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Reaction joining of SiC ceramics using TiB_2-based composites

Wubian Tian *, Hideki Kita, Hideki Hyuga, Naoki Kondo, Takaaki Nagaoka

National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Shimo-Shidami, Moriyama-ku, Nagoya 463-8560, Japan

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Abstract

SiC ceramics were reaction joined in the temperature range of 1450–1800 °C using TiB_2-based composites starting from four types of joining materials, namely Ti–BN, Ti–B_4C, Ti–BN–Al and Ti–B_4C–Si. XRD analysis and microstructure examination were carried out on SiC joints. It is found that the former two joining materials do not yield good bond for SiC ceramics at temperatures up to 1600 °C. However, Ti–BN–Al system results in the connection of SiC substrates at 1450 °C by the formation of TiB_2–AlN composite. Furthermore, nearly dense SiC joints with crack-free interface have been produced from Ti–BN–Al and Ti–B_4C–Si systems at 1800 °C, i.e. joints TBNA80 and TBCS80, whose average bending strengths are measured to be 65 MPa and 142 MPa, respectively. The joining mechanisms involved are also discussed.

Keywords: Silicon carbide; Joining; TiB_2-based composite; Microstructure; Mechanical properties

1. Introduction

Silicon carbide (SiC) has been known as a useful material for more than one century. SiC whiskers and compounds have been widely used in abrasives, cutting tools, structural parts, nuclear fuel elements, and so on.[1–3] Recently, SiC catalyst support and astronomical telescope mirror have also been developed.[4,5] Moreover, SiC ceramics are good candidates for high-temperature applications because of the good mechanical properties and thermal stability at elevated temperatures.[6,7] To produce large-size components and engineering parts that can serve at high temperatures, developments of SiC joints possessing desired high-temperature properties are very fundamental.

It is well-known that TiB_2 exhibits exceptional hardness and elastic modulus, high melting point, good corrosion resistance to chemicals or molten metal and oxidation resistance at temperatures up to 1100 °C.[8] TiB_2-containing ceramic composites usually possess superior properties than monolithic TiB_2 when they share similar microstructure after sintering, such as fracture toughness, mechanical strength and oxidation resistance.[9–13] Among the various methods to fabricate TiB_2-based composites, reactive sintering has been paid much attention because of relatively low sintering temperature, cheap starting powders and less consumption of sintering additives.[14]

Our motivation of present work, therefore, is to evaluate the possibility of using TiB_2-based composites to bind SiC ceramics with reactive sintering process. Four kinds of joining materials, i.e. Ti–BN, Ti–B_4C, Ti–BN–Al and Ti–B_4C–Si, were used to form the composite interlayers containing TiB_2 in the temperature range of 1450–1800 °C. The produced SiC joints were characterized and evaluated with XRD analysis and microstructure examination. Mechanical properties of dense joints were measured. In addition, the involved mechanisms for joining tests are discussed.

2. Experimental procedure

2.1. Joining materials preparation

The characteristics of starting constituents of interlayer, including titanium, boron nitride, boron carbide, aluminium and silicon, were listed in Table 1. Four kinds of joining materials were used to bind SiC sintered bodies, viz. Ti–BN, Ti–B_4C, Ti–BN–Al and Ti–B_4C–Si, as summarized in Table 2, where the labels of bonded samples, composition of interlayer and joining processes were also presented.

The starting powders were weighted according to designed compositions and blended in ethanol by ball milling for

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* Corresponding author. Tel.: +81 52 736 7120; fax: +81 52 736 7405.
E-mail address: w.b.tian@aist.go.jp (W. Tian).

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Table 1
Characteristics of starting powders.

Powder	Purity (%)	D50 (μm)	SSA (m^2/g)	Major impurities (elements/wt.%)	Maker
Ti	99.9	10	–	–	Kojundo Chemical Lab., Japan
BN	97.5	0.1	50	–	Zikusu Industry Co., Ltd., Japan
B_4C	HS grade	0.63	20	Si/0.1, Fe/0.01	H.C. STARCK, Germany
Al	99.9	20	–	Si/0.03, Fe/0.06	Kojundo Chemical Lab., Japan
Si	99.9	10	–	–	Kojundo Chemical Lab., Japan

–, Data unknown.

24 h using silicon carbide balls as media. After mixing, the slurry was dried using a vacuum evaporator and then placed into an oven at 70 °C for overnight. The dried mixtures screened through a 150 mesh sieve were served as joining materials.

2.2. Joining method

SiC plates with dimensions of 20 mm × 20 mm × 3 mm or 20 mm × 20 mm × 20 mm were used for joining tests. Prior to joining, SiC plate surface (20 mm × 20 mm) was polished down to 0.5 μm diamond suspension and ultrasonically cleaned in ethanol. The average surface roughness (Ra) of the polished SiC was measured to be 0.01 μm by a surface roughness measuring machine (Surftest SV-624, Mitutoyo, Japan). The powder-like joining materials were sandwiched between two polished SiC plates. Joining procedures were performed in a graphite elements furnace with 1 atm flowing Ar and proceeded in the temperature range of 1450–1800 °C for 60 min under a mechanical pressure of 12.5 MPa or 15 MPa.

2.3. XRD analysis and microstructure characterization

Phase constituents were determined by X-ray diffractometry (XRD, RINT2000, Rigaku, Japan) on the joint interlayers. The joined SiC samples were sectioned perpendicular to the interlayer and polished in the same manner as the polished surfaces of the SiC plates. Microstructure observations on the polished surfaces were conducted via SEM (JSM-5600, JEOL, Japan) equipped with energy dispersive spectrometer (EDS JED-2300, JEOL, Japan) or optical microscope (ECLIPSE ME600, Nikon, Japan).

2.4. Mechanical properties measurements

Vickers hardness was determined by means of indentation method (MVK-G3 hardness tester, Akashi, Japan) with a load of 9.8 N for 15 s. Room temperature 4-point bending strength was measured on 4 mm × 3 mm × 40 mm beams with outer and inner span of 30 mm and 10 mm, respectively, at a crosshead speed of 0.5 mm/min. The tensile surface was polished using the same procedure for the bonding surfaces of SiC blocks and the edges of tested specimens were beveled.

3. Results and discussion

3.1. Ti–BN and Ti–B_4C systems

For the joining material of Ti–BN system, XRD patterns of SiC joint interlayers bonded at 1450 °C and 1600 °C are presented in Fig. 1. It is clear that the interlayers joined at the two temperatures consist of TiB_2 and TiN major phases, and trace amount of un-reacted BN, suggesting the near completion of reactions between Ti and BN. These results are not surprised because the formation of TiB_2–TiN composite is found to be completed at temperatures higher than 1200 °C as starting from Ti and polyborazylene ($B_3N_3H_4$) polymer.[15] However, SiC substrates separate completely from the reaction-formed interlayer after the joining tests. These results point to a conclusion that Ti–BN joining material does not weld SiC substrates well at temperatures up to 1600 °C.

The joining tests of SiC using Ti–B_4C powder mixtures were also conducted at 1450 °C and 1600 °C, and the corresponding XRD patterns of interlayers are shown in Fig. 2. It is noted that the phase constituents of interlayers are similarly composed of TiB_2 and TiC compounds, suggesting that the for-

Table 2
Sample label, interlayer composition and joining process of bonded SiC ceramics.

Sample label	Interlayer composition (mole ratio)					Target constituents of interlayer	Joining process (°C/MPa/min)
	Ti	BN	B_4C	Al	Si		
TBN45	3	2	0	0	0	$TiB_2 + 2TiN$	1450/12.5/60
TBN60	3	2	0	0	0	$TiB_2 + 2TiN$	1600/12.5/60
TBC45	3	0	1	0	0	$2TiB_2 + TiC$	1450/12.5/60
TBC60	3	0	1	0	0	$2TiB_2 + TiC$	1600/12.5/60
TBNA45	1	2	0	2	0	$TiB_2 + 2AlN$	1450/12.5/60
TBNA70	1	2	0	2	0	$TiB_2 + 2AlN$	1700/12.5/60
TBCS70	2	0	1	0	1	$2TiB_2 + SiC$	1700/12.5/60

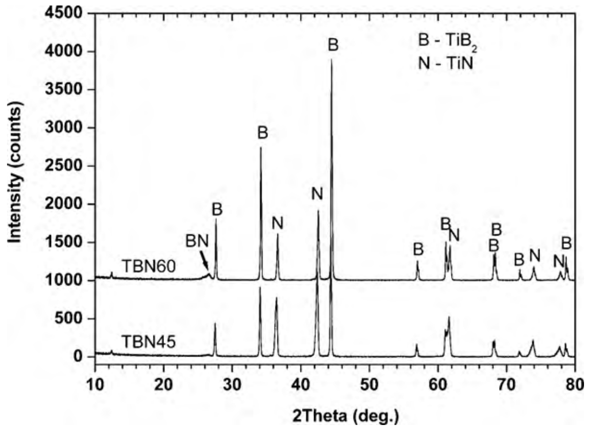

Fig. 1. XRD patterns of joints TBN45 and TBN60 in Ti–BN system that were joined at 1450 °C and 1600 °C, respectively.

mation of composite is finished at temperatures above 1450 °C. No reaction-formed layer is observed between interlayer and SiC substrate, where cracking along their interface takes place after the joining process. These results demonstrate that Ti–B_4C system does not yield good bond for SiC substrates at present joining conditions.

Reasons why Ti–BN and Ti–B_4C systems fail to adhere strongly to SiC substrate are mainly attributed to the following two aspects. On the one hand, the thermal expansion coefficients of composite interlayers are larger than that of SiC substrate, and therefore the residual stress in interlayer and the weak adhesion at interface occur within all SiC joints during cooling from the joining temperature. Choy et al. studied the adhesion of TiB_2, TiC and TiN protective coatings to SiC fibers and found an adhesion sequence in $TiB_2 > TiC > TiN$, which was strongly correlated with their thermal properties.[16] On the other hand, although the diffusion of Si and C from SiC base to starting Ti particles and the subsequent formation of TiC and Ti–Si silicide probably take place at these joining temperatures,[17] they are negligible because the contact area between Ti and SiC is small, which results from the large particle size of titanium that is surrounded by fine BN or B_4C (Table 1).

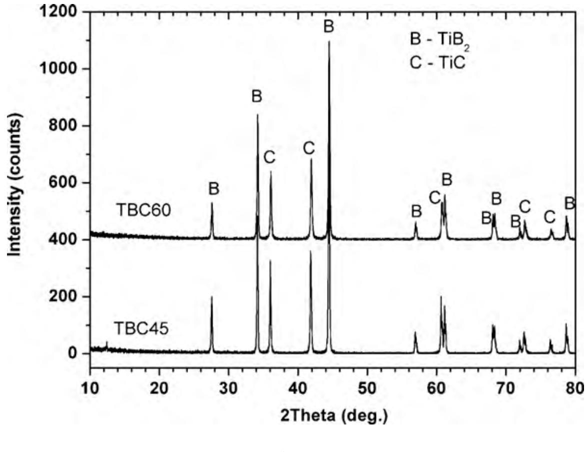

Fig. 2. XRD patterns of joints TBC45 and TBC60 in Ti–B_4C system that were bonded at 1450 °C and 1600 °C, respectively.

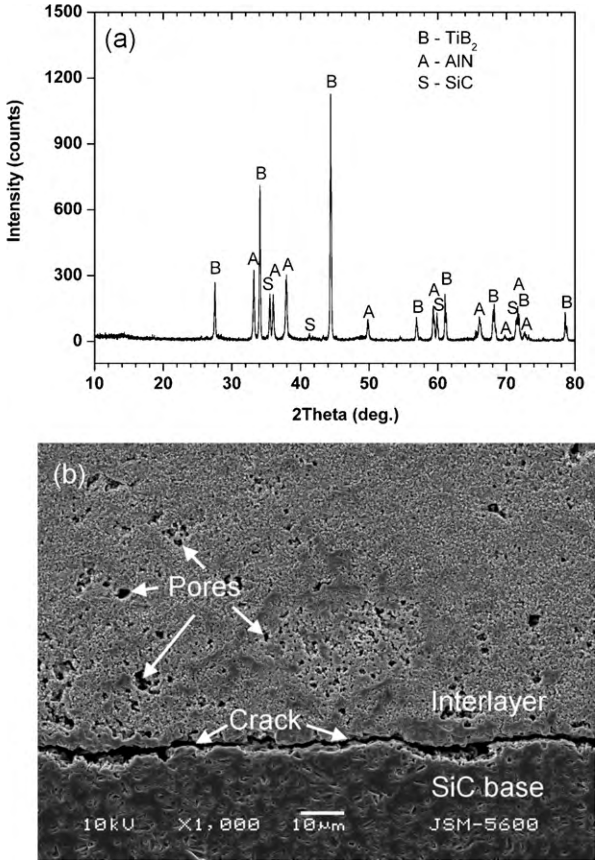

Fig. 3. (a) XRD pattern and (b) SEM image of joint TBNA45 that was sintered at 1450 °C using Ti–BN–Al joining materials.

3.2. Ti–BN–Al system

Reasonably, we add Al into the joining material Ti–BN, which not only improves the wetting properties of interlayer on SiC surface but also decreases the coefficient of thermal expansion of composite interlayer because AlN is formed instead of TiN. As expected, Ti–BN–Al joining material results in the connection of SiC plates at 1450 °C (TBNA45). The XRD pattern of interlayer suggests that the main phases are TiB_2 and AlN (Fig. 3(a)). The appearance of SiC phase in Fig. 3(a) comes from SiC substrate when conducting XRD measurement. Although SiC blocks are successfully bonded by Ti–BN–Al starting material, the resulted interlayer is not dense and cracks along interface are obvious (Fig. 3(b)). This suggests that the densification of joint is not accomplished and the adhesion of interlayer to SiC substrate is still weak at 1450 °C. Accordingly, high joining temperatures were applied to improve the interlayer density and slow cooling rate was used to compromise the cracking at interface.

Microstructural observations of SiC joints performed at 1700 °C (TBNA70) and 1800 °C (TBNA80) at a cooling rate of 5 °C/min are presented in Fig. 4(a) and (b), respectively. The XRD result of joint TBNA45 shows that the reaction formation of TiB_2–AlN composite from Ti–BN–Al is finished at 1450 °C (Fig. 3(a)), and therefore the phase constituents of joints TBNA70 and TBNA80 are fairly assumed to be the same as that of TBNA45. According to the color contrast of exposed

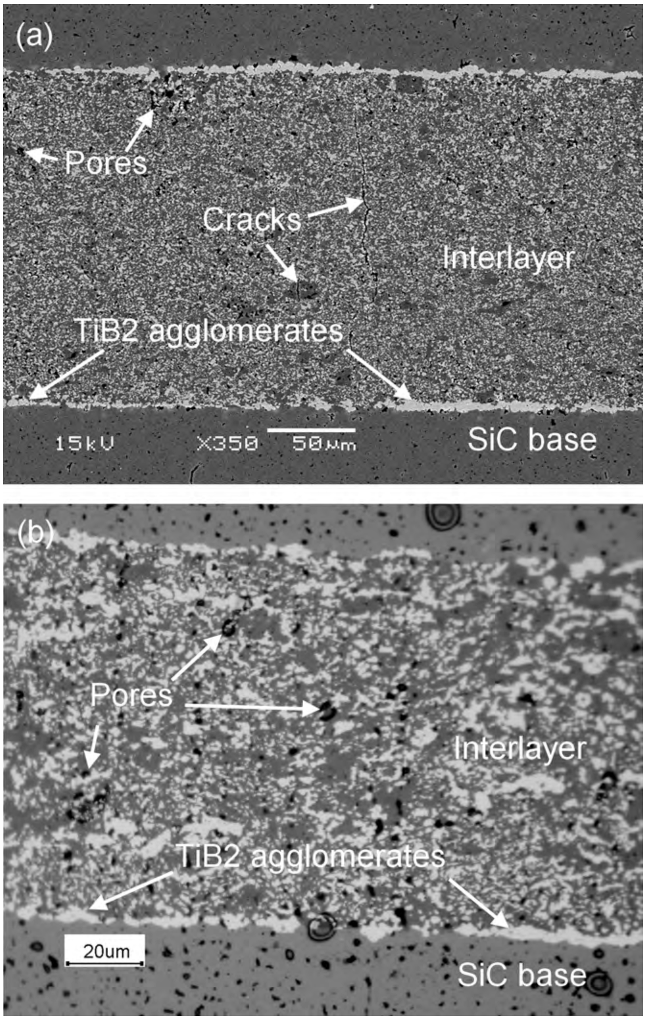

Fig. 4. (a) Backscattered SEM image of joint TBNA70 and (b) optical microstructure of joint TBNA80 in Ti–BN–Al system that were joined at 1700 °C and 1800 °C, respectively.

phases in interlayer, it is ease to conclude that the bright phase and the gray phase are TiB_2 and AlN, respectively, coexisting with small amount of dark pores. Note that two main phases distribute homogeneously inside interlayer and the interfaces between interlayer and SiC substrate are crack-free. Some cracks nearly perpendicular to interface are found inside SiC joints (as indicated in Fig. 4(a)), which are attributed to the thermal expansion mismatch between interlayer and SiC base, and the subsequently induced thermal stress.

It is interesting to find that some TiB_2 grains seem to agglomerate at interface in joint TBNA70 and TBNA80. This microstructure can be explained by the reaction path during joining process. ZrB_2–AlN composite prepared using Zr–Al–BN starting materials shows fine and homogeneous microstructure because of the low melting point of Al and the high solubility of Al in Zr.[18,19] The contact angle data suggest that the wetting of Al or aluminium alloy on BN and SiC is usually good.[20–23] These studies not only give an explanation of the uniform microstructure inside interlayer in present study but also remind the good spreading of Ti–Al liquid phase on SiC surface. Due to the faster diffusion coefficient of Al, the agglomerates of AlN are not remarkable. The slower diffusion of Ti, therefore, is responsible for the agglomerate of TiB_2 grains at interface. Similar phenomenon, e.g. agglomeration of a VN reaction layer at the interface of joint, was also reported for Si_3N_4/Si_3N_4 joint as brazed by Au–Ni–V filler alloys.[24]

3.3. Ti–B_4C–Si system

Following the same train of thought, the joining of SiC was conducted by adding Si into Ti–B_4C powder mixture and sintering at 1800 °C at a cooling rate of 5 °C/min (TBCS80). SEM image of joint TBCS80 is shown in Fig. 5(a), in which dense interlayer and crack-free interface between interlayer and SiC base are successfully produced. Representatively backscattered SEM around interface is shown in Fig. 5(b), in which the dark phase and the bright phase inside interlayer correspond to SiC and TiB_2, respectively, based on the EDS results in Fig. 5(c) and (d). Cracks generally normal to interface are also found in joint TBCS80 because the thermal stress within interlayer is compressive.[25,26] The reactions and thermodynamic calculation of some boride-containing composites were elaborated in reference [18], from which we can see that the reactions of Ti–B_4C–Si satisfy the thermodynamic possibility to run (the free enthalpy of reaction at 1500 K: −509.429 kJ) and are highly exothermic (the enthalpy of reaction: −569.526 kJ). Therefore, the TiB_2–SiC composite interlayer is formed preferably at present joining conditions.

The improved SiC joint in Ti–B_4C–Si system is attributed to some chemical reactions at interfaces, which are accelerated by the addition of element Si. Gottselig et al.[27] investigated the reaction behavior of Ti film sputtered on SiC in the temperature range of 1250–1500 °C and found that the formation of Ti_3SiC_2 leads to join strengths comparable to the strength of SiC substrate. Li et al.[28] studied the brazing of SiC at 1400 °C using Ti–78%Si alloy, in which TiC and Ti_5Si_3 phases are identified at the interface and responsible for the bonding of SiC. These results demonstrate that the reactions between Ti and SiC have significant influence on the microstructure and final mechanical properties of joints. For present study, Ti–Si intermetallic melt would be formed firstly and wetted with SiC substrate well at the joining temperature due to the good wettability.[28–30] Then B_4C particles and partial SiC substrates dissolve into the liquid according to their solubility. The following precipitations of TiB_2 and SiC phases on the SiC substrates as well as the reaction products of Ti–SiC at interface lead to the good bonding of joint. More detailed micro-analysis on the interface area will be helpful to understand the joining mechanisms.

3.4. Mechanical properties of SiC joints

For the dense joints TBNA80 and TBCS80, Vickers hardness of interlayer and bending strength of bonded SiC joint were measured, as listed in Table 3. We can see that both hardness and strength of TBNA80 are inferior to those of TBCS80. The higher hardness of the latter joint is due to the larger amount of hard TiB_2 phase formed in composite interlayer. The signifi-

Table 3
Summaries of the joining process and the characteristics of SiC joints.

Sample ID	Starting materials (mole ratio)	Joining processing (°C/min/MPa)	Interlayer thickness (μm)	Vickers hardness (GPa)	Bending strength (MPa)
TBNA80	Ti/2BN/2Al	1800/60/15	102	16.5 ± 0.8	65 ± 19
TBCS80	2Ti/B_4C/Si	1800/60/15	68	22.2 ± 1.0	142 ± 44
$TBCS80_t$	2Ti/B_4C/Si	1800/60/15	24	–	169 ± 60
$TBCS80_g$	2Ti/B_4C/Si	1800/60/15	69	–	148 ± 42

t, tape-like joining material; g, 400# ground SiC substrate.

cantly lower strength of TBNA80 (65 MPa) than that of TBCS80 (142 MPa) is related to the following aspects: on the one hand, the microstructure of interlayer, especially the agglomerate of TiB_2 phase at interface, affects mechanical properties. On the other hand, comparing with the reactive element Si in Ti–B_4C–Si system, element Al in Ti–BN–Al system melts at relatively low temperature and finally leads to high porosity in interlayer (comparing Fig. 4(b) with Fig. 5(b)). In addition, the cracks induced by thermal stress in both joining systems have effects on mechanical strength. However, since the tensile stress during bending tests is parallel to crack direction, this effect is not remarkable and predominant.[26]

To further alleviate the cracking issues in above SiC joints and improve the joint strengths, we prepared a SiC joint using a thin Ti–B_4C–Si tape as joining material at the same conditions to TBCS80, i.e. $TBCS80_t$. The strength of SiC joint is measured to increase from 142 MPa in TBCS80 to 169 MPa in $TBCS80_t$ with decreasing interlayer thickness from 68 μm to 24 μm, as listed in Table 3. Furthermore, SiC can join to itself through diffusion bonding or superplastic joining process, which requires good surface condition and fine microstructure of the host SiC material. The reaction bonding process used in present work, however, does not need such requirements, although these variables have close relationship with the final mechanical properties of SiC joints. To confirm this, we ground the SiC plates by 400# diamond wheel (average surface roughness Ra = 0.13 μm) and joined the ground SiC by Ti–B_4C–Si powder mixture at 1800 °C, namely $TBCS80_g$. The obtained SiC joint exhibits an average bending strength of 148 MPa, which is fairly close to that of TBCS80 (Table 3).

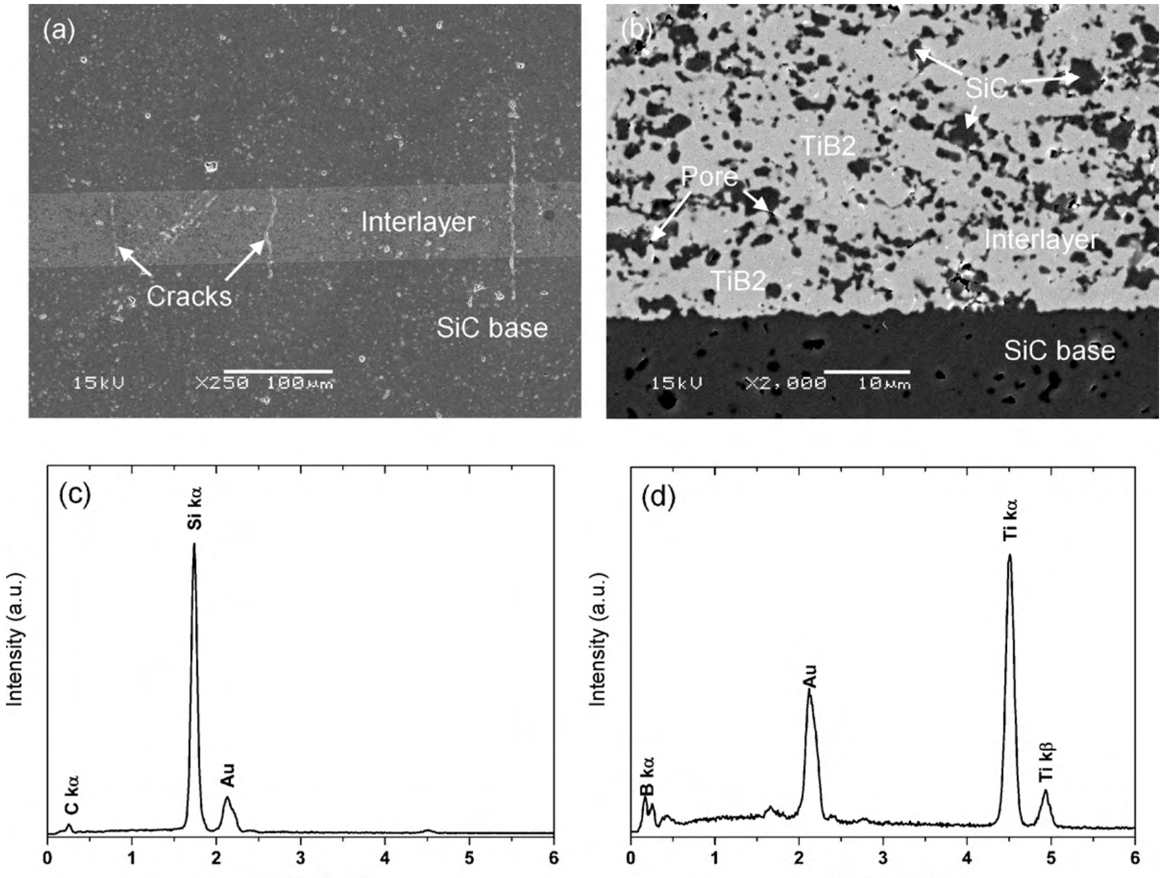

Fig. 5. (a) SEM image of joint TBCS80 that was bonded at 1800 °C at a cooling rate of 5 °C/min using Ti–B_4C–Si powder mixture. (b) The representatively backscattered SEM around the interface. EDS results of the dark phase and the bright phase in (b) are presented in (c) and (d), respectively.

4. Conclusion

SiC ceramics were reaction joined in the temperature range of 1450–1800 °C using TiB_2-based composites starting from four kinds of joining materials, namely Ti–BN, Ti–B_4C, Ti–BN–Al and Ti–B_4C–Si. For the former two systems, SiC substrates separate completely from interlayer after joined at temperatures up to 1600 °C. By adding Al into Ti–BN system, the connection of SiC substrates is achieved at 1450 °C and the main phases of interlayer are confirmed to be TiB_2 and AlN. Dense SiC joints with crack-free interface have been produced from Ti–BN–Al and Ti–B_4C–Si systems at 1800 °C, i.e. joints TBNA80 and TBCS80. Average bending strengths of joints TBNA80 and TBCS80 are 65 MPa and 142 MPa, respectively. The strength of TBCS80 joint can be further improved by decreasing the interlayer thickness.

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