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Fabrication of ultra high temperature ceramic matrix composites using a reactive melt infiltration process

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ABSTRACT

Fiber reinforced composites containing a ZrB_2 matrix are prepared by reactive melt infiltration, using a Zr based intermetallic compound. The reactive melt infiltration process is further characterized by determining the contact angle of the different melt and preform elements. Two different methods for boron powder impregnation of the preforms, which form ZrB_2 during Zr_2Cu melt infiltration, are evaluated. Degradation of fibers and different fiber coatings for Zr_2Cu melt are evaluated and the microstructure of the infiltrated samples is investigated by means of XRD and SEM.

1. Introduction

Ultra High Temperature Ceramics (UHTCs) define a group of ceramic materials which enable application in hypersonic engines, sharp leading edges, high lift reentry and fusion reactors. Hence, important characteristics are high melting point, good thermal shock behavior and oxidation resistance. To create enough lift in hypersonic flight, many concepts are based on slim designs with sharp leading edges, resulting in more variable reentry scenarios. The fact making UHTCs interesting for these cases is leading edge temperature, which rises inverse to the square root of the nose radius [1].

Monolithic UHTCs have been under investigation for these types of applications, especially the diboride system [2–7]. As most monolithic ceramics, UHTCs possess low fracture toughness making engineering of system parts difficult. In Ceramic Matrix Composites (CMCs) fracture toughness can be improved by adding fiber reinforcements. Focus of this paper is the development of a Reactive Melt Infiltration (RMI) process and manufacture fiber reinforced ZrB_2 matrix composites. The article discusses the characteristics of RMI important to fabrication as well as a study of fiber protection from melt infiltration.

2. State of the art

Further work on the diboride and refractory compositions were performed in the 1960s by ManLabs Inc. in the USA and from G.V. Samsonov in Russia. Both works already include ZrB_2 and HfB_2. ManLabs also performed the investigation of SiC additions to the diboride system. They also performed first tests on high temperature oxidation, mechanical and thermal properties. The addition of SiC influences properties such as strength [8,9], fracture toughness [8–10] and oxidation resistance at certain temperatures [11,12]. For sintering routes SiC also creates thermal residual stresses during cool down from process temperature. While the strength of pure ZrB_2 is mainly governed by the grain size, SiC doped diboride is effected by the SiC particle/grain size [13].

Beside the high melting points of Hf and Zr diborides, ZrB_2 being at ~3200 °C [5], they also exhibit high electrical conductivity (~11×10^6 S/m for ZrB2 at RT) due to the high degree of covalent bonding [14–16].

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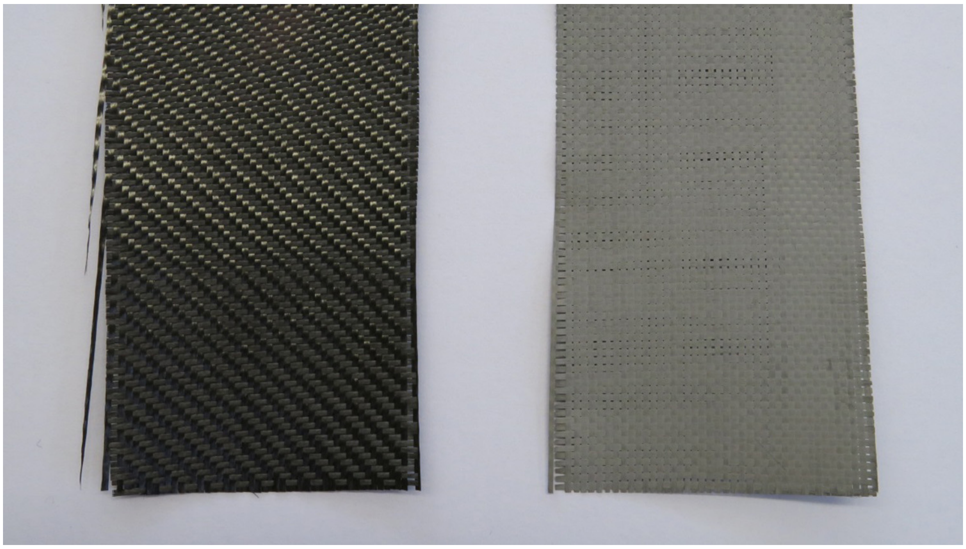

Fig. 1. Uncoated (left) and TiB_2 coated (right) C_f.

A comprehensive historical study by Guo [17] reviews various methods for creating ZrB_2. It includes hot pressing (HP) [18–21], spark plasma sintering (SPS) [22–24], reactive hot pressing [25], electron beam/laser sintering [26,27] and pressureless sintering. These methods usually use a ZrB_2 powder and various precursors which need to be manufactured at temperatures ranging from 1400 °C to 2250 °C. ZrB_2/HfB_2 with 20 vol.% of SiC are probably the most common UHTCs.

There are also fiber reinforced composites containing UHTCs as matrix. Corral [28] infiltrated a C/C composite with a slurry of ZrB_2 and B_4C. Hu [29] infiltrated a preform with polycarbosilan and ZrB_2 powder resulting in a composite with 23.3% porosity at 24.6 vol.% ZrB_2. Wang [30] combined this process with Chemical Vapor Infiltration (CVI). Levine [18] infiltrated a preform with a mixture of polycarbosilane, HfB_2 and SiC powder. Zhao [31] used a polymer to form a ZrC matrix during pyrolysis. Jayaseelan [32] infiltrated a porous C/C preform with ZrB_2 powder and ethanol in addition to a liquid chemical process to form ZrB_2 by a carbothermal reaction.

There is not a lot of literature dealing with the formation of ZrB_2 based UHTC through melt infiltration. Zhang [33] completed studies of melt infiltration at 1200 °C under vacuum. Zhang's paper includes the manufacturing of B_4C porous bars, along with the infiltration of these bars with Zr_2Cu. Dickerson [34] performed a Zr_2Cu infiltration of a porous WC preform to form a ZrC and W structure. The advantages and disadvantages of the Zr_2Cu RMI are comparable to the Liquid Silicon Infiltration (LSI) process, namely low porosity, residual melt and possible manufacturing of large parts. In case of a fiber reinforced ZrB_2 matrix composite, RMI achieves a lower temperature exposure of the fibers compared to HP or SPS, with no additional mechanical pressure. Conversely the fibers need to withstand the melt during the RMI process.

For melt infiltration processes key issue is wetting of the preform as well as wetting of reaction products, formed during infiltration. Beside the atmosphere, wetting is also influenced by small impurities of the substrate, for example Ni in ZrB_2 as shown in the work of Muolo et al. [35]. They showed that the contact angle of Cu drops by ~120° when using 4 wt.% of Ni as sintering aid. This may not only be the effect of Ni addition but also the influence of higher densification of the ZrB_2 substrate, as well as the formation of Ni_2B shown in the work of Voytovych et al. [36]. In addition Muolo et al. showed the time change of Cu contact angle, spreading kinetics, which decreased within a few minutes [35,37]. Another aspect which has to be taken into account is wetting of C by Cu. Compared to ZrB_2 contact angle of Cu and C is rather high, larger than 100° [38]. Beside spreading kinetics there is also an influence of temperature on the contact angle, as shown in by Samsonov et al. [5] the contact angle drops nearly 100° from 1100 °C to 1400 °C.

Liquid Silicon Infiltration (LSI) for manufacture of CMCs is documented in the literature from DLR [39–41]. Compared to the reaction of Zr-RMI, LSI is using C and molten Si to react to SiC, however basic infiltration mechanisms are similar for both methods. They both use capillary forces to infiltrate a porous preform with molten metal and create ceramics due to reaction while infiltrating. The reactions occurring during infiltration are:

$$Zr_2Cu + 4B \rightarrow ZrB_2 + Cu \tag{1}$$

$$Zr_2Cu + 2B + C \rightarrow ZrB_2 + ZrC + Cu \tag{2}$$

$$Zr_2Cu + 2B + SiC \rightarrow ZrB_2 + ZrC + uCu_xSi_y \tag{3}$$

Eq. (3) describes the infiltration of preforms from polycarbosilane and boron powder, Eq. (2) from phenolic and boron powder and Eq. (1) only boron powder.

In order to manufacture stoichiometric ZrB_2/SiC using RMI the following aspects have to be taken into account:

- Which porosity is necessary for the boron preform in order to produce a dense stoichiometric matrix
- Which pore size distribution is necessary to reach all boron
- Which ceramic yield is necessary for a dense stoichiometric matrix

$$V_{\text{total}} = V_{\text{ZrB}_2} = V_{\text{por}} + V_{\text{B}} \tag{4}$$

Eq. (5) can be related to the reaction in Eq. (1), therefore the volumes can be replaced by the molar volume. The division by the molar volume of ZrB_2 gives

$$e_{\text{B,stoich}} = \frac{V_{\text{por}}}{V_{\text{ZrB}_2\text{,mol}}} = 1 - \frac{V_{\text{B,mol}}}{V_{\text{ZrB}_2\text{,mol}}} \tag{5}$$

Beside the porosity an important factor is the capillary system. To describe these in hydrodynamics, it is necessary to solve the Navier-Stokes Equations. For incompressible Newtonian Flu-