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Preparation of tetragonal zirconia containing titanium nitride powder by *in-situ* selective nitridation

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A novel *in-situ* preparation technique has been developed for selective reaction in solid solution. A thermodynamic approach was employed to analyze the selective nitridation conditions of the (Zr,Ti)O_2 solid solution system and to define the temperature range of the selective nitridation. Tetragonal zirconia containing titanium nitride powder was synthesized by carbothermal reduction under a nitrogen atmosphere in the selected temperature range. The influence of reaction temperature on selective nitridation was evaluated by X-ray diffraction. Elemental quantitative analysis showed that the ratio of selective nitridation of titanium oxide reached about 93%. The morphology of the resultant powder was observed by scanning electron microscopy. The average particle size of the powders obtained was found to be in the range 300–400 nm.

Introduction

To date, the preferred fabrication technologies for ceramic materials have been those which allow the preparation of products with controllable microstructures. The Synergy Ceramics Project, which was put forward by the Japanese government, attaches much importance to the composite on a molecular or atomic scale using solid solution based preparation and modification technologies. Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) materials have excellent mechanical properties, but their modest hardness limits potential applications.[1,2] In order to compensate for this weakness and to improve their overall properties, composites of Y-TZP and non-oxides have been studied extensively during the last decade.[3–6] Titanium nitride possesses a series of interesting properties including hardness, low resistivity and good abrasion resistance. It has been used as a diffusion barrier in very large scale integrated (VLSI) devices and has become a promising material in III–V compound metal–semiconductor technology.[7] Among the ceramic composite materials, titanium nitride is often used as rigid particles dispersed into alumina or silicon nitride matrices for the formation of laminated composites.[8–10] Nevertheless, the studies performed on Y-TZP–TiN are not frequently reported.

The conventional mechanical powder processing usually causes inclusion agglomerates, and/or generates local component segregation which limits the degree of microstructural homogeneity in the final products. *In-situ* synthesis technology is an important method for reducing the microstructural heterogeneity. In this study, a novel *in-situ* preparation technique for selective reaction by a solid solution method was developed. Tetragonal zirconia containing titanium nitride powder was prepared by means of selective nitridation on zirconium and titanium oxide solid solutions. Ti^{4+} cations diffused out of the oxide solid solution to form the nitride (TiN) under the given conditions. The details of the procedure, theoretical analysis and results are described below.

Experimental

(a) Synthesis of a superfine powder of (Zr,Ti)O_2 solid solution

The main raw materials used to prepare a superfine powder of (Zr,Ti)O_2 solid solution were: $ZrOCl_2 \cdot 8H_2O$ (CP, Chemically Pure; Shanghai Chemical Reagent Corporation), $Y(NO_3)_3 \cdot 6H_2O$ (AR, Analytical Reagent; Beijing Chemical Plant) and $Ti(SO_4)_2$ (CP;Shanghai Yingfang Chemical Plant). At first, the hydroxide precipitates of the ZrO_2–TiO_2–Y_2O_3 system were synthesized using a chemical co-precipitation process. Then the precipitates were filtered and washed with deionized water to remove the impurity anions, such as Cl^-, which were adsorbed on the surface of the precipitates from the starting materials. Next the precipitates were washed with water-free alcohol which removed the oxo-bridging bond between zirconium hydroxide groups, with the help of H_2O molecules, and avoided the formation of hard agglomerates during calcination. Finally, the precipitates were dried at 80 °C and calcined at 800 °C for 1 hour to allow ZrO_2 to crystallize fully and allow the Ti^{4+} and Y^{3+} ions to dissolve into the crystal lattice. The titanium cation also had a stabilizing effect in causing the zirconia to form a tetragonal phase. The result was examined by X-ray diffraction and is shown in Fig. 2(a) (see later).

In the present experiment, the molar ratio of Y_2O_3 to ZrO_2 is 3 : 97, and the mole fraction of TiO_2 is about 28% in the solid solution powder. It can be seen from the phase diagram of the ZrO_2–TiO_2 system that ZrO_2 and TiO_2 can form a solid solution when the mole fraction of TiO_2 is less than 43%.[11]

(b) Preparation of *t*-ZrO_2–TiN powder

Tetragonal zirconia containing titanium nitride powder was prepared by a carbothermal reduction cum nitridation (CTR/N) route. A slight excess of activated charcoal powder (AR; Tientsin Binhai Chemical Plant) was used as the reducing agent, uniformaly mixed with the solid solution powder. The nitridation reactions were performed in a multi-function

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Table 1 Results of thermodynamic calculations

Reaction no.	$\Delta_r G_T^{0\,a}$/J mol^{-1}	Reaction temperature/K
(1)	$\Delta_r G_T^0 = -59.285T\ln T + 79.241 \times 10^{-3}T^2 + 0.385 \times 10^5 T^{-1} - 11.59 \times 10^{-6}T^3 - 183.00T + 760351$ (298–1100 K) $\Delta_r G_T^0 = 38.035T\ln T + 2.231 \times 10^{-3}T^2 - 59.907 \times 10^5 T^{-1} - 838.829T + 815789$ (1100–2143 K)	1453
(2)	$\Delta_r G_T^0 = -38.975T\ln T + 72.316 \times 10^{-3}T^2 - 8.904 \times 10^5 T^{-1} - 11.59 \times 10^{-6}T^3 - 341.79T + 1022402$ (298–1100 K) $\Delta_r G_T^0 = 58.345T\ln T - 4.694 \times 10^{-3}T^2 - 69.196 \times 10^5 T^{-1} - 998.29T + 1078077$ (1100–1478 K) $\Delta_r G_T^0 = 68.051T\ln T - 12.225 \times 10^{-3}T^2 - 55.138 \times 10^5 T^{-1} - 1047.86T + 1062188$ (1478–2500 K)	1901
(3)	$\Delta_r G_T^0 = -43.588T\ln T + 59.5 \times 10^{-3}T^2 + 0.6465 \times 10^5 T^{-1} - 9.00 \times 10^{-6}T^3 - 92.4T + 530954$ (298–1100 K) $\Delta_r G_T^0 = 29.402T\ln T + 1.734 \times 10^{-3}T^2 - 44.573 \times 10^5 T^{-1} - 0.3145 \times 10^{-6}T^3 - 584.5T + 572704$ (1100–2143 K)	1555
(4)	$\Delta_r G_T^0 = -37.985T\ln T + 56.383 \times 10^{-3}T^2 - 2.299 \times 10^5 T^{-1} - 8.692 \times 10^{-6}T^3 - 140.32T + 674493$ (298–1100 K) $\Delta_r G_T^0 = 35.00T\ln T - 1.3745 \times 10^{-3}T^2 - 47.518 \times 10^5 T^{-1} - 632.66T + 716240$ (1100–1478 K) $\Delta_r G_T^0 = 39.858T\ln T - 5.14 \times 10^{-3}T^2 - 40.489 \times 10^5 T^{-1} - 657.49T + 708316$ (1478–2500 K)	1931
(5)	$\Delta_r G_T^0 = 20.769T\ln T + 1.255 \times 10^{-3}T^2 - 29.238 \times 10^5 T^{-1} - 0.629 \times 10^{-6}T^3 - 330.3T + 329619$ (1100–2500 K)	1892

$^a\Delta_r G^0{}_T = -\Delta A_1 T\ln T - 1/2\Delta A_2 \times 10^{-3}T^2 - 1/2\Delta A_3 \times 10^5 T^{-1} - 1/6\Delta A_4 \times 10^{-6}T^3 - 1/6\Delta A_5 \times 10^8 T^{-2} + A_7 T + A_6$.

furnace (Model FRET-20, Japan) under a high purity nitrogen atmosphere (99.999%, 5 atm) for 1.5 hours, and TiO_2 was nitrided while keeping ZrO_2 unchanged over the selected temperature range.

(c) Characterization

X-Ray diffraction (XRD, D/max-IIIB) analysis was used for phase identification of the resultant powder; X-ray fluorescence spectroscopy (XRF, Model XRF-1700) was carried out for elemental quantitative analysis; the morphology and the particle size of the resultant powder were observed by scanning electron microscopy (SEM, JEOL6301F).

Results and discussion

(a) Thermodynamic analysis of selective nitridation

The carbothermal reduction cum nitridation (CTR/N) route is an established method for the preparation of ceramic nitride powder.[12–15] However, whether or not the selective nitridation can be realized is based upon whether there is enough difference between the nitridation temperature of titania and zirconia to make the nitridation reactions take place in turn. Moreover, the reaction system for carbothermal reduction and nitridation is complex, it is probable that carbonization reactions of zirconia and titania would occur under the conditions used. The reactions that could occur are as follows:

$$2TiO_2 + 4C + N_2 \rightarrow 2TiN + 4CO \quad (1)$$

$$2ZrO_2 + 4C + N_2 \rightarrow 2ZrN + 4CO \quad (2)$$

$$TiO_2 + 3C \rightarrow TiC + 2CO \quad (3)$$

$$ZrO_2 + 3C \rightarrow ZrC + 2CO \quad (4)$$

$$2TiN + 2C \leftrightarrow 2TiC + N_2 \quad (5)$$

Based on the fundamental principle of thermodynamics, when the Gibbs free energy of the reaction is less than or equal to zero, the reaction can take place. According to the thermodynamic data for the different reaction species provided in the literature,[16,17] the equations for the standard Gibbs free energies for these reactions, as a function of temperature, were calculated by the authors and are shown in Table 1. The relationship between the calculated standard Gibbs free energies and temperature for reactions (1)–(4) is shown in Fig. 1. As can be seen from Table 1 and Fig. 1, reaction (1) can occur at 1453 K, while reactions (2) and (4) can occur above 1901 K and 1931 K, respectively, *i.e.* they would not interfere with reaction (1). Reaction (3), however, can occur at 1555 K. From reciprocal reaction (5) it can be concluded that titanium nitride is the predominant product when the reaction is carried out under a high concentration of nitrogen below 1892 K. Therefore, the selective nitridation can be realized, at least in theory, when the nitridation temperature is in the range 1453–1892 K.

Although pure TiN can be obtained when the nitridation temperature is in the range 1453–1555 K, the rate of reaction is slow. Prolonging the reaction time would cause excessive crystal grain growth to occur. In order to investigate the influence of reaction temperature on the extent of nitridation and to optimize the conditions of selective nitridation, the reaction temperatures chosen were: 1673 K, 1773 K, 1873 K and 1973 K.

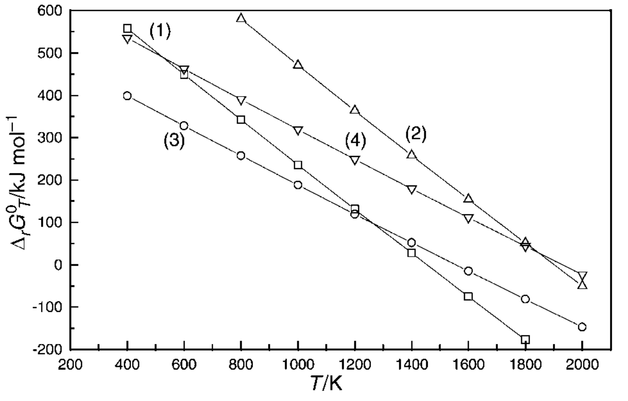

Fig. 1 $\Delta_r G_T^0$ for reactions (1) to (4) as a function of reaction temperature, T.

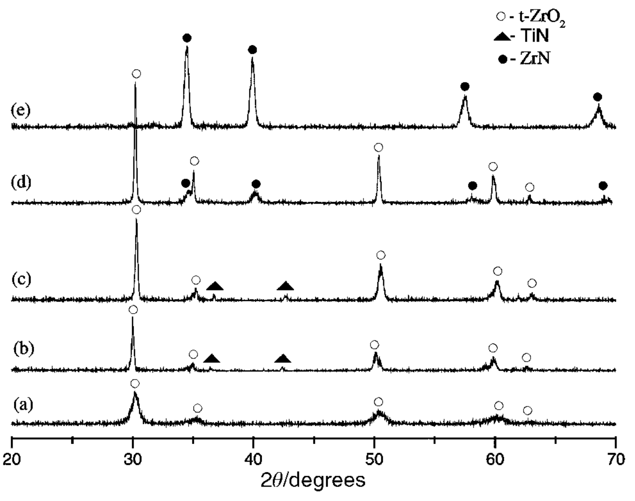

Fig. 2 XRD patterns of the powder before (a) and after 1.5 h selective nitridation at: (b) 1673 K, (c) 1773 K, (d) 1873 K and (e) 1973 K.

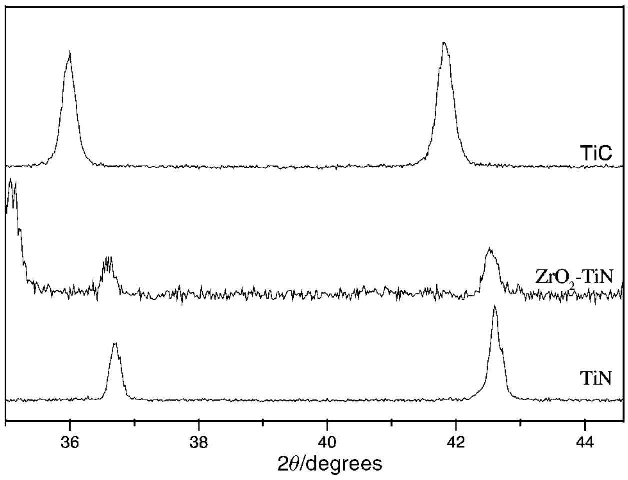

Fig. 3 The comparison of XRD patterns of titanium nitride, the nitrided powder and titanium carbide.

(b) The influence of reaction temperature on nitridation

The XRD patterns of the powder before nitridation (a) and after nitridation at different temperatures (b–e) are shown in Fig. 2. The powder before nitridation was composed of tetragonal zirconia, and no rutile or other types of titania crystal were present.

When the nitridation temperature was 1673 K or 1773 K, the tetragonal zirconia containing titanium nitride powder could be synthesized. The yield of titanium nitride increased at 1773 K indicating that the higher nitridation temperature allowed Ti^{4+} ions to diffuse out of the solid solution more readily and take part in the reaction. These results also supported the thermodynamic analysis.

However, at nitridation temperatures above 1873 K, with carbon in excess, zirconia began to be nitrided. The formation temperature of zirconium nitride was found to be lower than the temperature calculated by the thermodynamic data shown in Table 1. The reason for this was that our nitridation system was not closed (as assumed for the calculations) and the reaction conditions did not agree with the standard conditions used for the calculations. Since ZrN and TiN can also form a solid solution, Ti^{3+} will dissolve into the ZrN crystal lattice, thus, there are no peaks for TiN in the XRD pattern. When the reaction temperature was 1973 K, the diffraction peaks in the XRD pattern were all characteristic of zirconium nitride, indicating that the solid solution $(Zr,Ti)O_2$ had transformed into a solid solution of (Zr,Ti)N. The complete nitrided powder was brown in color.

(c) Effect of nitridation

Since titanium nitride and titanium carbide both have a cubic crystal structure, the difference in their lattice parameters is small, the individual values are 0.42414 nm and 0.43274 nm respectively, and the values and intensities of their characteristic peaks in the XRD chart are very similar. A comparison of the XRD spectrograms for titanium nitride, the nitrided powder and titanium carbide in the range $2\theta = 35$–$45°$ is shown in Fig. 3. XRD patterns were collected at a scanning rate of $0.005°\ s^{-1}$ and a step size of 0.02°. The diffraction peaks for the nitrided powder were in agreement with the characteristic peaks of titanium nitride.

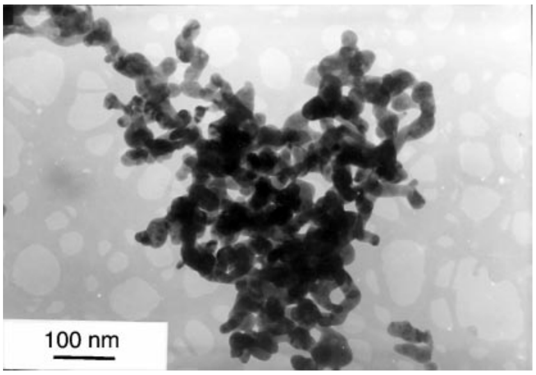

Fig. 4 TEM micrograph of the starting powder.

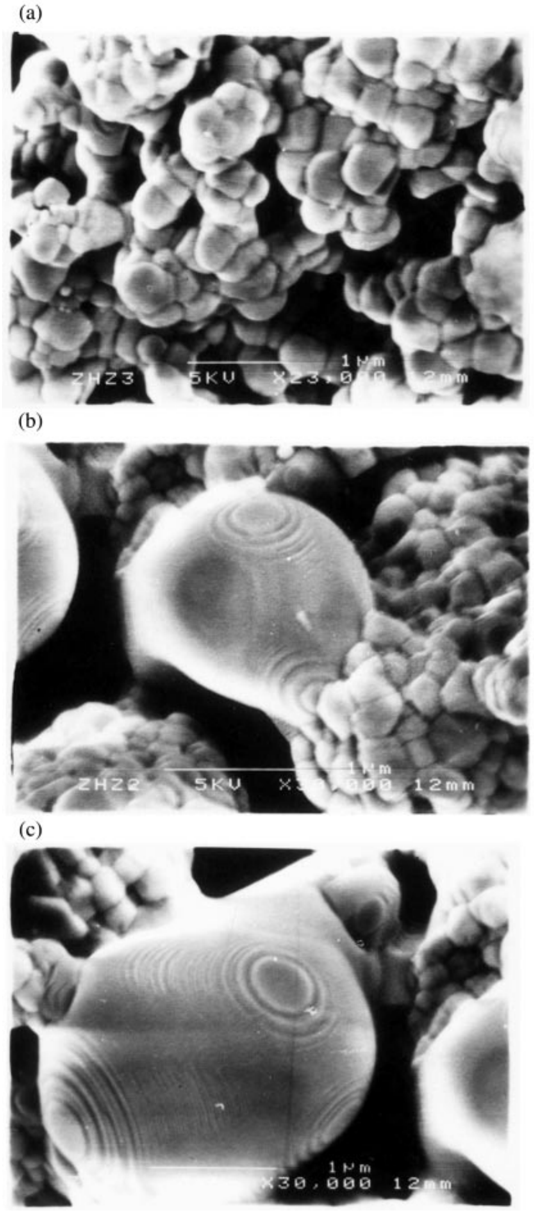

Fig. 5 SEM micrographs of the nitrided powder (a) common particles, (b) and a big particle with a growth step (c).

Ainger *et al.* developed an empirical equation for calculating the mole fraction of nitrogen:[18]

$$a(x,T) = 0.43193 - 0.0088x + (2.216 + 0.122x)10^{-6}T + (0.8455 + 0.2258x)10^{-9}T^2 \pm 0.0002\text{nm}$$

where a is the lattice parameter, x is the mole content of nitrogen and T the absolute temperature. The value of the lattice parameter of the nitrided powder is 0.4248 nm. Given the value of T is 298 K, the value of x is calculated as about 0.9039, *i.e.* the mole fraction of nitrogen is 90.39%.

X-Ray fluorescence spectroscopy was carried out on the compacted final powder for elemental quantitative analysis, which was performed by the Center of Measurement and Analysis of Tsinghua University. The result shows: Y is 2.64 wt%, Ti is 12.83 wt%, N is 3.50 wt%, O is 21.86 wt% and Zr is 60.18 wt%. The nitridation ratio of TiO_2 is about 93.33% by calculation.

(d) Morphology of the nitrided powder

The morphology and the primary crystal grain size of the solid solution superfine powder was characterized by transmission electron microscopy (TEM, JEM-200CX). Fig. 4 shows the primary crystal grain size of the starting powder is about 20–30 nm. The morphology of the resultant powder, which was nitrided at 1773 K for 1.5 hours without being ground, was observed by SEM. Fig. 5 shows that most of the particles are in the size range 300–400 nm. It is difficult to clearly illustrate the method of formation of TiN and point out where the TiN grains are located just from the SEM photograph of the nitrided powder. However, combined with the results of the bulk materials, which will be reported later, the formation of TiN appears to be mainly through the preferential diffusion of Ti^{4+} ions out of the crystal lattice of the t-ZrO_2 solid solution. Therefore, TiN grains formed as separate grains in the t-ZrO_2 powder. Moreover, the size of the TiN grains obtained is far smaller than those of ZrO_2, which, combined with the even grain distribution makes the intensity of the XRD peaks of TiN lower.

Since the grains in the powder grew under unrestricted conditions, some of the grains reached sizes of 1–2 μm, and interesting striation patterns could be seen on growth surface of the big grains, these were seldom seen by other workers. The formation of these patterns may suggest the involvement of vapor transport phenomena during high temperature nitridation reaction and its relationship with the defect chemistry of zirconia. A better understanding needs to be developed.

Conclusions

The preparation of t-ZrO_2–TiN powder by the selective nitridation of $(Zr,Ti)O_2$ solid solution has been attempted. The temperature range for the selective nitridation reaction has been defined by thermodynamic analysis. The nitrided powder obtained has been characterized by XRD, XRF and SEM with the following results:

(1) Tetragonal zirconia containing titanium nitride powder is prepared by *in-situ* selective nitridation. The nitridation ratio of titanium oxide is about 93% and the average grain size of the nitrided powder obtained is in the range of 300–400 nm.

(2) The theoretical temperature range for selective nitridation, according to thermodynamic calculations, is 1453–1892 K and the optimal reaction conditions are nitridation at a temperature of 1773 K for 1.5 hours.

(3) The selective nitridation of TiO_2 can be realized through the diffusion of Ti^{4+} ions out of the t-ZrO_2 solid solution crystal lattice and their preferential involvement in the nitridation reaction, allowing the TiN grains to be evenly dispersed throughout the t-ZrO_2 powder.

We believe that the *in-situ* preparation technique of selective reaction in solid solution can be used to effectively design the microstructure of ceramic materials.

Acknowledgements

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