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Design of the multiple transition metals interlayer process to diffusion bond ZrC_x ceramics

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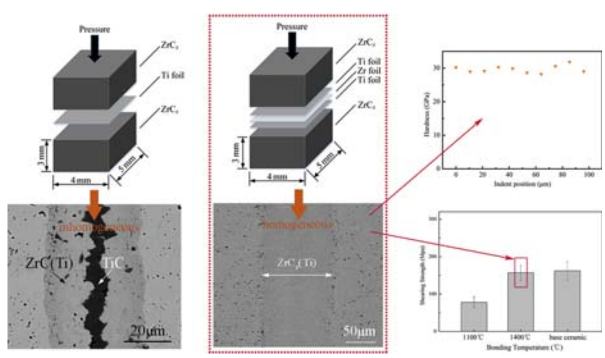
HIGHLIGHTS

- A Ti/Zr/Ti interlayer was designed to join ZrC_x via forming homogeneous joint zone.
- The homogenization of ZrC joint was achieved at 1400 °C/1 h/20 MPa.
- Decreasing the thickness of Ti/Zr/Ti interlayer reduces the bonding temperature.
- The joint strength (162 MPa) and hardness (30.1 GPa) approach that of the ceramic.

GRAPHICAL ABSTRACT



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ABSTRACT

In the study summarized in this paper, it is hypothesized that ZrC_x with fewer carbon vacancies (e.g. stoichiometric ZrC) could form a homogenous joint when using a new multilayered design of the interlayer, consisting of a set of transition metals Ti/Zr/Ti. The proof of the hypothesis is obtained by performing diffusion bonding of ZrC with Ti/Zr/Ti interlayer under different temperature and time conditions, notably at 1400 °C/1 h/20 MPa. This design also applies to ZrC_x with a larger population of carbon vacancies, like $ZrC_{0.85}$. It is established that the mechanical integrity of the joint zone has been dramatically improved by the homogenization of the joint, which is comparable to that of the base ceramics. The homogeneous microstructure and outstanding mechanical properties demonstrate the great potential of this multiple interlayer design.

1. Introduction

Ultra-high temperature nonstoichiometric transition metal carbides (TMCs) from groups IV and V of the Periodic Table (ZrC_x, TiC_x, TaC_x VC_x, etc.) are interstitial compounds (x from 0.47 to 1.0 [1,2]) due to the existence of the structural carbon vacancies located in the octahedral interstices surrounded by the metal sub-lattices [3,4]. They have excellent physical and chemical properties, such as ultra-high melting temperature, extreme hardness and stiffness, good thermal

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shock resistance, excellent electrical and thermal conductivities, good magnetic susceptibility, great wear and corrosion resistance and chemical inertness, etc. [1–3,5–7]. They also possess radiation resistance due to the existence of structural vacancies [3]. These remarkable properties have made them appealing candidates for a wide range of high temperature applications like cutting tools, aerospace applications, nuclear industry components and rocket engine parts [1,2,7–10].

In these high temperature applications, it is often necessary to join the transition metal carbides to metals or to themselves. Some but few investigations of joining of pure transition metal carbides have been reported, involving solid diffusion bonding [10–12], partial transient liquid phase (PTLP) diffusion bonding [13–15], self-propagation high-temperature synthesis (SHS) [16]. Review of the published literature indicates that two key obstacles are encountered when producing joints for service at high temperature: (i) the residual stress caused by the large thermal expansion mismatch between the heterogeneous materials (between ceramics and the residual interlayer, if any) including the heterogeneous phases across the joint [13], and (ii) the insufficient high-temperature resistance of the joint [12].

Motivated by the listed issues, in a recent study [17], we succeeded in forming a homogenous joint for the ceramic containing a *large number of carbon vacancies*, e.g., $ZrC_{0.7}$ ceramic, but by using Ti as an interlayer. However, in previous studies we didn't resolve the problem of achieving the homogenous bond with *near stoichiometric ZrC ceramics.* Resolving this opens a possibility for uncovering not only the mechanism of joint homogenization, but for achieving a practical implementation in terms of targeted properties. Hence, in this study, first of all, to explore the potential of Ti forming homogenous joints with ZrC_x with near $x = 1$, diffusion bonding of ZrC/Ti/ZrC were investigated for the first time. Then a hypothesis that cross-diffusion phenomena in complex multilayered bonding interface zone may assist the joint's homogenization has been explored. To verify the hypothesis, an alternative new design of the interlayer with a combination of multiple transition metals (Ti/M/Ti, M = Zr, Hf, Nb and Ta, respectively) is proposed to obtain the homogenous joints of ZrC_x. In present study, we take Ti/Zr/Ti as a representative of the family of transition metals in a composite interlayer. Forming homogenous joints of ZrC_x by using a multiple transition metal interlayer has been successfully accomplished.

In this paper, the microstructural features of the ZrC_x joints made by using both single and multiple layered transition metals' designs were characterized. In addition, the mechanical property characterizations (four-point bending tests and nano-indentation measurements) were performed.

2. Experimental procedure

The ZrC_x ceramics analyzed in this study include ZrC and $ZrC_{0.85,}$ prepared by the hot-pressed sintering. The hot sintering procedure and the process outcome were described in our previous paper, [18], but for the sake of completeness, these are summarized here. HPS uses graphite ($D_{90} \approx 1.3$ μm, purity > 99.9%; Qingdao Hua Tai Lubricant Sealing S&T Co., Ltd., China) and ZrH_2 ($D_{90} \approx 15$ μm; purity 99.94%; Beijing Xing Rong Yuan Technology Co., Ltd., China) powders as the raw materials. The different value of x indicates the different concentration of carbon vacancies (e.g. $1 - x$), which can be controlled when weighting the two powders proportionally. The hot-pressing was performed in a hot zone of a controlled atmosphere furnace (High-Multi 1000, Fuji, Nihon Dempa Kogyo Co., Ltd.) with a pure Ar (purity > 99.8%) for 1 h under 40 MPa pressure at 2000 °C and 1900 °C, respectively. The bulk densities of the resultant ZrC_x ceramics were 6.52 g/cm^3 and 6.67 g/cm^3, for $x = 1$ and 0.85, respectively. The densities were estimated using the Archimedes' principle.

Each of the resultant ZrC_x ceramics were cut into (i) 5 mm × 4 mm × 3 mm pieces for a microstructure analysis, and (ii) 18 mm × 4 mm × 3 mm specimens for mechanical four-point bending testing. Prior to bonding, the specimen surfaces (to be joined) were polished using diamond millstones, from 500-grit to 2000-grit. The transition metal's foils, either Ti (10 μm) or Zr (30 μm and 10 μm, respectively), used in this study are commercially available (Goodfellow) and have a high purity (higher than 99.7%). The foils were cut into 6 mm × 6 mm squares. An interlayer made of Ti is selected because (i) Ti forms an infinite solid solution with Zr [19], as can be seen from Ti-Zr binary phase diagram [20], and (ii) Ti belongs to the transition metal family, the same group with Zr. Transition meal carbides (except VC) have a unique feature, which is to form solid solutions with each other under certain conditions. As a result, after a diffusion takes place, the newly formed TiC is expected to dissolve into ZrC, making homogenization possible. Prior to the assembly, all pieces to be joined (i.e., the mating ZrC_x pieces and the interlayer foils) were ultrasonically cleaned for 20 min in acetone. The transition metal interlayer (single Ti or multiple Ti/Zr/Ti) was sandwiched between two ZrC_x pieces, followed by vacuum diffusion-bonding (10^{-6} Torr, CVI M60, Centorr Vacuum Industries, Nashua, NH, USA). The schematic diagram of the assemblies' design is shown in Fig. 1. The assemblies of ZrC_x ceramics were subsequently heated to 700 °C at 20 °C/min and held at that temperature for 10 min. Then, the assemblies were heated to the peak bonding temperatures (ranging from 900 °C to 1500 °C) at a rate of 10 °C/min and were held at the peak temperature between 10 min and 5 h. The specimens were slowly cooled to 400 °C at a rate of 10 °C/min, and ultimately to the room temperature. During the process, 20 MPa pressure was applied to the assemblies.

After bonding, microstructure characterization of the joints was performed by the scanning electron microscopy (SEM, HELIOS NanoLab 600i) equipped with an energy dispersive spectroscopy (EDS) in the back-scattering mode at 15 kV (with the resolution of 0.9 nm) on the polished cross-sectional surfaces of the joints. The interfacial phases were identified using a transmission electron microscopy (TEM, FEI Talos F200x) on the polished cross-sections of different ZrC_x joints and also by the X-ray diffraction analysis (XRD, Philips X'Pert, Holland) with Cu/Kα1 radiation on the surfaces of the joints. The sample for XRD analysis was grinded layer by layer across the joint. Initial grinding was executed close to the joint and then the XRD analysis was performed. Subsequently the analysis was repeated after removal of the next layer of material. This cycle is repeated until all of the joint has been consumed. The four-point bending strength of the joints was measured by Instron-1186 universal mechanical testing machine, at room temperature with a displacement rate of 0.5 mm/min. The average value of each experimental condition was calculated from at least 5 measurements. Nano-indentation testing was performed by using a nano-indentation equipment (Nano Indenter G200, Agilent) with an indent depth of 30 nm and peak holding time of 10 s on the polished cross-sections of different ZrC_x joints. The average value of the hardness of each layer under each experimental condition was calculated and the standard deviation of each layer was estimated.

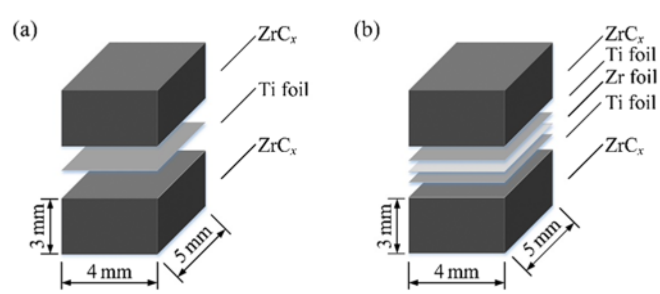

Fig. 1. The schematic diagram of the assemblies of ZrC ceramics using (a) a single Ti as the interlayer, and (b) the multiple Ti/Zr/Ti as the interlayer.