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Preparation of nanocrystalline ultra-high temperature Ta_4ZrC_5 ceramics by joint processes of solvothermal and carbothermal reaction

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ABSTRACT

An attractive way to prepare nanocrystalline tantalum zirconium carbide ternary ceramics was proposed and confirmed experimentally. The experimental results showed the Ta_4ZrC_5 powders were successfully fabricated by joint processes of solvothermal and carbothermal reaction. The thermodynamic change process in the Ta_2O_5-ZrO_2-C system was studied. The reactions were substantially completed at relatively lower temperatures (~1873 K/1 h) and the synthesized powders had a small average crystallite size (~10 nm). The crystalline structure and the nitrogen sorption isotherms patterns of the product were studied. Besides, a monolithic Ta_4ZrC_5 ceramics was densified without sintering additives by pressureless sintering.

1. Introduction

Among the family of ultra-high temperature ceramics (UHTCs), tantalum carbide (TaC) and zirconium carbide (ZrC) are appealing candidates for space and aerospace ultra-high temperature applications, due to high melting point (>3500 K), high elastic modulus (>450 GPa), high hardness (15–20 GPa), and superior thermal and chemical stability [1–5]. Besides, TaC and ZrC can form a continuous single-phase cubic Ta-Zr-C solid solution, due to they have the same NaCl-type structure (B1, space group Fm-3m) [6]. And the Ta_4ZrC_5 is reported to possess the highest melting point for the TaC-ZrC systems [7].

The majority of researches focus on the hot pressing and spark plasma sintering of starting TaC/ZrC mixable powders [8,9]. However, their high covalent bonds and low self-diffusion coefficients make sintering of these powders particularly challenging. Search for appropriate methods to synthesize Ta_4ZrC_5 ceramics remains topical [10,11]. In recent years, the hydrothermal/solvothermal process has been widely used to prepare nano-size to micrometer materials [12,13]. The high dispersible powders with uniform size and shape by solvothermal process are desirable materials for sintering. So attempts to produce Ta_4ZrC_5 powders by joint processes of solvothermal treatment and carbothermal reaction lead to the study of this paper. However, Ta_4ZrC_5 powders fabricated by solvothermal treatment still have not been reported so far.

In this study, an attractive way to prepare Ta_4ZrC_5 powders by solvothermal treatment and carbothermal reduction reactions is proposed for the first time. The morphology, the phase composition and the nitrogen sorption isotherms pattern of the as-synthesized Ta_4ZrC_5 powders were also characterized. Furthermore, using the as-synthesized Ta_4ZrC_5 powders, a monolithic Ta_4ZrC_5 ceramics was densified without sintering additives by pressureless sintering.

2. Experimental procedure

Analytical grade tantalum pentachloride ($TaCl_5$; Ningxia Orient Ta Ind Co., Ltd, an average particle size of 30–70 μm), zirconium chloride ($ZrCl_4$; China New material Ind Co., Ltd, an average particle size of 100–130 μm) and acetylacetone (Hacac), used to prepare tantalum zirconium precursors. Phenolic resin (THC-400; Shanxi Taihang Impedefire Polymer Limited Company, China) was used as the carbon source. The carbon yield of phenolic resin was about 60 wt%.

Stoichiometric amount of $TaCl_5$ (35.85 g, about 0.1 mol) and $ZrCl_4$ (5.825 g, about 0.025 mol) were dissolved in a mixture of 100 ml ethanol and 25 ml acetylacetone (about 0.25 mol). After concentration in an oil bath for 1–2 h, stoichiometric amount of phenolic resin was blended homogeneously to produce the

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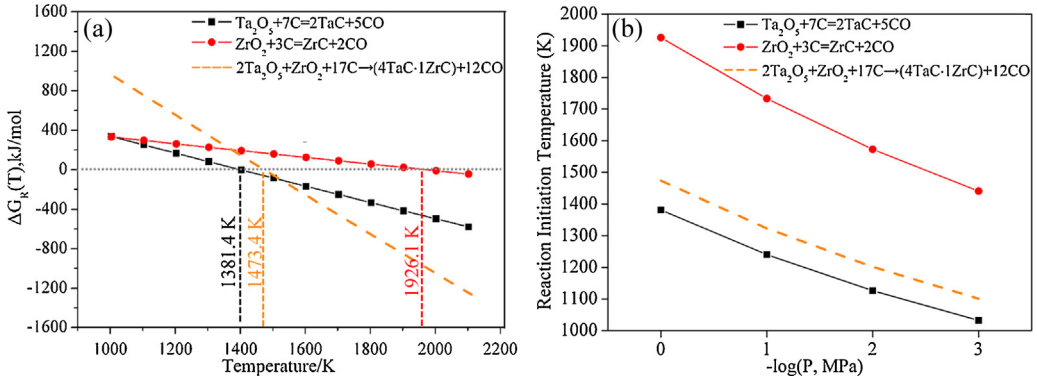

Fig. 1. (a) ΔG(T) for carbothermal reaction from 1000 to 2100 K in the standard state and (b) Changes in reaction initiation temperature as a function of pressure.

tantalum zirconium carbide sol and then the obtained sol was transferred into Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 473 K for 24 h. After the autoclave was cooled to room temperature, the precipitate was separated from the solution by centrifugation and washed with anhydrous ethanol one time. The obtained precipitate was dried in an oven at 333 K for 48 h. The subsequent heat treatment was performed in vacuum at a heating rate of 15 K/min to the desired temperature.

The thermal behavior of the precursor was investigated by thermal gravimetric analysis (TG) (STA49C, NETZSCH, Germany). The crystal structure and the phase composition of powders were determined by X-ray diffraction with a Bruker D8 Advance using Cu Kα radiation (λ = 1.5406) operated at 30 mA and 40 kV. The microstructure of the samples was evaluated with scanning electron microscopes (SEM, S4800) operating at 10 kV, with accessorial energy-dispersive spectroscopy (EDS, 15 kV). Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100 microscope operated at 200 kV. The particle-size distribution of the Ta_4ZrC_5 powder was analyzed using a laser particle size analyzer (Brookhaven Zeta PALS, USA). Micro/mesopores were characterized by nitrogen adsorption-desorption isotherms using a Quantachrome instrument. The surface area was determined by the Brunauer-Emmett-Teller method, and the pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method using desorption branch. Ta_4ZrC_5 powders were pressed into disks (15 mm in diameter, 3–4 mm in thickness).The heat treatment to observe the sintering behaviour was performed at a heating rate of 15 K/min to the desired temperature of 2073 K, 2273 K, 2473 K and 2673 K for 0.5 h in flowing Ar atmosphere. Then sintered materials were measured for apparent density (Archimedes method), and accordingly on which the relative density was calculated by assuming the theoretical density equal to 12.94 g/cm^3 for Ta_4ZrC_5 ceramics. All specimens for SEM/EDS analyses were prepared by incised, ground and polished with a series of diamond pastes to a surface finish of 0.5 μm. The mean grain size (MGS) were determined by image analyses on SEM images using Image-Pro Plus 6.0. More than 50 grains were measured to give out average diameter for each sample.

3. Results and discussion

To estimate the direction of carbothermal reaction between carbon and metal oxides, thermodynamics calculations in the standard state were conducted. All reactants and products were assumed to be pure and in their stable states. The standard Gibbs free energy of included phase was obtained came from Chase [14]. As can be seen in Fig. 1a, however, for ZrO_2-3C system under the same pressure, the Gibbs free energy for the carbothermal synthesis of ZrC

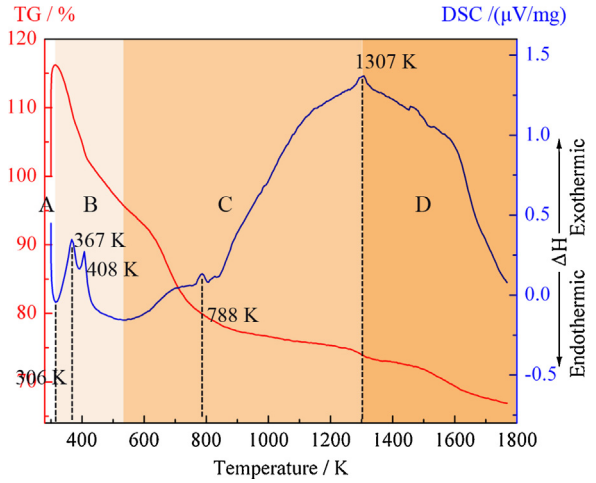

Fig. 2. TG-DSC curves of the Ta-Zr-C precursor from room temperature to 1773 K.

becomes negative at temperatures that are more than 500 K higher than those for TaC (Fig. 1a). Because no standard thermodynamics data for Ta_4ZrC_5 was available, the thermodynamic estimation for the formation of Ta_4ZrC_5 was conducted by combining ZrO_2-3C and Ta_2O_5-7C systems together. The reaction for formation of 4TaC·1ZrC was estimated to be favorable as low as 1473 K in the standard atmospheres from the thermodynamic perspective. Moreover, the initiation temperature for the carbothermal reaction in a vacuum becomes lower than that in the standard state for $2Ta_2O_5$-ZrO_2-17C system as can be seen in Fig. 1b.

So the thermal behavior of the precursor was examined from room temperature to 1773 K in vacuum (Fig. 2). The TG curve showed a total mass loss of 33 wt% at 1773 K. There are four stages (A-D, in different color depth) of mass change in TG curve. At A stage (below 306 K, with approximate mass increase of 16 wt%), nitrogen adsorption might be conducted, associated with an endothermic DSC peak measured at about 306 K. At B stage (306–523 K, with approximate mass loss of 5 wt%), an exothermic peak could be observed at around 367 K in the DSC curve, probably due to the nitrogen desorption and pyrolysis of $TaOCl_3$ and $ZrOCl_2$ [15]. The other exothermic peak at 408 K might be caused by the release of structural water from the precursor. C stage between 523 K and 1307 K was that of a typical mass loss of 20 wt%. The exothermic peak at 788 K might be attributed to the decomposition of phenolic resin. The TG curve of this stage has a downward-sloping shape, which might be due to the precipitation of Ta_2O_5 and ZrO_2 crystal and formation of pyrolyzed carbon. Above 1307 K, an increasing mass loss showed at D stage indicated the onset of the carbothermal reduction for Ta_2O_5-7C system [16]. Owing to the reactants being