
High-performance Self-lubricating Ceramic Composites with Laminated-graded Structure

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<http://dx.doi.org/10.5772/62538>

Abstract

High-performance ceramic composites are potential candidates for the application of wear-resistance components because of their excellent properties. Nevertheless, many problems, such as high friction coefficient of ceramic material and poor mechanical properties of ceramic-matrix self-lubricating composites, limit a wider range of applications of these composites in tribological areas. Therefore, improving high-toughness ceramic-matrix self-lubricating materials for practical applications is significant. This study proposes a new design for ceramic self-lubricating composites to overcome the conflict between their mechanical and tribological properties. Complying with the design principle of bionic and graded composites, two kinds of self-lubricating ceramic composites with laminated-graded structure were prepared, and their mechanical and tribological properties were studied. The results show that this newly developed ceramic composite has achieved satisfactory strength and tribological properties compared with the traditional ceramic self-lubricating composites. The bending strength reached the same level as the properties of general monolithic ceramics. In the temperature range of 25-800 °C, the friction coefficient of composites was less than 0.55, which was about half of that of monolithic ceramics.

Keywords: Functionally graded material, Laminated structures, Ceramic, High temperature, Self-lubricating

1. Introduction

Ceramic materials are promising candidates for wear-resistance components owing to their excellent properties such as high strength and resistance to corrosion and oxidation stability at high temperature. Nevertheless, both the high coefficient of friction of this kind of material under dry sliding and the brittleness of ceramic-matrix itself limit its practical application in

tribological areas. Generally, incorporating solid lubricants (SLs) in ceramic matrixes solves the friction problems, which can reach a positive effect. Moreover, compound lubricants can exhibit excellent self-lubricating abilities in a wide range of temperatures because the lubricants can promote the formation of well-covered lubricating films on the surfaces of ceramics that can work effectively under different temperature [1-3]. Unfortunately, subsequent studies have shown that these composites are homogenous in terms of mechanical and tribological properties. Thus, the strength of ceramics and the lubrication of SLs cannot be fully utilized. Because the continuity of ceramic phases is destroyed by the layered structural SL phase, the mechanical property of this type of material is reduced [4,5]. In these situations, it is necessary to develop a high-strength and high-toughness self-lubricating ceramic composites.

Lamination is one of the new strategies being used to enhance the mechanical properties of ceramics. The ideas of laminated composites inspired from natural biomaterials, such as shells and teeth, are made of layered architectures combining materials with different properties. During the past decade, there are large amounts of layered ceramic composites that have been fabricated and studied [6-8]. These kinds of materials have non-catastrophic fracture behavior and damage tolerance, which exhibit much higher fracture toughness and work of fracture in them than in monolithic ceramics. Moreover, the unique configurations of the layered material allow design flexibility. Therefore, the combination of the laminated design of ceramic materials and self-lubricating ceramic composites with excellent lubricating property is a promising way to achieve the integration of mechanical and tribological properties [9-12].

For laminated self-lubricating ceramic composites, interfacial residual stress between the adjacent layers may have an important effect on their mechanical properties. Any modification or change of the interfacial structure and composition will be a determining factor in the strength of the interfacial bond and will eventually affect the toughness, strength, and fracture behavior of laminated composites [13]. Therefore, a reasonable residual stress between the adjacent layers is essential to improve the mechanical properties. Previous studies have shown that the graded design of the materials is an effective method to eliminate the interface stress of dissimilar material system [14-16]. This design concept of functionally graded materials (FGMs) was first raised by Japanese scientists in 1987 as reported in reference [14]. That is, components with different properties or structures disperse by a gradient change along with one direction instead of a homogeneous manner. Thus, the composite can exhibit different properties that are mutually exclusive at the same time, and the gradient change can eliminate the interface between components. This new-style and non-uniform composite realized the integration of structure and function, making it to have a wider prospect of application in extreme conditions.

Based on the above background, the authors prepared high-performance structural/lubricating-functional integration ceramic composites using the design of graded laminated structure [4,17,18]. This design is conducive to the combination of mechanical and tribological properties while retaining all the advantages of these materials. The aim of this chapter is to illustrate the design, fabrication, and properties of alumina and zirconia self-lubricating composites with laminated-graded structure and to provide guidance for the optimum design of these materials.

2. Design, fabrication, and properties of laminated ceramic composites

2.1. Design and fabrication of laminated composites

Figure 1 illustrates the schematic and the design concept of laminated composites. The thickness of the A layer and B layer are d_1 and d_2 , respectively, where the A layer is the Al_2O_3 or $\text{ZrO}_2\text{-Al}_2\text{O}_3$ and the B layer is $\text{Al}_2\text{O}_3\text{-ZrO}_2$ or ZrO_2 . Commercially available Al_2O_3 , ZrO_2 , Y_2O_3 , CuO , and TiO_2 were used in this study. The material was manufactured using the following steps [17-20]: (1) ball-milling of powder, (2) sequential stacking of layers in steel mold, and (3) hot-pressing in graphite mold. Hot-pressing was performed at 1350-1400 °C and 25 MPa using graphite die in an argon atmosphere for 100-120 minutes. Monolithic Al_2O_3 and ZrO_2 with sintering aids were also sintered at same condition as comparisons. The microstructures of the composites were observed using scanning electron microscopy (JSM-5600LV). The sintered specimens were sliced into test bars for bending strength and work of fracture.

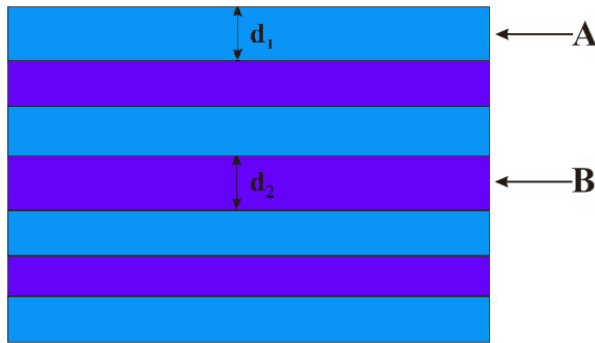


Figure 1. Schematic of laminated composite structure.

An example of the microstructure of the $\text{ZrO}_2(3\text{Y})\text{-Al}_2\text{O}_3/\text{ZrO}_2(3\text{Y})$ -laminated composites is shown in Figure 2, where the dark layer is the $\text{ZrO}_2(3\text{Y})\text{-Al}_2\text{O}_3$ layer and the light layer is the $\text{ZrO}_2(3\text{Y})$ layer. The multilayer structure with a relatively straight interface can be observed without clear delamination. It can also be seen from Figure 2 that the $\text{ZrO}_2(3\text{Y})\text{-Al}_2\text{O}_3$ layer and $\text{ZrO}_2(3\text{Y})$ layer have the same thickness of approximately 160 μm .

2.2. The mechanical properties of laminated composites

The geometric parameters of the layered structure are the key factors for the optimal design of laminated composites. These parameters mainly include the layer numbers and thickness ratio of the two layers. The mechanical properties of $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3\text{-}10\text{wt.}\%\text{ZrO}_2(3\text{Y})$ -laminated composites with different layer numbers are shown in Figure 3 [19,20]. As shown in Figure 3, a relatively large number of layers are likely to improve the mechanical properties of the materials. When the number of layers is 41, the bending strength and work of fracture of materials reach the maximum value. The relationship between the mechanical properties and

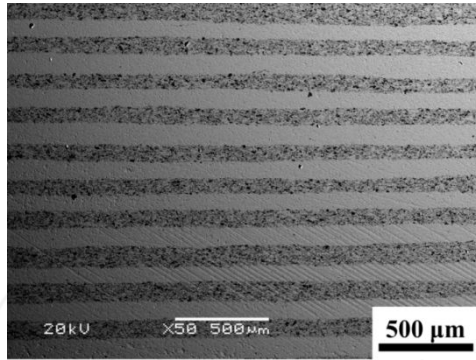


Figure 2. SEM photograph of profile of laminated composites.

layer thickness ratio is displayed in Figure 4 [19,20]. One can see that the layer thickness ratio also has an enormous effect on the mechanical properties of laminated composites. The bending strength and work of fracture of all of the laminated materials are higher than that of the monolithic materials and decrease with the increase of the layer thickness ratio. When the layer thickness ratio is 1:1 and the thickness of each layer is 80 μm, the bending strength and work of fracture of the $Al_2O_3/Al_2O_3-ZrO_2(3Y)$ laminated composites could reach to 740 MPa and 3892 J m⁻², respectively [19,20].

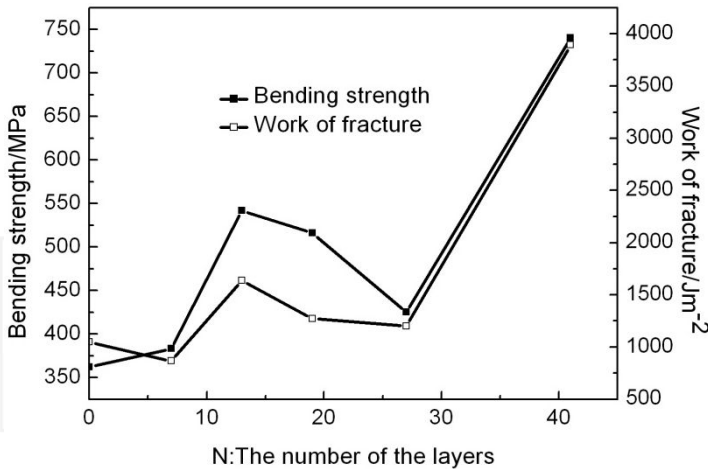


Figure 3. Effect of the layer numbers on the bending strength and work of fracture.

In addition, the compositions of the two layers also have significant effects on the mechanical properties of the laminate composites. The bending strength and work of fracture of $Al_2O_3/Al_2O_3-ZrO_2(3Y)$ -laminated composites with different content of $ZrO_2(3Y)$ in $Al_2O_3-ZrO_2(3Y)$

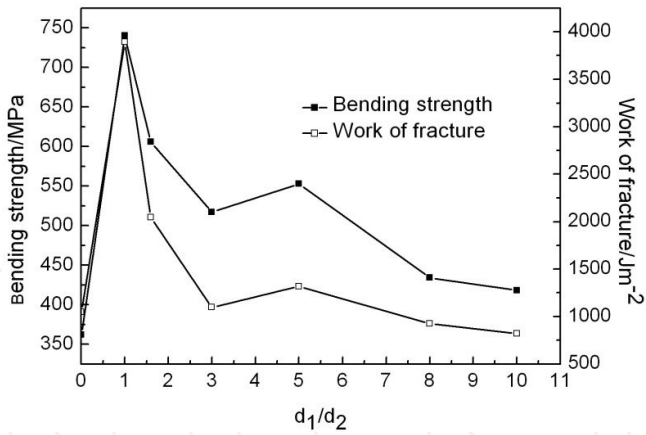


Figure 4. Effect of the thickness ratio on the bending strength and work of fracture.

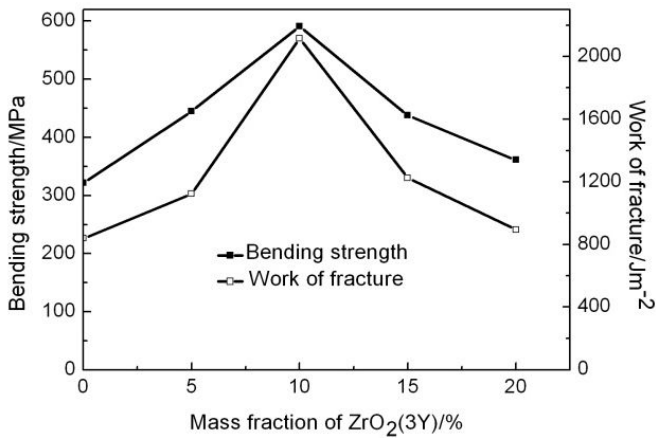


Figure 5. Relationship between mechanical properties of $Al_2O_3/Al_2O_3-ZrO_2(3Y)$ -laminated composites and content of $ZrO_2(3Y)$ in the $Al_2O_3-ZrO_2(3Y)$ layers.

layers are shown in Figure 5 [19,20]. As can be seen from the figure, with the increase of the content of $ZrO_2(3Y)$, first, the bending strength and work of fracture of the material increase and then they decrease gradually. When the mass content of $ZrO_2(3Y)$ is 10%, both bending strength and work of fracture reach the optimal value. This is mainly because the variation of content of $ZrO_2(3Y)$ in $Al_2O_3-ZrO_2(3Y)$ layers causes significant changes in the residual stresses between adjacent layers and the contribution of phase transformation toughening to the crack propagation energy of the materials, thus realizing the optimization of the materials [19,20]. The same design principles used for designing $Al_2O_3/Al_2O_3-ZrO_2(3Y)$ -laminated composites apply to designing $ZrO_2(3Y)-Al_2O_3/ZrO_2(3Y)$ material. When the mass content of Al_2O_3 in

ZrO₂(3Y)-Al₂O₃ layers is 15 %, the bending strength and work of fracture of the ZrO₂(3Y)-Al₂O₃/ZrO₂(3Y)-laminated composite reach to 968 MPa and 3751 J m⁻², respectively (Fig. 6a and b).

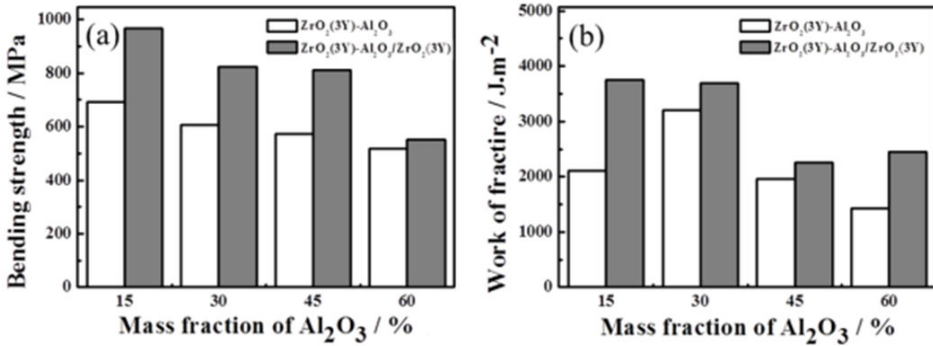


Figure 6. Mechanical properties of ZrO₂(3Y)-Al₂O₃/ZrO₂(3Y)-laminated composites and monolithic ceramic.

3. Graded structure and tribology design for optimal lubricating properties in laminated ceramic composites

3.1. Design and preparation of laminated-graded self-lubricating ceramic composites

From the results above, it can be concluded that the layered structure design is a good strategy to enhance the mechanical properties of monolithic ceramics, which can efficiently improve the bending strength and work of fracture. Nevertheless, the friction and wear rate of these materials under dry sliding conditions are still high. To overcome this problem, the laminated-graded structure self-lubricating ceramic composites were designed. Figure 7 shows the schematic of self-lubricating ceramic composites with laminated-graded structure, where $d_1=d_2$, the A layer is the Al₂O₃ or ZrO₂-Al₂O₃, and the B layer is Al₂O₃-ZrO₂ or ZrO₂. The center area is composed of laminated composites that are similar to that of in the section 2, which provides high strength for the whole material. The content of SLs is graded, increased from center to two sides, and finally reaches a fixed value on the surface to ensure the excellent lubricating function of the materials. In this study, each couple of ZrO₂(3Y)-Al₂O₃ and ZrO₂(3Y) or Al₂O₃ and Al₂O₃-ZrO₂ has the same SL content. The SL content of each couple $f(x)$ is determined by the following equation [18]:

$$f(x) = (x/m)^p \times f(s) \quad (1)$$

Where x is the number of the couple, m is the total number of the couples in the gradient area, p is the gradient exponent, and $f(s)$ is the content of SLs in surface layers. Commercially

available Al_2O_3 , ZrO_2 , Y_2O_3 , CuO , TiO_2 , and SLs (graphite+ CaF_2 + BaSO_4 and graphite+ CaF_2 in two kinds of laminated-graded structure self-lubricating ceramic composites, respectively) were used. Experimental details for preparation and characterization are described in these references [17, 18].

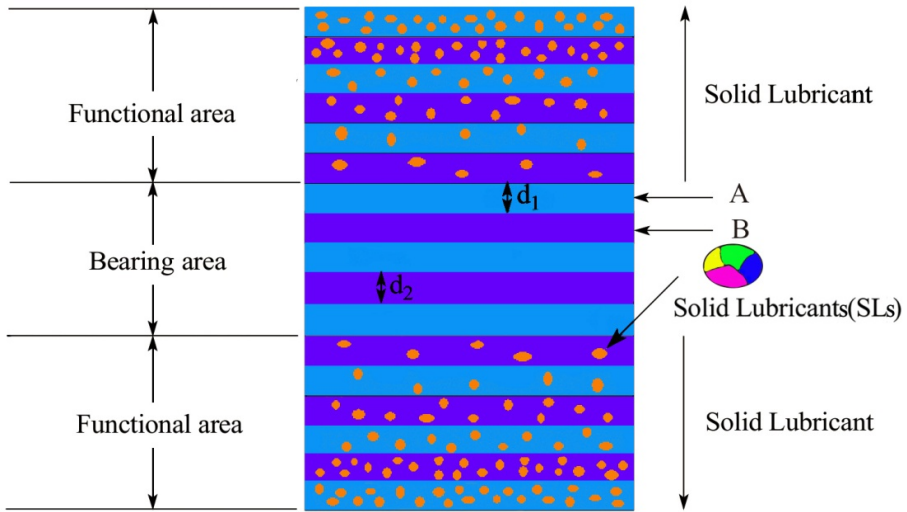


Figure 7. Schematic of the laminated-graded structure self-lubricating composites.

3.2. The mechanical and tribological properties of traditional self-lubricating ceramic composites

For comparison, the mechanical and tribological properties of traditional self-lubricating ceramic composites were first conducted. Figure 8 shows the microstructure of two kinds of traditional self-lubricating ceramic composites. It can be seen that there are lots of tiny pores in the sintered samples. There is no doubt that these defects will greatly degenerate the mechanical properties of the materials. The mechanical properties of two kinds of traditional self-lubricating ceramic composites (Al_2O_3 -graphite and Al_2O_3 - LaF_3 composites) are given in Figure 9. It can be seen clearly that the bending strength and work of fracture decrease rapidly with the increase of the content of SLs. For the Al_2O_3 - LaF_3 composites, when the volume content of lubricants increase to 40%, the bending strength and work of fracture reduced to as low as 67 MPa and 44 J m^{-2} , which were 6.3 and 2.9 times lower than those of monolithic Al_2O_3 ceramic. Therefore, the traditional self-lubricating ceramic composites exhibit poor mechanical properties mainly because of the lots of SLs that destroyed the continuity of ceramic matrix. The ceramic composites may exhibit good lubricating properties when proper amounts of lubricants were added [1,4]. Nevertheless, this kind of ceramics possesses poor anti-destructive and reliability, which is the key obstacle to its practical application. Therefore, as mentioned

earlier, improving high-strength and high-toughness ceramic-matrix self-lubricating materials for practical applications is significant.

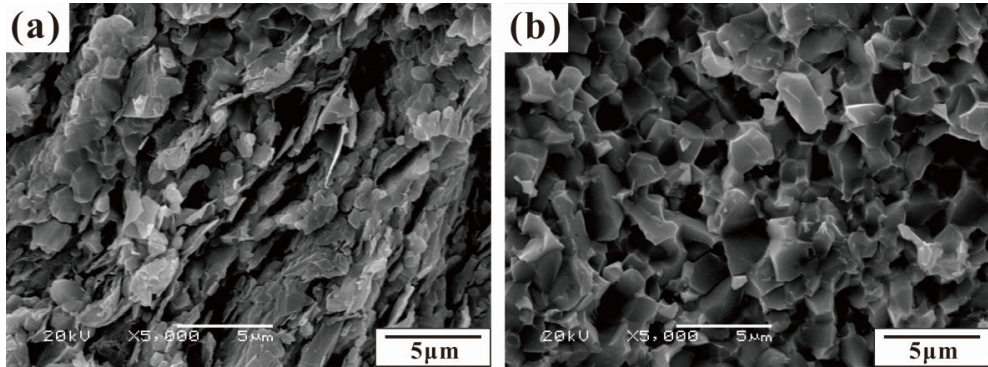


Figure 8. SEM micrographs of fracture surface of traditional Al_2O_3 -graphite (a) and Al_2O_3 - LaF_3 (b) self-lubricating ceramic composites.

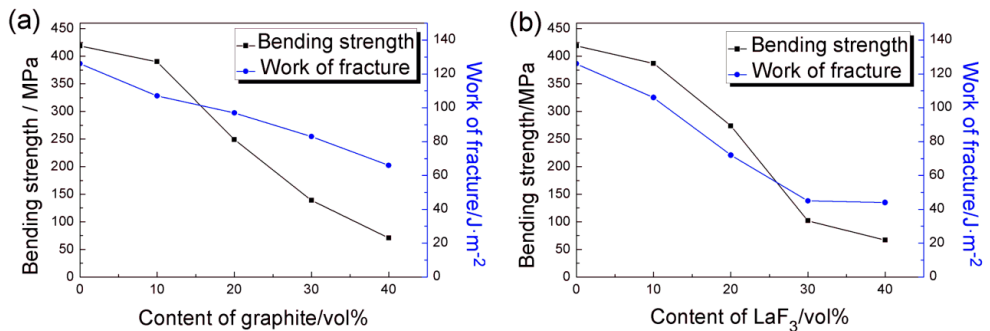


Figure 9. Mechanical properties of Al_2O_3 -graphite (a) and Al_2O_3 - LaF_3 (b) self-lubricating composites.

3.3. The performance of laminated-graded structure self-lubricating ceramic composites

Compared to the traditional self-lubricating ceramic composites, laminated-graded structure self-lubricating ceramic composites exhibit excellent mechanical properties. Table 1 describes the bending strength of Al_2O_3 -laminated-graded structure self-lubricating ceramic composites and of some monolithic self-lubricating ceramic composites. It can be seen from Table 1 that the bending strength of laminated-graded structure self-lubricating ceramic composites are much higher than any one of monolithic materials. The bending strength reached 348 MPa, which is approximately five times higher than that of the traditional monolithic Al_2O_3 /SL and Al_2O_3 - $\text{ZrO}_2(3\text{Y})$ /SL ceramics, and which basically approached the properties of general monolithic Al_2O_3 and Al_2O_3 - $\text{ZrO}_2(3\text{Y})$ ceramics [17].

Additionally, the gradient exponent p has a remarkable influence on the mechanical properties of laminated-graded structure self-lubricating composites [18]. As shown in Figure 10, the bending strength of the $ZrO_2(3Y)-Al_2O_3/ZrO_2(3Y)/SL$ FGM increased, with the increase of p up to 2.0, and then decreased rapidly when p exceeds 2.0. This phenomenon is caused by the residual stress between the adjacent layers in gradient area. The variation of p causes the change of content of SLs in gradient layers, and then the residual stress that is generated from the thermal mismatch because of the difference in thermal expansion coefficients between the adjacent graded layers (as shown in Figure 11) is influenced. This shows that a reasonable residual stress is essential to adjust the mechanical properties of these materials.

Materials	Bending strength (Mpa)
$Al_2O_3/Al_2O_3-10wt.\%ZrO_2(3Y)/SL$ FGMs	348
Al_2O_3/SL	68
$ZrO_2(3Y)-Al_2O_3/SL$	69

Table 1. Bending strength of laminated-graded structure self-lubricating ceramic composites [17].

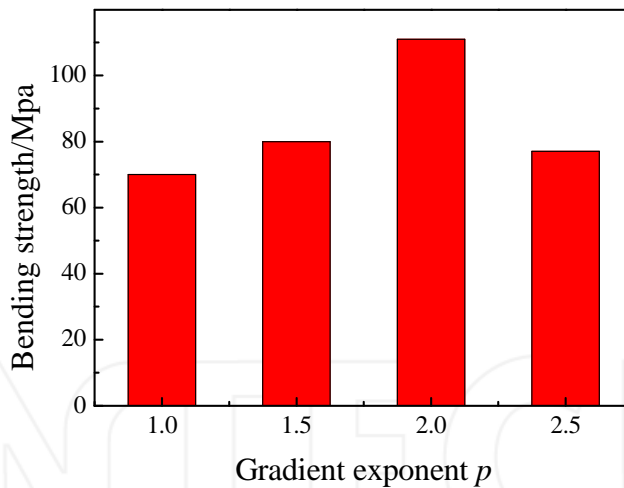


Figure 10. The bending strength of $ZrO_2(3Y)-Al_2O_3/ZrO_2(3Y)/SL$ FGMs varies with the gradient exponent.

The laminated-graded structure ceramics not only showed excellent mechanical properties, it also maintained good tribological performance. As shown in Figure 12, in the temperature range of 25–800 °C, the friction coefficient of Al_2O_3 and $ZrO_2(3Y)$ laminated-graded structure composite was less than 0.55, which was approximately half of that of monolithic Al_2O_3 and ZrO_2 ceramics. The decrease of friction coefficients were achieved by the presence of graphite, CaF_2 , and $BaSO_4$, which have excellent lubricating property under different temperatures.

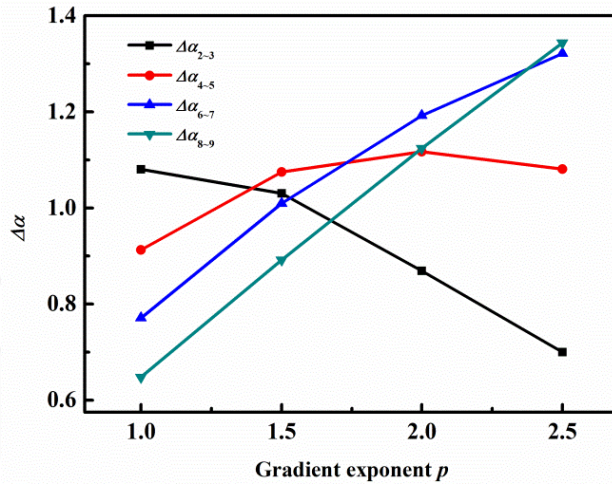


Figure 11. Variation of the difference value of coefficients of thermal expansion between the adjacent layers with the gradient exponent p [18].

Graphite has a good lubricating property at room temperature to 300 °C, and CaF_2 at 250 °C to 1000 °C. In addition, BaSO_4 also possesses excellent self-lubricating performance over a broad temperature range. During the sliding process, these SLs form the self-lubricating film that is helpful to reduce direct contact between the ceramics and further improved the tribological properties of the materials [17,18].

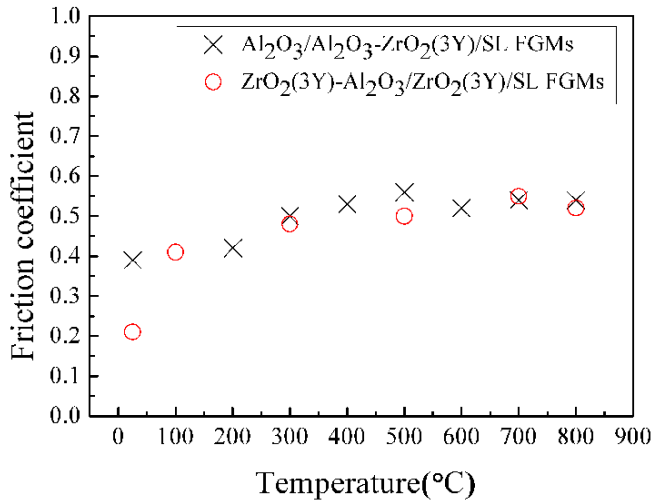


Figure 12. The friction coefficients of two kinds of laminated-graded self-lubricating composites at room temperature to 800 °C.

In conclusion, laminated-graded structure self-lubricating ceramic composites realize the integration of mechanical and tribological properties. Their excellent mechanical and tribological properties indicate that the laminated-graded structure self-lubricating ceramic composites have numerous high-technology applications and promising prospect as structural materials.

Acknowledgements

The authors acknowledge the financial support from the Foundation for National Innovation of Chinese Academy of Sciences (CXJJ-15M059), the Gansu Province Science Foundation for Youths (1107RJYA043) and the Youth Innovation Promotion Association CAS (2013272).

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