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Oxidation behaviour of a pressureless sintered HfB_2–$MoSi_2$ composite

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Abstract

The thermal stability of a 80-vol.% HfB_2 + 20 vol.% $MoSi_2$ composite is tested under oxidizing environment. Oxidation tests are carried out in flowing synthetic air in a TG equipment from 1000 to 1400 °C with exposure time of 30 h. At temperatures ≥1200 °C the silica resulting from oxidation of molybdenum disilicide seals the sample surface, preventing hafnium diboride from fast degradation. Analysis of the kinetics is carried out through fitting of the thermogravimetric curves. Between 1200 and 1400 °C, the kinetic curves deviate from a parabolic behaviour, being more close to a logarithmic–parabolic behaviour.

Keywords: Ceramic; Microstructure; Oxidation; Borides

1. Introduction

Hafnium diboride is gaining increasing attention as a highly refractory compound with superior properties at high temperature. Nowadays the design and production of new materials suitable to withstand high temperatures are stimulated by an increasing demand for applications in the field of thermal protection systems and for several industrial sectors like foundry. HfB_2-based composites display a number of unique properties including hardness, high thermal and electrical conductivity and chemical stability.[1–12] HfB_2–SiC composites are able to withstand very high temperatures[5–7] and can maintain their room temperature strength up to 1500 °C in air.[6,7] The addition of $MoSi_2$ to borides seems to be very promising as it allows the densification of composites by pressureless sintering and the resulting composites retain their strength up to 1500 °C.[10,11] HfB_2–$MoSi_2$ composites have also been tested in an arc jet facility at 1900 °C showing excellent stability due to the development of a silica-based scale.[12] So far, oxidation studies reported in the literature have concerned pure HfB_2,[13,14] HfB_2–SiC[5,8] materials, and HfB_2–Si_3N_4[15] materials. Oxidation data for pure HfB_2 between 1200 and 1700 °C could be fitted to a parabolic rate equation. Around 1700 °C there was an abrupt increase of the oxidation rate due to transition from monoclinic to tetragonal HfO_2.[13] More recently, a mechanistic model that interprets the oxidation behaviour of Zr and Hf borides in the range 1000–1800 °C has been formulated.[14] At temperature below 1400 °C, the rate limiting step is the diffusion of dissolved oxygen through liquid boria, while at higher temperatures boria is lost by evaporation and the oxidation rate is limited by diffusion of molecular oxygen between columnar blocks of HfO_2.[14] Silica has very low diffusivities for oxygen and is a very protective scale at moderate temperatures. Hence, SiC, Si_3N_4 and transition metal silicides are considered very useful additives for improving the oxidation resistance in the middle temperature range. HfB_2–SiC materials[5,8] were reported to withstand temperatures as high as 1700 °C thanks to the formation of a borosilicate glass containing HfO_2 crystals, which is an effective barrier against the inward diffusion of oxygen. For HfB_2–Si_3N_4 materials oxidation studies were carried out[15] up to 1400 °C. At temperatures in the 900–1200 °C range, the main oxidation products were HfO_2, B_2O_3 and borosilicate glass. In the 1200–1400 °C range, SiO_2 and $HfSiO_4$ were detected. Kinetic curves recorded at 1450 and 1600 °C were shown to be parabolic.In this work, the oxidation behaviour of a HfB_2-20 vol.% $MoSi_2$ composite is tested in the middle temperature range, i.e. between 1000 and 1400 °C. Actually, $MoSi_2$ was already found to be beneficial for improving the oxidation resistance of ZrB_2–20 vol.% $MoSi_2$ composites in the same temperature range.[16–18]

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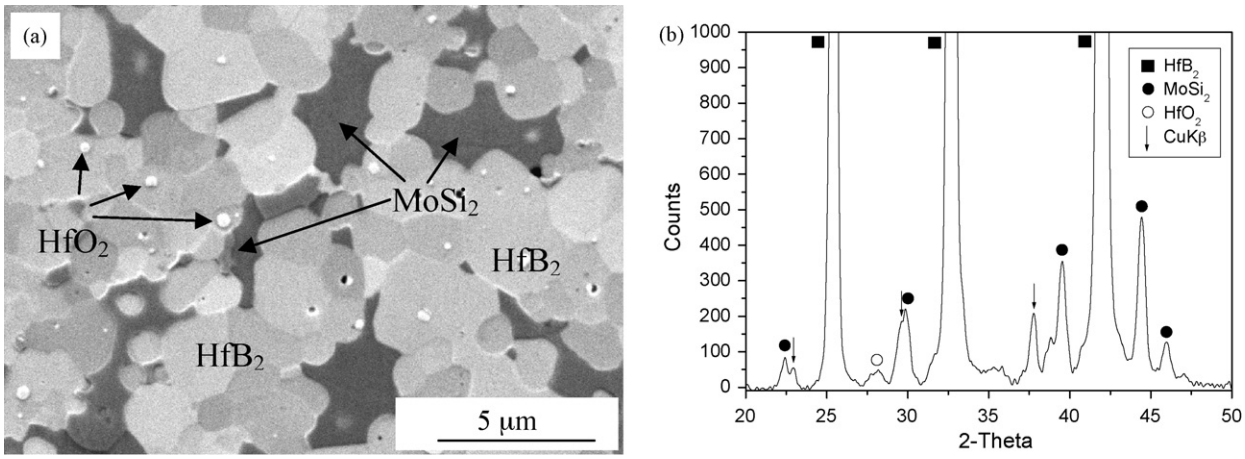

Fig. 1. (a) Polished microstructure and (b) X-ray diffraction of as-sintered HfB_2–20 vol.% $MoSi_2$.

2. Experimental procedure

2.1. Material

Commercial powders were used for the preparation of the composite material: HfB_2 (Cerac Incorporated, Milwaukee, USA), particle size range 0.5–5 μm. Impurities: Al (0.07%), Fe (0.01%), Zr (0.47%); $MoSi_2$ (<2 μm, Aldrich, Milwaukee, USA), mean particle size 2.8 μm and oxygen content of about 1 wt.%. Dense pellets were prepared by pressureless sintering at 1950 °C. Details on the material's processing are reported elsewhere.[11]

2.2. Oxidation tests

Rectangular plates sized 9.0 mm × 8.0 mm × 1.0 mm were cut from the sintered pellet. The specimens were cleaned in ultrasonicated acetone bath, dried and weighed (accuracy 0.01 mg). The oxidation tests were carried out in a thermogravimetric analyser (model STA449, NETSCH, Geraetebau GmbH, Selb, Germany), in synthetic air (composition: 80 vol.% N_2 + 20 vol.% O_2, with 30 ml/min gas flow) between 1000 to 1400 °C with isothermal exposure time of 30 h for each experiment, heating rate 30 °C/min and free cooling. The fast heating-up stage prior to the isothermal period was applied to minimize oxidation effects before reaching the target temperatures. The mass variation was recorded continuously with 10^{-3} mg of sensitivity. The TG measurements evaluation was performed with the subtraction of Buoyancy effect corrections. As-sintered and oxidized sample surfaces were analysed by X-ray diffraction (Cu Kα radiation, Miniflex Rigaku, Tokyo, Japan). Surfaces and polished cross-sections were analysed by scanning electron microscope (SEM, Leica Cambridge S360, Cambridge, UK) and energy dispersive microanalysis (EDS, Model INCA energy 300; Oxford Instruments, High Wycombe, UK).

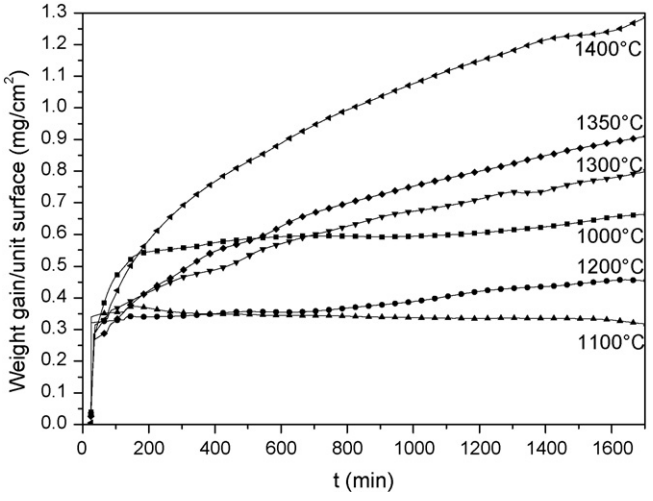

Fig. 2. Thermogravimetric curves of the HfB_2–20 vol.% $MoSi_2$ composite in the range 1000–1400 °C.

3. Results

3.1. Microstructure of the as-sintered material

The sintered material contained a low amount of residual porosity, 2%, as ascertained by SEM analysis and density measurements. Crystalline HfB_2, $MoSi_2$ and traces of HfO_2 were identified by X-ray diffraction (Fig. 1a). An example of the polished section is displayed in Fig. 1b. HfB_2 grains have a rounded shape while the $MoSi_2$ phase has a very irregular morphology with very low dihedral angles. This peculiar characteristic indicates that $MoSi_2$ was very ductile at the sintering temperature or could have formed a liquid phase, which is not surprising since the sintering temperature was close to its melting point (2020 °C). The analysis of secondary phases by EDS confirmed the presence of HfO_2, HfC and traces of a Mo–B phase. Further details are reported elsewhere.[11]

3.2. Oxidation curves

Thermogravimetric curves recorded during the oxidation of the composite 80 vol.% HfB_2 + 20 vol.% $MoSi_2$ are displayed in Fig. 2. With the exception of the curve collected at 1100 °C showing a mass loss, in all of the cases a weight gain was recorded. The weight gain after oxidation at 1200 °C was