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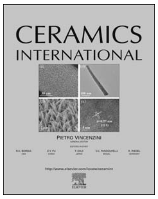

Synthesis of ZrN powders by aluminum-reduction nitridation of ZrO_2 powders with $CaCO_3$ additive

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ABSTRACT

ZrN powders were synthesized from mixtures of ZrO_2 and Al metal powders using $CaCaO_3$ as an additive. The effects of various heating temperatures, nitrogen pressures and amounts of $CaCO_3$ additive on the phase assemblage and morphologies of the final products were investigated using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Impurity contents and particle sizes of the final powders were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), oxygen gas analysis, Energy Dispersive Spectroscopy (EDS) and ImageJ software. The results show that without adding $CaCO_3$, the products were mostly composed of ZrN and $ZrAl_3O_3N$, and a small amount of other ZrO_xN_y phases. However, both of the $ZrAl_3O_3N$ and ZrO_xN_y were stable in acid, and it was not possible to separate the ZrN powders. Suitable $CaCO_3$ concentration, heating temperature and nitrogen gas pressure were employed to avoid the formation of $ZrAl_3O_3N$ and ZrO_xN_y and resulted in powders composed of ZrN, calcium-aluminates and calcium-zirconate phases. The by-products, calcium-aluminates and calcium-zirconate were subsequently dissolved by HCl acid to obtain single phase ZrN. The impurity elements contents are less than 2% and the mean particle size is around 0.96 µm. The optimum parameters for synthesis of ZrN were: $CaCO_3$ concentration of 26.83 ~29.53 wt%, heating temperature of 1400 °C and nitrogen gas pressure of 0.4 MPa.

1. Introduction

As a kind of transition metal mononitride, zirconium nitride (ZrN) has attracted much attention due to its excellent physical and chemical properties [1]. ZrN has a NaCl-prototype cubic structure with a lattice parameter a=0.4586 nm and exhibits both covalent and metallic bonding characteristics. ZrN has many excellent properties [2–4], such as, melting point up to 2982 °C, hardness reaches about 25 GPa, the coefficient of thermal expansion is $7.2\times10^{-6}\ K^{-1}$ and the coefficient of thermal conductivity is 21.9 $Wm^{-1}K^{-1}$, high shear modulus and high Young's modulus, due to the covalent bonding. On the other hand, ZrN still has some metallic properties, like good electrical conductivity and good superconductivity with transition temperature of approximately 10 K because of its metallic bonding. At present, the research focus for ZrN is concentrated on ZrN coatings or ZrN thin films because of its excellent hardness and corrosion resistance [5–7]. There are many methods used to prepare this film material, such as physical vapor deposition (PVD) [3,8], including magnetron sputtering, micro-arc oxidation and electrophoresis; chemical vapor deposition (CVD) [9] plasma chemical vapor deposition and metal organic chemical vapor deposition. Lamni et al. [10] used magnetron sputtering to study the optical properties of sputtered ZrNx with x ranging from 0.81 to 1.35. From the results, with the chemical composition change, the compounds had an o-Zr_3N_4 crystal structure and the optical properties continuously changed from metallic to semiconducting behavior. Musil et al. [11] employed a $ZrSi_2$ alloyed target to sputter a type of Zr–Si–N film with a high Si content on steel and silicon substrates. With a change of nitrogen pressure and substrate temperature, the deposited film had a high hardness (as high as 30 GPa) and high oxidation resistance in flowing air (greater than 1300 °C). In addition for use as a coating material, ZrN also has promising applications as particulate or powdered materials. ZrN can be introduced into a matrix as a reinforcing or toughing phase because of excellent chemical and physical properties. Zhao et al. [12] introduced ZrN nano-particles to reinforce AlON composites to improve the mechanical properties and fracture resistance. In some researches, ZrN was employed as a secondary phase to form new composites, such as, ZrN-ZrB_2 composites with needle-like ZrN to improve mechanical properties [13], and electrically conductive β-Sialon/ZrN nano-composites [14].

ZrN is a kind of refractory material due to its many outstanding

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properties, such as, high hardness, high melting point, wear resistance and abrasive resistance. However, it is difficult to get high density bulk ZrN [15,16]. Some new sintering methods, such as hot pressing sintering (HP) and spark plasma sintering (SPS) [9], have been used to get high density ZrN using commercially available ZrN powders as starting powders. These sintering methods are good for obtaining high-density bulk ceramics. However, they have some disadvantages in that they need high temperatures and expensive equipment which will limit large scale production. ZrN particles have been synthesized by several methods, such as magnesium reduction and nitridation [17,18], the benzene-thermal method [19], a wire explosion process method [20], and a mechanical alloying [21]. However, there are some drawbacks for these methods, such as high energy consumption (mechanical alloying), potential dangers in the process (toxic and high-temperature organic solvents were used in benzene-thermal route) and normally high cost of high-purity starting materials (such as, Zr metal, $ZrCl_4$, $ZrOCl_2 \cdot 8H_2O$ or Li_3N).

In this paper, Al metal powders were employed to react with zirconia to form pure ZrN powders at different reaction temperatures and nitrogen pressures. $CaCO_3$ was chosen as an additive for some experiments. The effect of reaction temperatures, nitrogen pressures and the amounts of additive content on phase assemblage and morphologies of the product was investigated. The scope of this work was to synthesize high purity ZrN particles, to be used as the electrically conductive phase to form electrical conductive composite, which can be machined by EDM for complex component shapes.

2. Experimental work

2.1. Materials and methods

In the first set of experiments, Zirconia (> 99%, ZrO_2 Sigma-Aldrich Ltd., average particle size of 5 µm.) and Al metal (> 99.5%, LR from ECP Ltd. average particle size < 40 µm) powders were chosen as raw materials. For subsequent experiments, $CaCO_3$ (> 99%, Sigma-Aldrich Ltd.,) was used as an additive. The raw materials were mixed base on the following stoichiometric equations.

$$6ZrO_2(s)+8Al(s)+3N_2(g)=6ZrN(s)+4Al_2O_3(s) \quad (1)$$

$$6ZrO_2+8Al+2CaCO_3+3N_2=6ZrN+2CaAl_4O_7+2CO_2(g) \quad (2)$$

$$6ZrO_2+8Al+4CaCO_3+3N_2=6ZrN+4CaAl_2O_4+4CO_2(g) \quad (3)$$

The theoretical amounts of $CaCO_3$ based on Eqs. (2) and (3) are 17.33–29.53 mass %. In this study, additional compositions both within this range, and a higher $CaCO_3$ containing powder were prepared, giving $CaCO_3$ contents (mass %) of 17.33%, 20.76%, 23.91%, 26.83%, 29.53% and 33.33%, respectively.

The powder mixtures were ball milled in isopropanol for 4 h with Si_3N_4 balls, then dried in a rotary evaporator and passed through a 250 µm sieve. The precursor powders were placed in boron nitride (BN) crucibles and fired in a graphite gas pressure furnace in high purity oxygen free nitrogen. The powders were nitrided at different temperatures and nitrogen pressures for 6 h, following the schedule of nitridation shown in Fig. 1. Following the nitridation, the furnace was cooled down to 1000 °C at 10 °C min^{-1}, and then free cooled down to room temperature. After the nitridation, part of the products were dissolved by HCl acid (20 wt% HCl) for 48 h or 72 h at room temperature, and then washed by distilled water to obtain the final material.

2.2. Characterisation

Crystalline phase identification was carried out using XRD analysis with a Bruker 2D Phaser with CuKα radiation. Data were collected over the range 2θ =10–70° with a Lynxeye detector (~ 4° wide) a step count of 0.2 s and a step size of 0.02°. The morphologies of powders were observed with a field-emission gun scanning electron microscope (ESEM, FEI Quanta 200 F, USA). For viewing the samples, the samples were coated with conductive Pt or gold. The impurity content of the samples were analysed by EDS, ICP-MS (Agilent 7700, USA) and Oxygen gas analysis (ON736, LECO, USA) using a commercially available ZrN powder as comparison (> 99%, ZrN Sigma-Aldrich Ltd., average particle size of 1–2 µm). The mean particle size of the acid-dissolved powders was measured on representative SEM micrographs using ImageJ by counting 150 particles.

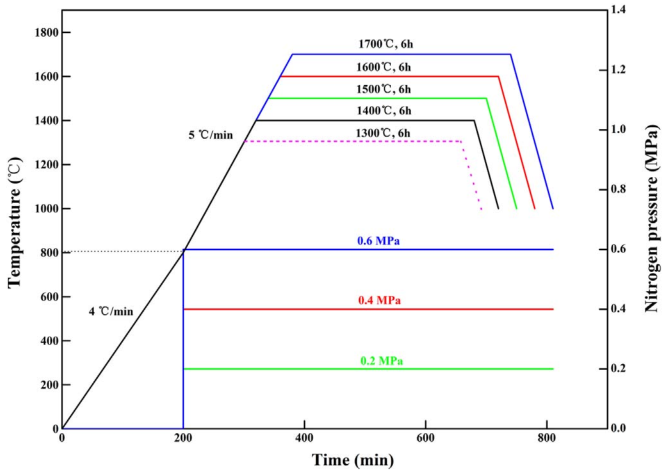

Fig. 1. The schedule of heating temperatures and nitrogen pressures of the nitridation stage of ZrN.

3. Results and discussion

3.1. Effects of nitride temperatures and nitrogen pressures on the products formed from ZrO_2 and Al

For the samples produced from ZrO_2 and Al based on Eq. (1), the standard Gibbs free energy of the compounds was shown in Table 1[22].

The Gibbs free energy of Eq. (1) could be calculated by Table 1, given as following:

$$\Delta G_1 = -2361200+642.76T-3RT\ln P_{N_2}/P^{\theta} \quad (4)$$

Where R is gas constant (8.314 J mol^{-1}. K^{-1}), T is reaction temperature, P_{N2} is the pressure of nitrogen, and P^{θ} is the pressure of standard atmosphere. According to the experimental parameters, the value of ΔG_1 is always less than zero, indicating that theoretically the reaction based on Eq. (1) could produce ZrN and Al_2O_3. The phase assemblage of the products from ZrO_2 and Al powders are shown in Fig. 2. The main phases of the products were ZrN and $ZrAl_3O_3N$ at all temperatures and pressures. At 1400 °C, residual ZrO_2 existed as monoclinic zirconia (m-ZrO_2) and tetragonal zirconia (t-ZrO_2) in the products under a nitrogen pressure of 0.2 MPa and 0.4 MPa respectively, but was not seen in the samples fired under 0.6 MPa. Zirconium oxynitride (ZrO_xN_y) phases existed in the products fired under 0.2 MPa and 0.6 MPa at all temperatures but the intensity decreased with increasing temperature. AlN and α-Al_2O_3 also appeared in these samples at lower

Table 1
The standard Gibbs free energy of compounds (ZrO_2, ZrN and Al_2O_3).

Name	Reaction equation	Standard Gibbs Free Energy $\Delta_f G^{\theta}/J \cdot mol^{-1}$
ZrO_2	$Zr(s)+O_2(g)=ZrO_2(s)$	−1092000+183.7 T (25 °C < T < 1850 °C)
ZrN	$Zr(s)+0.5N_2(g)=ZrN(s)$	−363600+92.0 T (25 °C < T < 1850 °C)
Al_2O_3	$2Al(l)+1.5O_2(g)=Al_2O_3(s)$	−1682900+323.24 T (660 °C < T < 2042 °C)