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SiC whisker reinforced multi-carbides composites prepared from B_4C and pyrolyzed rice husks via reactive infiltration

Hongyan Wu [a], Mingxia Gao [a,*], Dan Zhu [a], Shengcai Zhang [a], Yi Pan [a], Hongge Pan [a], Yongfeng Liu [a], Filipe J. Oliveira [b], Joaquim M. Vieira [b]

[a] State Key Laboratory of Silicon Materials & Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China
[b] Department of Ceramics and Glass Engineering/CICECO, University of Aveiro, Aveiro 3810-193, Portugal

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Abstract

SiC whisker reinfored carbide-based composites were fabricated by a reactive infiltration method by using Si as the infiltrate. Rice husks (RHs) were pyrolyzed to SiC whiskers, particles and amorphous carbon, and were then mixed with different contents of B_4C as well as Mo powders. The mixtures were molded to porous preforms for the infiltration. The SiC whiskers and particles in the preform remained in the composite. Molten Si reacted with the amorphous carbon, B_4C as well as Mo in the preform during the infiltration, forming newly SiC, $B_{12}(C,Si,B)_3$ as well as $MoSi_2$. The upper values of elastic modulus, hardness and fracture toughness of the composites are 297.8 GPa, 16.8 ± 0.8 GPa, and 3.8 ± 0.2 MPa $m^{1/2}$, respectively. The influence of the phase composition of the composites on the mechanical properties and the fracture mechanism are discussed.

Keywords: B. Composites; C. Mechanical Properties; D. Carbides; Reaction infiltration; Pyrolyzed rice husks, Microstructure

1. Introduction

Carbide ceramics have high mechanical wear resistance, hardness, thermal and chemical stability. SiC ceramics are most important materials for advanced engineering applications due to their excellent high-temperature strength, high hardness, good oxidation, corrosion, wear and thermal shock resistance [1,2]. A variety of applications of the SiC ceramics in the industry can be found, including wear parts, light-weight armor, cutting tools, high temperature structural parts, etc. Hot-pressing and pressureless sintering are two common ways to prepare the SiC ceramics. However, the former needs extra pressure and the latter needs extremely high temperature, which all lead to high material fabrication cost and costly equipments. An alternative economic approach to fabricate dense SiC-based ceramics is reactive infiltration [3–5], in which green preforms or partially sintered preforms of carbon are infiltrated by molten Si, forming composites after solidification. The molten Si reacts with the carbon, forming SiC. The residual Si remains in the ceramics.

B_4C is one of the hardest materials of the world. Its hardness reaches as high as 27–35 GPa. The application of the B_4C ceramics in industry is also extremely important [6,7]. The reactive infiltration method is also applicable to fabricate B_4C-based ceramics by infiltrating molten Si into B_4C-based preforms [8–10]. In the B_4C/Si infiltration system, Si reacted with B_4C, forming newly SiC and other boron-rich carbides [8,9].

In the recent years, multi-carbides ceramics based on B_4C and SiC are considered to be able to provide improved mechanical properties compared with the single carbide ceramics [9,11–15]. SiC and boron-rich carbides were formed in situ in the fabrication process [12–15]. It was reported that the in situ formed SiC in the $(SiC,TiB_2)/B_4C$ composites introduced new grain boundaries, leading to a higher grain boundary energy and a higher crack propagation resistance, thus improving the fracture toughness of the composite.

Introduction of whiskers or fibers is an effective strategy in improving the fracture tolerance and/or the strength of ceramics [16]. SiC whiskers (SiC_w) are promising material in strengthening and toughening composite ceramics and light metal alloys for

* Corresponding author. Tel.: +86 571 87952615; fax: +86 571 87952615.
E-mail address: gaomx@zju.edu.cn (M. Gao).

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structural use [17]. SiC_w can enhance crack bridging and deflection and in turn resulting in improved fracture toughness [18]. An economic route to prepare SiC_w is the pyrolysis of the rice husks (RHs), but high content of amorphous carbon also exists in the product. Previous studies were mostly focused on the fabrication technique of the SiC_w and the structure analysis of the pyrolyzed RHs [19–23]. The study of the utilization of the pyrolyzed RHs is hardly reported. Moreover, the separation of the SiC_w and the carbon is difficult. Therefore, the practical application of the SiC_w produced from pyrolyzed RHs has also not been realized. RHs were produced year by year all over the world, and they are mostly taken as agricultural wastes. The study of the RHs converted SiC whiskers and also the SiC particles as well as carbon in the application of ceramic materials should be a meaningful work.

In the present work, RHs were converted to SiC whiskers and particles as well as carbon, which were used as one of the starting materials to fabricate SiC whisker introduced carbides-based composites. The pyrolyzed RHs were mixed with B_4C as well as a little amount of Mo, and molded to porous preform, which was subsequently infiltrated by molten Si. Molten Si is supposed to react with the carbon and B_4C in the preform, forming newly carbides. The SiC whiskers and particles in the preform will be preserved in the composite. The addition of Mo is intended to form $MoSi_2$ by the reaction with Si, which is hopefully favorable to the overall properties of the composites, as $MoSi_2$ is a less brittle phase compared with Si and it has a high melting temperature of 2030 °C, favoring high temperature properties of the composite. The microstructure and mechanical properties including elastic modulus, fracture toughness and hardness of the composites have been studied. For comparison, parallel studies of the composite prepared from preform without Mo addition were also conducted. The results are hopefully to be able to provide some new experiment results for the use of RHs in the fabrication of ceramic materials.

2. Experimental

Raw RHs were pre-treated by washing, drying and sieving to eliminate the residual rice and clay particles firstly, and then were coked at 900 °C for 2 h in vacuum in a tube furnace. The intermediate coke was further pyrolyzed at 1550 °C for 6 h under Ar atmosphere in a graphite furnace. A heating rate of 10 °C/min and furnace cooling were used. The pyrolyzed RHs powder was mixed with purchased B_4C as well as metallic Mo by ball-milling with agate balls for 3 h at a rate of 650 rpm. Alcohol was used as milling medium. The composition of the mixtures is listed in Table 1. The particle size of B_4C ranges from 5 to 10 μm (Dalian Jinma Technology Co., Ltd., China. The residual free carbon is ca. 1.8 wt.%), and the particle size of Mo powder is ca. 3 μm. Fig. 1(a) is a scanning electron microscopy (SEM, S-4800, Hitachi) morphology of the as-purchased B_4C. The mixtures were dried and molded to porous preforms with dimension of 50 mm × 50 mm × 5 mm by being uniaxially cold pressed at 96 MPa in a stainless steel mold. The preforms were pre-sintered at 1550 °C for 2 h prior to the infiltration in order to release the organic ingredients and intend to increase the relative density of the preforms. The apparent density of the pre-sintered preforms was estimated according to their mass and volume. The volume of the preforms was measured by a conventional Vernier calliper. A balance with accuracy of 0.1 mg was used for weighing in the present study. The theoretical density of the performs was calculated by the equation of

Table 1
The composition and the relative density of the preforms.

Samples	The composition of green preforms (wt.%)			The relative density of the preforms (%)
	Pyrolyzed HRs	B_4C	Mo	
S1	20	70	10	50
S2	40	50	10	48
S3	60	30	10	46
S4	66.7	33.3	0	46

$$d_T = \frac{\sum M_i}{\sum M_i/d_i} \quad (1)$$

where M_i is the mass of the B_4C, free carbon, SiC and Mo in the preform. d_i is the theoretical density of B_4C, carbon, SiC and Mo, which is taken as 2.52, 1.85, 3.21 g/cm^3 and 6.28 g/cm^3, respectively. The relative density of the preforms is denoted as the percentage of the apparent density to its theoretical density. The recorded value of the relative density for each preform is the average of five pieces.

Infiltration was performed at 1480 °C × 30 min. The heating and cooling rates were 5 and 10 °C/min, respectively, for both the pre-sintering and infiltration. Sufficient Si fragments, the amount of which was estimated by pre-testing were put on the top of the preform. Both the pre-sintering and the infiltration were carried out in a graphite furnace under a vacuum of 10^{-2} Pa.

The phase structure of the pyrolyzed RHs and the composites was analyzed by X-ray diffraction (XRD, PANalytical, X'Pert PRO) using Cu Kα radiation (λ = 1.54056 Å) with a step interval of 0.02° and a count time of 1 s per step. The phase composition of the composites was further analyzed by XRD Rietveld refinement method. The morphology of the pyrolyzed RHs was observed by SEM. The microstructure of the composites was observed by both SEM and optical microscopy (OM, Leica, DMLM). Energy dispersive spectrometry (EDS, Horiba) under SEM was used in the estimation of the compositions of the pyrolyzed RHs and the phases in the composites. The content of free carbon of the pyrolyzed RHs was estimated roughly by a burning method based on the previous study [24], i.e., heating the pyrolyzed RHs at 700 °C for 3 h in air atmosphere and then measuring the weight loss, which was supposed to be caused by the oxidation of the free carbon. The microstructure of the composites was observed on their polished sections.

The infiltrated parts were cut into bars and further grounded with a diamond plated wheel of 0.5 μm as final for Vickers hardness and fracture toughness tests. Hardness of the