Homogenization of the zirconium carbide–titanium interface domain

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ABSTRACT

An excellent homogenization of the ceramic (ZrC_x)–metal (Ti) interface domain has been successfully achieved. A non-stoichiometric ZrC_x under certain diffusion bonding conditions leads to a total consumption of the metal Ti interlayer, and to a formation of a homogeneous interface domain. The combined impact of a presence of carbon vacancies in zirconium carbide, and the mutual solubility between transition metal carbides, is instrumental in achieving the homogenization. This has, to the best knowledge of authors, never been reported.

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Transition metal carbide ceramics have been considered as candidates for ultra-high-temperature applications [1–3]. This is due to (i) an extraordinarily high melting point, (ii) a high wear and corrosion resistance, (iii) an extreme hardness, and (iv) a relatively low thermal expansion. Highly stringent operating conditions demand inevitably a presence of high quality transition-metal-carbide ceramic-to-metal joints. So far, several bonding approaches were investigated, such as (i) high-temperature brazing [4], (ii) in situ forming [5], or (iii) doping fillers with ceramic particles [6]. These methods do improve the properties of the joints, but only to a certain degree and with a significant limitation. Namely, a recommended long time operating temperature must still be less than 800 °C [4–7]. Hence, such joints cannot meet the requirements of an intended application.

A Partial Transient Liquid Phase (PTLP) bonding has been used to further increase the operating temperature of a ceramic joint [8]. This is achieved by a composition homogenization of a melting-point depressant inserted into the core layer at the interface of the ceramics [9,10]. Most often Mo, Ti, Pd, Nb and Ni-Cr alloys have been used as high melting core composite interlayers [11]. For example, Hong et al. [8] have successfully increased the operating temperature of Al_2O_3 up to 2000 °C by using Ni/Nb/Ni as an interlayer. However, the PTLP applications have been facing yet another problem — an appearance of significant residual stress. Residual stress occurs due to markedly different thermal expansion coefficients between the ceramics and the residual core metal interlayer [8,11–14].

To solve this adverse effect, single or multi-layered soft metals [15] have been used. These possess sufficient plasticity and low yield strength. The use of some metals having expansion coefficients close to that of ceramics, such as W or Mo [16], has been attempted as well. Furthermore, composites [16,17], have been used as interlays. Doping (SiC [18], Al_2O_3 [19], carbon fibers [20] or TiB whiskers [21]) has also been investigated. Still, the problem of a significant residual stress caused by prominent heterogeneity stays unresolved. Besides, the low melting points of residual metals within the interlayers after bonding result in a low thermal performance [22].

Apparently, the issues associated with these problems have not been resolved by any of the current methods. The problem is of a fundamental nature — a highly homogeneous domain, from a highly non-homogeneous initial configuration, has not been achieved. So, in practical terms, a new bonding method for transition metal carbide ceramics needs to be developed. Its main objective would be a successful high level homogenization of the interface zone.

In our study, it is hypothesized that an impact of the presence of carbon vacancies on (i) the element's diffusion, and (ii) the mutual solubility among the transition metal carbides, would lead to a formation of a homogenous joint. Hence, the interface zone composed of refractory carbides would be obtained by diffusion bonding under adequate physical conditions. To the best knowledge of the authors, this has never been reported.

To verify this hypothesis we have designed a series of experiments involving multiple nominal composition ZrC_x ($x = 1$, 0.85, 0.7, 0.55) ceramics. The objective was to uncover the range of the physical conditions likely to lead to a transition from a highly non-homogeneous to a highly homogeneous ZrC_x–Ti–ZrC_x reactive diffusion bonding domain.

The bonding was performed by using Ti as the reactive interlayer sandwiched between two ZrC$_x$ domains. If the supposed effect is effective enough, a homogenous joint zone should form.

The ZrC$_x$ ceramics employed in the study were prepared by Hot Pressed Sintering (HPS) for 1 h under 40 MPa pressure at 2000 °C, 1900 °C, 1700 °C and 1600 °C, respectively, using (i) ZrH$_2$ (D$_{90}$ ≈ 15 μm; purity 99.94%; Beijing Xing Rong Yuan Technology Co., Ltd., China), and (ii) graphite powders (D$_{90}$ ≈ 1.3 μm, purity > 99.9%, Qingdao Hua Tai Lubricant Sealing S&T Co., Ltd., China). Each of the ZrC$_x$ ceramics was cut into 5 mm × 5 mm × 3 mm pieces. The surfaces to be joined were polished using diamond millstones (500-grit, 800-grit, 1000-grit and 1200-grit, respectively). Both 50 μm and 10 μm thick Ti foils (Baoji Tian Yu Rare Metal Co., Ltd., China) with purity higher than 99% were cut into 7 mm × 7 mm pieces. Both surfaces of the titanium pieces were acid pickled using a hydrofluoric acid aqueous solution (5% HF + H$_2$O) in an ultrasonic cleaner for a duration of 1 min. Each of the Ti foil pieces was subsequently sandwiched between two ZrC$_x$ specimens. Prior to the assembly, all the pieces to be joined were ultrasonically cleaned for 20 min in acetone. The assembly of the pieces was inserted between two graphite blocks. The diffusion bonding experiments with ZrC$_x$ featuring different proportions of carbon vacancies were performed within a range of different peak temperatures (from 1000 °C to 1400 °C), and different holding times (from 10 min to 2 h) with a loading of 20 MPa in a vacuum furnace (10^{-6} Torr). After the holding time, the specimens were slowly cooled up to 400 °C (cooling rate 5 °C/min). Ultimately, the samples were cooled in the furnace until reaching the room temperature.

The polished surfaces of the joints were analyzed by (i) scanning electron microscopy (SEM, Quanta 200FEG) equipped with an energy dispersive spectroscopy (EDS, AMETEK) in a back scattering mode at 30 kV (with the resolution of 2.5 nm), and by (ii) the transmission electron microscopy (TEM, Tecnai G2 F30).

Figs. 1a–d show the microstructures of ZrC$_x$ (x = 1, 0.85, 0.7 and 0.55, respectively) ceramic joints, diffusion bonded at 1300 °C for 1 h under 20 MPa pressure with 50 μm Ti foil as interlayer. It can be observed that the ZrC, ZrC$_{0.85}$, ZrC$_{0.7}$ and ZrC$_{0.55}$ ceramics are successfully joined to themselves respectively using Ti foil as the interlayer. The results of a line scan along the white lines in Figs. 1a–d are presented in Figs. 1e–f, respectively, and show sharp boundaries and limited diffusion.

A typical microstructure of ZrC$_x$ ceramic joints can be described as follows. As shown in Fig. 1a, three reaction layers from the edge of the

Table 1
Average chemical compositions (points in Fig. 1a); ZrC$_x$ joints by EDS (at.%).

Point	Elements (at.%)			Possible phase
	Zr	Ti	C	
A	39.43	08.22	52.35	ZrC (Ti)
B	13.85	62.96	23.19	TiC(Zr)
C	08.59	74.62	16.79	α-Ti(Zr, C)
D	22.82	43.22	33.96	β-Ti(Zr, C)
E	34.95	0.78	55.28	ZrC

base material to the center of the joint can be identified. These are marked respectively as: I (a light gray diffusion layer with a thickness of 6 ± 1 μm), II (dark phase layer which is 13 ± 3 μm thick), and III (a dark gray needle-like and white "matrix" phase, thickness of 72 ± 3 μm).

The light gray layer I and the dark layer II can be identified as (i) ZrC$_x$(Ti) diffusion layer, and (ii) TiC layer dissolving a certain quantity of Zr atoms, respectively, see Table 1. However, the phase composition of the layer III, (composed of a needle shaped phase and of a "matrix" white phase), is difficult to identify based only on the composition analysis due to its complex micromorphology.

Consequently, a transmission electron microscopy (TEM) analysis was employed to identify the species of the reaction products. The typical TEM micrograph of the marked rectangular zone (shown in Fig. 1b) in the bonding seam of ZrC$_{0.85}$ is shown in Fig. 2.

The corresponding selected area features electron diffraction (SAED) patterns as illustrated in Figs. 2b–e. The formation of TiC layer is confirmed. The dark gray needle shaped phase and the white phase in the layer III are identified as α-Ti and β-Ti, respectively. It would be expected that β-Ti is a stable phase at the bonding temperature (1300 °C) and that the transformation to α-Ti during cooling should follow by an allotropic transition [23]. However, our system features β-Ti retained within α-Ti at the room temperature. This is most likely due to the interdiffusion across the interface. Such diffusion can influence the process of allotropic transformation, forming the α-Ti needles and stabilizing the β-Ti matrix by dissolving Zr and C atoms [23].

Moreover, it can also be concluded, from Fig. 1, that the interfacial microstructures of different ZrC$_x$ ceramic joints were greatly influenced by different proportions of carbon vacancies. With the carbon to Zr ratio in ZrC$_x$ base ceramics decreasing from 1 to 0.55, the total thickness of
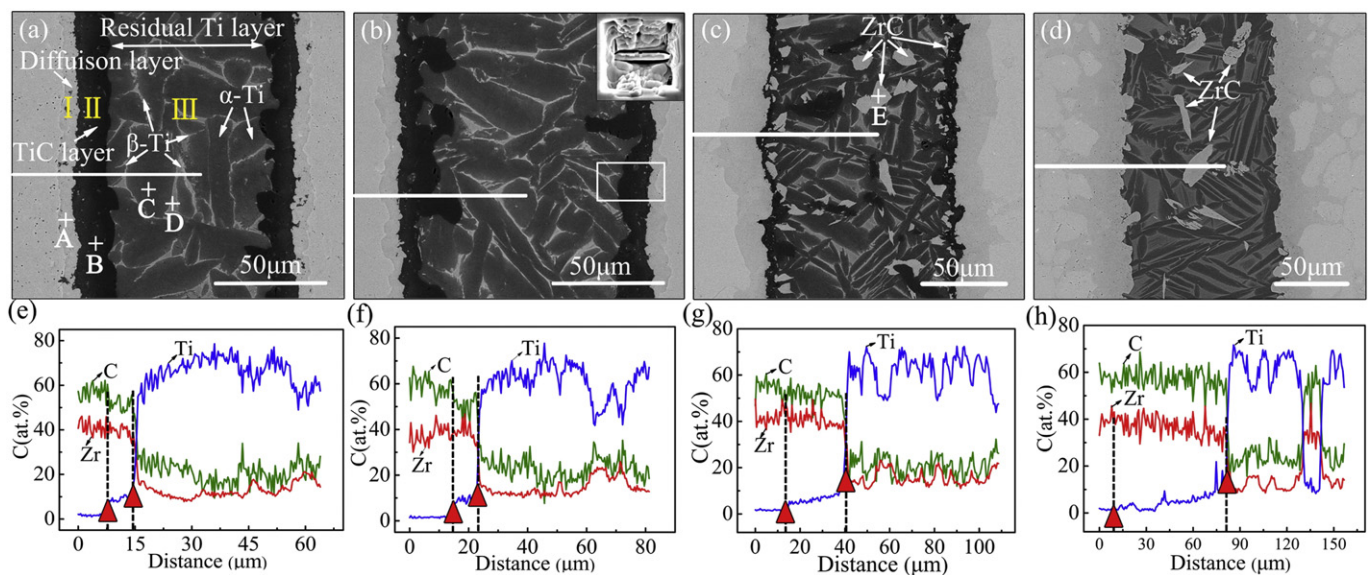

Fig. 1. SEM images of the microstructure and the line scans (along the marked white line) of ZrC$_x$ diffusion bonded ceramics. Ti foil interlayer was 50 μm. (The peak, 1300 °C; 1 h under 20 MPa pressure). (a and e) ZrC; (b and f) ZrC$_{0.85}$, the inset in (b) shows the morphology of the marked rectangular zone after Focused Ion Beam (FIB) cutting; (c and g) ZrC$_{0.7}$; (d and h) ZrC$_{0.55}$.