

High-Temperature Chemical Stability of Plasma-Sprayed $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ Coatings on Nicalon/SiC Ceramic Matrix Composite and Ni-Based Superalloy Substrates

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The potential application of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ (CS50) as a corrosion-resistant coating material for Si-based ceramics and as a thermal barrier coating material for Ni-based superalloys was explored. A ~ 200 μm thick CS50 coating was prepared by air plasma spray with commercially available powder. A Nicalon/SiC ceramic matrix composite and a Ni-based superalloy coated with a ~ 200 μm thick metallic bond coat layer were used as substrate materials. Both the powder and coating contained ZrP_2O_7 as an impurity phase, and the coating was highly porous as-deposited. The coating deposited on the Nicalon/SiC substrate was chemically stable upon exposure to air and $\text{Na}_2\text{SO}_4/\text{O}_2$ atmospheres at 1000°C for 100 h. In contrast, the coating sprayed onto the superalloy substrate significantly reacted with the bond coat surface after similar oxidation in air.

I. Introduction

THE class of ceramics commonly referred to as NZPs and named after their parent composition $(\text{NaZr}_2\text{P}_3\text{O}_{12})^{1-3}$ possess several unique properties for consideration as protective coating materials for high-temperature structural applications. An interesting property of NZPs is their very low thermal conductivity (~ 1 $\text{W}/(\text{m}\cdot\text{K})$ for dense, slip-cast materials³). This thermal conductivity value is essentially as low as that of air-plasma-sprayed (APS), porous Y_2O_3 -stabilized ZrO_2 coatings that are currently used as thermal barrier coatings for advanced gas turbines. Most NZP materials have low coefficients of thermal expansion (CTE) of about 1×10^{-6} to $3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, and generally exhibit anisotropic behavior. However, some NZP compositions such as $\text{Ba}_{1+x}\text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24}$ (where $0 \leq x \leq 1$), $\text{Ca}_{x-1}\text{Sr}_x\text{Zr}_4\text{P}_6\text{O}_{24}$, and $\text{Ca}_{x-1}\text{Mg}_x\text{Zr}_4\text{P}_6\text{O}_{24}$ can be tailored to obtain isotropic thermal expansion characteristics.²⁻⁴ Young's modulus of NZPs is reported to be rather low for a ceramic (~ 70 GPa).³ The melting point of NZPs is typically higher than 1800°C . Because of their crystal structure, oxygen diffusivity in the NZPs is also expected to be relatively low, although it has not been accurately measured.¹

A potential application of NZP coatings may be to protect Si-based ceramics and ceramic matrix composites from hot

corrosion induced by impurity deposits such as Na_2SO_4 .^{6,7} From the perspective of minimizing residual and thermal stresses, the low CTE and low modulus of NZPs could be attractive as coating materials for Si-based materials, since the CTE of most Si-based materials is also relatively low (e.g., 3×10^{-6} for Si_3N_4 and 5×10^{-6} for SiC).^{6,7} In our earlier work,⁶ the stability of several NZP bulk compositions was tested in a corrosive environment containing Na_2SO_4 at 1000°C . In brief summary, $\text{Ba}_{1.25}\text{Zr}_4\text{P}_5\text{Si}_{0.5}\text{O}_{24}$ and $\text{Ca}_{0.6}\text{Mg}_{0.4}\text{Zr}_4\text{P}_6\text{O}_{24}$ experienced extensive cracking and delamination upon reaction with $\text{Na}_2\text{SO}_4/\text{O}_2$ after 100 h. It appeared that the cracking occurred due to the formation of $\text{NaZr}_2\text{P}_3\text{O}_{12}$ as a reaction product, which caused volume changes as well as anisotropic thermal expansion. On the other hand, $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ (CS50) remained structurally intact, and did not exhibit significant weight changes. However, the ion exchange between Na^+ ions and Ca^{2+} ions was observed to be sufficiently rapid to allow the substitution of the Na^+ ions into the CS50 structure.

In another possible application, the low thermal conductivity of NZPs might render them useful as thermal barrier coating materials.⁸ From a mechanical standpoint, the CTE mismatch between a NZP coating and a Ni-based superalloy substrate ($\sim 16 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) is large. More critically, the chemical compatibility of NZP materials with respect to Ni-based superalloys in turbine environments is largely unknown.

In view of its observed structural stability in hot corrosion, the first objective of the present study was to further assess the potential of CS50 as a corrosion-resistant coating material for Si-based ceramics. Specifically, in this work, a CS50 coating was prepared by APS on Nicalon/SiC ceramic matrix composite substrates, and the chemical stability of the coating-substrate interface in corrosive environments was examined. The second objective of this study was to address the chemical compatibility between the CS50 coating and a Ni-based superalloy substrate in an oxidative atmosphere.

II. Experimental Procedure

A CS50 coating was prepared using APS equipment (Metco, Westbury, NY) with commercially available CS50 powder (CS50, LoTEC, Salt Lake City, UT). A number of coating specimens were prepared, but it was generally difficult to plasma spray the as-received CS50 powder because the particle size was smaller than what is typically desired for spraying (~ 40 μm). The particle size distribution was bimodal and centered around 2 and 20 μm . An example of the processing difficulties encountered in this work is that it took 110 spray passes to apply ~ 200 μm CS50 with a deposition efficiency of less than 30%.

The CS50 coating was directly applied to Nicalon/SiC composite coupons (1.9 cm \times 1.9 cm \times 0.64 cm) to a thickness of ~ 200 μm . The Nicalon/SiC composite consisted of Nicalon

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SiC fiber cloth (Nippon Carbon, Japan) which was chemical vapor infiltrated with a SiC matrix. The procedure for preparing the Nicalon/SiC composites is described elsewhere in detail.⁹ A Ni-based superalloy (Mar-M-247) was also used as a substrate material (disk shape with 2.54 cm diameter X 0.316 cm thickness). This alloy contains 8.4 wt% Cr, 10.0% Co, 0.15% C, 1.1% Ti, 5.5% Al, 0.65% Mo, 10% W, 0.015% B, 1.4% Hf, 3.1% Ta, 0.055% Zr, and Ni as the balance. A metallic CoNi-CrAlYSi bond coat layer with a thickness of $\sim 200 \mu\text{m}$ was also applied by APS to improve the adhesion between the CS50 layer and the substrate. The composition of the bond coat material (Co-260, Praxair, Indianapolis, IN) was 32% Ni, 22% Cr, 12% Al, 0.75% Y, 1.5% Si, and Co as the balance.

Some of the coated specimens were subjected to oxidation in an open tube furnace at 1000°C . The specimens were placed on an Al_2O_3 holder, and slowly heated to temperature and slowly cooled after the desired exposure time duration. The superalloy and Nicalon/SiC specimens were tested separately. Some Nicalon/SiC specimens coated with CS50 were also tested for hot corrosion. In this test, the CS50 coating surface was loaded with -40 mg/cm^2 of Na_2SO_4 using a procedure described elsewhere.^{6,7,10} The Na_2SO_4 -loaded specimens were placed on an Al_2O_3 holder and exposed for 100 h to a flowing oxygen environment ($200 \text{ cm}^3/\text{min}$) at 101 kPa in a quartz tube heated to 1000°C . It is noted that this gas environment creates a higher Na_2O activity in the Na_2SO_4 salt (i.e., more basic) than a carrier gas containing SO_2 .¹¹

A Scintag PAD V X-ray diffractometer (XRD) and a JEOL Superprobe 733 electron microprobe analyzer (EMPA) were mainly used for microstructural and compositional characterization. The coating specimens after oxidation and corrosion tests were mounted in epoxy and polished using kerosene as a lubricant to examine the formation of any reaction products and coating-substrate interfacial features.

III. Results and Discussion

The as-sprayed CS50 coating adhered well to the superalloy substrate and Nicalon/SiC substrate. The polished cross section of the as-sprayed CS50 layer was porous as shown in Fig. 1. A significant degree of particle pull-out was suspected to occur during polishing because of the low modulus of the CS50 material. Figure 1 suggests that the CS50 and the CoNiCrAlYSi bond coat surface did not react during plasma spraying. It was determined by XRD that the as-received CS50 powder contained a significant level of ZrP_2O_7 incorporated as an impurity phase. The presence of both CS50 and ZrP_2O_7 as crystalline phases was detected in the plasma-sprayed coating deposited on both the superalloy and Nicalon/SiC substrates. It also appeared that the coating deposited on the superalloy substrate contained an amorphous phase as evidenced by a broad rise on the baseline. However, the XRD analysis could only be qualitative because some diffraction peaks could not properly be indexed.

One issue identified in this study was the need to prepare CS50 powder with a larger particle size and more homogeneous distribution, and without the incorporation of ZrP_2O_7 . The ZrP_2O_7 phase is known to be highly anisotropic in thermal expansion. Consequently this material tends to microcrack when prepared as a bulk structure. It appeared that the reaction to form CS50 was incomplete when the powder was calcined at 1150°C by the powder supplier. A higher calcining temperature ($>1300^\circ\text{C}$) is suggested for future powder preparation. Also, several methods for increasing the average particle size could be explored, such as agglomerating as-calcined powder by pressing and sintering, followed by crushing and sieving, or possibly a spray drying operation.

The substrates coated with the CS50 layer were subjected to 1000°C in air for 100 h to determine their high-temperature stability. The CS50 coating deposited on the bond coat surface of the superalloy substrate delaminated from the bond coat surface on cooling to room temperature. In the XRD pattern

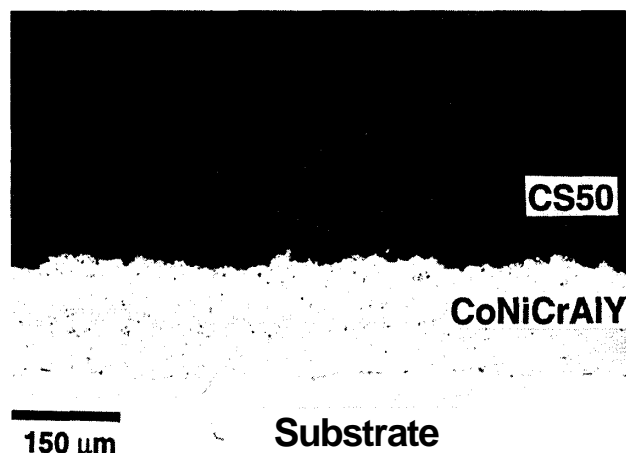


Fig. 1. Polished cross section of an air-plasma-sprayed CS50 coating ($\sim 200 \mu\text{m}$) deposited on a Mar-M-247 superalloy substrate with a CoNiCrAlYSi bond coat layer ($\sim 200 \mu\text{m}$).

obtained from the delaminated coating, most of the diffraction peaks could be assigned to CS50. This observation suggested the disappearance of the ZrP_2O_7 and amorphous phases in the coating layer after the oxidation treatment. A backscatter electron micrograph and X-ray elemental maps in Fig. 2 show that substantial reactions occurred at the CS50-CoNiCrAlYSi interface. It appears that the reaction zone, which was about $20 \mu\text{m}$ thick, contained oxides of constituent metal elements including Al, Cr, and Ni. The presence of a microcrack was observed within the reaction zone (Fig. 2).

The results from the oxidation experiment were not sufficient to determine major reasons for the CS50 layer delamination. There could be many contributing factors such as reaction at the interface, crystallization, phase change, CTE mismatch, etc. Nevertheless, the observed chemical incompatibility between the CS50 and CoNiCrAlYSi layers discourages the use of this particular NZP material for thermal barrier coating applications. However, since CS50 appears to be inert with respect to Al_2O_3 ,¹² the possibility of using Al_2O_3 as an interface material between the CS50 and metallic bond coat phases could be considered. In this system design, the CS50 material provides thermal insulation, while Al_2O_3 acts as a buffer material to minimize the reaction between the CS50 and metallic phases, and also to reduce the CTE mismatch between the CS50 and the metal. Also, other NZP compositions could be explored to determine their chemical compatibility with Ni-based superalloys.

In contrast, the CS50 coating deposited on the Nicalon/SiC composite adhered well to the substrate after the oxidation treatment at 1000°C for 100 h. The coated specimen lost a small amount of weight (0.44 mg/cm^2). As in the case of the CS50 coating deposited on the metallic substrate, the presence of ZrP_2O_7 in the coating was no longer observed after oxidation. The coating-substrate interface was metallographically analyzed, and was observed to be chemically stable.

Two as-sprayed CS50-Nicalon/SiC specimens were exposed to the hot corrosion atmosphere for 100 h. At this temperature, Si-based ceramics severely react with Na_2SO_4 to form sodium silicates." After the corrosion test, the CS50 coating still adhered well to the Nicalon/SiC substrates except for some very minor delamination by edge lifting at two of the four corner locations of the square substrate surface. The samples lost 10.1 and 9.2 mg/cm^2 , which were substantially higher than the weight loss measured for the oxidation sample. The XRD analysis also indicated the disappearance of ZrP_2O_7 in the coating structure. More interestingly, Fig. 3 shows that there were no major chemical or microstructural changes at both Na_2SO_4 -CS50 and CS50-substrate interfaces. The formation of any sodium-containing reaction product at the substrate interface was not apparent, at least within the resolution of the EMPA technique ($\sim 0.5 \text{ wt}\%$). However, it should be mentioned that,

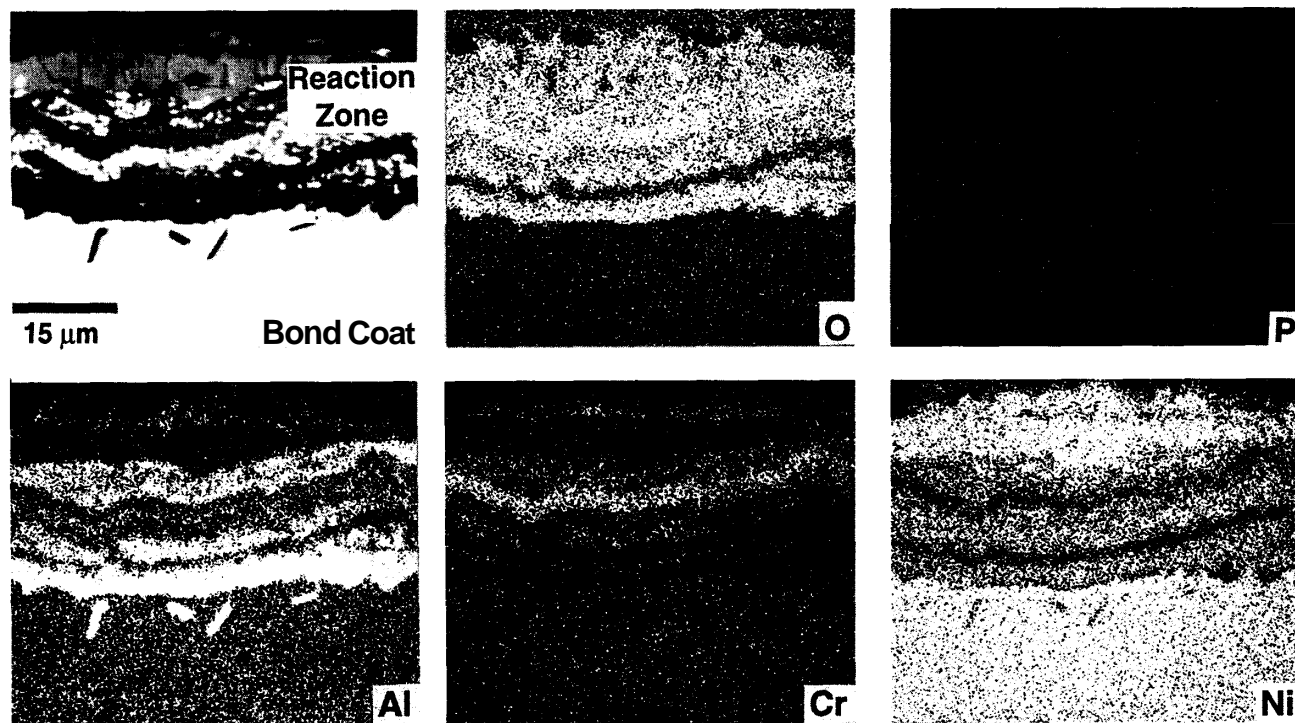


Fig. 2. Backscattered electron image and X-ray elemental maps at the bond coat interface from which the CS50 coating delaminated after oxidation in air at 1000°C for 100 h.

while the use of a more basic salt under the present experimental conditions (i.e., oxygen carrier gas) creates a more aggressive environment with respect to reaction of SiO_2 with Na_2SO_4 , it reduces the driving force in the reaction of the CS50 with the salt.^{11,13}

The presence of Na was detected in the CS50 coating structure. This observation is consistent with our earlier work with slip-cast CS50 bulk specimens.⁶ As mentioned above, the ion exchange between Na^+ ions and Ca^{2+} ions was sufficiently rapid to allow the substitution of the Na^+ ions into the specimens in 100 h. Interestingly, the surface of the Nicalon/SiC substrate was not affected by the presence of the Na^+ in the coating structure. It seems that the CS50 coating acted as a "chemical getter" for the Na^+ ions. Furthermore, the Na^+ ions,

once trapped in the coating, had the attribute of not being able to react to form sodium silicates at the substrate surface.

IV. Conclusions

This study explored the use of CS50 as a corrosion-protection coating material for Nicalon/SiC composites and a thermal barrier coating material for Ni-based superalloys. The CS50 coating could be prepared by APS processing although there were several problems with the commercially available CS50 powder such as small particle size for spraying and the presence of an impurity phase. The plasma-sprayed CS50 coating significantly reacted with the CoNiCrAlYSi bond coat material upon exposure to air at 1000°C for 100 h, suggesting their chemical incompatibility in oxidative environments. However, the CS50 coating deposited on the Nicalon/SiC substrate was stable under oxidative environments. Furthermore, the CS50 coating protected the surface of the Nicalon/SiC composite from hot corrosion, although it was a porous coating. It appeared that the CS50 coating acted as a getter for Na^+ during the corrosion test. These observations were encouraging for the possible use of CS50 as a corrosion-resistant coating material for Si-based ceramic materials; however, there are many other issues which need to be considered in future studies. For example, it would be interesting to examine the effects of long-term and higher temperature exposures as well as of other corrosive environments (i.e., basic salts, coal ash, etc.) on the chemical stability and the protective capability of the CS50 coating.

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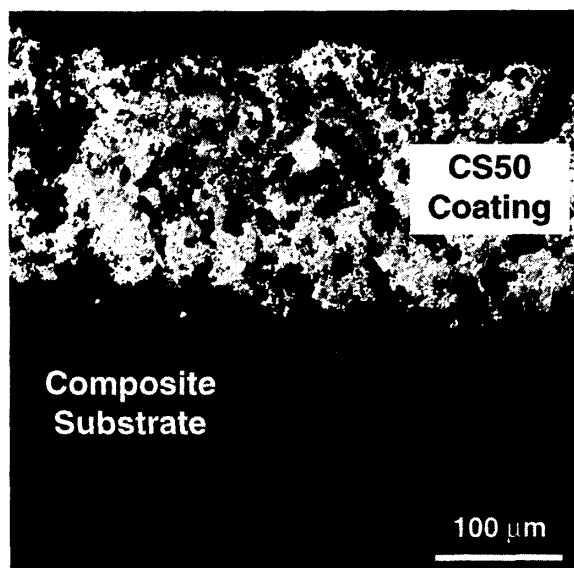


Fig. 3. Backscattered electron image of the CS50 coating on the Nicalon/SiC substrate after hot corrosion in $\text{Na}_2\text{SO}_4/\text{O}_2$ at 1000°C for 100 h.

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