Design and Preparation of Wave-Transmitting Reinforcing Coatings for Multifunctional Ceramic Composite Antenna Windows

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Abstract. For obtaining multifunctional ceramic composite antenna windows with integrated function including low density, wave-transmission and thermal insulation, the design and preparation of reinforcing coatings on ceramic matrix was discussed in detail in this work. With quartz glass chopped fiber as the major constituent for matrix, borosilicate glass was selected as the main phase for reinforcing coatings, and functional filler was added to match the coefficient of thermal expansion between the two components. According to the performance testing of the as-prepared samples, content of B₂O₃ in SiO₂/B₂O₃ binary system and sintering temperature showed a marked impact on the microstructure, density and thermal behaviour of the ceramics. Densified coatings were prepared at 1160°C after sintering for 1h with 20% B₂O₃ in borosilicate glass, which bond well with the substrate and have radiation coefficient of 0.85 and linear expansion coefficient of (1.77~2.39)×10⁻⁶/°C (200~1000°C). Stronger matrix, better ablation resistance and dielectric properties are expected to be integrated in the obtained sample pieces, which can be a good candidate as effective thermal insulation materials for aerospace aircrafts at high flight Ma.

1. Introduction
Rigid thermal insulation materials with ceramic fibers as raw materials, has excellent thermal insulation performance [1], wave permeability [2,3], anti-erosion [4] and shape retention, as well as superior mechanical properties at high temperature [5], which has become a good candidate for multifunctional ceramic composite antenna windows integrating low density, wave-transmission and thermal insulation qualities. The service temperature of these materials is mainly in intermediate region from 600 to 1260°C [6]. In order to avoid being destroyed by high-speed airflow scour and reduce the incoming heat, densified coatings with good anti-erosion properties, high radiation coefficient and excellent thermal shock resistance are usually applied on the surface of the ceramic matrix [7].

Borosilicate glass is known to be a kind of material system with heat-resistance, low expansion, good thermal shock resistance and erosion resistance [8]. Moreover, borosilicate glass shows good chemical and physical compatibility with ceramic matrix using silica fibers as main components [9]. Therefore, high-performance borosilicate glass coatings were designed and prepared in this work,
through systematically investigating the effects of chemical component and sintering temperature on the phase composition and microstructure of borosilicate glass coatings. The expansion coefficient, dielectric property and radiation coefficient of the obtained coatings were also characterized as well.

2. Materials and Methods

Coating slurries were prepared by ball-milling raw materials for 30min with ratios listed in Table 1. Spray finishing was employed to coat the slurries on the surface of the multifunctional ceramic matrix, which was then dried and sintered above 1000°C for 1h to obtain coating samples for further characterization with scanning electron microscope (SEM).

| No. | SiO₂ | B₂O₃ | Al₂O₃ | Y₂O₃ |
|-----|------|------|-------|------|
| 1   | 90   | 10   | 2     | 2    |
| 2   | 85   | 15   | 2     | 2    |
| 3   | 80   | 20   | 2     | 2    |

To investigate the effect of sintering temperature on the microstructure of coatings, SEM characterization was carried out with samples sintered with slurries in No.3 ratio for 1h at 1100°C, 1130°C and 1160°C respectively. Besides, back-scattering electron (BSE) imaging, expansion coefficient, dielectric properties and radiation coefficient were also tested for coating samples sintered at 1160°C for 1h in No.3 ratio.

3. Results and Discussions

3.1. Effect of slurry components on the microstructure and phase composition of sintered coatings

Figure 1 shows the microstructure of coatings sintered at 1160°C for 1h, with slurries in different components. As can be seen from section images shown in Figure 1a, 1c and 1e, melting degree increases and internal porosity decrease with the increasing amount of B₂O₃ from 10% to 20% in slurries, indicating the increasing density of sintered coatings. Specifically, fine particles in slurries become to melting and joining with each other, while many interconnected holes can be found in Figure 1a. When B₂O₃ increases to 15%, particles in slurries gradually fused and grow up to form larger glass phase, with less interconnected holes owing to the reduction of intergranular space, as shown in Figure 1b. While the amount of B₂O₃ is up to 20%, continuous glass phase is obtained with almost no intergranular space and few isolated pores in Figure 1c.

As for surface images shown in Figure 1b, 1d and 1f, continuous fused glass phase is form gradually with the increase of B₂O₃ in slurries. Specifically, particles begin to melting and joining in Figure 1b with more space, which is further reduced to form larger fused area in Figure 1d. A nearly continuous glass phase is obtained with few isolated pit areas in Figure 1f when B₂O₃ increases to 20%. Therefore, B₂O₃ in slurries act as effect adhesive to form fused phases, and continuous densified coatings are obtained with the increasing amount of B₂O₃ in slurries. Coating slurries with raw materials in No.3 ratio are used for further experiments in this work because of its better microstructure.

The binary phase diagram of SiO₂-B₂O₃ [10] was consulted to further confirm the phase composition of the coatings sintered at 1160°C with different amount of B₂O₃ in coating slurries. When content of B₂O₃ is 10%, the coating is composed of more solid phase of molten quartz and less liquid phase of borosilicate glass. With B₂O₃ of 15%, the coating is composed of less molten quartz solid phase and more borosilicate glass liquid phase. As for B₂O₃ increasing to 20%, the coating is composed of single borosilicate glass liquid phase. At 1160°C, the solid phase of molten quartz formed in the coating gradually decreases and the liquid phase of borosilicate glass gradually increases, with the increasing B₂O₃ content. That is, the only liquid phase of borosilicate glass existing in samples No.3 with 20% B₂O₃ accounts for the densified coatings obtained in this work.
Figure 1. SEM images of coatings sintered with slurries in different components: (a) Section of No.1, (b) Surface of No.1, (c) Section of No.2, (d) Surface of No.2, (e) Section of No.3, (f) Surface of No.3.

3.2. Effect of sintering temperature on the microstructure of the coatings
Figure 2 shows the microstructure of coatings sintered with slurries in No.3 ratio for 1h at 1100°C, 1130°C and 1160°C respectively. As can be indicated from Figure 2, the melting degree of the coatings increases with decreasing pores and the density is gradually increasing, as the increase of sintering temperature. It is interesting to find that, the sintering temperature has similar effect on the microstructure of the coatings, which is indicated in detail in section images (Figure 2a, 2c, 2e) as well as surface images (Figure 2b, 2d, 2f).

The binary phase diagram of SiO$_2$-B$_2$O$_3$ [10] with 20% B$_2$O$_3$ was consulted to further confirm the phase composition of the coatings sintered at different temperature. At 1100°C, the coating is composed of more solid phase of molten quartz and less liquid phase of borosilicate glass. At 1130°C, the coating is composed of less molten quartz solid phase and more borosilicate glass liquid phase. At 1160°C, the coating is composed of single borosilicate glass liquid phase. In brief, densified coatings
have been obtained with raw materials in No.3 ratio by sintering slurries at 1160°C for 1h, which is further characterized for microstructure and properties in the following sections.

**Figure 2.** SEM images of coatings sintered with slurries in No.3 ratio at different temperature: (a) Section at 1100°C, (b) Surface at 1100°C, (c) Section at 1130°C, (d) Surface at 1130°C, (e) Section at 1160°C, (f) Surface at 1160°C.

### 3.3. The microstructure and composition of the coatings

Figure 3 shows the SEM and BSE images of typical coating samples prepared at optimized conditions mentioned above. As seen from Figure 3a, continuous densified structure is formed in the section of the coatings, with few isolated closed pores. Some pits and semienclosed pores are found on the surface of the coatings, as shown in Figure 3c. According to corresponding BSE images in Figure 3b and 3d, relatively brighter particles as circled in red are identified as Y$_2$O$_3$, which are uniformly distributed in the section and surface of the coatings. To further confirm the component analysis, Energy Dispersion Spectrum (EDS) in different areas in the coating samples was collected and the results are shown in Figure 4 and Table 2.
**Figure 3.** SEM and BSE images of the coatings.
(a) SEM of section, (b) BSE of section, (c) SEM of surface, (d) BSE of surface.

**Figure 4.** EDS images of the coatings.

**Table 2.** eZAF Smart Quant Results.

| Element | Selected Area 1 Atomic % | Selected Area 2 Atomic % | Selected Area 3 Atomic % |
|---------|---------------------------|---------------------------|---------------------------|
| B K     | 48.39                     | 49.40                     | 47.58                     |
| O K     | 35.91                     | 39.84                     | 35.02                     |
| Al K    | 0.07                      | 0.89                      | 0.41                      |
| Si K    | 5.47                      | 5.10                      | 16.99                     |
| Y L     | 10.15                     | 4.76                      | /                         |
Based on the results of EDS, it can be seen that the elements in typical coating samples include B, O, Si and Al, indicating the generation of aluminum borosilicate glass with low aluminum content. Y is found to be accumulated in both selected area 1 and 2, while no Y is observed in selected area 3. The main substances in area 3 are SiO₂, B₂O₃, and a small amount of Al₂O₃, which is supposed to be aluminum borosilicate glass. That is, filler Y₂O₃ particles are evenly dispersed in the coated borosilicate aluminum glass independently and do not react with SiO₂, B₂O₃ and Al₂O₃ to form glass solid solution.

3.4. The matching of expansion coefficient between coating and matrix
Thermal matching plays key effect on the high-temperature behavior of the composite multifunctional materials. Therefore, the expansion coefficient of matrix and coatings is measured from 200°C to 1000°C, which is demonstrated in Figure 5. The coatings present larger expansion coefficient than matrix with maximum and minimum difference of 1.5×10⁻⁶/K⁻¹ and 0.4×10⁻⁶/K⁻¹ in the whole testing range, respectively. The relatively small difference in the expansion coefficient of matrix and coatings means the fewer cracks possibly appeared during the period of their service, and the better thermal insulation properties obtained in this work.

![Figure 5. Expansion coefficient of matrix and coatings.](image)

4. Conclusions
Dense coatings have been obtained in this work, with raw materials containing 20% B₂O₃ by sintering slurries at 1160°C for 1h. Filler Y₂O₃ particles are evenly dispersed in the coated borosilicate aluminum glass independently, which are supposed to increase the porosity of the coatings and correspondingly provide stronger resistance against thermal shock. Moreover, the relatively small difference in the expansion coefficient of matrix and coatings indicates better thermal match and thermal insulation properties of the as-prepared sample pieces, which can be a good candidate as effective thermal insulation materials for aerospace aircrafts at high flight Ma.

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