Effect of Fluoric Resin Coating on Bending Strength of Ceramics

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1. Introduction

Compared to metal, ceramics offer superior corrosion and heat resistance, high stability and low density. Therefore, a ceramic-particle-dispersed alloy shows high strength at elevated temperatures due to the strengthening effect of the ceramic particles and the excellent corrosion resistance against oxidation and/or molten metals. Thus, the ceramic/metal composite is expected to combine the superior properties of both ceramics and metal. Furthermore, as ceramics are extremely hard and have various kinds of wear resistance, they outperform other materials without lubrication. On the other hand, fluoric resin consists of three elements: hydrogen (H), carbon (C) and fluorine (F). Among these three elements, fluorine atom is the most chemically stable. The fluoric resins also have superior wear resistance due to their low friction coefficient and superior electrical resistivity. They are often used as coatings to improve the function of the metal surface. We surmise that the combination of dissimilar materials, such as ceramics and polymer, will markedly improve their mutual properties. Particularly, a fluoric resin coating, which involves infiltrating fluoric resin into sintered ceramics, may be used for improving wear resistance and electrical insulation, etc.

On the other hand, recently, it has become indispensable for coating materials to endure the severe environment in various industrial fields. It is well-known that the strength properties of the coated material are significantly affected by the mechanical and thermal properties of the coating layer. Particularly, the cracking and delamination behaviors of the coated material are strongly affected by the residual stress characteristics of the coating layer. As a matter of course, the strength of a substrate is strongly affected by the cracking of the coating layer due to the residual stress; namely, compressive residual stress improves the strength of ceramics and tensile residual stress produces the opposite effect. In the same manner, the authors analyzed the residual stress induced by the mismatch of the thermal expansion coefficients for the tungsten matrix composite with Y2O3 particles, using the finite element method. Because of the high tensile residual stress induced in the Y2O3 particles, the Y2O3 particles became the crack initiation sites of the tungsten matrix composite during the fabrication process. However, the basic properties of fluoric resin coatings, such as mechanical properties and residual stress characteristics, which are formed by infiltrating the fluoric resin into the sintered ceramics, have not been clarified so far. Also, the strength of the ceramics/fluoric resin composites has not been confirmed so far.

From the point of view of residual stress characteristics as described above, the bending strength of sintered ceramics with various kinds of fluoric resin coatings was investigated by finite element analysis in this study. It is clarified that the stress and residual stress distributions of sintered ceramics with fluoric resin coatings were investigated by paying attention to effects of the mismatch of Young’s modulus and the thermal expansion coefficient on the stress concentration at the edge of the sintered ceramic pores. Furthermore, the effect of fluoric resin (tetra fluoro ethylene-perfluoro alkylvinyl ether copolymer: PFA) coating on the bending strength of sintered Al2O3-SiO2 is experimentally confirmed.

2. Stress analysis

The authors have previously investigated the residual stress characteristics of ceramic coatings and clarified that the residual stress induced by the mismatch of the thermal expansion coefficient and Young’s modulus promoted the cracking of the coating layer. Similarly, some analytical investigations have been carried out to determine the stress distribution characteristics of various ceramics with various fluoric resin coatings. The material constants used for the stress analysis are shown in Fig. 1 and Poisson’s ratio of all the materials is assumed to be 0.3. Nine kinds of ceramic substrates, such as Al2O3, ZrO2, SiC, Si3N4, SiAlON, Mullite, MgO partially stabilized ZrO2, WC-Co and TiC-Ni, and seven kinds of fluoric resin coatings, such as ETFE, PVDF, PCTFE, ECTFE, PFA, FEP and PTFE, were selected.* It was found that the fluoric resins have low Young’s modulus and high thermal expansion coefficient in comparison with

* Dupont Teflon (R) coating, Catalogue, Dupon K. K., S2125-06-98 (1998)
The analyses of thermal stress in the ceramics with the fluoric resin coating were carried out using the analytical solution of a multi-layered infinite plate based on strain suppression and Timoshenko's beam theory. In these analyses, the thermal expansion in the thickness direction was not taken into account for evaluating the thermal stress. It was confirmed that the one-dimensional thermal stress distributions in each layer plane obtained by this method showed good agreement with the results of finite element analysis in the case where the coating thickness was sufficiently small in comparison with the other dimensions of plate width and length. The residual stress due to the fluoric resin coating process can be analyzed as the thermal stress during a uniform cooling process. For example, Fig. 2 shows the residual stress distribution in the thickness direction during the fluoric resin coating process (423 K→293 K) in the case of Al₂O₃ substrate with PFA coating. The thickness of PFA coatings is 0.05 mm and the substrate thickness is 3 mm. It is clear that the tensile residual stress is induced at the PFA coating layer and the bending stress is induced at the Al₂O₃ substrate by the PFA coating. The compressive residual stress exists at the coating interface of the Al₂O₃ substrate. The same tendency of the residual stress characteristics due to the PFA coating could be obtained for other ceramics with other fluoric resin coatings. The tensile residual stress, 33.6 MPa, and the compressive residual stress, -2.3 MPa, can be obtained in the case of Al₂O₃ substrate with PFA coating. Throughout the analyses, the maximum tensile residual stress, 35.1 MPa, and the maximum compressive residual stress, -2.4 MPa could be obtained in the case of Si₃N₄ substrate with PFA coating. Although the residual stress is proportional to the difference of the thermal expansion coefficient, the induced residual stress value is comparatively low due to the low Young's modulus of the PFA coating. These analytical results show that the strength of the Al₂O₃ substrate is slightly increased by the compressive residual stress induced by fluoric resin coatings. However, the residual stress effect is minimal and the maximum strength increase is 2.4 MPa at most for the compressive residual stress of -2.4 MPa in the case of Si₃N₄ substrate with PFA coating.

On the other hand, another analysis has been carried out to determine the stress distribution characteristics of the ceramic substrates whose pores are filled with the fluoric resin. In particular, it is considered very important to clarify the residual stress characteristics in the vicinity of fluoric resin particles during the coating process in order to investigate the strength behavior of the ceramics whose pores are filled with the fluoric resin. From this point of view, thermoelastic finite element analysis (the rectangular elements in the plane strain state) was used to determine the thermal stress generated when the ceramics with the fluoric resin were heated uniformly to the coating temperature (423 K) and then cooled to room temperature (the difference in temperature was equal to 130 K). It was assumed that the two-dimensional analysis models were perfectly elastic bodies, i.e., plastic deformation was not taken into account in the analysis. In order to clarify the residual stress distribution around the pores filled with PFA, analysis models of the shape of PFA were circular and square, as shown in Figs. 3 (a) and (b). The interaction between the pores filled with PFA is not taken into account in this analysis, and so the plate size is ten times as wide as a central pore filled with PFA. Also, the analysis is carried out in the case of uniform tension in the y-direction by paying attention to the stress concentration at the edge of a central pore filled with PFA.

Figure 4 shows the stress distribution under uniform tension and the residual stress distribution during the fabrication process generated in the vicinity of the circular pore filled with PFA in sintered Al₂O₃. The stress concentration under uniform tension is induced by the mismatch of Young's modulus between the Al₂O₃ matrix and the PFA. In the case of the circular pore infiltrated with PFA in sintered Al₂O₃, the stress concentration, σ₂/σ₃ = 2.82, could be ob-
served at the edge of the circular pore. In the case of the square pore filled with PFA in sintered Al₂O₃, the higher stress concentration, \( \sigma_y/\sigma_n = 3.93 \) could be observed at the corners of the pore. On the other hand, when the infiltrating (coating) temperature was 423 K, the compressive residual stress, \( \sigma_y = -28.2 \text{ MPa} \), was generated at the edge of the circular pore infiltrated with PFA, as shown in Fig. 4, in agreement with the stress concentration position induced under uniform tension. It was confirmed that the compressive residual stress could be induced around the ceramic pores filled with fluoric resins by the mismatch of the thermal expansion coefficient between the ceramics and the fluoric resins. In the case of the square pore infiltrated with PFA in sintered Al₂O₃, a high stress concentration, \( \sigma_y = -64.29 \text{ MPa} \), could be obtained at the corners of pores filled with PFA in comparison with the circular pore infiltrated with PFA. These analytical results show that the strength of the Al₂O₃ substrate is fairly increased by the compressive residual stress due to the infiltration of PFA into sintered Al₂O₃ pores.

Figure 5 shows the effect of Young's modulus of various ceramic substrates on the stress concentration in the vicinity of the pore infiltrated with PFA under uniform tension. The stress concentration factor increased slightly with increasing Young's modulus of the ceramic substrates. Although the change of stress concentration factor was minimal, the stress concentration factor increased markedly with decreasing corner radius of the pore filled with PFA. It is well known that the stress concentration factor of an infinite plate with a circular hole under uniform tension is equal to 3.0. Compared with the stress concentration factor of 3.0, it was found that the effect of stress reduction by PFA in ceramic pores was minimal. In the same manner, the effect of the thermal expansion coefficient of ceramic substrates on the residual stress in the vicinity of the pore filled with PFA during the coating process is shown in Fig. 6. The residual stress increased slightly with increasing thermal expansion coefficient of the ceramic substrates. Although the change of residual stress was minimal, it was all because of the much higher thermal expansion coefficient of the fluoric resins than that of the ceramics. The compressive residual stress increased with decreasing corner radius of the pore filled with PFA. As described in Fig. 5, the effect of stress reduction by PFA infiltration into the ceramic pore is minimal. However, it was found that the effect of compressive residual stress due to the coating process became marked with decreasing corner radius of the pore.

Figure 5. Effect of Young's modulus of ceramic matrices on stress concentration factor at the edge of pore filled with PFA.

3. Experimental method
We described herein the experimental investigation car-
ried out to clarify the four-point bending strength of sintered ceramics with fluoric resin coating and compared it with that of sintered ceramics without the fluoric resin coating. We used two kinds of sintered Al$_2$O$_3$–SiO$_2$ as substrates for the fluoric resin coating. One is sintered 20 mass% Al$_2$O$_3$–74 mass% SiO$_2$–clay (sintering condition: 1573 K-36 ks, density: 2.305 g/cm$^3$) and the other is sintered 95 mass% Al$_2$O$_3$–5 mass% SiO$_2$ (sintering condition: 1833 K-36 ks, density: 3.673 g/cm$^3$). The density of the sintered ceramics was measured by the Archimedes method. Tetra fluoro ethylene-perfluoro alkylvinyl ether copolymer (PFA) was used as the fluoric resin coating. The PFA powder was layered on the ceramic substrates by the electrostatic coating method. These coated substrates were heat-treated at 423 K for 3.6 ks in air.

Figure 7 shows typical examples of the microstructure of the 20 mass% Al$_2$O$_3$–SiO$_2$ with the PFA coating. The PFA coating layer of nearly 50 µm thickness is formed over the 20 mass% Al$_2$O$_3$–SiO$_2$ substrate and spherical pores of 10-50 µm diameter exist in the sintered substrate. Figure 8 shows typical examples of the microstructure of the 95 mass% Al$_2$O$_3$–SiO$_2$ with PFA coating. The PFA layer of nearly 50 µm thickness is formed on the 95 mass% Al$_2$O$_3$–SiO$_2$ substrate and variously shaped of pores of 2–5 µm size exist in the sintered substrate. The microstructure reveals that 95 mass% Al$_2$O$_3$–SiO$_2$ is denser than 20 mass% Al$_2$O$_3$–SiO$_2$, and the pores of 95 mass% Al$_2$O$_3$–SiO$_2$ have sharper corners.

Four-point bending specimens, which were 4 mm wide, 40 mm long and 3 mm thick, were tested at room temperature (296 K) and a displacement speed of 0.5 mm/min. All specimens exhibited brittle failure. The load at final fracture was recorded, and the four-point bending strength was determined using the fracture load according to the Japanese Industrial Standards (JIS R-1601).

4. Experimental results and consideration

Figure 9 shows the two-parameter Weibull distributions of the four-point bending strength in case of 20 mass% Al$_2$O$_3$–SiO$_2$ specimens with and without PFA coating. Ten samples were used for determining the four-point bending strength at room temperature. The relationships between the accumulated probability using the mean rank method and the four-point bending strength were well represented by two straight lines for 20 mass% Al$_2$O$_3$–SiO$_2$ specimens with PFA coating and those without PFA coating. The shape parameter, $m$, and the mean value, $\sigma_m$, are indicated...
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Therefore, it was confirmed that the four-point bending strength and the scatter of sintered 20 mass% Al$_2$O$_3$–SiO$_2$ specimens was improved by PFA coating. The improved value of the four-point bending strength, 20 MPa, was nearly agreement with the compressive residual stress in Fig. 6 generated at the edge of square pore infiltrated with PFA. This means that the actual pore shape of 95 mass% Al$_2$O$_3$–SiO$_2$ specimens is sharper than that of the square pore model in Fig. 3(b).

5. Conclusions

First, the strength properties of various ceramics with fluoric resin coating were investigated analytically by focusing on the residual stress behaviors. Residual stress analyses were conducted for nine kinds of ceramic substrates and seven kinds of fluoric resin coatings. The fluoric resin coatings were low Young’s modulus and high thermal expansion coefficient in comparison with the ceramic substrates. It was clarified that the tensile residual stress could be induced at the fluoric resin coating layer and the bending stress was induced at the ceramic substrate by the fluoric resin coating. The compressive residual stress exists at the coating interface of the ceramic substrate. Although the residual stress is proportional to the difference of the thermal expansion coefficient, the induced residual stress value is comparatively low due to the low Young’s modulus of fluoric resin coating. However, the residual stress effect is minimal and the strength increase is nearly 2–3 MPa at most.

On the other hand, the residual stress characteristics of ceramic composite, induced by the infiltration of fluoric resin into sintered ceramic pores, were analyzed by finite element analysis. Because of the much higher thermal expansion coefficient of the fluoric resins than that of the ceramics, the compressive residual stress of ~20–30 MPa was induced in the case of the circular pore infiltrated with PFA in the sintered ceramics. The compressive residual stress increased with decreasing corner radius of the pore filled with PFA. As described above, the effect of stress reduction by PFA infiltration into the ceramic pore was minimal. However, it was found that the effect of compressive residual stress due to the coating process became marked with decreasing corner radius of the pore.

The analytical results showed that the strength of the ceramic substrates was fairly increased by the compressive residual stress produced by the infiltration of fluoric resin into the ceramic pores. Finally, the bending strengths of sintered 20 mass% Al$_2$O$_3$–SiO$_2$ and sintered 95 mass% Al$_2$O$_3$–SiO$_2$ with tetra fluoro ethylene-perfluoro alkylvinyl ether copolymer (PFA) coating were improved by PFA infiltration in comparison with the as-sintered samples. Also, the large scatter in the four-point bending strength was reduced by the PFA coating. These tendencies were in agreement with the analytical results of the compressive residual stress due to the coating process.

References