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ScienceDirect

Ceramics International 40 (2014) 2793–2798

CERAMICS INTERNATIONAL

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Effects of copper on microstructure and mechanical properties of C_f/ZrC composites fabricated by low-temperature liquid metal infiltration

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Received 13 July 2013; received in revised form 9 October 2013; accepted 9 October 2013
Available online 18 October 2013

Abstract

Carbon fiber-reinforced zirconium carbide matrix (C_f/ZrC) composites were fabricated by a liquid metal infiltration process at 1200 °C, using low melting Zr_7Cu_{10}, ZrCu and Zr_2Cu alloys as infiltrators. The effects of Cu on microstructure and mechanical properties of the composites were investigated. The results indicated that the products were composed of either single- or polycrystalline ZrC, C and Cu. With increasing Cu content in the infiltrators, the yield of ZrC decreased from 43.7 vol% to 27.9 vol%. When ZrCu was used as an infiltrator, the obtained composites exhibited a better bending strength of 98.2 ± 3.1 MPa. What is more, the use of Zr_2Cu could provide the highest fracture toughness of the composites with a moderate debonding.

Keywords: B. Composites; B. Microstructure; C. Mechanical properties; D. Carbides; Liquid metal infiltration

1. Introduction

Zirconium carbide (ZrC) is usually referred to as an ultra-high temperature ceramic (UHTC) for its unique properties such as extremely high melting point, relatively low density, high strength [1–4], and superior ablation resistance at high temperatures [5,6], which enables it to be used in extreme environments associated with hypersonic flight and rocket propulsion [1,2,7]. However, the poor plasticity of ZrC ceramic restricts its development and applications [6,7]. A potentially effective approach to improve its toughness is introduction of long continuous carbon fibers into the ceramic as reinforcement [6–9].

Among the fabrication processes for continuous fiber reinforced ceramic matrix composites, the liquid metal infiltration (LMI) has many advantages, including short fabrication period, low cost, near net shape, etc. [10–13]. This process has been adopted to prepare C_f/ZrC composites, by infiltrating porous C_f/C preforms with molten Zr [6,9]. But due to the high melting point of Zr (1850 °C) [14], the infiltration process can only be operated above 1900 °C, resulting in a great damage to the fibers. Recently, Zr_2Cu alloy has been used as an infiltrator to produce C_f/ZrC composites at temperature as low as 1200 °C [7,15]. However, the effects of Cu additive on microstructure and performance of the final composites have not been reported so far.

In this paper, C_f/ZrC composites were prepared at relatively low temperature, by vacuum infiltrating porous C_f/C preforms with low melting Zr–Cu alloys. The influences of Cu content in the melts on microstructure and mechanical properties of the composites were investigated.

2. Experimental procedure

2.1. Materials preparation

Porous C/C preform with porosity of about 40% was fabricated by a needle-punching technique combined with the PIP method, using phenolic resins as the precursor. The carbon

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http://dx.doi.org/10.1016/j.ceramint.2013.10.037

fiber (T300, an average diameter of about 7 μm, Toray in Japan) fraction is about 30 vol%.

Three Zr–Cu alloys with Zr/Cu molar ratios of 7:10, 1:1 and 2:1 were used as reactive infiltrators for this study. The alloy ingots were received from Hunan Rare Earth Metal & Material Institute, prepared with spongy Zr pieces (99.6% purity) and electrolytic Cu plates (99.99% purity) by arc melting.

The preparation of C_f/ZrC composites included stages as follows: Zr–Cu alloys were placed in graphite crucibles and heated up to 1200 °C in a vacuum of 0.5 Pa. After the alloys melted completely, C_f/C preforms were mechanically driven into the melts, kept there for 1–3 h, then separated from the liquid Zr–Cu baths and cooled spontaneously to room temperature.

2.2. Characterization

The volume fractions of solid phases and the theoretical porosities of the specimens were determined by inductively coupled plasma (ICP) and chemolysis, based on the theoretical densities of 6.63 g cm^{-3} for ZrC, 1.55 g cm^{-3} for deposited C, 8.96 g cm^{-3} for Cu, 6.49 g cm^{-3} for Zr and 1.76 g cm^{-3} for T300 fibers. The details were described elsewhere [7,16]. The open porosities were measured on five samples using the Archimedes method. The phases were analyzed by X-ray diffraction with a Bruker D8 Advance instrument. The microstructures were observed by scanning electronic microscopy (SEM, Quanta-200) and transmission electron microscopy (TEM; JEOL, Tokyo, Japan; JEM-2010F). The TEM sample was prepared by grinding a bulk sample to about 80 μm in thickness and then a 3 mm diameter disc was cut out. The disc was subsequently dimpled and ion milled.

2.3. Mechanical properties tests

Flexural strength and elastic modulus were measured using a four-point bending test (Model 5566, Instron Corp., High Wycombe, UK), according to GB/T 6569-2006 and GB/T 10700-2006 Standard (China), respectively. Length of the force arm was 15 mm and crosshead speed was 0.5 mm min^{-1}. At least 10 specimens with a dimension of 3.0 mm × 4.0 mm × 60 mm and a span of 45 mm were tested to obtain the average data. Fracture toughness was evaluated by the single-edged notched-beam test according to GB/T 23806-2009 Standard (China). Five samples with a span of 30 mm were measured at a crosshead speed of 0.05 mm min^{-1}. Length of the force arm was 15 mm. The test bars, 3.0 mm × 6.0 mm × 40 mm, were notched by electromachining with a 0.2 mm-diameter Mo line. The notches were about 0.2 mm in width and 3.0 mm in depth.

3. Results and discussion

3.1. Thermodynamics consideration

Assuming a complete consumption of Zr in the alloys, the reactions between carbon and Zr–Cu melts can be expressed as follows:

$$C(s)+\frac{1}{2}Zr_2Cu(l)\rightarrow ZrC(s)+\frac{1}{2}Cu(l) \quad (1)$$

$$C(s)+ZrCu(l)\rightarrow ZrC(s)+Cu(l) \quad (2)$$

$$C(s)+\frac{1}{7}Zr_7Cu_{10}(l)\rightarrow ZrC(s)+\frac{10}{7}Cu(l) \quad (3)$$

The changes of Gibbs free energy (ΔG°) were calculated to estimate the feasibility of the above reactions. The results (Fig. 1) show that ΔG° of all three reactions at temperature above 1200 K is negative. Thereby it is thermodynamically favorable to form ZrC phase from reactions between C and alloys. It is worth noting that ΔG° of reaction (3) is more negative than that of others, indicating that the formation of ZrC from Zr_7Cu_{10} is the most favorable. According to Zhang et al. [17], the increase of Cu could promote and accelerate Zr–C reaction occurrence by prior formation of liquids at a low temperature.

3.2. Composition and microstructure

XRD patterns of the obtained C_f/ZrC composites are shown in Fig. 2. It can be found that all the specimens have the same

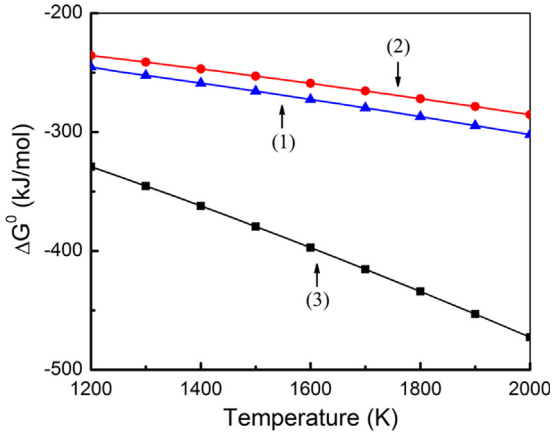

Fig. 1. Changes in Gibbs free energy for reactions (1)–(3).

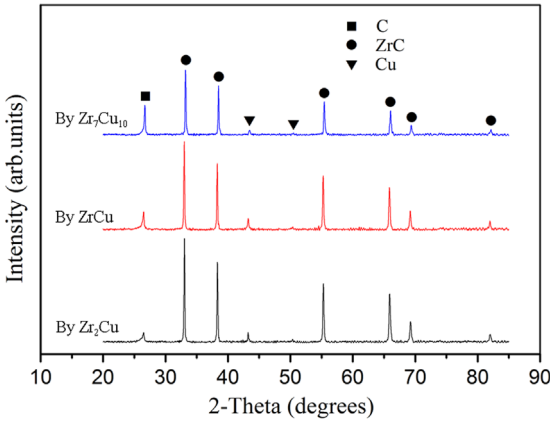

Fig. 2. XRD patterns of the C_f/ZrC composites fabricated by Zr–Cu alloys.