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Short communication

Harmonized toughening and strengthening in pressurelessly reactive-sintered $Ta_{0.8}Hf_{0.2}C$-SiC composite

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ABSTRACT

$Ta_{0.8}Hf_{0.2}C$-27 vol%SiC (99.0% in relative density) composite was toughened and strengthened via pressurelessly in-situ reactive sintering process. HfC and β-SiC particles were formed after reaction of $HfSi_2$ and carbon black at 1650 °C. $Ta_{0.8}Hf_{0.2}C$ was obtained from solid solutioning of HfC and commercial TaC. The β-α phase transformation of SiC proceeded below 2200 °C. High aspect ratio, platelet-like α-SiC grains formed and interconnected as interlocking structures. Toughness and flexural strength values of 5.4 ± 1.2 MPa $m^{1/2}$ and 443 ± 22 MPa were measured respectively. The toughening mechanisms by highly directional growth of discontinuous α-SiC grains were crack branching, bridging and deflection behaviors.

1. Introduction

$Ta_{1-x}Hf_xC$, belonging to the family of ultra-high temperature ceramics (UHTCs), has attracted considerable attention due to high melting point, superior thermal and chemical stabilities [1]. The solid solution formation not only contributes to densification by decreasing the diffusion activation energy across grain boundaries [2], but may also improve mechanical properties than their monolithic carbide counterparts: relationship between hardness and x values of $Ta_{1-x}Hf_xC$ (x = 0, 0.2, 0.5 and 0.8) was reported to vary as an open-down quadratic function, which could be attributed to solid solution strengthening effect [3]. Notably, $Ta_{0.8}Hf_{0.2}C$ was proved to have the highest melting point 3942 ± 82 °C among the $Ta_{1-x}Hf_xC$ solid solutions [4]. $Ta_{0.8}Hf_{0.2}C$ is the candidate material for thermal protection systems (TPS) as sharp leading edges, nose caps and flight control components of aerospace vehicles that can be exposed to extreme environments with temperatures exceeding 2000 °C by dissociated air operate at hypersonic speeds.

Owing to its extremely strong covalent bonding, $Ta_{0.8}Hf_{0.2}C$ is difficult to densify. Advanced techniques including hot pressing, spark plasma sintering [5] and hot isostatic pressing [6] have been attempted to enhance the sintering driving force. Pressureless sintering (PLS) is beneficial to fabricate cost-effective and near-net-shape ceramic components. Researches on the field-less densification techniques of $Ta_{0.8}Hf_{0.2}C$ were rather scarce. Quite recently, we reported pressureless densification of $Ta_{0.8}Hf_{0.2}C$-based composites with fine mechanical/thermal properties [7].

The critical application of $Ta_{0.8}Hf_{0.2}C$-based composites as thermal protection systems (TPS) is restricted by the poor thermal shock resistance, including thermal shock fracture and damage resistance. The maximum thermal shock fracture parameter (R) is one of crucial importance to impede the fracture inside bulk ceramics [8]. Thermal shock damage resistance is considered on the basis of toughness (K_{IC}), with the pre-existing cracks after fracture initiation, when the maximum stress intensity factor K_{max} reaches the material toughness K_{IC} [8].

Therefore, UHTCs need to improve their damage tolerance via increasing both strength and toughness for TPS application [9]. To meet such demand, incorporating a hard secondary phase to strengthen, together with further extrinsic toughening [10], such as crack deflection and bridging is an effective strategy. Investigations are needed for the optimization of $Ta_{0.8}Hf_{0.2}C$-SiC mechanical performance, typically in-situ strengthening and toughening.

SiC, introduced in-situ inside the (Ta,Hf)C bulk, were tailored to be platelet-like with high aspect ratio of 15.6 after soaking 2 h at 2200 °C. Homogeneous HfC and SiC formed after reaction between $HfSi_2$ and

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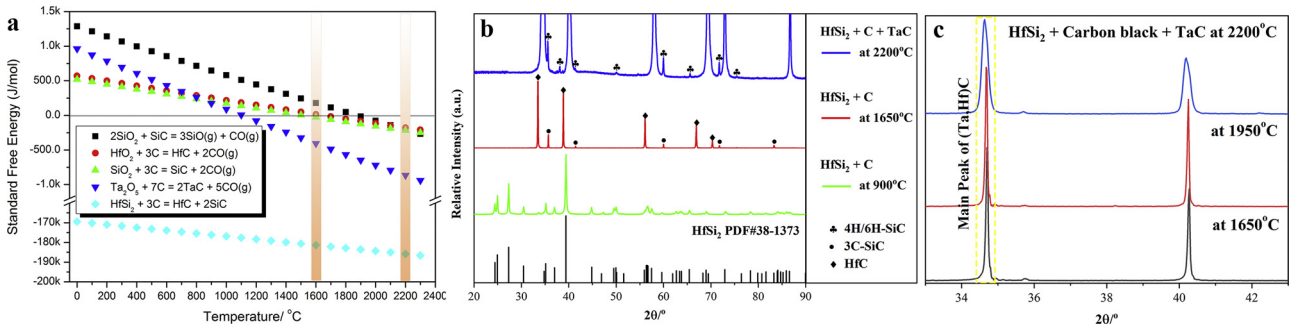

Fig. 1. (a) Thermodynamics analysis of the reactions for TaC-$HfSi_2$-carbon black system; XRD patterns of (b) $HfSi_2$ and carbon black reaction and (c) $HfSi_2$ and carbon black reaction in TaC matrix from [33°, 43°] at different temperatures.

carbon black at 1650 °C. $Ta_{0.8}Hf_{0.2}C$ was generated via inter-diffusion among raw TaC and in-situ HfC. The phase and microstructure evolution of SiC proceeded during the high-temperature densification progress. The in-situ toughening mechanism was investigated.

2. Experimental procedure

TaC and $HfSi_2$ powders (Haotian Nano Technology Co., Ltd, Shanghai, China) had a purity of 99.9% and an average particle size of 1 μm. The median size of carbon black (Anyang Delong Chemical Co., Ltd., Henan, China) was ~200 nm. Phenolic resin (P. R.) (Shanghai QiNan Adhesive Material Factory, Shanghai, China) with a carbon yield of 50 wt% was used as binder. The oxygen contents of TaC and $HfSi_2$ were analyzed using infrared method after fusion under an inert gas atmosphere (TC-600C, LECO Instrument LD, MI, USA). TaC, $HfSi_2$ and carbon contents were precisely calculated for obtaining $Ta_{0.8}Hf_{0.2}C$-27 vol% SiC in stoichiometric and volume ratio based on the reaction below [11]:

$$HfSi_2 + 3C = HfC + 2SiC \quad \Delta G = -167385 - 7.456T \tag{1}$$

Where ΔG: Gibbs' free energy (J/mol), and T: Temperature (K). The starting powders were blended with 4 wt% phenolic resin in ethanol, and ball-milled for 4 h using a planetary mill (QM-3SP4, Nanjing NanDa Instrument plant, Nanjing, China) with WC balls (5 mm in diameter) and Teflon-coated tanks (Φ 100 mm × 120 mm) at a speed of 400 rpm. Wear debris contamination was ≤0.2 wt % after milling. The slurries were dried, crushed, sieved and pressed uniaxially in a steel die at 45 MPa (6 mm × 8 mm × 48 mm), followed by cold isostatic pressing at 280 MPa for 300 s. The green compacts were pressurelessly sintered at 1650 °C and 2200 °C for 0, 1 and 2 h in argon (purity 99.999% with $O_2 \leq 1.5$ ppm), at a heating rate of 10 °C min^{-1} in a graphite resistance furnace (Zhuzhou Norbert High Temperature Instrument Ltd. Co., China).

Phase analysis was performed by X-ray diffraction (XRD; Ultima IV diffractometer, Rigaku, Tokyo, Japan) with Cu Kα radiation (λ = 1.5406 Å). The microstructure and crack introduced by indentation in hardness test on polished surface were analyzed by scanning electron microscopy (SEM; Magellan 400, FEI, Hillsboro, American) equipped with EBSD (INCA SERIES, Oxford Instrument, UK). The electron backscatter diffraction pattern (EBSP) was acquired at an angle of 60° and an acceleration voltage of 15 kV, and Aztec software was used to clarify the phase. In transmission electron microscopy (TEM; Tecnai G2 F20, FEI Co., Hillsboro, USA) observation, high-resolution transmission electron microscopy (HRTEM) was conducted. The bulk density was measured by the Archimedes method. The theoretical density was determined based on the rule of mixtures (densities of $Ta_{0.8}Hf_{0.2}C$ and SiC are 14.05 and 3.21 g cm^{-3} respectively).

Three-point bending strength (3 mm × 4 mm × 36 mm) was measured by a universal tester (Instron-1195, Instron, Canton, MA, USA) using a 30 mm span and a cross-head speed of 0.5 mm min^{-1}. Vickers hardness was measured by the indentation technique (Model 300, Tukon, Canton, MA, USA) using a load of 3 kg and dwell time of 10 s. The indentation fracture resistance (K_{IC}) was calculated on the basis of the equation as reported by Evans and Charles [12].

$$K_{IC} = 0.16(c/a)^{-1.5} \cdot H \cdot a^{1/2}$$

Where K_{IC} is fracture toughness, a is the half average length of the diagonal of the Vickers indentations (μm), c is the average length of the cracks obtained in the tips of the Vickers indentations (μm), and H is the Vickers hardness.

3. Results and discussion

To obtain desired properties of (Ta,Hf)C-SiC composite, the chemical reactions in TaC-$HfSi_2$-C system were investigated. Oxide impurities were coated on the surfaces of raw powders, eg: Ta_2O_5 on TaC (oxygen contents: 0.59 wt%), and HfO_2 and SiO_2 on $HfSi_2$ (oxygen contents: 1.73 wt%). The complexity of the chemical reactions in TaC-$HfSi_2$-C system increases due to the surface oxide impurities. Carbon was an effective reducing agent. Following chemical reactions should be considered [13,14]:

$$Ta_2O_5 + 7C \rightarrow 2TaC + 5CO(g) \tag{2}$$

$$HfO_2 + 3C \rightarrow HfC + 2CO(g) \tag{3}$$

$$SiO_2 + 3C \rightarrow SiC + 2CO(g) \tag{4}$$

$$2SiO_2 + SiC \rightarrow 3SiO(g) + CO(g) \tag{5}$$

The Gibbs free energy (ΔG) of each reaction was calculated by thermodynamic simulation software (HSC Chemistry 6.1), and they were shown in Fig.1a. To complete the reactions above, adequate amount of carbon black was added to react with oxide impurities. The thermal decomposition of P. R. occurred before densification initiation, during which all P. R. will be removed from the green body at 1000 °C. 0.9 wt% of pyrolytic carbon from P. R. removal was added into the total carbon contents precisely for obtaining $Ta_{0.8}Hf_{0.2}C$-27 vol% SiC. Reactions (2)–(4) occurs since 1600 °C, while Reaction (5) starts at above 1900 °C as shown in Fig. 1a. Besides, since SiO_2 impurity could not be eliminated during the sintering of monolithic SiC without the presence of carbon additive, Reactions (2)–(4) were considered to occur for removing the surface impurities.

Reaction (1) was taken out and investigated individually. The XRD patterns of $HfSi_2$-carbon black sintered at 900 °C (P. R. removal) and 1650 °C (reaction (1) initiation) were shown in Fig.1b. Peaks of mixed $HfSi_2$ and carbon black were consistent with the $HfSi_2$ (PDF#38-1373) at 900 °C. Well-defined HfC (PDF#39-1491) and β-SiC (PDF#29-1129, 3C-SiC) peaks were detected after the sintering at and above 1650 °C together with the complete disappearance of $HfSi_2$ peaks, which indicated that reaction (1) was completed. After the temperature reached 2200 °C, existence of α-SiC phases in Fig.1b (PDF#29-1127, PDF#49-