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Oxidation behavior and mechanism of oxidation of Si₃N₄/TiC micro-nanocomposite ceramic materials

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Oxidation behavior of hot-pressed Si₃N₄/TiC micro-nanocomposite ceramic materials with Al₂O₃ and Y₂O₃ as sintering additives was investigated at a dry air temperature of 800-1250 °C. The experimental study included analyses of oxidation behavior and mechanism. The results show that the relationship between oxidation mass gain and oxidation time is parabolic, where gains in the oxidation mass increase with the growth of TiC content. The surface layer composition of materials after oxidation was investigated with X-ray diffraction. The oxide layer is composed mainly of SiO₂ and TiO₂, and a small amount of Si_3N_4 or TiC phase can be found on the oxidation surface layer, thereby implying that the surface layer is significantly covered with oxides after oxidation at 1250 °C for 100 hrs. Scanning electron microscopy (SEM) reveals that the oxidation behavior results in a large number of microcracks and holes in the oxide layer.

Key words: Silicon nitride, Micro-nanocomposite ceramic, Oxidation, Mechanism.

Introduction

Silicon nitride (Si₃N₄) was first investigated in 1859[1], but was gradually applied to refractory materials nearly a century later. Until the 1980s, silicon nitride is clearly useful in structural applications [2]. At present, Si₃N₄ ceramics are ubiquitous in internal combustion engines, cutting tools, ball bearing, and high-temperature gas turbines given its relatively hightemperature strength, high thermal conductivity, high thermal shock resistance, and low thermal expansion coefficient [3-5]. However, the defects of Si₃N₄ ceramics, such as comparatively low hardness and wear resistance, limit its application. Numerous improvements have been introduced through synergistic toughening effects such as adding and whisking nanoparticles into the Si₃N₄ matrix or developing self-reinforced microstructures that consist of elongated grains [6,7].

In the machining field, the development of cutting tools, machine tools, and high-speed machining has led to the widespread application of high-speed cutting that enhance machining productivity [8]. Given its high thermal resistance and good chemical stability, Si₃N₄ ceramic cutting tools are widely used in machining difficult-to-cut materials, especially high-speed cutting of cast iron. However, the heat generated from high speed machining is concentrated on the cutting edge region near the tool-work interface, thereby resulting in a rapid increase of cutting temperature. The maximum cutting temperature can reach up to 1300 °C [9-11]. The high-temperature oxidation of non-oxide ceramics significantly influences their high-temperature properties and may limit their use in structural applications [12, 13]. Subsequently, addressing the issues of oxidation kinetics and mechanism provides a clear understanding of ceramic composites.

The dispersion of TiC nanoparticles in Si₃N₄ matrix composites considerably improves the mechanical properties, possibly overcoming inherent defects [6, 14, 15]. For Si₃N₄/TiC micro-nanocomposites, an interlocking microstructure has an "intra/inter" morphology that is distinct from microcomposites [6, 16]. Meanwhile, particulate additions make the oxidation of micronanocomposites more complex at elevated temperatures. Currently, the attention given to oxidation mechanisms of Si₃N₄/TiC micro-nanocomposites is insufficient, despite their practical applications at higher temperatures as ceramic cutting tool materials.

In the present study, Si₃N₄/TiC micro-nanocomposites, made from the mixing of a Si₃N₄ sub-micron matrix with Si₃N₄ and TiC nanopowders, were hot-pressed with Al2O3-Y2O3 additives. The oxidation resistance and mechanism of Si₃N₄/TiC nanocomposites were investigated at an air temperature of 800-1250 °C. Based on the literature data, scanning electron microscopy (SEM) findings, and X-ray diffraction (XRD) results, we propose a simplified model that describes the oxidation mechanism of the Si₃N₄/TiC micro-nanocomposite material.

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Sample	Si ₃ N ₄ (0.5 μm)	Si ₃ N ₄ (140 nm)	TiC (50 nm)	TiC (130 nm)	$Y_2O_3 + Al_2O_3$	Flexural strength <i>o</i> _f /MPa	Fracture toughness $K_{?c}$ /MPa·m ^{1/2}	Vickers hardness <i>HV</i> /GPa	Relative density
А	70	10	15		5	1025	8.5	13.75	\geq 98%
В	70	10		15	5	980	8.3	12.75	\geq 98%
С	80		15		5	810	6.5	13.21	\geq 98%
D	57	10	28		5	920	7.1	16.95	\geq 98%

Table 1. Composition and mechanical properties of samples in wt%.

Experimental

Material preparations

High-purity α -Si₃N₄ (> 99%) particles with mean sizes of 0.5 µm and 130 nm and TiC (> 99%) particles with average sizes of 50 nm and 130 nm were used. Al₂O₃ and Y₂O₃ were used as additives. Furthermore, polyethylene glycol (PEG) functioned as a nanomaterial dispersant in preparing well-agglomerated and stable suspensions. The suspensions were manufactured by ball milling in anhydrous ethanol for 36 hrs with alumina grinding balls and vacuum-dried at 120 °C. The dry product was milled through a sieve with 120 µm apertures to crush the soft agglomerates. The powders were then hot-pressed for 60 min under a nitrogen atmosphere in a boron nitride-coated graphite die at 1750 °C and 30 MPa.

The sintered discs were cut into square specimens with dimensions of 3 mm \times 4 mm \times 30 mm by an inner diameter slicer and mechanically polished to 1 μ m. The densities of sintered specimens were determined using the Archimedes principle in distilled water. The edges of square samples were chamfered to eliminate machining flaws that can act as fracture origins.

The mean flexural strength of the samples was measured by a three-point bending test with a universal testing machine at a load rate of 0.5 mm/min. The average of at least six measurements was obtained to achieve the reported value. The hardness was measured by Vickers indentation at a load of 196 N for 15 sec. Fracture toughness values were calculated through Vickers indentation based on the radial crack lengths [17].

The composition and mechanical properties of the samples are listed in Table 1.

Oxidation tests

All rectangular test samples were accurately measured, cleaned ultrasonically in ethanol, placed on high-purity alumina rods, and exposed to air at 800-1250 °C for 100 hrs. Heating and cooling rates were 20 °C /min. The samples were weighed with high precision (0.0001 g) before and after oxidation, and the structural characteristics of the oxide scales were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Results and Discussion

Oxidation Kinetics

Fig. 1 shows typical parabolic curves for the oxidation of sample A. The figure shows a rapid initial mass gain followed by a much lower secondary stage.

The curve of changes in weight versus time for specimens can be expressed by the following equation [18]:

$$W^2 = k_p t \tag{1}$$

where W, t, and k_p are the weight change per unit area, oxidation time, and the parabolic rate constant,



Fig. 1. Weight gain versus oxidation time for sample A.



Fig. 2. W^2 versus *t* for sample A.

respectively.

Fig. 2 demonstrates the relation between the square of the weight-change (W^2) and the oxidation time (*t*) at different oxidation temperatures. The parabolic rate constants (k_p) of the oxidation of sample A at 800-1250 °C, can be calculated from the slopes of the straight lines in Fig. 2.

The Arrhenius equation is expressed as:

$$k_p = k_o exp(-E_d/RT) \tag{2}$$

where E_a is the activation energy, k_0 is a constant of the given material, *T* is the absolute temperature, and *R* is the Boltzmann constant. According to the Arrhenius equation and the parabolic rate constant, k_p , the relationship between the ln ($\Delta w^2/t$) and 1/*T* is shown in Fig. 3.

The value of $-E_a/R$ was obtained from the slope of the best-fit line in the plot of Fig. 3. At 800-1250 °C, the activation energy for the oxidation of sample A is 215 kJ/mol. Because the activation energy of Si₃N₄/TiC micro-nanocomposites is lower than that of monolithic Si₃N₄ materials (260-630 kJ/mol) [19], the former can undergo oxidation more quickly than the latter.

Typical weight changes of the micro-nanocomposite materials containing different TiC amount that oxidized in air at 1250 °C, are shown in Fig. 4. The parabolic weight changes indicated that diffusion through the oxide layer is an important step during the entire oxidation process [20].

As shown in Fig. 4, Sample A shows the highest oxidation resistance at 1250 °C; the oxidation resistance of sample B is about equal to C; sample D is the least resistant. TiC reinforcement into the Si_3N_4 -based materials seems to have a distinct effect on the overall kinetics of oxidation, which is essentially governed by the formation of a passivating oxide layer, thus resulting in a parabolic type of kinetics over the entire temperature range.

Fig. 5 shows the XRD analyses of sample A after 10 hrs and 100 hrs oxidation at 1250 °C. The amount of β -Si₃N₄ and TiC significantly decreased in the oxidized surface, while the level of crystalline TiO₂ slightly varied with increasing oxidation time. Cristobalite (SiO₂) phase formed in the oxidized sample surface after 10 hrs at 1250 °C and increased remarkably after 100 hrs.

The oxidized surface morphology of sample A after 100 hrs oxidation at 1250 °C is shown in Fig. 6.

Fig. 6(a) indicates that the oxidized surface is gray, and TiO_2 and SiO_2 cover the uneven surface, which is clearly shown from the X-ray image in Fig. 5. In addition, interface cavities denote the outward pervasion of possible gaseous products such as CO_2 or N_2 [21]. Moreover, the surface oxide was badly cracked and formed a crack network, which is clearly visible from the partially enlarged view of Fig. 6(b). The observed



Fig. 3. Arrhenius plot of $\ln k_p$ versus 1/T for sample A.



Fig. 4. Weight gains versus oxidation time for Si₃N₄/TiC samples.



Fig. 5. XRD patterns from sample A after oxidation at 1250 °C for 10 hrs and 100 hrs.

scale cracking is most probably related to the mismatches in thermal expansion caused by repeated cooling from high temperature to room temperature during measurement of weight changes. Furthermore, volume changes induced by oxide formation, such as SiO₂ and TiO₂, also initiate surface cracking. The densities of SiO₂ (2.2-2.66 g/cm³) and TiO₂ (3.4 g/cm³) are lower than Si₃N₄ (3.12-3.22 g/cm³) and TiC (4.93 g/cm³), respectively,

and the difference in density leads to volume changes during the oxidation process. Thus, the oxide layers deteriorate and peel off at the interface as a result of the weak adhesive force and the internal stress, which accelerate the oxidation of the material.

Mechanisms of oxidation

 Si_3N_4 /TiC micro-nanocomposites undergo numerous possible chemical reactions upon oxidation in the air. These reactions depend on temperature, ceramic composition, physical properties of the oxidation layer, additive composition, and additive quantities[22-24].

The oxidation of Si_3N_4/TiC micro-nanocomposites initially involves the oxidation of TiC to outer TiO_2 (rutile) layers, according to the following reaction (3):

$$TiC(s) + 2O_2(g) \rightarrow TiO_2(s) + CO_2(g)$$
(3)

The diffusion of molecular oxygen through TiO_2 mainly controls the oxidation of TiC, and the titanium diffusion is relatively fast at above 1000 °C or within monocrystalline TiO_2 [25, 26]. Therefore, the inward diffusion of oxygen and the outward diffusion of titanium result in the rutile crystal growth.

The oxidation of silicon nitride is comparatively slow and hardly detectable by XRD below 1100 °C [20, 25]. Mass transfer and surface reaction jointly control the oxidation behavior [27]. At high air temperature, the passive oxidation of Si_3N_4 initiates [28], forming a thin protective SiO_2 film according to reaction (4):

$$Si_3N_4(s) + 3O_2(g) \rightarrow 3SiO_2(s) + 2N_2(g)$$
 (4)

Previous studies have also found the formation of Si_2N_2O layer underneath the SiO_2 layer [23, 29, 30], which cannot be observed by XRD in this test. The reaction equation is given as follows:

$$4Si_{3}N_{4}(s) + 3O_{2}(g) \rightarrow 6Si_{2}N_{2}O(s) + 2N_{2}(g)$$
(5)

$$2S_{12}N_2O(s) + 3O_2(g) \rightarrow 4S_1O_2(s) + 2N_2(g)$$
 (6)

A thin layer of crystalline oxynitride (Si_2N_2O) separates the SiO₂ layer from the matrix material. The outer cover is formed from the conversion of Si_3N_4 and Si_2N_2O into SiO₂, and its rate of formation depends on the diffusion of oxygen through the oxide. The thickness ratio of Si_2N_2O to SiO_2 is about 1:9 [29]. The products appear at the Si_2N_2O/SiO_2 and Si_3N_4/Si_2N_2O interfaces, affecting the diffusion and interfacial reactions of oxygen.

According to reactions (3)-(6), the bubbles accounted for the nitrogen gas and the evolution of carbon dioxide at the interfaces of $Si_3N_4(s)$ -SiO₂(s) and TiC(s)-TiO₂(s). When the gas pressure in these bubbles surpasses the ambient pressure, the release of bubbles from the sample surface generates micro-cracks on the oxide layer and a network of fine pores, as shown in Fig. 6.



(a) oxide layer (b) enlarged view of region A Fig. 6. SEM micrographs from surface of sample A after oxidation at 1250 °C for 100 hrs



Fig. 7. Simplified oxidation model of Si_3N_4 /TiC micronanocomposite materials.

Based on the microstructural investigations of oxidized materials and the literature on oxidation mechanisms of Si_3N_4 and TiC, a proposed simplified model describes the oxidation process of Si_3N_4 /TiC micro-nanocomposites at 800-1250 °C, as presented schematically in Fig. 7.

Conclusions

This paper provides a better understanding of oxidation kinetics and mechanisms of Si_3N_4 /TiC nanocomposites. The results are as follows:

(1) The oxidation of Si_3N_4 /TiC micro-nanocomposite materials containing Y_2O_3 and Al_2O_3 additives show a parabolic oxidation kinetics at air temperature range of 800 °C-1250 °C.

(2) With TiC reinforcement into the Si_3N_4 -based materials, the content of TiC has a distinct effect on the overall kinetics of oxidation. Oxidation resistance decreases with the increasing TiC content.

(3) After 100 hrs oxidation at 1250 °C, TiO₂ and SiO₂ constitute the rough oxide surface. The escape of CO₂ and N₂ gases forms pores in the oxide layer as a result of TiC and Si₃N₄ oxidation. The layers cracked severely and apparently consisted of more than one phase. The formation of cracking is mainly from the volume effect, and mismatch of thermal expansion between matrix materials and the oxidation products.

(4) A proposed simplified model describes the oxidation of Si_3N_4 /TiC micro-nanocomposite materials, which demonstrates that several diffusion mechanisms control the oxidation process.

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