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Short communication

Contact-mechanical properties at intermediate temperatures of ZrB_2 ultra-high-temperature ceramics pressureless sintered with Mo, Ta, or Zr disilicides

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Abstract

The elasto-plastic properties and contact damage evolution of ZrB_2 ultra-high-temperature ceramics (UHTCs) pressureless sintered at 1900 °C with $MoSi_2$, $TaSi_2$, or $ZrSi_2$ additive were evaluated by Hertzian indentation tests in air up to 800 °C. It was found that liquid-phase sintering occurred in the three cases, but with severe decomposition of the $TaSi_2$ and $ZrSi_2$ additives and extensive formation of $(Zr_{1-m}Si_m)B_2$ solid-solutions in the case of the $ZrSi_2$ additive. Furthermore, ZrB_2 sintered with $ZrSi_2$ underwent severe peptization at 800 °C, raising questions as to its utility as a UHTC. It was also found that ZrB_2 sintered with $MoSi_2$ exhibits the best combination of contact-mechanical properties, being harder, stiffer, and more resistant to quasiplastic damage and radial cracking than ZrB_2 sintered with $TaSi_2$ or $ZrSi_2$, as well as equally resistant to ring/cone cracking from ~600 °C onwards. Implications of interest for the UHTC community are discussed.

Keywords: ZrB_2; Ultra-high-temperature ceramics; Contact-mechanical properties; Pressureless sintering

1. Introduction

Ultra-high-temperature ceramics (UHTCs) based on ZrB_2 with additions of a Si-rich source (i.e., metal disilicides or SiC) are being widely investigated as leading candidate materials for their use in the critical aerosurfaces of the future hypersonic and supersonic vehicles, and more in general in all those structural applications involving extremely high temperatures and oxidizing atmospheres [1–3]. This is because these UHTCs combine the excellent physical and chemical properties of ZrB_2 (as, for example, high melting point (~3250 °C), elevated hardness (~23 GPa), moderate density (~6.2 g cm^{-3}), high elastic modulus (~490 GPa), low thermal expansion coefficient (~5.9×10^{-6} °C^{-1}), and high thermal conductivity (~60 W m^{-1} K^{-1}), to name just a few) with the improved oxidation resistance provided by the SiO_2 phase resulting from the Si-rich source [1,3,4]. Clearly, this justifies the ongoing research into the oxidation and high-temperature mechanical behaviour of these ZrB_2-based UHTCs.

So far, the studies of high-temperature mechanical properties of ZrB_2-based UHTCs have mostly focused on the evaluation of the flexural strength and creep [1,3,5–34]. Very little information exists on other aspects such as their contact-damage resistance, which is an important gap that needs to be filled. The evaluation of contact-mechanical properties is necessary for various reasons. First, experience demonstrates that the aerosurfaces of the UHTCs used in aerospace applications are not exempt from suffering potential spurious contacts, which might lead to dramatic consequences as has been learnt from the disaster of the space shuttle Columbia [35]. And second, the safe use of UHTCs, and in general of any structural ceramic, in structural applications necessarily requires the evaluation of their limitations under contact loads up to pre-creep temperatures at least in the static loading regime. There has only been one such study on UHTCs, in particular, on a hot-pressed

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ZrB_2 + 30 vol%SiC by Hertz indentation tests as a function of temperature in air up to 800 °C [36]. Clearly, parallel studies on other relevant ZrB_2-based UHTCs will have to be systematically conducted with a view to properly establishing the correlation between processing, microstructure, and contact-mechanical properties. With this in mind, we here apply the Hertzian testing to investigate the contact-mechanical properties at intermediate temperatures of ZrB_2 UHTCs pressureless sintered with $MoSi_2$, $TaSi_2$, or $ZrSi_2$. The details of the experiments and the major findings will be described below.

2. Experimental procedure

Commercially available micrometre powders (H.C. Starck, Berlin, Germany) of ZrB_2 (>99%, $d_{50} \sim$ 1.5–3 μm, $\rho = 6.09\ g\ cm^{-3}$), $MoSi_2$ (>99%, $d_{50} \sim 3.5$–5 μm, $\rho = 5.9\ g\ cm^{-3}$), $TaSi_2$ (>99%, $d_{50} \sim 5$–10 μm, $\rho = 9.14\ g\ cm^{-3}$), and $ZrSi_2$ (>99%, $d_{50} < 6$ μm, $\rho = 4.88\ g\ cm^{-3}$) were used as starting materials to prepare three different UHTC compositions. To that end, the ZrB_2 powder was first mixed individually with each of the three metal disilicides in appropriate proportions to obtain UHTCs with the nominal composition ZrB_2 + 20 vol%$MeSi_2$ (Me = Mo, Ta, or Zr). Mixing was performed with a high-energy centrifugal planetary mixer (Are-250, Thinky, Japan) operated at 600 rpm for 6 min, using WC balls (6.7 mm in diameter) and a powder-to-ball weight ratio of 4. Subsequently, to reduce the particle sizes of the ZrB_2 and of the metal disilicides, as well as to promote their more intimate mixing, the powder mixtures were ball-milled using a high-energy shaker mill (Spex D8000, Spex CertiPrep, USA) operated at about 1060 back-and-forth cycles per minute for 30 min, again utilizing the same type of WC balls at a ball-to-powder weight ratio of 4.

The ball-milled powder mixtures were then cold-pressed into compacts by uniaxial pressing (C, Carver Inc., USA) at 50 MPa followed by isostatic pressing (CP360, AIP, USA) at 350 MPa. Next, the resulting pellets (∽2.5 cm diameter, ∽1 cm thickness) were placed inside graphite crucibles and pressureless sintered in a graphite furnace (1000-3560-FP20, Thermal Technology Inc., USA) at a maximum temperature of 1900 °C for 1 h. To promote the elimination of B_2O_3 impurities, the sintering cycle involved isothermal soakings at 1450 °C and 1650 °C for 1 h each, and smooth heating and cooling ramps of 10 and 20 °C min^{-1}, respectively, and the pressureless sintering was performed in vacuum up to the end of the 1650 °C soaking and under a flowing Ar-gas atmosphere of 99.999% purity thenceforward. The sintered UHTCs were ground off 1 mm and polished to a 1-μm finish using routine ceramographic methods for the microstructural analyses and mechanical tests.

The microstructure of the three UHTCs was characterized using scanning-electron microscopy (SEM) and X-ray diffractometry (XRD). The SEM observations were done on polished and chemically-etched (attacked with molten NaOH for 2 s) surfaces using backscattered electrons (Quanta 3D, FEI, The Netherlands), and on fracture surfaces using secondary electrons (S-3600N, Hitachi Ltd., Japan), in both cases without the typical surface metallization. The XRD patterns were collected in the step-scanning mode (20–55°2θ interval, 0.02°2θ step, 5 s counting time) using a high-resolution laboratory diffractometer (D8 Advance, Bruker AXS, Germany) with Cu$K\alpha_1$ radiation (λ = 1.5406 Å), and the crystalline phases present were identified with the aid of the PDF2 database.

The UHTCs were also characterized mechanically using both Vickers and Hertz indentation tests, the former to determine the hardness (H_V) and toughness (K_{IC}) at room-temperature, and the latter to evaluate the contact-damage resistance as a function of temperature. In particular, 10 separate Vickers tests were performed at ambient conditions under 98 N load using a hardness tester (MV-1, Matsuzawa, Japan), and H_V and K_{IC} were calculated through standard formulae from the length of the diagonal of the residual impression and the total length of the surface trace of the radial cracks as measured by optical microscopy (Epiphot 300, Nikon, Japan) [37,38]. The Hertzian contact tests were performed in air at 25, 200, 400, 600, and 800 °C using a universal testing machine (AG-IS 100 kN, Shimadzu Corp., Kyoto, Japan) equipped with a split furnace; the indentation sequences required to construct the indentation stress–strain curves were carried out at a constant crosshead speed of 0.05 mm min^{-1} over the peak load range of 25–7000 N, using a Si_3N_4 half-sphere of 3 mm radius as an indenter. The elastic moduli (E) were then calculated from the linear stretch of each indentation curve using the Hertzian relation for elastic contacts [39,40], and the yield stresses (Y) were computed from the contact pressure at which the indentation curve deviates from linearity using Hertzian theory [39,40]. The critical loads for the initiation of quasiplasticity (P_Y) were calculated from the previously determined Y values using the relationship derived for the Hertzian mechanical contact [39,40]. Finally, the critical loads for the onset of fracture in the form of ring/cone cracks (P_C) and radial cracks (P_R) were taken as the lowest applied load at which such a cracking mode was observed during the post-test examination of the specimens.

3. Results and discussion

Fig. 1A–C show representative SEM images of the microstructure of the ZrB_2 + 20 vol%$MeSi_2$ (Me = Mo, Ta, or Zr) UHTCs fabricated for the present study. It can be seen that the three UHTCs are dense and that the densification occurred by liquid-phase sintering, as expected. Also, it is evident that ZrB_2 + 20 vol%$ZrSi_2$ (Fig. 1C) has a larger ZrB_2 grain size than ZrB_2 + 20 vol%$MoSi_2$ (Fig. 1A), which in turn has a larger ZrB_2 grain size than ZrB_2 + 20 vol%$TaSi_2$ (Fig. 1B). These grain size trends are consistent with the refractoriness of the metal disilicides used as sintering additives. The SEM images of the fracture surface of these ZrB_2 + 20 vol%$MeSi_2$ (Me = Mo, Ta, or Zr) UHTCs, shown as insets in Fig. 1, corroborate the complete densification and the aforementioned trend of the ZrB_2 grain sizes, and also indicate that the fracture is predominately intergranular in the three cases.

Fig. 2 shows the XRD patterns of the three ZrB_2 + 20 vol%$MeSi_2$ (Me = Mo, Ta, or Zr) UHTCs. It is seen that ZrB_2 + 20 vol%$MoSi_2$ contains ZrB_2 (with Mo solute) and $MoSi_2$, as well as Mo_5Si_3. ZrB_2 + 20 vol%$TaSi_2$ contains ZrB_2 (with Ta solute) plus $ZrSi_2$, Ta and Si, not