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Titanium metallization of Si_3N_4 ceramics by molten salt reaction: Mechanism and interfacial structure

PAN WEI, JIAN CHEN, YONG HUANG
Department of Materials Science & Engineering, Tsinghua University, Beijing 100084, People's Republic of China
E-mail: panw@mail.tsinghua.edu.cn

In the present work, a new method of molten salt reaction for titanium metallization of Si_3N_4 has been developed. It was found that the decomposition of the titanium divalent compound led to the formation of a titanium coating. The thickness or weight gain per surface area of the coated sample increased with treating time and temperature. When the treating temperature was below 1123 K, the deposition process was controlled by the combination of interfacial reaction and the diffusion of N, Ti or Si in the coating layer, but when the temperature was above 1123 K, the process was only controlled by the diffusion of these elements. Field emission SEM observation revealed the multi-layer structure of TiN and Ti_5Si_3 at the interface. Based on the thermodynamic calculations and other analysis, the possible reactions were determined. © *2000 Kluwer Academic Publishers*

1. Introduction

Si_3N_4 ceramics are emerging as very important engineering materials due to their excellence mechanical properties. However, its brittleness and too hard to be processed deter it from wide use. Si_3N_4 brazing, as a solution to the problem, has been developed in the passed years.

An essential consideration in the brazing of Si_3N_4 to metal or itself is the need to promote the wetting of Si_3N_4 surface by liquid braze filler metals. One common approach is to treat Si_3N_4 surfaces to form metallic coatings.

Metallization of ceramics followed by plating and brazing has been established for several decades. Metal coated ceramic surfaces can be brazed with standard commercial braze filler metals so that this approach offers considerable flexibility for selecting joining materials that are compatible with processing or joint property constraints. The most widely used method to coat a ceramic surface is a molybdenum-manganese process which is usually used for oxide ceramics. In this process, a thin layer of molybdenum paint containing manganese is applied to the surface of ceramics and then fired at about 1773 K in a reducing atmosphere. During the sintering, the glass phase from the ceramics would migrate into the molybdenum layer, which assists the molybdenum layer in adhering to the ceramic [1]. Another variation of the metallizing approach is the use of a vapor deposited coating of metal which is typically made by the sputter coating process or the electron beam vapor coating process. This process can be used for most ceramics. Examples of the use of this technique include sputter-deposited coatings of titanium used to enhance the wetting of Si_3N_4 [2], but it is too expensive for application on an industrial sale. Gotman *et al.* [3] have obtained a titanium coating layer by putting Si_3N_4 in a TiH_2 powder bed and treating in an evacuated stainless bag at a temperature of 1273 K for 1 hour. However, this coating layer was weakly bound to the Si_3N_4 substrate and often spalled off.

In the present work, a new method of molten salt reaction has been developed for the metallization of Si_3N_4 ceramics which is simple, cheap and can be applied in the industrial area. The deposition mechanism and the possible reactions between titanium coating and Si_3N_4 substrate are also discussed.

2. Experimental

In the experiment, a mixture of equimolar NaCl-KCl (>99.0%, BAC Co., China) and proportional amounts of (5–10 wt%) potassium fluorotitanate (>99.5%, BAC Co., China) were put in an alumina crucible and heated to the reaction temperature (973 K–1373 K) in a SiC resistance furnace under a flowing argon atmosphere. The Si_3N_4 samples were made by pressureless sintering of Si_3N_4 powder (SN-10, UBE Industries, Japan) with 5 wt% MgO (>99.0%, BAC Co., China) as a sintering additive. At the required temperature, samples were immersed into the molten bath by Mo wires and at known intervals, then these samples were taken out of the bath and cooled in the cold zone of the furnace. After the experiment was finished, these samples were cleaned, dried, weighed and the coating area was accurately measured. The microstructure of the titanium coating and the interface between the titanium coating and Si_3N_4 ceramics were determined by means of a scanning electron microscope (SEM; Opton

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CSM950, Germany), and a field emission scanning electron microscope (FE-SEM; Amray1910E, USA) with an energy dispersive spectroscopy (EDS). To further determine the fine microstructure of the interface, transmission electron microscopy(TEM; JEM-200CX, Japan) was used. For the preparation of the TEM samples, the coated specimens were first sliced into 3 × 0.5 mm slabs, two slabs were then glued together with the titanium-coated sides facing each other. After that, the specimens were polished to 50 μm and then dimpled to 20 μm. Finally, ion beam milling of these specimen was conducted.

In addition, X-ray diffraction (XRD; Rigaku D/MAXIIIA, Japan) was employed to detect whether there were chemical reactions between the titanium coating and the Si_3N_4 substrate.

3. Results and discussion

3.1. Coating mechanism

It is considered that when potassium fluorotitanate in the salt reacted and reached equilibrium with titanium, the following reaction occured, i.e.

$$Ti^{4+} + Ti = 2Ti^{2+} \tag{1}$$

$$3Ti^{4+} + Ti = 4Ti^{3+} \tag{2}$$

$$2Ti^{3+} + Ti = 3Ti^{2+} \tag{3}$$

As the Si_3N_4 samples were immersed into the bath, the titanium divalent ions produced by reaction (1), (3) were easily decomposed onto the surfaces of the ceramic substrate, so a titanium coating layer could be obtained.

$$2Ti^{2+} = Ti^{4+} + Ti \text{ (on substrate)} \tag{4}$$

Figs 1–3 summarise the influences of reaction temperature, treating time and the initial concentration of potassium fluorotitanate on the weight gain per surface area (g/cm^2) of Si_3N_4 samples. It can be seen that the weight gains increased with the temperature and treating time, respectively. When the initial concentration of potassium fluorotitanate was lower than 11 wt%, the weight gain increased with the initial concentration, but decreased when the concentration was higher than 11 wt%.

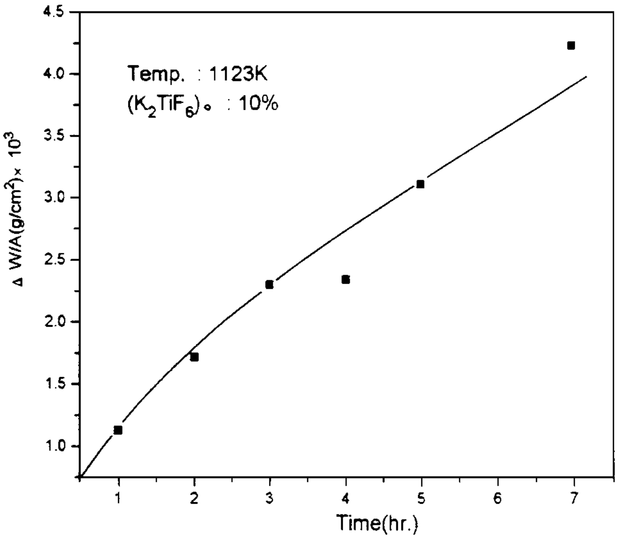

Figure 1 Weight gain of the Si_3N_4 sample per surface area versus coating time.

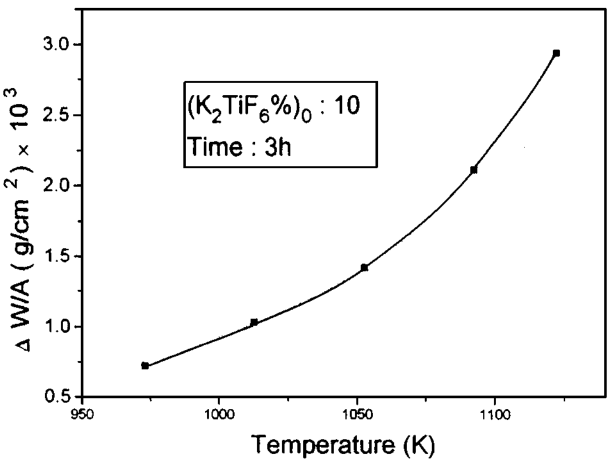

Figure 2 Weight gain of the Si_3N_4 sample per surface area versus coating temperature.

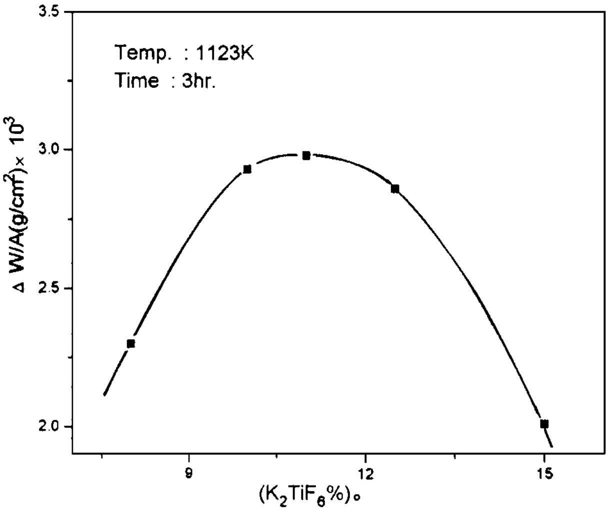

Figure 3 Effect of initial concentration of Potassium fluorotitanate on the weight gain of the Si_3N_4 sample per surface area.

Taking the weight gain per surface area as a function of the treating time, it was found that, when the coating temperature was lower than 1123 K, the relationship between weight gain per surface area of Si_3N_4 sample and treating time could be described as follows (as shown in Fig. 4):

$$\Delta W/A = kt^{2/3} \tag{5}$$

where k is the reaction rate constant and t is the treating time. This relationship shows that the coating process may be controlled by both the surface reaction (reaction (4)) and the diffusion of N, Ti, Si in the coating layer. However, when the coating temperature was higher than 1123 K, the relationship obeyed a parabolic law (as shown in Fig. 5).

$$\Delta W/A = kt^{1/2} \tag{6}$$

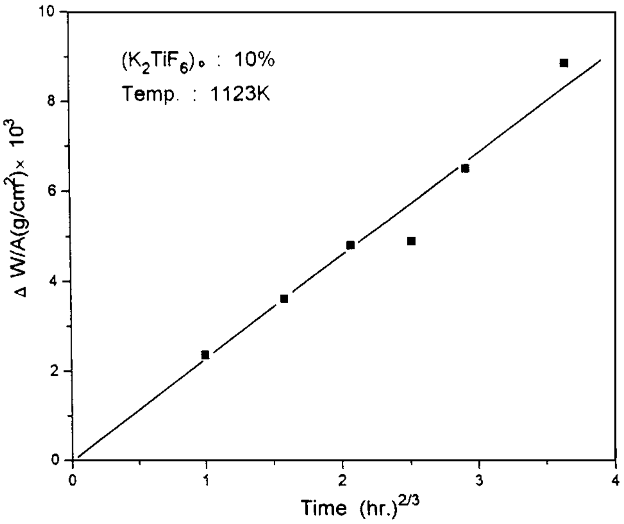

Figure 4 Weight gain of the Si_3N_4 sample per surface area versus $t^{2/3}$.

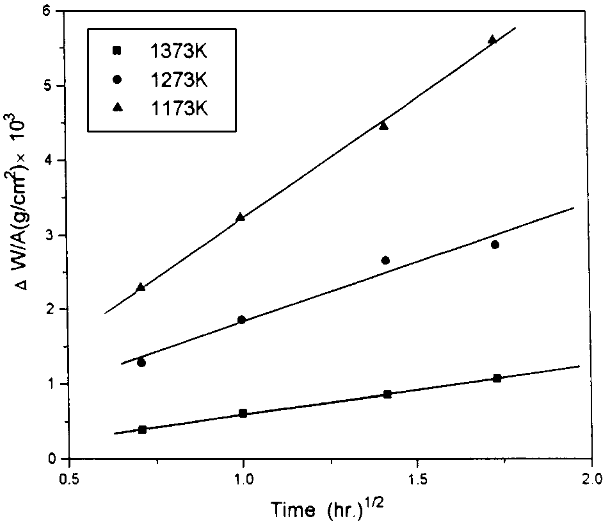

Figure 5 Weight gain of the Si_3N_4 sample per surface area versus $t^{1/2}$.

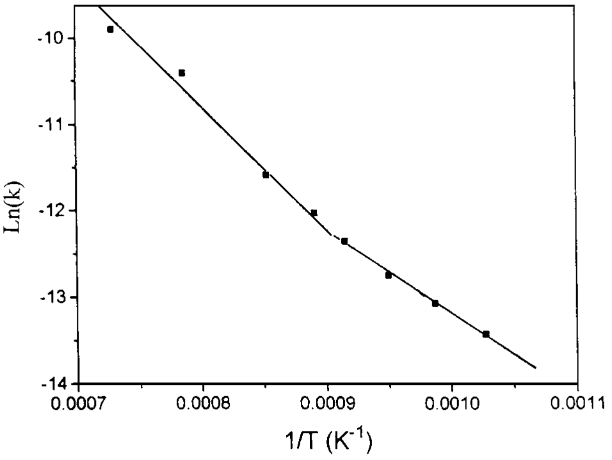

Figure 6 Relationship between rate constant k and the coating temperature.

This indicates that the process is controlled by diffusion of the elements in the surface coating layer. These relationships at different temperatures suggest different limiting steps in the coating process.

The plot of log(k) versus $1/T$ is illustrated in Fig. 6. From the slope of the straight part of the line, the apparent activation energy can be calculated, which shows that, when the coating temperature was lower than 1123 K, the apparent activation energy was 78.264 KJ/mol and when the coating temperature was higher than 1123 K, it was 113.85 KJ/mol.

3.2. Interfacial reactions and structure

Fig. 7 is the surface SEM micrograph of the titanium coating. The micrograph shows that continuous coating has been successfully obtained. XRD patterns of samples treated at different temperatures show that the titanium coating reacted with Si_3N_4 to yield TiN and Ti_5Si_3 (Fig. 8). Note that under the experimental conditions, the metallized titanium coating was Ti_2O, which may be explained by considering the diffusion of oxygen from the grain boundary phase, which consisted of MgO and SiO_2 to the coating layer.

The possible reactions that relate to the formation of Ti_5Si_3 and TiN when Si_3N_4 meets titanium are as the followings [4, 5]:

$$\mathrm{Ti(s)} + 1/4\mathrm{Si_3N_4(s)} = \mathrm{TiN(s)} + 3/4\mathrm{Si(s)} \qquad (7)$$

$$\begin{aligned}\Delta G^\circ &= -155.02 + 0.0143T\\ &= -135.39\ \mathrm{KJ/mol\ (at\ 1373\ K)}\end{aligned}$$

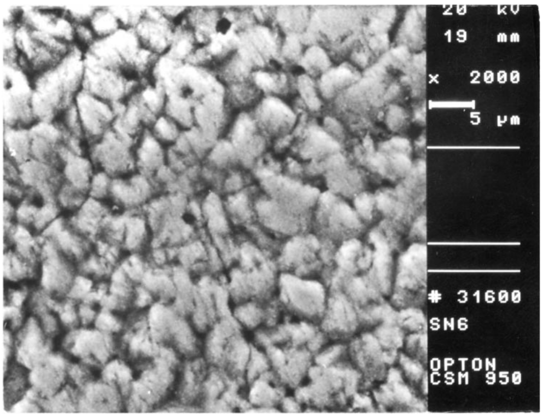

Figure 7 Surface micrograph of metallized Si_3N_4 ceramics(SEM).

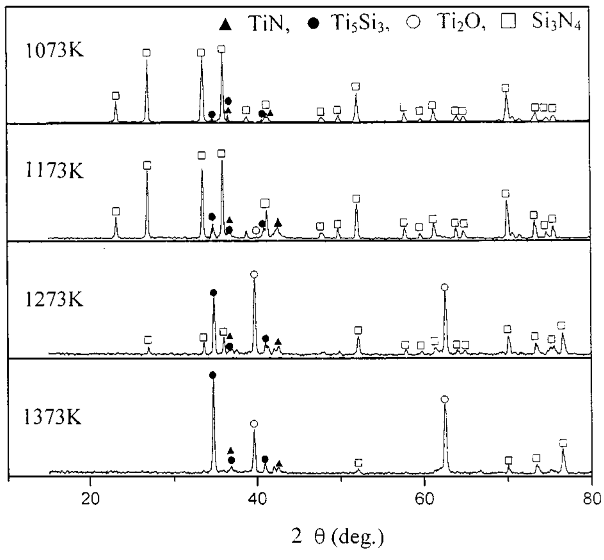

Figure 8 XRD patterns of sample treated at different temperature.

$$\mathrm{Ti(s)} + 1/5\mathrm{Si_3N_4(s)} = 1/5\mathrm{Ti_5Si_3(s)} + 2/5\mathrm{N_2(g)} \quad (8)$$

$$\Delta G^\circ = -5.36 - 0.0418T$$

$$= -62.75\ \mathrm{KJ/mol\ (at\ 1373\ K)}$$

$$\mathrm{Ti(s)} + 1/9\mathrm{Si_3N_4(s)} = 4/9\mathrm{TiN(s)} + 1/9\mathrm{Ti_5Si_3(s)} \quad (9)$$

$$\Delta G^\circ = -152.20 + 0.018T$$

$$= -127.49\ \mathrm{KJ/mol\ (at\ 1373\ K)}$$

It is obvious that reaction (1) is the most thermodynamically favorable among the above reactions from the calculated standard Gibbs free energy at 1373 K. On the other hand, the work of Sambasivan *et al.* [6] have proved that Si_3N_4 is not stable with any of the titanium silicides, indicating that reaction (3) could not occur. In order to decide whether reaction (2) occurs, an equal volume mixture of Ti and Si_3N_4 powder was examined by thermogravimetric analysis under an argon atmosphere up to 1673 K. The analysis demonstrated that there was no mass loss, suggesting reaction (2) was impossible. Thus, Si_3N_4 reacted with titanium would give Ti_5Si_3 and Si and the released Si reacted with titanium to produce Ti_5Si_3.

A fine interfacial structure between the titanium coating and the Si_3N_4 substrate is shown in Fig. 9. The micrograph clearly shows that between the titanium coating and the Si_3N_4 there were two different layers: the layer (marked as A) adjacent to Si_3N_4 consisted of ultra-fine grains which had a very high titanium content from EDS analysis, the other layer (marked as B) consisted of coarse grains, of which the titanium/silicon atomic ratio was about 5 : 3. Thus, it is reasonable to deduce that the coarse grain was Ti_5Si_3 while the ultra-fine grain was TiN. A further observation on the microstructure of Si_3N_4 near the interface between the ultra-fine TiN and Si_3N_4 by TEM clearly shows that before the outside continuous TiN layer formed, the titanium had diffused through the grain boundaries into Si_3N_4 bulk and reacted with the oxynitride glassy phase to form ultra-fine TiN (as shown in Fig. 10). It is not known why the TiN grains were ultra-fine under these experimental conditions, we guess this was the released Si from the reaction between Si_3N_4 and Ti that interfered with the growth of TiN grains. The coarsening of Ti_5Si_3 grains may be due to their rapid growth.

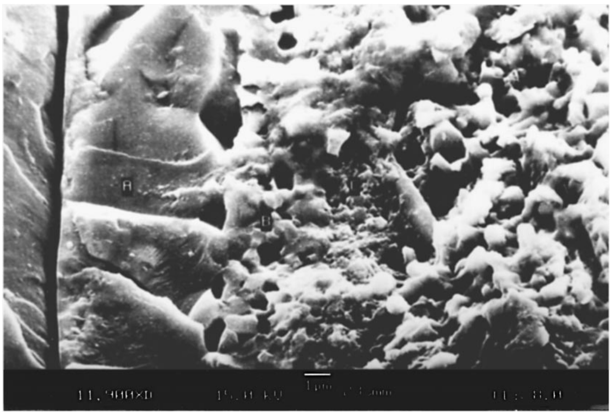

Figure 9 Cross-sectional field emission SEM micrograph of the interface between Si_3N_4 and titanium coating.

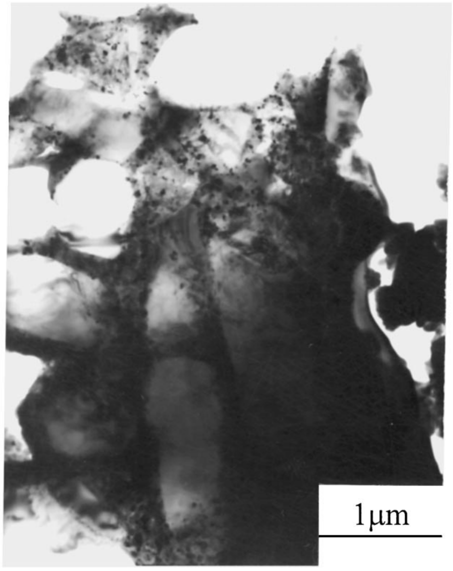

Figure 10 TEM micrograph of Si_3N_4 grainboundaries near the interface.

TiN is usually used as diffusion barrier in microelectronics field, such as the diffusion barrier between aluminum and PtSi, $CoSi_2$ [7]. But at such high temperatures of the present experiment, the barrier effect of the TiN would be lost. However, the ultra-fine TiN and Ti_5Si_3 multi-layers structure are still beneficial in retarding the reaction between titanium and Si_3N_4. Again in Fig. 8, it can be seen that when TiN and Ti_5Si_3 multilayer structure have formed, the reaction between titanium and Si_3N_4 would be determined by the diffusion of titanium atoms since they travel slower compared with nitrogen and silicon atoms [8]. Thus, the titanium coating can reach its highest thickness by considering both the titanium deposition rate and the chemical reaction rate at the interface. But when the treating temperature further increased, the reaction between titanium and Si_3N_4 would become more severe due to the increase of diffusion rate of titanium atoms. This would lead to more consumption of titanium, which is harmful for the mechanical strength of the joints if the metallized Si_3N_4 is to be used as joining specimen.

4. Conclusions

A new method of molten salt reaction has been developed for the titanium metallization of Si_3N_4 ceramics. It was found that the weight gains per surface area or thickness of the coating increased with treating temperature and time. Moreover, when the treating temperature was below 1123 K, the relationship between weight gains per surface area and the treating time could be described by Equation 5 while the temperature was above 1123 K, the relationship obeyed parabolic law (Equation 6), indicating different limiting steps in the coating process. The apparent activation energy of the different limiting process was 78.26 KJ/mol and 113.85 KJ/mol, respectively.

At the treating temperature, a TiN and Ti_5Si_3 layered structure was formed at the interface. Thermodynamic calculations and other analyses suggested that the titanium coating layer first reacted with the Si_3N_4 substrate to yield ultra-fine TiN, and Si and the released Si reacted with titanium to produce Ti_5Si_3. TEM observation further indicated that ultra-fine TiN had already formed in the Si_3N_4 bulk near the interface before the outer TiN and Ti_5Si_3 multi-layers formed.

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