CSG slurry stability, as evidenced through the slower settling time. The 12 h ball-milled A40 CSG showed the settling rate of 0.16 mm/min for the first 15min while no sedimentation was observed in the 24 h ball-milled A40. Based on these results, A40 has been selected as an appropriate CSG concentration for the spray coatings of thick dielectric alumina films on AA5052.

#### (ii) chemical bonding of the CSG films

Chemically bonded composite sol-gel (CB-CSG) technique provides decreasing process temperature to 300°C. CB-CSG also increases the adhesion (to the level of 10MPa) between AA5052 and the alumina coatings and as such increases the system resistance to thermal mismatch stresses. The aluminum phosphate bonds the alumina filler particles, and thus provides denser and harder ceramic than that of ordinary sol-gel process.

#### (iii) multi-layer coating deposition

The thickness limit of a single layer deposition without coating failure was experimentally determined to be ~40  $\mu$ m, due to excessive residual stress accumulation in thicker coatings caused by the relatively large thermal expansion mismatch between the coating and the substrate. Therefore, multi-layer deposition reduces the stresses in total alumina coating thickness of ~200  $\mu$ m is deposited with 5 multi-layers of ~40  $\mu$ m thick each without failure of coatings.

#### (iv) citric acid derived bond coats

Citric acid (CA) melts and partially decomposes during the 300 °C heat treatment in

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coating processing, providing poorly defined CAD ("citric acid derivative") amorphous phase, forming a CAD+sol derived alumina amorphous bond coat at the interface with AA5052. Three point bending test was applied to quantify the effect of CAD-based bond coat on stress mitigation in the system, with constant force of 18N to the coated sample for 60 min. After the force removal, it was observed that alumina coatings on AA5052 without CAD bond coat recovered in 120 minutes ~99 % of the deformation, while only ~92 % of the recovery was observed for the same time for the CAD bond coat containing samples. This was presumably related to the viscoelastic behavior of the CAD bond coat, and it allows deposition of films of up to 200 µm thickness.

#### (v) residual stress in the films

Residual stresses in the coating, after accumulation of consecutive coating layers, were evaluated by curvature measurement and XRD method. The maximum residual tensile stress of ~150±30 MPa was observed after first layer deposition (at ~40  $\mu$ m) while the residual compressive stress of -60±20 MPa was reached at the fourth layer, the thickness of ~160  $\mu$ m. XRD method demonstrated the same trend of the stresses. The maximum residual tensile stress of 100±60 MPa has been determined for the first layer, ~40  $\mu$ m, and the residual compressive stress of -40±60 MPa for the fourth layer, at ~160  $\mu$ m.

#### (vi) dielectric strength of the films

Dielectric strength of the CB-CSG alumina coated AA5052 aluminum was determined from the measurements of the breakdown voltage (in AC). As expected, the breakdown voltage (kV) increased proportionally to the coating thickness. The dielectric

strength reached a maximum of about 15 kV/mm for the first layer, and subsequently decreased to reach minimum of about 10 kV/mm for the fifth coating layer. The most rapid decrease of the dielectric strength was found between the first layer of ~40  $\mu$ m and the second layer (total coating thickness ~80  $\mu$ m), and it gradually decreased thereafter. It is believed that this decrease in the dielectric strength after the first layer is caused by increased density of cracks in the coating, as also evidenced by decrease of the residual stress in the coatings.

### **CHAPTER 8** 'RECOMMENDATIONS FOR FUTURE WORK

Although it has been shown that the combination of the CB-CSG technique and CAD organo-ceramic bond coats substantially expanded the possibilities of deposition of thick dielectric ceramic films on light metals, the effects of CAD on the coating behavior and properties have not been fully clarified. This issue is important if the technology is to be transferred to other coating systems. Therefore, further investigations including theoretical and experimental approaches are required to verify the influence of CAD bond coats on the coatings and system characteristics.

The composition of CAD organo-ceramic bond coats was determined by EDX and it is observed that such bond coats are made of partially decomposed CA and alumina gelderived sol. No exact chemical composition was determined. Therefore, it is recommended to investigate the bond coat composition by using XPS, XRD and other methods such as DTA/TGA. The hypothesis regarding viscoelastic behaviour of the CAD organo-ceramic bond coats has not been fully confirmed in this study. Therefore, it is recommended that detailed nano-indentation studies are performed on the interlayer, to support (or reject) the hypothesis on the viscoelastic behavior of CAD organo-ceramic bond coats.

Adhesion of the CB-CSG coatings, even with use of CAD bond coats, remains relatively low at ~10 MPa. This is believed to be due to the large difference in CTE between alumina and AA5052. It is recommended to evaluate further methods to decrease the effect of the large difference in CTE on bonding strength of the coatings. Particle size-graded multi-layers and controlled porosity (low stiffness) layers may be deposited and evaluated. The use of composite films may also be promising to increase the adhesive strength of the films. Alumina/silica composites may be introduced by dispersing alumina in silica sol. It is anticipated that better coating adhesion would result due to the presence of amorphous phase of silica. In addition, the dielectric strength of the coating would be increased due to high dielectric strength of the silica (i.e., 25-40 kV/mm).

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#### APPENDIX

### Fig.A-1 Effect of the Sand-blasting on the shape of AA5052



## **3-Dimensional Interactive Display**

Date: 4/26/2005 Time: 11:36:46



Title: 30.150753 Note: 30.150753

(a) As-received AA5052 after cutting in a beam shape



#### **3-Dimensional Interactive Display**

Date: 4/26/2005 Time: 11:45:39



Title: 30.150753 Note: 30.150753

Ra: 34.31 um

Rq: 40.43 um

Rt: 162.76 um

(b) After sand-blasting with silica grit (size of 60)

Fig.A-2 Comparison of Stress/Strain Curve between As-received AA5052 and Alumina coated AA5052 (~100 µm coating thickness) with/without CA





(c) 3<sup>rd</sup> layer





(e) 5<sup>th</sup> layer





The peaks in (a) are for as-received fine alumina powders (0.5  $\mu$ m), the peaks in (b) are for as received coarse alumina powders (5  $\mu$ m), and the peaks in (c) are for the phosphated alumina CB-CSG (mixed with 40/60 of fine/coarse particles) under the stress free state



(a) Alumina CSG coating on AA5052
 without chemical bonding by using phosphoric acid. The complete coating failure (i.e., delamination) occurred at the thickness of the coating about 100 μm



(b) CA-free alumina CB-CSG coatings on AA5052. The partial coating failure (i.e., delamination) occurred at the thickness of about 200 μm



(c) CA-containing alumina CB-CSG coatings on AA5052. The coating thickness is about 200 μm and no coating failure (i.e., delamination) occurred during the process.

			Strain		Stress	Young's	
# of	Thickness,	Width,	constant,	Strain,	constant,	modulus,	
layer	mm	mm	Kε	3	$K_{\sigma}$	E (Gpa)	
substrate	1.62	6.4	0.006075	0.000304	35258.06	66.7	
1	1.67	6.45	0.006263	0.000313	32921.21	63.52	
1	1.674	6.45	0.006278	0.000314	32764.07	64.16	
2	1.704	6.43	0.00639	0.00032	31718.91	61.24	
2	1.704	6.43	0.00639	0.00032	31718.91	60.87	
3	1.771	6.5	0.006641	0.000332	29048.11	61.15	
3	1.771	6.51	0.006641	0.000332	29003.49	61.12	
4	1.809	6.56	0.006784	0.000339	27585.92	56.64	
4	1.781	6.5	0.006679	0.000334	28722.83	55.87	
5	1.883	6.57	0.007061	0.000353	25421.57	52.03	
5	1.868	6.57	0.007005	0.00035	25831.48	52.12	

Table A-1 Parameters for obtaining average Young's Modulus of aluminacoated AA5052 using 3-Point Bending

# Comparison Comparison</t

Maximum Force	18N		
Minimum Force	0.0001N		
Force Resolution	0.00001N		
Strain Resolution	1 nm		
Modulus Range	$10^3$ to $3 \times 10^{12}$ Pa		
Modulus Precision	±1%		
Tano Sensitivity	0.0001		
Tano Resolution	0.00001		
Frequency Range	0.01 to 200 Hz		
Dynamic Sample Deformation Range	±0.5to 10,000 μm		
Temperature Range	-150 to 600 °C		
Heating Range	0.1 to 20 °C/min		
Cooling Rate	0.1 to 10 °C/min		
Isothermal Stability	±0.1 °C		
Time/Temperature Superposition	Yes		

δ (ppm)	δ (ppm) Group Family		Example	
		$(\delta \text{ of italicized carbon})$		
220-165	>C=O		(CH <sub>3</sub> ) <sub>2</sub> CO	(206.0)
· · · · · · · · · · · · · · · · · · ·			(CH <sub>3</sub> ) <sub>2</sub> CHCOCH <sub>3</sub>	(212.1)
		Aldehydes	CH <sub>3</sub> CHO	(199.7)
		α,β-Unsaturated	CH <sub>3</sub> CH=CHCHO	(192.4)
		carbonyls	CH <sub>2</sub> =CHCOCH <sub>3</sub>	(169.9)
		Carboxylic acids	HCO <sub>2</sub> H	(166.0)
			CH <sub>3</sub> CO <sub>2</sub> H	(178.1)
		Amides	HCONH <sub>2</sub>	(165.0)
			CH <sub>3</sub> CONH <sub>2</sub>	(172.7)
		Esters	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	(170.3)
			CH <sub>2</sub> =CHCO <sub>2</sub> CH <sub>3</sub>	(165.5)
140-120	>C=C<	Aromatic	C <sub>6</sub> H <sub>6</sub>	(128.5)
		Alkenes	CH <sub>2</sub> =CH <sub>2</sub>	(123.2)
			CH <sub>2</sub> =CHCH <sub>3</sub>	(115.9,136.2)
			CH <sub>2</sub> =CHCH <sub>2</sub> Cl	(117.5, 133.7)
			CH <sub>3</sub> CH=CHCH <sub>2</sub> CH <sub>3</sub>	(132.7)
125-115	-CN	Nitriles	CH <sub>3</sub> -CN	(117.7)
80-70	<u>-CC-</u>	Alkynes	НССН	(71.9)
			CH <sub>3</sub> CCH <sub>3</sub>	(73.9)
70-45	-C-O	Esters	CH <sub>3</sub> OOCH <sub>2</sub> CH <sub>3</sub>	(57.6, 67.9)
		Alcohols	HOCH <sub>3</sub>	(49.0)
			HOCH <sub>2</sub> CH <sub>3</sub>	(57.0)
40-20	-C-NH <sub>2</sub>	Amines	CH <sub>3</sub> NH <sub>2</sub>	(26.9)
			CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	(35.9)
30-15	-S-CH <sub>3</sub>	Sulfides (thioethers)	C <sub>6</sub> H <sub>5</sub> -S-CH <sub>3</sub>	(15.6)
30-(-2.3)	-С-Н	Alkanes, cycloalkanes	CH <sub>4</sub>	(-2.3)
			CH <sub>3</sub> CH <sub>3</sub>	(5.7)
			CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	(15.8, 16.3)
			CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	(13.4, 25.2)
			CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	(13.9, 22.8, 34.7)
		Cyclohexane		(26.9)

.

# Table A-3 <sup>13</sup>C-NMR Absorptions of major functional groups [2.55]

Thickness (mm)	Breakdown Voltage (V)							
	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Point 7	
40	570	570	572	617	619	668	680	
80	812	819	918	918	967	1118	1118	
120	1088	1116	1216	1317	1366	1466	1504	
160	1440	1468	1517	1665	1865	2015	2166	
200	1744	1767	1916	2066	2365	2516	2674	

•

# Table A-4 Full Data set for Dielectric Breakdown Voltages of the AluminaCoated AA5052