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Effect of carbon on the thermal and electrical transport properties of zirconium diboride

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Abstract

The thermal and electrical properties were studied for zirconium diboride (ZrB_2) containing 0–2 wt% carbon. Thermal conductivity was evaluated from 25 to 2000 °C and electrical resistivity measured from 25 to 800 °C and linearly extrapolated to 2000 °C. Estimated values for the Lorenz number for each composition ranged from 2.04×10^{-8} to 2.26×10^{-8} W Ω K^{-2} and were used to separate the electron (84–95%) and phonon (5–16%) contributions to thermal conductivity. The estimated Lorenz numbers were lower than the theoretical value, which indicated the electron mean free path for thermal conduction in ZrB_2 was less than the mean free path for electrical conduction. Thermal conductivities ranged from 99 to 87 W/m K at 25 °C and 76 to 72 W/m K at 2000 °C. Increasing carbon content, either as a second phase or in solid solution, decreased thermal conductivity across the entire temperature range by decreasing the electron contribution to thermal transport.

Keywords: UHTC; Zirconium diboride; Thermal conductivity; Lorenz number; Carbon

1. Introduction

Zirconium diboride is a prospective material for use in applications involving extreme physical and chemical environments, such as leading/trailing edges of hypersonic and re-entry vehicles.[1,2] High thermal conductivities (k) are one of the properties that make ZrB_2 an attractive material for these applications, and others such as electronic substrates.[3,4] Thermal conductivity values up to 133 W/m K at room temperature,[5] and as high as 82 W/m K at 2000 °C[6] (nearing the highest evaluated temperatures), have been reported for nominally phase pure ZrB_2. In contrast, k values as low as 56 W/m K[7] at 25 °C and 55 W/m K[8] at 2000 °C have also been reported. Other applications, which may be best served by a material with lower conductivities, are molten metal crucibles and scram jet engine components.[9,10] Additives and impurities can have a strong influence on the thermal conductivity of ZrB_2.

The bonding of ZrB_2 is a mix of covalent, ionic, and metallic types.[11] Due to the metallic bonding, ZrB_2 exhibits low electrical resistivities (6–23 μΩ cm at 25 °C).[7,12] Therefore, the total k includes significant phonon (k_p) and electron (k_e) contributions. Typically, phonon and electron conductivities are separated by evaluating k and electrical resistivity (ρ_e, or electrical conductivity ($\sigma_e = \rho_e^{-1}$)). Then, k_e is calculated using the Wiedemann–Franz law (Eq. (1)) while k_p is estimated using Eq. (2).[13]

$$k_e = \frac{TL_o}{\rho_e} \tag{1}$$

$$k = k_e + k_p \tag{2}$$

Eq. (1) uses the theoretical Lorenz number (L_o, Eq. (3)) that was derived by Sommerfeld[14] as a combination of constants, π, Boltzmann's constant (k_B), and the charge on an electron (e).

$$L_o = \frac{\pi^2 k_B^2}{3e^2} = 2.44 \times 10^{-8}\text{W } \Omega\,\text{K}^{-2} \tag{3}$$

However, L_o assumes that the mean free paths for thermal transport (ℓ_t) and electrical transport (ℓ_e) by electrons are the same.[15] However, ℓ_t and ℓ_e can differ depending on the inelastic

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scattering events experienced by electrons, which would cause the Lorenz number to vary from the theoretical value.[13,16]

Separation of phonon and electron contributions can be used to study the effects of processing and composition on the total thermal conductivity. For example, McClane et al. showed that the solid solution of transition metals (including Hf, a common, natural impurity in commercial ZrB_2 powder and thus ceramics produced using this powder) results in a decrease in k for ZrB_2 based ceramics due to a reduction in k_e.[17] Like Hf, carbon is commonly present in ZrB_2-ceramics and may also affect k. Commercial ZrB_2 powders are commonly produced using boro-carbothermal and carbothermal reduction processes, which result in typical commercial C contents between 0.25 and 1.5 wt%.[18–21] In addition, carbon is a sintering aid that is often added intentionally to ZrB_2-ceramics to react with and remove surface oxide impurities from powder particles.[22–24] Previous researchers have investigated the effect of carbon additions, showing that increasing the volume fraction of carbon (typically graphitic in nature), as a second phase, decreases k.[6,23,25] The overall decrease in k was attributed to the orientation of the graphite between the ZrB_2 grains.[21] The structure and orientation of graphite as a second phase is significant due to the highly anisotropic nature of pyrolytic graphite. Differences in bonding between the graphene layers (⊥ to a-direction) vs. along the sheets (∥ to a-direction), can result in thermal conductivities of ∼2 W/m K (⊥) to ∼500 W/m K (∥) at 300 K.[26] Therefore, if the graphite is preferentially oriented such that the ⊥ direction dominates, it would be expected to decrease the overall k of the composite. The same should be true if the graphite were disordered, due to the increase in incomplete bonding within the structure.

The role of the carbon in solid solution in ZrB_2 has not been evaluated. In addition, previous studies, such as the one performed by Thompson et al., did not evaluate the effects of C on "pure" ZrB_2. Those ceramics contained WC contamination that was introduced by a milling process. In Thompson's study, the presence of WC reduced the overall k[23] and the role of the $(Zr,W)B_2$ solid solution on k has been supported by McClane et al.[17]

The present study investigated the thermal conductivity of nominally pure ZrB_2 with additions of carbon from 0 to 2 wt%. Thermal diffusivity and electrical resistivity were measured to determine the electron and phonon contributions to total thermal conductivity. Second phase and compositional analyses were performed to relate changes in k to the effects of the carbon additions.

2. Experimental procedure

2.1. Powder processing

Materials used in this study were ZrB_2 (Grade B, H.C. Starck, Goslar, Germany), phenolic resin (GP 2074, Georgia-Pacific, Atlanta, GA) with a 41 wt% carbon yield, and ZrH_2 (Grade S, Chemetall GmbH, Frankfurt, Germany). All powder batches were ball milled for 2 h at 60 rpm using ZrB_2 media and acetone as the liquid. The ZrB_2 and ZrH_2 (1 wt% based on previous research[24]) were dispersed together for the first 1.5 h and the desired phenolic amount was introduced for the final 30 min. After mixing, slurries were dried by rotary evaporation (Rotovapor R-124, Buchi, Flawil, Switzerland). Before densification, the dried powders were ground and sieved to −100 mesh.

2.2. Hot pressing and billet preparation

Processed powders were loaded in a 5.08 cm diameter graphite die lined with graphite foil that had been coated with BN spray. The dies were then loaded in a graphite element furnace (HP50-7040G, Thermal Technologies LLC, Santa Rosa, CA) for hot pressing. A low temperature isothermal hold was performed under flowing Ar-10%H_2 at 600 °C for 30 min to pyrolyze the phenolic. The atmosphere was then switched to a mild vacuum (≤200 mTorr or ∼27 Pa) for three isothermal reaction holds at 1250, 1450, and 1600 °C for 1 h each. After the final hold, a flow of Ar-10%H_2 was established and the furnace was heated under full power to 2150 °C where the heating rate steadily decreased from ∼130 to ∼80 °C/min. Upon stabilization of the furnace temperature, the force was applied to achieve 50 MPa of pressure. After pressing for 70 min, the furnace was shut off and allowed to cool naturally and the force was released at 1600 °C. Hot pressed billets were fabricated to be ∼8 mm thick to allow for the removal >1.5 mm of material from the top and bottom faces of each billet to eliminate the sampling/testing of any of the reaction layer between the ZrB_2 and the graphite spacers. The billets were then diamond machined to produce specimens that were 1.27 cm^2 and 0.27–0.28 cm thick for thermal diffusivity and one disk 2.5 cm in diameter and 0.1 cm thick for electrical resistivity testing.

2.3. Characterization

Bulk densities (ρ) were evaluated using the Archimedes method with water as the immersing medium. Density values were corrected for temperature for use in thermal conductivity calculations using thermal expansion data from Touloukian.[27] Specimens were ground and polished to a 0.05 μm finish for scanning electron microscopy (SEM; S-570, Hitachi, Ibaraki, Japan) and confocal Raman spectroscopy (633 nm He–Ne laser, Aramis LabRAM, Horiba Jobin Yvon, Edison, NJ). Image analysis (ImageJ, National Institutes of Health, West Bethesda, MD) was performed on SEM images to analyze the volume fractions of porosity and second phases. Transmission electron microscopy (TEM; Tecnai F20, FEI, Hillsboro, OR) was also performed to identify a second phase in the composition with the lowest carbon addition. The TEM specimen was produced by focused ion beam (FIB; Helios Nanolab 600, FEI) liftout. X-ray diffraction (XRD; X'Pert Pro, PANalytical, Almelo, Netherlands) analysis was also used for phase identification. Carbon content was quantified (CS600, Leco Corporation, St. Joseph, MI) for the densified materials after grinding to −200 mesh using an alumina mortar and pestle. In addition, several other impurities were analyzed for the highest conductivity material (0.2 wt% added C) to allow for direct comparisons with