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Preparation of in-situ TiO_2/O′-Sialon multiphase ceramics by selective-oxidation

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Abstract

On the basis of thermodynamic and thermal analysis, in-situ TiO_2/O′-Sialon multiphase ceramics were prepared from TiN/O′-Sialon materials by selective-oxidation at 800–1000 °C in air. The samples were characterized by XRD and EPMA. Selective-oxidation kinetics and effect of partial pressure of oxygen on oxidation process were studied. The results indicate that the increase of oxidation temperature and partial pressure of oxygen in the atmosphere accelerates the selective-oxidation of the materials. Logarithm rule, i.e., $\Delta m/A = k \log t + C$ can describe the selective-oxidation process perfectly with an apparent activation energy of 56.1 kJ/mol. There is no protective scale formed on the surface of the materials and diffusion of gas through gradually closed pores is believed to be the rate-limiting step.

Keywords: TiN/O′-Sialon; Selective-oxidation; In-situ TiO_2/O′-Sialon; Kinetics

1. Introduction

Combining structural and functional properties is becoming one of the developing tendencies of advanced ceramics in recent years [1], which can be performed by the incorporation of a functional phase into a structural ceramic matrix. Sialon is considered to be the most promising structural ceramics and O′-Sialon has shown great research prospects for its high-temperature strength and excellent oxidation and heat shock resistance. TiO_2 is an important inorganic functional material and is widely utilized for its unique properties such as photocatalytic activity [2], dielectric property [3], photoelectric conversion [4], gas-sensitive and humidity-sensitive effect [3], etc. However, as a result of the chemical incompatibility between TiO_2 and Si_3N_4, Si_2N_2O [5] and the fact that high purity O′-Sialon powder has not been prepared so far, multiphase ceramic of O′-Sialon composited with TiO_2 cannot be obtained by conventional "one step" and "two step" methods. In-situ TiN/O′-Sialon, a new multiphase ceramics has been prepared by the authors and has shown superior comprehensive properties [5]. Compared with O′-Sialon, TiN has poor oxidation resistance and is easy to be oxidized into TiO_2. Thus, an idea was proposed that by controlling process conditions, selective-oxidation of TiN/O′-Sialon may happen, i.e., TiN will be oxidized into TiO_2 whereas the oxidation of O′-Sialon will not occur, consequently in-situ TiO_2 composited O′-Sialon may be obtained. On the basis of thermodynamic and thermal analysis, the selective-oxidation behavior of TiN/O′-Sialon was studied and in-situ TiO_2/O′-Sialon, a new multiphase ceramics with combined structural–functional properties, were successfully prepared by this process. Oxidation kinetics as well as the effect of atmosphere on oxidation behavior is also discussed in the present paper.

2. Experimental procedures

In-situ TiN/O′-Sialon was in situ synthesized by pressureless sintering of Si_3N_4, SiO_2 and Al_2O_3 as raw materials

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of the primary phase and nano-TiO_2 as precursor of TiN. Sm_2O_3 was used as sintering additive. The content of TiO_2 in the composition is selected as 20% in mass fraction, and the solid solubility of O′-Sialon [$Si_{2-x}Al_xO_{1+x}N_{2-x}$], i.e., x, is set as 0.3 in all the samples. The powders were carefully weighed and wet milled in absolute alcohol followed by ultrasonic vibration. Then the dried powder mixtures were uniaxially pressed into pellets in a steel die under 120 MPa and then cold isostatically pressed under 210 MPa for 10 min. In all cases, samples were placed in an alumina crucible and packed in a protective powder bed containing equimolar Si_3N_4 and SiO_2 before firing in high purity nitrogen (⩾99.999%)for 2 h at 1500 °C. During the synthesis process, TiN was in situ formed through reaction between TiO_2 and other raw material. The growth of TiN, the formation of primary phase O′-Sialon, and the densification of the composite were accomplished in one step. For comparison, single-phase O′-Sialon was also prepared by the analogical process in which only TiO_2 was not added.

Perkin Elermer 7 thermal analyzer was employed to investigate the starting temperature and reaction course of the oxidation of the samples in air [5]. Specimens with regular shape were cut from the sintered pellets, wet-polished, ultrasonically cleaned in acetone, and then dried. Selective-oxidation experiments were conducted using a SiC electric furnace and TG7297 thermobalance at different temperatures in air. Isothermal oxidation under different partial pressure of oxygen was performed in Metteler 851 thermal analyzer. After oxidation, the samples were cut off by a diamond saw. The phases of cross-section were analyzed by XRD, and the morphologies of surface and cross-section were observed by electron-probe microanalysis (EPMA).

3. Thermodynamic analysis

Due to the interaction of two phases, oxidation behavior is assumed to be more complex for in-situ TiN/O′-Sialon. O′-Sialon is a solid solution of Si_2N_2O and Al_2O_3 and the latter is not oxidized, so it can be considered that the oxidation of whole material is constituted by the oxidation process of two species. One is TiN and the other is Si_2N_2O. The oxidation reactions are as follows, respectively:

$$TiN_{(s)} + O_{2(g)} = TiO_{2(s)} + \tfrac{1}{2}N_{2(g)} \tag{1}$$

$\Delta G_1^\theta = (-604.700 + 0.08431T)\,\mathrm{kJ\,mol^{-1}}$ (298–1943 K) [6].

$$\Delta G_1 = \Delta G_1^\theta + RT \ln \frac{p_{N_2}^{1/2}}{p_{O_2}}$$

$$Si_2N_2O_{(s)} + \tfrac{3}{2}O_{2(g)} = 2SiO_{2(s)} + N_{2(g)} \tag{2}$$

$\Delta G_2^\theta = (-1151.220 + 0.21576T)\,\mathrm{kJ\,mol^{-1}}$ (294–1685 K) [6,7]

$$\Delta G_2 = \Delta G_2^\theta + RT \ln \frac{p_{N_2}}{p_{O_2}^{3/2}}$$

The calculation results have shown that the variation in the Gibbs free energy of the two reactions 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.

4. Results and discussion

4.1. Oxidation process analysis

Figs. 1 and 2 show the DTA and weight gain curves of O′-Sialon and TiN/O′-Sialon during the non-isothermal oxidation process in air, respectively. By combining the results of the two figures, a conclusion may be drawn that the first and second exothermic peak in the DTA curve of TiN/O′-Sialon corresponds to the oxidation reactions of TiN and O′-Sialon, respectively, and the starting temperatures are about 600 °C and 1050 °C, respectively. Therefore, it can be expected that when TiN/O′-Sialon is oxidized at 600–

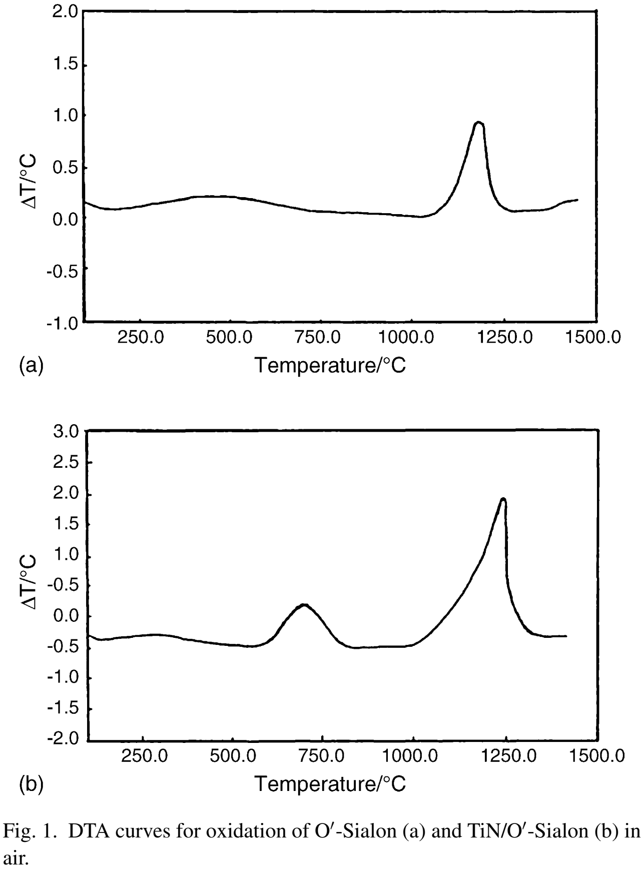


Fig. 1. DTA curves for oxidation of O′-Sialon (a) and TiN/O′-Sialon (b) in air.

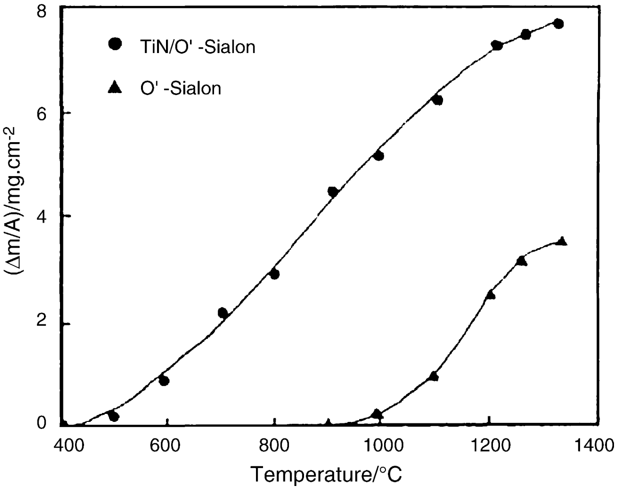


Fig. 2. Weight gain curves for oxidation of O′-Sialon and TiN/O′-Sialon in air.

1000 °C, only the oxidation of TiN takes place, whereas O′-Sialon will not be oxidized. If the exposure time is long enough, TiN will be completely oxidized into TiO_2, and O′-Sialon multiphase ceramic which is composited with TiO_2 will be produced. To verify the above analysis, three temperatures were selected at which isothermal oxidation experiments of TiN/O′-Sialon in air were conducted. The weight change of the samples was monitored continuously and the experiments were terminated until the weight gain reached the theoretical value calculated by the complete oxidation of TiN into TiO_2, and did not change anymore. Fig. 3 shows the XRD patterns of TiN/O′-Sialon and those which have undergone the above oxidation process. It can be seen that in all the oxidized samples, TiN disappeared thoroughly and only two phases, O′-Sialon and TiO_2(rutile), are observed. The results significantly confirmed the previous assumption, i.e., selective-oxidation process of TiN/O′-Sialon indeed occurred in which all TiN was oxidized into TiO_2, whereas O′-Sialon was not oxidized, indicating that in-situ TiO_2 composited O′-Sialon has been prepared. Taking into account the fact that there is no thermodynamic equilibrium between Si_2N_2O and TiO_2, which has been illustrated by thermodynamic analysis [5], the prepared in-situ TiO_2/O′-Sialon can be regarded as a metastable material.

4.2. Kinetic model and parameters of oxidation process

The isothermal mass gain curves for TiN/O′-Sialon at 800, 900 and 1000 °C in air are shown in Fig. 4. It can be found that oxidation extent is enhanced with the increase in temperature when exposed for the same time. During the initial stage, mass gain is obvious, but subsequently the oxidation rate decreases gradually with the extended exposure time.

On the basis of kinetic theory for gas–solid reaction [8,9], the whole oxidation process of TiN/O′-Sialon composites consists of the following steps: (1) diffusion of O_2 molecular in atmosphere into the surface of the material through the gas boundary-layer (external diffusion); (2) diffusion of O_2 inward the reaction interface (internal diffusion); (3) oxidation occurring at the reaction interface, including adsorption, chemical reaction and

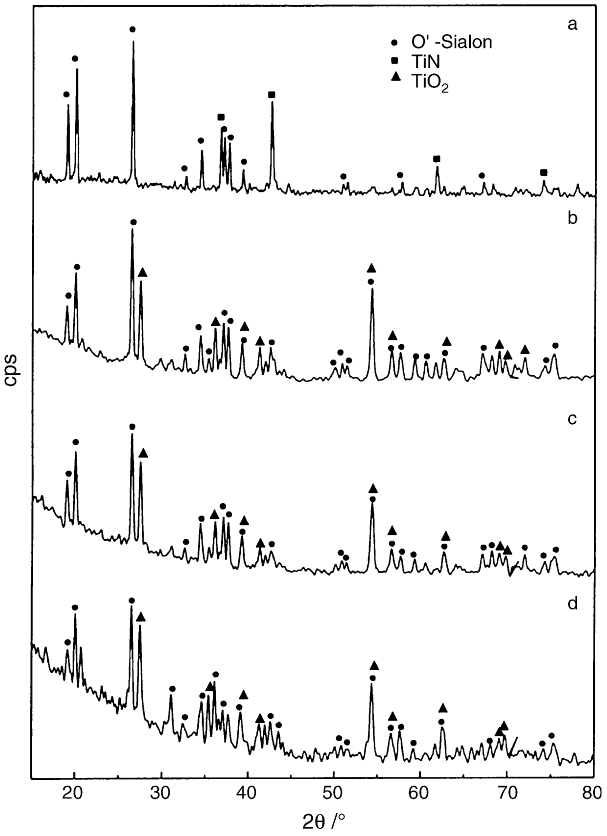


Fig. 3. XRD patterns of TiN/O′-Sialon (a) and the samples oxidized in air (b–d) (b: 800 °C, 19 h; c: 900 °C, 6 h; d: 1000 °C, 5 h).

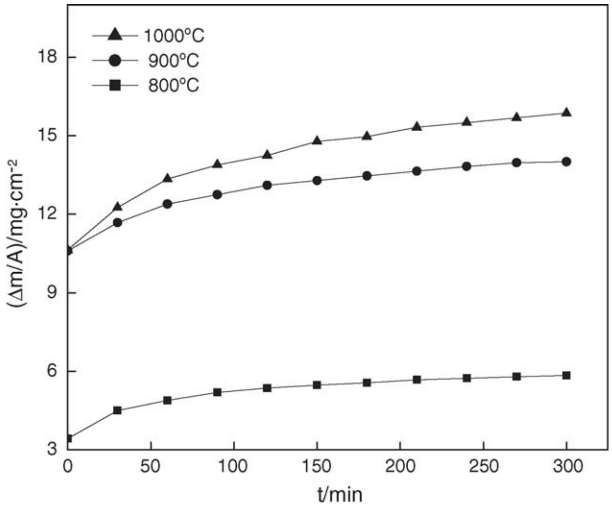


Fig. 4. Mass gain curves for TiN/O′-Sialon oxidized at different temperatures in air.

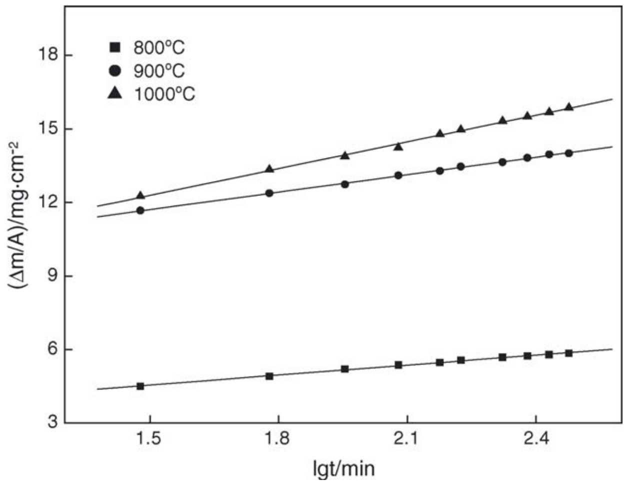


Fig. 5. Plots showing linear relation between $\Delta m/A$ and log t.

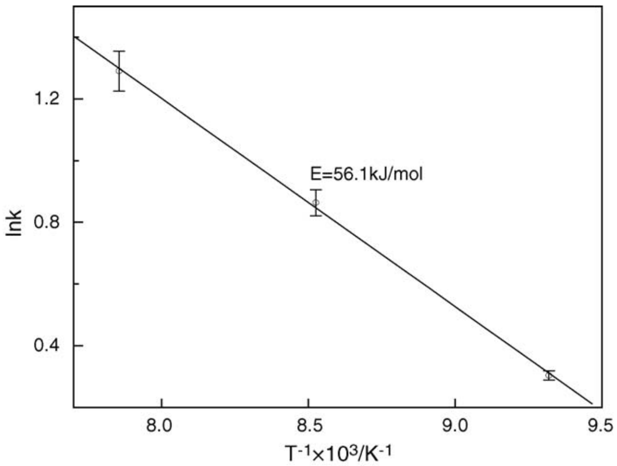


Fig. 6. Arrhenius plot for the selective-oxidation of TiN/O′-Sialon.

desorption; (4) internal diffusion of N_2 as the gas product through oxidized layer; (5) external diffusion of N_2. The oxidation kinetics of Si_3N_4 or Si_2N_2O matrix ceramics at high temperatures have been previously described by a classic parabolic law, which means that the rate of process is controlled by the diffusion of O_2 through oxidized layer or the diffusion of metal ions in intergrannular outward oxidized layer [9–13]. Study of oxidation behavior of TiN/O′-Sialon at high temperatures (>1300 °C) has demonstrated that a dense fusing silicate layer will form on the surface of some materials under the experiment conditions, which acts as a ‘‘protective scale’’ by blocking pores and retarding further oxidation [5]. In that case, diffusion is the rate-limiting step of the oxidation process and its kinetics fits the parabolic law very well. However, a different oxidation kinetics model is followed in the present study, as shown in Fig. 4. Fig. 5 shows the plots of $\Delta m/A$, mass gain per unit surface area, versus the logarithm of time t. A perfect linear relationship was found over the entire temperature range, which suggests that the oxidation kinetics follows the logarithm law:

$$\frac{\Delta m}{A} = k \log t + C \tag{3}$$

where k is the apparent reaction rate constant and C a numerical constant.

It has been shown that in-situ TiN/O′-Sialon has a relatively high porosity (about 25%), as there was generation of gas products during the in situ synthesis process of the materials. When exposed at lower temperatures, oxidation of O′-Sialon does not occur. Moreover, another effect is that it is difficult for interior metal ions or impurities to diffuse outward, and concentrate on the surface because of their slow diffusion rate. As a result, silicate liquid with low eutectic-temperature cannot be formed, i.e., the dense ‘‘protective scale’’ cannot be developed to cap the surface pores, which results in an easy diffusion of O_2 via pores. During the oxidation process of TiN into TiO_2, there accompanies a volume expansion of about 59.4%, which may close the cracks and pores, and in turn reduce the effective reaction area. Thus, diffusion of gas phase through gradually closed pores becomes the rate-controlled step [14–16], and the logarithm oxidation behavior is presented.

Arrhenius formula can be expressed as follows:

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{4}$$

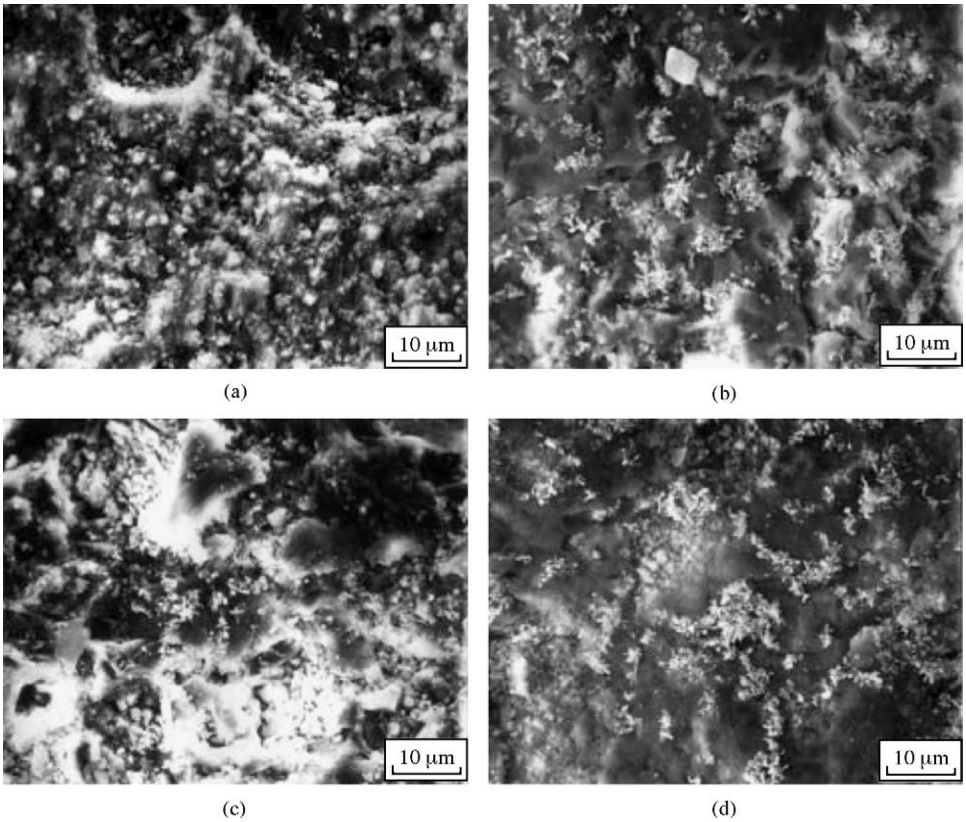
or

$$\ln k = \ln A - \frac{E}{RT} \tag{5}$$

where E is the apparent activation energy, A the apparent frequency factor, R the gas constant (8.314) and T the absolute temperature. Fig. 6 shows the plot of the logarithm of the rate constant k, which was determined from the slopes of the straight lines in Fig. 5, versus $1/T$. A linear relationship was found in Fig. 6 and the values of E and A for the oxidation process were calculated from the slope and intercept of the line, respectively. All the kinetic parameters are listed in Table 1.

Table 1
Kinetic parameters for the oxidation of TiN/O′-Sialon at 800–1000 °C

Apparent rate constant, k			Apparent activation energy, E (kJ/mol)	Apparent frequency factor, A	Correlation coefficient, R
800 °C	900 °C	1000 °C			
1.355	2.372	3.635	56.1	7.34×10^2	−0.9996



(a) (b) (c) (d)

Fig. 7. Cross-section (a) and surface (b–d) morphologies of TiN/O′-Sialon exposed at 900 °C for 6 h under various partial pressures of oxygen (a and b: $p_{O_2}/p^\theta = 0.21$; c: $p_{O_2}/p^\theta = 0.16$; d: $p_{O_2}/p^\theta = 0.10$).

Table 2
Mass gain of TiN/O′-Sialon exposed at 900 °C for 6 h under the atmosphere with various partial pressures of oxygen

Partial pressure of oxygen, p_{O_2}/p^θ	0.10	0.16	0.21
Mass gain ($\Delta m/m_0$) (%)	2.1	2.5	3.6

4.3. Effects of partial pressure of oxygen on oxidation behavior

Table 2 shows the isothermal mass gain of TiN/O′-Sialon exposed at 900 °C for 6 h under the atmosphere with various partial pressures of oxygen p_{O_2}. With the increase of p_{O_2}, mass gain increases significantly. It is easy to understand that there is a lower p_{O_2} but higher p_{N_2} in interior cracks and gas pathways compared with that at external region, which is thermodynamically unfavorable for the inward-proceeding of the oxidation reaction. When p_{O_2} increases on the surface of the material, a larger concentration gradient of O_2 and N_2 between the inner and outer, i.e., a greater diffusion driving force for them will be formed, which will promote the transportation of O_2 and N_2 in pores and in turn result in an increase of p_{O_2} and a decrease of p_{N_2} in the interior gas pathways. Therefore, the interior oxidation reaction will be accelerated by increasing p_{O_2} in atmosphere, which contributes to the increase in the amount of oxidized TiN and consequently the total mass gain of the samples when exposure temperature and time are given. Considering the influence of p_{O_2}, this viewpoint has been further approved that the diffusion of gas phase through gradually closed pores is the rate-limiting step. Furthermore, it also can be anticipated that at the same exposure temperatures, the time required for the completion of the selective-oxidation of TiN/O′-Sialon will be reduced by increasing p_{O_2}.

Fig. 7 shows the cross-section and surface morphologies of the samples exposed at 900 °C for 6 h under different partial pressures of oxygen as revealed by EPMA. It is clear that there is no ‘‘protective scale’’ formed on the surface. Short rod-like TiO_2 grains are observed aggregating in the grain-boundaries and it seems that the size of TiO_2 increases as p_{O_2} in atmosphere increases. In addition, TiO_2 grains on the surface are larger in size than those in the interior, which may be attributed to a weaker restriction to TiO_2 exerted by the surrounding matrix, and thereby a smaller resistance to the grain growth of TiO_2 or grain-boundary movement on the surface.

5. Conclusions

Selective-oxidation of TiN/O′-Sialon occurs at 800–1000 °C, in which TiN is selective-oxidized into TiO_2 whereas O′-Sialon is not oxidized. A new type of metastable in-situ TiO_2/O′-Sialon composites have been prepared by exposing TiN/O′-Sialon for an enough time, which decreases with the increase in exposure temperature.

During the selective-oxidation process, the kinetics can be satisfactorily described by the logarithm law, $\Delta m/A = k \log t + C$, with an apparent activation energy of 56.1 kJ/mol. There is no ‘‘protective scale’’ formed on the surface and the rate-limiting step is supposed to be the diffusion of gas phase through gradually closed pores.

Increasing the partial pressure of oxygen in atmosphere accelerates the selective-oxidation process.

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