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High temperature oxidation behavior of electroconductive TiN/O'-Sialon ceramics prepared from high titania slag-based mixture

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Abstract: The oxidation behavior of electroconductive TiN/O'-Sialon ceramics prepared using high titania slag as main starting material was studied at 1 200–1 300 °C in air. The isothermal and non-isothermal oxidation processes were investigated by DTA–TG Phase compositions and morphologies of the oxidized products were analyzed by XRD, SEM and EDS. The results indicate that the oxidation of TiN and O'-Sialon occurs at about 500 °C and 1 050 °C, respectively. After oxidation at 1 200–1 300 °C, a protective scale that consists of Fe₂MgTi₃O₁₀, SiO₂ and TiO₂ is formed on the surface of the materials, which effectively prevents the oxidation process. The formation of a protective scale is relative to TiN content and apparent porosity of the samples, the amount of SiO₂ and amorphous phase in the oxidation product. At the initial oxidation stage, the oxidation kinetics of the materials follows perfectly the linear law with the apparent activation energy of 1.574×10^5 J/mol, and at the late-mid stage, the oxidation of the samples obeys the parabolic law with the apparent activation energy of 2.693×10^5 J/mol. With the increase of TiN content, mass gain of the materials increases significantly.

Key words: TiN/O'-Sialon; high titania slag; electroconductive ceramics; oxidation behavior

1 Introduction

O'-Sialon (Si_{2-x}Al_xO_{1+x}N_{2-x}, $0 \le x \le 0.3$) has excellent oxidation stability, low thermal expansion and excellent mechanical properties in a wide temperature range [1, 2], but the poor strength and hardness restrict its application as engineering materials. In order to further improve the comprehensive performance of O'-Sialon, O'/ β '-Sialon [3, 4], ZrO_2/O' -Sialon [5], $TiN/\beta'-O'$ -Sialon [6], TiN/O'-Sialon [7], etc, multiphase ceramics are prepared by different methods to improve the strength and toughness of O'-Sialon through granule dispersion strengthening and phase transformation toughening. All of these materials show better mechanical, physical and properties than single-phase O'-Sialon. chemical However, these composites are hard, brittle and cannot be machined efficiently by conventional diamond tools. As a result, electric-discharge machining (EDM) would be an attractive alternative technique. Although EDM has higher efficiency, higher machining accuracy than traditional machining and can process complex shape of parts, decrease material wastage and processing cost, it requires materials with electrical conductivity higher than 100 Ω ·cm, which is usually not obtainable for most ceramics. To match this requirement, considerable work been conducted to improve the electrical has conductivity of ceramics. One of efforts is through the composite approach, i.e., by adding a conductive second phase into ceramics. As a reinforcing material, TiN offers several unique advantages such as high melting temperature (2 950 °C), excellent stiffness (600 GPa), high hardness, good chemical durability, high electrical conductivity $(4.6 \times 10^6 \ \Omega^{-1} \cdot m^{-1})$ [8], and the chemistry compatibility with O'-Sialon ceramics. As a result, the addition of TiN to O'-Sialon ceramics is expected to increase not only the toughness but also their electrical conductivity. Electroconductive TiN/O'-Sialon ceramics which are modified by TiN can be processed by EDM and are expected to be used as electrode or

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heating materials.

Although O'-Sialon has excellent oxidation resistance, TiN as a nitride is readily oxidized at high temperature. So, it is important to investigate the high temperature oxidation behavior of TiN/O'-Sialon for achieving their application. Recently, the oxidation behaviors of O'-Sialon [9], β '-Sialon [10], Si₃N₄ [11] and TiN/Si₃N₄ [12] were studied. But there were no reports about TiN/O'-Sialon ceramic. Therefore, the oxidation behavior of TiN/O'-Sialon ceramics prepared using high titania slag as the staring material in air at high temperature and the effect of TiN content on the oxidation process are studied in this work.

2 Experimental

Electroconductive TiN/O'-Sialon ceramics were prepared by two-step method in this work. First, TiN/O'-Sialon powder was synthesized using high titania slag, silica fume and bauxite chamote as the starting materials by carbothermal reduction-nitridation in a nitrogen atmosphere with a N2 flow rate of 400 mL/min at 1400 °C for 7 h. The phases of the products are composed of O'-Sialon, TiN, small amounts of β '-Sialon and the unreacted TiO₂. Subsequently, the powder was pressed into pellets with 15 mm in diameter at 200 MPa, then put into the graphite crucible and buried with powder (the mole ratio of Si_3N_4 to SiO_2 is 1:1). TiN/O'-Sialon ceramics were prepared by pressureless sintering at 1500 °C for 2 h. The samples were marked with T₁₀, T₂₀, T₃₀, T₄₀ and the number indicated the content of TiO₂ in the starting materials. Phase compositions and properties of TiN/O'-Sialon ceramics are shown in Table 1.

Setsys Evolution 16 comprehensive thermal analyzer was employed to investigate the starting temperature and reaction course of the oxidation of the samples in air. The heating rate was 10 °C/min to confirm the oxidation temperature. Specimens with regular shape were cut from the sintered pellets, wet polished, ultrasonically cleaned, dried, and then measured the surface area. Oxidation experiments were conducted using a MoSi₂ resistance furnace at different temperatures in air. The mass gain was measured by MettlerA04 type electronic balance whose precision was 0.1 mg. In the whole oxidation process, the air with a flow rate of 80 mL/min was continuously blown into the furnace. After oxidation at 1200, 1260 and 1300 °C for 2 h, the samples were removed and cooled to the room temperature.

Phase identification of the oxidized layers was performed by D/MAX-RB X-ray diffractometer (XRD) using nickel-filtered Cu K_{α} radiation, and the morphologies of surface and cross section were observed by SSX–550 scanning electron microscope (SEM). The element analysis of characteristic grain on the oxidized surface was carried out by energy dispersion spectroscopy (EDS).

3 Results and discussion

3.1 Oxidation process analysis

The oxidation processes of TiN/O'-Sialon ceramics are composed of TiN and O'-Sialon. The oxidation reactions are as follows:

$$TiN(s)+O_2(g) = TiO_2(s)+0.5N_2(g)$$
(1)
$$\Delta G_1^{\Theta} = -604.700 + 0.08431T, 298-1943 \text{ K} [13]$$

$$\Delta G_1 = \Delta G_1^{\Theta} + RT \ln \frac{p_{\rm N_2}^{0.5}}{p_{\rm O_2}}$$

$$Si_{1.7}Al_{0.3}O_{1.3}N_{1.7}(s)+1.275O_2(g) = 1.7SiO_2(s)+0.15Al_2O_3(s)+0.85N_2(g)$$
(2)
$$\Delta G_2^{\Theta} = (-1164.454+0.21573T, 298-1685 \text{ K} [14]$$

$$\Delta G_2 = \Delta G_2^{\Theta} + RT \ln \frac{p_{N_2}^{0.85}}{p_{O_2}^{1.275}}$$

Thermodynamic analysis results show that the variation in the Gibbs free energy of reactions (1) and (2) is far less than 0 at room temperature up to 1673 K in air, which implies that the oxidation of both TiN and O'-Sialon is thermodynamically favorable. Therefore, thermal-analysis tests are necessary to determine the exact starting temperatures of the two reactions.

Figure 1 shows the DTA-TG curves of TiN/O'-Sialon in air. There are four obvious exothermic peaks in DTA curve for TiN/O'-Sialon, in the meanwhile the obvious mass change in TG curve. The beginning temperature of the first exothermic peak is 500 °C and

 Table 1 Phase compositions and properties of TiN/O'-Sialon prepared at 1 500 °C for 2 h

Sample	Phase composition	Apparent porosity/ %	Bulk density/ (g·cm ⁻³)	Flexure strength/ MPa	Electric resistivity/(Ω·cm)
T ₁₀	O'-Sialon $\gg\beta$ '- Sialon TiN	30.2	2.2	64	6.3×10 ⁸
T ₂₀	O'-Sialon>TiN>>β'-Sialon	8.20	2.8	100	2.1×10^{7}
T ₃₀	O'-Sialon≈TiN>>β'-Sialon	1.60	3.1	169	5.3×10 ⁻³
T ₄₀	TiN>O'-Sialon>>β'-Sialon	16.9	2.5	87	1.3×10^{-3}



Fig. 1 DTA-TG curves for oxidation of TiN/O'-Sialon in air

the forth one is 1050 °C. According to Ref. [15], the first peak is exothermic peak of TiN and the forth one is O'-Sialon. The other two peaks could come from the oxidation of impurity phases. According to the analysis results of DTA-TG, the isothermal oxidation experiments were carried out at 1200, 1260 and 1300 °C for 2 h.

3.2 Oxidation behavior at high temperature

Figure 2 shows the XRD pattern of the oxidized surface of the sample T_{30} at 1260 °C for 2 h. The oxidized layer mainly consists of Fe₂MgTi₃O₁₀, TiO₂ and SiO₂. The morphologies of the surface and the

cross-section of the sample T_{30} which is oxidized at 1200 and 1260 °C for 2 h are shown in Fig. 3. Large amounts of lath-shaped Fe₂MgTi₃O₁₀ grains are observed and confirmed by XRD and EDS analysis (Fig. 4). The Fe elements mainly derived from impurity phases of the starting materials. As shown in Figs. 3(a) and (c), these lath-shaped grains are covered by a layer of SiO₂ and glass phases and no obvious pores can be observed. With the temperature increasing, the lath-shaped grains grow continually. Three obvious layers can be observed on the cross-section of the sample T_{30} after oxidation at 1200 and 1260 °C (Figs. 3(b) and (d)). The outer layer is a protective scale layer formed by molten oxide, and its



Fig. 2 XRD patterns of oxidized sample T_{30} at 1 260 °C for 2 h in air



Fig. 3 SEM images of surface and cross-section of sample T_{30} after oxidation for 2 h in air: (a) 1200 °C, surface; (b) 1200 °C, cross-section; (c) 1260 °C, surface; (d) 1260 °C, cross-section



Fig. 4 EDS spectrum of lath-shaped grain in oxidation layer of sample T_{30}

thickness is about 90 μ m. The protective scale formed at 1200 °C is more compact than that formed at 1260 °C. The middle layer is solid-phase oxide layer and part of which has been oxidized before the outer protective scale formed. Many pores caused by the diffusion of metal ions to the outside layer were observed. The inner layer is unoxidized TiN/O'-Sialon matrix.

Figure 5 shows the isothermal TG curves of the sample T_{30} at 1200, 1260 and 1300 °C. As shown in Fig. 5, the mass gain increases obviously at the initial oxidation stage, which indicates that on the sample surface, an effective protective scale cannot form. At this stage, the chemical reaction is the rate-limiting step of the oxidation process and the oxidation of the samples follows the linear law with the apparent activation energy of 1.574×10^5 J/mol (Fig. 6(a)). With the oxidation time prolonging, the thickness of protective scale increases and closes the surface pores and prevents the oxygen from diffusing to the interior of the sample through the oxidation layer. In that case, the oxidation kinetics of the materials can be described by a class parabolic law with an apparent activation energy of 2.693×10^5 J/mol



Fig. 5 Isothermal TG curves for sample T_{30} at different temperatures



Fig. 6 Oxidation kinetic curves of samples: (a) Initial stage; (b) Late-mid stage

(Fig. 6(b)), which means that the diffusion of O_2 through the oxidized layer to the reaction layer or the diffusion of metal ions through the product layer to the outer layer is the rate-limiting step of the oxidation process. The researches have shown that the oxidation kinetics of Si₃N₄ and Si₂N₂O matrix ceramics at high temperatures also followed the parabolic rule [16–18].

3.3 Effect of TiN content on oxidation process

Figure 7 shows the XRD patterns of the oxidized surfaces of the samples $T_{10}-T_{40}$ at 1260 °C for 2 h. As indicated in Fig. 7, Fe₂MgTi₃O₁₀, TiO₂ and SiO₂ are found in all the samples, but their contents are different. The SiO₂ content of the oxidation layer of sample T_{10} is high and contains large amounts of amorphous phase. The SiO₂ content in sample T_{20} obviously decreases, but the product still contains large amounts of amorphous phases. The SiO₂ content of sample T_{30} and amorphous phase are little, but the TiO₂ content obviously increases. Fe₂MgTi₃O₁₀ is only phase in sample T_{40} , and SiO₂ and amorphous phase do not exist.

Figure 8 shows the isothermal TG curves of the samples T_{10} - T_{40} at 1 260 °C. As shown in Fig. 8, with the increase of TiN content, the mass gain per unit area



Fig. 7 XRD patterns of samples T_{10} - T_{40} after oxidation at 1260 °C for 2 h



Fig. 8 Isothermal TG curves of samples T₁₀-T₄₀ at 1 260 °C

increases obviously in the initial stage of the oxidation process, which is due to the fact that TiN is easier to be oxidized at lower temperature. Although the porosity in samples T₁₀ is high (see Table 1), large amounts of molten SiO₂ formed at the initial oxidation stage close the pores on the surface rapidly and prevent the oxygen from diffusing into the interior of the sample. So, the passive oxidation occurs and the mass gain is little in the initial oxidation stage. The molten SiO₂ is reserved as the amorphous phase in the following cooling processes. Although the molten SiO_2 of sample T_{20} on the surface decreases obviously in the initial oxidation stage, the pores on the sample surface still are closed rapidly due to lower porosity compared with sample T_{10} . TiN content of sample T_{20} is higher than that of sample T_{10} , so the mass gain of the oxidation process is higher. Although the content of SiO₂ generated on the sample surface is little, its porosity is very low and the large amounts of TiO₂ generated on the sample surface reduce the liquid phase formation temperature, which effectively leads to formation of the protective scale. The mass gain in the initial oxidation stage is obvious caused by the high TiN content in the sample T_{30} . There is an effective protective

scale formed on the surface of sample T_{40} due to high porosity of the material and no molten SiO₂ and TiO₂ produced, so the oxidation process aggravated. As a whole, the amount of SiO₂ and TiO₂ formed by O'-Sialon and TiN oxidation and apparent porosity of the materials have a great influence on the formation of a protective scale, but the effect of Fe₂MgTi₃O₁₀ is not significant.

4 Conclusions

1) The oxidation processes of TiN/O'-Sialon ceramics are composed of TiN and O'-Sialon oxidations which begin at about 500 °C and 1050 °C, respectively.

2) At 1200–1300 °C, the oxidation kinetics of the materials at the initial stage follows a linear law and no effective protective scale is formed and the apparent activation energy is 1.574×10^5 J/mol. The oxidation kinetics at the late-mid stage obeys a parabolic law and an effective protective scale is generated on the specimen surface. In that case, the diffusion of the oxygen through gradually closed pores is considered to be the rate-limiting step and the apparent activation energy of the oxidation is 2.693×10^5 J/mol, exhibiting good oxidation resistance.

3) The formation of a protective scale is connected with the amounts of SiO_2 and amorphous phases generated on the oxidized surface and apparent porosity of the materials. With the increase of TiN content, mass gain of the materials increases significantly.

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TiN/O'-Sialon 导电陶瓷的高温氧化行为

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摘 要:以高钛渣为主要原料制备的 TiN/O'-Sialon 导电陶瓷为研究对象,研究 TiN/O'-Sialon 材料在 1200~1300 ℃ 下的抗空气氧化行为。采用 DTA-TG 法研究材料的恒温和变温氧化过程,利用 X 射线衍射、扫描电镜和能谱分析检测方法对氧化产物的相组成和显微结构进行表征。结果表明: TiN 和 O'-Sialon 的氧化分别从 500 ℃ 和 1 050 ℃ 左右开始进行。在 1200~1300 ℃ 下氧化后的材料表面可形成由 Fe₂MgTi₃O₁₀、SiO₂和 TiO₂组成的较致密的保 护膜,其形成主要与材料中 TiN 含量、氧化产物中 SiO₂和非晶相数量以及材料显气孔率有关。材料氧化前期遵 循直线规律,中后期遵循抛物线规律,其表观活化能分别为 1.574×10⁵ J/mol 和 2.693×10⁵ J/mol。增加材料中 TiN 的含量从而导致材料单位面积氧化质量显著增加。

关键词: TiN/O'-Sialon; 高钛渣; 导电陶瓷; 氧化行为

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