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Original Article

High toughness integrated with self-lubricity of Cu-doped Sialon ceramics at elevated temperature

Qichun Sun[a,b], Jun Yang[a], Bing Yin[a], Jun Cheng[a], Shengyu Zhu[a], Shuai Wang[a], Yuan Yu[a], Zhuhui Qiao[a,*], Weimin Liu[a]

[a] *State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, China*
[b] *University of Chinese Academy of Sciences, Beijing, China*

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ABSTRACT

High toughness integrated with self-lubricity of β-Sialon composites at elevated temperature containing second phase particles were successfully fabricated. It was found that the fracture toughness can be substantially improved by addition of Cu powder. The fracture toughness can be reached 6.75 MPa $m^{1/2}$ and 4.42 MPa $m^{1/2}$ at 25 and 900 °C, respectively. Meanwhile, the tribological properties of Cu-doped Sialons have a tremendous improvement at high temperature. Especially when the content of Cu powder is above 10 wt%, the wear rate decreases by two orders of magnitude and the friction coefficient reduces to 0.56–0.65 at 900 °C. In addition, the microstructure of composites was characterized, and crack propagation behavior and tribological behavior were discussed to clarify the toughening mechanisms and self-lubrication mechanisms. The results show that the principal toughening mechanisms are crack deflection and crack bridging. The tribo-chemical reaction and generated CuO films with lubricity are the main self-lubrication mechanisms.

1. Introduction

The Sialon ceramics possess unique combination of promising properties including outstanding mechanical properties, excellent thermal shock resistance, good chemical stability, high-temperature oxidation resistance, and so on [1–4]. These advantages make them as one of the most competitive high-temperature materials [5,6]. Meanwhile, the low density and high-temperature resistance make them as a potential material for aircraft engines [4,7]. Nevertheless, the Sialon ceramics show poor toughness and tribological behavior at elevated temperature [8,9], which need to be enhanced for various structural applications. Therefore, designing and preparing high-toughness ceramic-matrix materials with self-lubrication property for actual applications at high temperature is very significant.

It has been widely recognized that the major limitation of ceramics for structural application is their low fracture toughness, which can be toughened by introducing a ductile phase [10–12]. This concept of ductile phase toughened brittle materials was originally proposed by Krstic [13] as a means of increasing the energy dissipation in brittle materials. Since this pioneering work, there have been considerable efforts paid to improve the fracture toughness of brittle materials by the incorporation of ductile phases [4,14–16]. Some researchers [14,15] studied the influence of particle size on the toughness of ceramics composite. Experimental results highlighted that the interface of small particles is easily fractured and thus reduce the maximum toughness. The composite with larger grain size, however, displayed better damage tolerance and higher resistance to crack growth. Some researchers [4,16] also investigated the influence of metal and alloy on the toughness of Sialon-based ceramics at room temperature. The results exhibited that the toughness of these ceramics can significantly improve by addition FeMo alloy. However, until now, the influence of Cu powder on the crack growth behavior of ductile phase-toughened β-Sialon composites at wide range temperature has not been explored.

Moreover, it is observed the previous studies mainly focused on the tribological properties of Sialons at room temperature [17–22], while the thorough research on their elevated temperature tribological properties is quite limited. According to our previous study [8], the β-Sialon composites have poor tribolgical properties at elevated temperatures. The wear rate and friction coefficient of β-Sialon composites reached up to 10^{-4} mm^3/Nm and 0.7–0.95 with different *z* values at high temperatures, respectively. This is ascribed to that the β-Sialons are incapable of self-lubricity at elevated temperature. Thus, designing and preparing self-lubrication β-Sialon ceramics is very important. The previous studies have been demonstrated that the tribological behavior of ceramic compositions can be improved by adding the material which possess or can generate the lubrication effect during the wear process

* Corresponding author.
E-mail address: zhqiao@licp.cas.cn (Z. Qiao).

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[23–26]. However, the studies about improving the tribological behavior of Sialon-based ceramics, especially at elevated temperature are very few.

Based on the mentioned above, few work has been done on the design and preparation of toughened Sialon-based ceramics integrated with self-lubrication properties by the addition of metal/alloy particles at elevated temperature. The principal objective of the present study was to develop a Sialon-matrix composite integrated with high toughness and self-lubrication properties by incorporating varying amounts of copper powder. The microstructure of the composite was characterized, the fracture toughness and the tribological properties of the composite were determined, and crack propagation behavior was also observed. According to the experiment results, the toughening and self-lubrication mechanisms of the composites were also discussed.

2. Experimental procedure

The $Si_4Al_2O_2N_6$ containing definite amounts of Y_2O_3 were chosen as the matrix in this study. Commercially available Si_3N_4 (99.7%, grain size: < 0.7 μm), Al_2O_3 (99.9%, grain size: < 0.5 μm), AlN (99.5%, particle size: < 0.5 μm), Y_2O_3 (99.9%, grain size: < 0.5 μm) and Cu powder (99.7%, grain size: 15 μm) were used as raw powders. The raw materials were mixed according to a stoichiometric ratio to synthesize $Si_4Al_2O_2N_6$ with Cu. Various proportions of copper content were added: 0, 10, 20, and 30 wt% to obtain samples designated as S0-S3. The designed starting compositions for each sample are summarized in Table 1.

The powders were homogeneously mixed by ball milling for 15 h in ethyl alcohol using silicon nitride balls at a ball-to-sample mass ratio of 8:1. The slurries were then dried in a vacuum evaporator and sieved with a mesh size of 250 μm. In order to prevent sticking, due to the reaction of the powders with the graphite die, the graphite foil was placed between the powders and the die. The samples were sintered by spark plasma sintering (SPS, LABOX-3010KF, Sinter Land Incorporation, Ltd, Japan) in a vacuum atmosphere at 30 MPa and 1600 °C for 10 min, and the furnace were naturally cooled to room temperature.

The fracture toughness of the samples were determined using the Vickers indentation method (HTV-PHS30, Archimedes Industry Technology Co. Ltd., England) with a load of 10 Kg at a duration of 10 s on a polished surface. The fracture toughness (K_{IC}) has been evaluated using the indentation fracture (IF) toughness technique. In the present work, the indentation fracture toughness K_{IC} (MPa $m^{1/2}$) was calculated from measurements of the crack length due to indentation by using Eq. (1) [27],

$$K_{IC} = \frac{0.15 \times k \times HV \times a^{1/2} \times (c/a)^{-3/2}}{\varphi} \quad (1)$$

Where K_{IC} is the fracture toughness (MPa $m^{1/2}$), φ is the constant (3), HV is the Vickers hardness (GPa), k is the correction factor (3.2 for high c/a values), c is the mean length of crack (m), a is the half of horizontal length of diagonal (m). Both the indent diagonal and crack length were carefully measured from SEM images of the indented surfaces. The reported fracture toughness values are the average of at least seven indentation measurements.

Dry sliding wear tests were carried out by a rotational ball-on-disc tribometer (HT-1000, China). The discs of the Cu-doped Sialon ceramics were employed as the bottom samples. The upper samples were Si_3N_4 balls with a diameter of 6.25 mm and a hardness of 15.12 GPa. The tests were conducted at a sliding velocity of 0.10 m/s, with a rotation radius of 4 mm at 25, 600, 800 and 900 °C. The tribological tests were run at load of 5 N and the total sliding distance was set at 200 m. During the tests, the values of the friction coefficient were automatically and digitally recorded. The wear volume (V) of disc was calculated by $V = AL$, where A is the wear area from the profile in mm^2 and L is the perimeter of wear circle in mm. Volumetric wear rate was determined as $W = V/Ps$, while P is the applied load and s is the total sliding distance in m. Three repeated tests were conducted for each test to obtain the mean value and error bar.

The morphology, composition and phase identification of the samples were examined by scanning electron microscope (JSM-5600LV) and an X-ray diffractometer (XRD), respectively. Raman spectroscope (Lab RAM HR Evolution, with 532 nm laser excitation) analyses were conducted to determine the composition of the worn surface. The topography profile of worn surface was determined by a stylus profilometer (KLA Tencor).

Table 1
The composition of the starting raw materials (wt%) with different contents of Cu.

Samples	Si_3N_4	Al_2O_3	AlN	Y_2O_3	Cu
S0	64.21	23.39	9.40	3.00	0
S1	57.79	21.05	8.46	2.70	10.00
S2	51.37	18.71	7.52	2.40	20.00
S3	44.96	16.36	6.58	2.10	30.00

3. Results

3.1. Phase and microstructure characterization

Fig. 1 shows the XRD patterns of β-Sialon ceramics with different addition of Cu. As demonstrated in Fig. 1, without Cu content, the S0 is mainly composed of $Si_4Al_2O_2N_6$ phase. Observe the XRD patterns of S1, S2 and S3, it can be seen that the phases are mainly $Si_4Al_2O_2N_6$, $Cu_{0.83}Si_{0.17}$ and a little Cu metal, which suggested that $Cu_{0.83}Si_{0.17}$ alloy was in-situ generated by the reaction of Si_3N_4 and Cu during sintering process. Moreover, it is noted that the addition of Cu has a significant impact on the full-width at half-maximum of β-Sialon phase. The full-width at half-maximum firstly increases with 0–20 wt% Cu addition, then slightly change with increase of Cu. According to the well-known Scherrer equation [28,29], the average grain size decreases with the full-width at half-maximum increasing. Hence, the average grain of β-Sialon phase firstly decreases with 0–20 wt% Cu addition, then no distinct difference change with the addition of Cu increase.

The SEM micrographs of Cu-doped β-Sialon composite are shown in Fig. 2. In this micrograph, the darker and bright phases are β-Sialons and Cu-Si alloy, respectively. The Cu-Si particles are uniformly dispersed in the matrix. Meanwhile, with the increase of the addition Cu, the Cu-Si particle size becomes bigger.

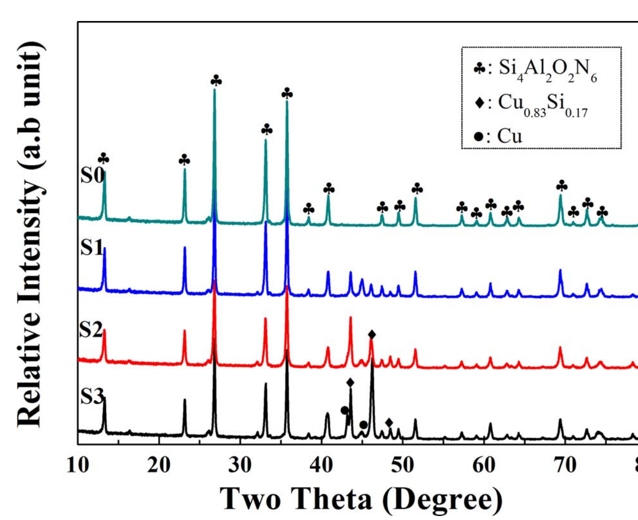

Fig. 1. XRD patterns of samples with different addition of Cu.