Elsevier Editorial System(tm) for Materials Characterization

Manuscript Draft

Manuscript Number: MTL-17021R3

Title: Effect of holding time on microstructure and mechanical properties of SiC/SiC joints brazed by Ag-Cu-Ti+B4C composite filler

Article Type: Research paper

Keywords: brazing, holding time, composite filler, nano-indentation

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Abstract: The composite fillers have a number of advantages comparing with the traditional filler metals, and have been widely used for brazing ceramics. However, previous researches mainly focus on the strengthening mechanism of either whiskers or particles. It is still of great interest to investigate the reinforcement effect with the presence of both whiskers and particles. In this study, Ag-Cu-Ti+B4C composite filler was developed to braze SiC ceramics, and effects of holding time on the microstructure evolution and mechanical properties of the joints were investigated in detail. With the prolongation of holding time, the overall thickness of Ti3SiC2+Ti5Si3 layers adjacent to SiC ceramic was increased correspondingly and the reaction between active Ti and B4C particles were promoted more extensively. The bending strength of the joints increased with holding time until the maximum bending strength of 140 MPa was reached and then decreased dramatically. The hardness and Young's modulus of the joints were characterized by nano-indentation to reveal the strengthening of the brazing seam. In addition, the strengthening mechanism of the joints brazed by the Ag-Cu-Ti+B4C composite filler was proposed on the basis of experimental observation and theoretical analysis.

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To: Editor, *Materials Characterization*

Dear Editor:

On behalf of my co-authors, we thank you very much for giving us an opportunity to revise our manuscript. We appreciate editors and reviewers very much for their positive and constructive comments and suggestions on our manuscript entitled "Effect of holding time on microstructure and mechanical properties of SiC/SiC joints brazed by Ag-Cu-Ti+B_4C composite filler".

We have studied editors' comments carefully and tried our best to revise our manuscript according to the comments. Attached please find the revised version, which we would like to submit for your kind consideration. We would like to express our great appreciation to you and editors for comments on our paper. Looking forward to hearing from you.

Thank you and best regards.

Sincerely yours,

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Detailed Responses to Reviewers

Reviewers' comments:

Reviewer #1:

Thank you for your comments. We are very sorry for all the mistakes in this paper. According to your helpful recommendation, the written style in the English language has been modified and the mistakes have been corrected in the revised manuscript. In addition, the corrections recommended regarding the content of the paper have been listed as follows.

1. At the beginning of first paragraph of page 5 it says: "The load-carrying ability of the Ti_3SiC_2+Ti_5Si_3 layers could be weakened when its thickness exceeds a certain value." It is necessary to specify what value is that.

Response: Thank you for your comments. Based on your recommendation, the thickness of Ti_3SiC_2+Ti_5Si_3 reaction layers was added. Based on the experimental data, the load-carrying ability of Ti_3SiC_2+Ti_5Si_3 layers could be weakened when their thickness exceeded 2.1 μm.

Revised manuscript, Page 5 Paragraph 1

Based on the experimental data, the load-carrying ability of Ti_3SiC_2+Ti_5Si_3 layers could be weakened when their thickness exceeded 2.1 μm.

2. At the middle of second paragraph of page 5 it says: " The EDS result revealed that this grey phase was made up of $Ti_{69.5}Cu_{21.6}Ag_{8.9}$ (at.%). Based on the previous research [26], the grey phase was likely to be the mixture of TiB and TiC phases." If the grey phase was a mixture of TiB and TiC phases, where were the Cu and the Ag detected during the EDS analysis?

Response: Thank you for your comments. The grey domain was likely to be a mixture of TiB and TiC phases, which was distributed in the Cu-based solid solution.

Revised manuscript, Page 5 Paragraph 2

The EDS result revealed that this grey domain was made up of $Ti_{69.5}Cu_{21.6}Ag_{8.9}$ (at.%). Based on the previous research [26], the grey domain was likely to be a mixture of TiB and TiC phases, which was distributed in the Cu-based solid solution.

Title page

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Effect of holding time on microstructure and mechanical properties of SiC/SiC joints brazed by Ag-Cu-Ti+B_4C composite filler

Abstract

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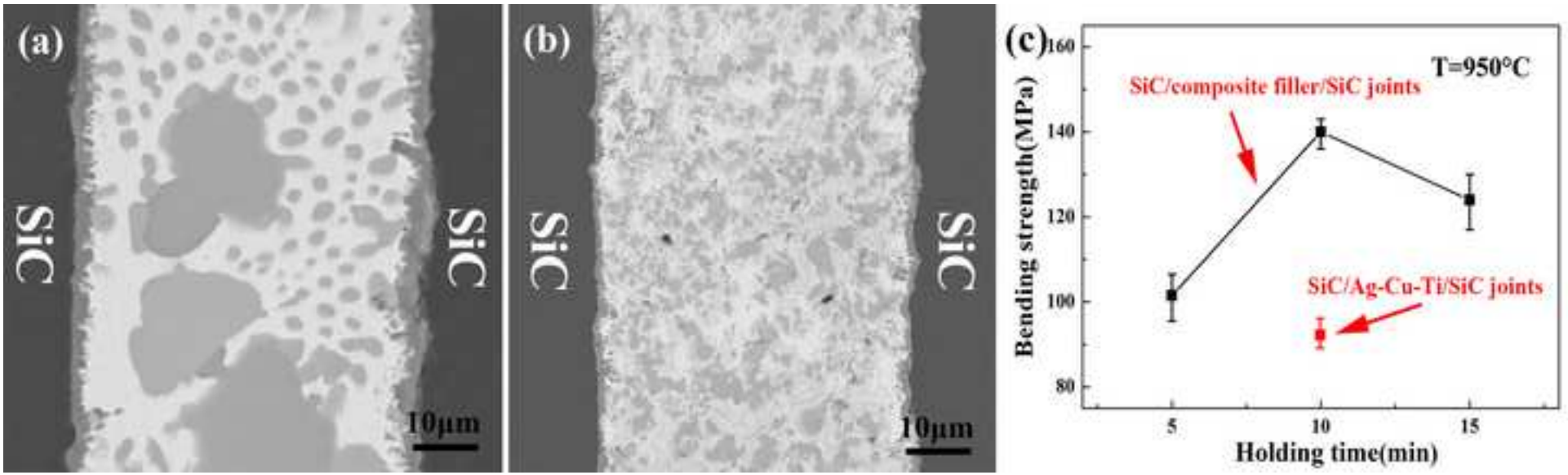
Graphical Abstract



***Highlights (for review)**

1. Ag-Cu-Ti+B_4C composite filler was developed to braze SiC ceramic.

2. Effects of holding time on microstructure and mechanical properties were studied.

3. The maximum bending strength increased from 92 MPa to 140 MPa with B_4C addition.

4. The strengthening mechanism of the joints brazed by composite filler was discussed.

Effect of holding time on microstructure and mechanical properties of SiC/SiC joints brazed by Ag-Cu-Ti+B_4C composite filler

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Abstract

The composite fillers have a number of advantages comparing with the traditional filler metals, and have been widely used for brazing ceramics. However, previous researches mainly focus on the strengthening mechanism of either whiskers or particles. It is still of great interest to investigate the reinforcement effect with the presence of both whiskers and particles. In this study, Ag-Cu-Ti+B_4C composite filler was developed to braze SiC ceramics, and effects of holding time on the microstructure evolution and mechanical properties of the joints were investigated in detail. With the prolongation of holding time, the overall thickness of Ti_3SiC_2+Ti_5Si_3 layers adjacent to SiC ceramic was increased correspondingly and the reaction between active Ti and B_4C particles were promoted more extensively. The bending strength of the joints increased with holding time until the maximum bending strength of 140 MPa was reached and then decreased dramatically. The hardness and Young's modulus of the joints were characterized by nano-indentation to reveal the strengthening of the brazing seam. In addition, the strengthening mechanism of the joints brazed by the Ag-Cu-Ti+B_4C composite filler was proposed on the basis of experimental observation and theoretical analysis.

Keywords: brazing, holding time, composite filler, nano-indentation

1 Introduction

SiC ceramic is an important structural material for aerospace, nuclear and transportation industry applications because of its excellent mechanical properties and chemical stability at high temperature [1-3]. However, it is almost impossible to machine SiC ceramic due to its extreme hardness and brittle

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nature. Therefore, the most popular approach for fabricating SiC ceramic component is to join small or simple ceramic pieces together to form the desired structures [4-6].

A wide range of technologies have been developed for joining ceramics, for example, brazing, transient liquid phase bonding and diffusion bonding [7-11]. Among all the available joining methods, brazing is a versatile technique to join the ceramics to themselves or to metals because of its convenience, cost-effectiveness and high-quality [12-13]. Unfortunately, two main problems need to be solved to achieve a successful brazing. The first one is that most filler metals have poor wettability on ceramics [14-15]. This problem can be solved by using active filler metals consisting of Ti or Zr. The active element Ti in filler metals can alter the surface chemistry of the ceramics by forming Ti_3SiC_2+Ti_5Si_3 layers reducing the wetting angle of the molten filler metals on the ceramics [16]. The second problem is the thermal mismatch between ceramics and filler metals. The difference of coefficient of thermal expansion (CTE) leads to a high level of tensile residual stresses in the joints, which seriously reduces the strength of the joint. The problem can be alleviated by adding low CTE materials (particles or fibers) into filler metals. The addition of low CTE materials will release the CTE mismatch between ceramics and the brazing seam, therefore improve the joint strength significantly [17-18]. He et al. [19] indicated that the addition of 10 vol.% Mo particles into Ag-Cu-Ti filler resulted in up to 114.7% improvement in the bending strength of the Si_3N_4/Si_3N_4 joints. Wang et al. [20] introduced TiN particles as reinforcement in Ag-Cu-Ti filler for joining of Si_3N_4 ceramic to 42CrMo steel. The bending strength of the joints containing 30 vol% TiN particles was about 100% higher than that of the joints brazed without TiN particles. Therefore, these low CTE materials are usually called reinforcements. Unfortunately, directly adding reinforcements has many intrinsic disadvantages, such as heterogeneous distribution and poor wetting ability [21-22]. Hence, in situ synthesized reinforcements were developed with considerable advantages, such as fine size, uniform distribution and favorable cohesion with matrix [23]. Zhu et al. [24] reported that, by introducing 12 vol% short carbon fibers into Ag-Cu-Ti filler, TiC particles were formed in the brazing seam and an approximately 30% increase in the shear/tensile strength of the stainless steel/alumina joints was observed. Qiu et al. [25] investigated the shear strength of the Al_2O_3/TC4 brazed joints with the reinforcement of in situ formed TiB whiskers, which was about 36% higher than that of the joints brazed without TiB whiskers. The above investigations revealed the great benefits of using synthesised whiskers or particles as reinforcement in the brazing seam. Unfortunately, brazed joints co-enhanced by both whiskers and

particles were rarely reported. In our previous study [26], B_4C reinforced Ag-Cu-Ti composite filler was developed to braze SiC ceramic and the characteristic of interfacial microstructure was initially analyzed. However, the strengthening mechanism and effects of holding time on the joints still remain to be clarified.

In this investigation, Ag-Cu-Ti+B_4C composite filler was adopted to braze SiC ceramic. The effect of holding time on the microstructure evolution and mechanical properties of the joints was systematically investigated. Nano-indentation was employed to analyze the mechanical properties of the brazing seam of the joints. In addition, the strengthening mechanism of the joints was proposed.

2 Materials and experimental procedures

The base SiC ceramic material used in the experiment was provided by Shanghai Institute of Ceramics, which was produced by pressureless sintering. The dimension of the ceramic for brazing was 3 mm × 4 mm × 20 mm. The surfaces to be joined together were coarsely ground using SiC papers and polished with diamond suspensions with a minimum grain size of 1 μm. Then the specimens were degreased and cleaned with acetone in an ultrasonic bath for 15 min prior to brazing. The composite filler consisted of Ag powders, Cu powders, TiH_2 powders (the average particle sizes of above three powders are less than 50 μm) and B_4C powders with an average particle size of 10 μm. The content of Ag, Cu, TiH_2 and B_4C in composite filler was (in wt.%): 65.5%, 25.5%, 7.5% and 1.5%, respectively. TiH_2 powers were employed to replace Ti powers in the filler metal, because Ti powers tended to be oxidized during mechanical milling. During brazing, when the heating temperature reached 600-800 °C, TiH_2 powers were decomposed into Ti by the following reaction [27]:

$$TiH_2 = Ti + H_2 \quad (1)$$

The mixture was argon atmosphere-milled for 1 h in a QM-SB planetary ball mill to prepare composite filler. The overall weight of the composite filler for each joint was fixed to be 20 mg. The as-milled composite filler was mixed with a small amount of high viscosity cellulose nitrate binder to form a composite brazing paste. Then the composite paste was carefully coated between SiC ceramic plates and the assembly was held in a graphite jig. A compressive load of 0.015 MPa was applied normal to the joint surface to prevent any unfavorable movement. The joint assembly was heated to the brazing temperature of 950 °C at a rate of 10 °C/min, isothermally soaked for 5-15 min and then cooled down

to room temperature at 5 °C/min. The brazing process was carried out in a vacuum of 1.3×10^{-3} - 1.7×10^{-3} Pa.

After brazing, the microstructure of the joints was analyzed using scanning electron microscope (SEM, Helios NanoLab 600i) equipped with an energy dispersive spectroscopy (EDS). The morphology and diffraction patterns for phase identification of the reaction phases were analyzed by transmission electron microscopy (TEM, Tecnai G^2 F30). The TEM sample with a thickness of 200nm was prepared by using focused ion beam (FIB, Helios NanoLab 600i) technique. The phases in the joint were also employed by an X-ray diffraction spectrometer with Cu-Kα radiation (XRD, D8-Advance). The hardness and Young's modulus across the joints were characterized by using a nano-indenter with a Berkovich indenter tip. The bending strength of the joints produced with different holding time was evaluated and each test was repeated five times, as demonstrated in Ref. [26]. In addition, the fracture surfaces of the joints were also observed by SEM.

3 Results and Discussion

3.1 Effect of holding time on the microstructure evolution of the SiC/SiC joints

Fig. 1 shows the microstructure evolution in backscattered electron (BSE) mode of the joints brazed with composite filler at 950 °C for different holding time. It could be seen that the microstructure of the joints changed significantly with the prolongation of holding time. The joints were mainly composed of two reaction zones: Ti_3SiC_2+Ti_5Si_3 layers adjacent to SiC ceramic substrates and the brazing seam reinforced by TiB whiskers and TiC particles, as demonstrated in our previous study [26]. When the holding time was 5 min, the reaction between Ti and B_4C particles was insufficient, which resulted in the aggregation of B_4C particles in the brazing seam. Thus, the amount of in situ synthesized TiB and TiC reinforcements in the brazing seam was decreased. As the holding time reached 10 min, almost all of the B_4C particles reacted with Ti during the brazing process. The reaction products such as TiB whiskers and TiC particles were dispersed homogeneously in the brazing seam, which made the brazed joint appear as a metal matrix reinforced by whiskers and particles.

High magnification BSE images of the microstructure in the joints brazed at 950 °C for different holding time are shown in Fig. 2. It could be seen that the holding time had a significant effect on the interfacial microstructure of the joints. With the increase of holding time, the overall thickness of Ti_3SiC_2+Ti_5Si_3 layers increased correspondingly. At the shorter holding time of 5 min, the average

thickness of Ti_3SiC_2+Ti_5Si_3 layers was only about 1.2 μm and cracks were formed adjacent to the substrates due to the insufficient reaction between Ti and SiC ceramic. When the holding time was increased to 15 min, Ti_3SiC_2+Ti_5Si_3 layers grew further and reached approximately 2.7 μm. Based on the experimental data, the load-carrying ability of Ti_3SiC_2+Ti_5Si_3 layers could be weakened when their thickness exceeded 2.1 μm. Microcracks were also formed due to the brittleness of Ti_3SiC_2+Ti_5Si_3 phases, which deteriorated the mechanical properties of the joints. Based on the above analysis, it could be concluded that the increase of holding time could facilitate the diffusion of Ti toward SiC ceramic and enhance the interfacial reaction since diffusion was a thermally activated process. Longer holding time resulted in the faster growth of Ti_3SiC_2+Ti_5Si_3 layers, thus favored the increase of total thickness of Ti_3SiC_2+Ti_5Si_3 layers. In addition, the increase of holding time also stimulated the reaction between Ti and B_4C particles. Hence, in situ synthesized TiB and TiC reinforcements were dispersed more homogeneously in the brazing seam, which was beneficial for the uniformity and refinement of the microstructure of the brazing seam.

3.2 Microstructure around B_4C_p reinforcement

With the addition of B_4C particles in composite filler, the microstructure of the brazing seam is dramatically changed. Fig. 3 illustrates the backscattered electron image and the corresponding elemental distribution images of B_4C particles in the joint brazed at 950 °C for 10 min. Due to the limitation of analyzing light elements by the EDS detector in this study, B and C elements are not presented. It could be observed that the B_4C particles were intimately embedded in the Ag-Cu-Ti filler matrix and a grey domain marked by A in Fig. 3(a) was formed surrounding the B_4C particles. According to Fig. 3(d), Ti-rich region was detected around the B_4C particles, which indicated that Ti segregated outside B_4C particles. The EDS result revealed that this grey domain was made up of $Ti_{69.5}Cu_{21.6}Ag_{8.9}$ (at.%). Based on the previous research [26], the grey domain was likely to be a mixture of TiB and TiC phases, which was distributed in the Cu-based solid solution. In order to determine the reaction phases in the brazing seam, XRD analysis was performed and the result was given in Fig. 4. The peaks of TiB and TiC phases confirmed their existence in the brazing seam which in turn supported the above analysis of the microstructure.

The morphology and crystal structure of reaction products around B_4C particle were shown in Fig. 5. The specimen for TEM analysis was firstly hand-polished and finally cleaned using focused ion beam (FIB). According to the selected-area electron diffraction patterns in Fig. 5 (b) and (c), the

needle-shaped reinforcements were TiB whiskers, while the equiaxed reinforcements were TiC particles. The average diameter of TiB whiskers was approximately 20 nm and the average aspect ratio of TiB whiskers was calculated to be approximately 15.4. The formation of these two phases confirmed that B_4C particles could react with active Ti in the molten filler.

He et al. [19] suggested that new phases in the melt usually preferred to precipitate around impurity according to the crystallographic theory. The TiB whiskers and TiC particles in the molten filler could act as nucleation sites for Ag-based and Cu-based solid solution. Therefore, the higher amount of TiB whiskers and TiC particles in the molten filler, the more nucleation centers would be supplied for Ag-based and Cu-based solid solutions. It was beneficial for the uniformity and refinement of the microstructure of the brazing seam. And a desired homogenous microstructure in the brazing seam was obtained due to the addition of B_4C particles, as shown in Fig. 1(b). The reaction equation between Ti and B_4C particles was as below:

$5Ti+B_4C=4TiB+TiC$

$\Delta G^0(kJ/mol)=0.006T-181.53$ (2)

The ΔG_0 value of forming TiB and TiC phases calculated by reaction (2) was about -175.83 kJ/mol at 950 °C. The Gibbs free energy of formation of TiB and TiC phases was negative, which indicated that Ti could react with B_4C particles to form TiB and TiC phases. However, the reaction between Ti and B_4C particles is still arguable. Lin et al. [28] investigated the B_4C substrate by molten Ni-Ti alloys using sessile drop method. The improved wettability was attributed to the formation of TiB_2 and TiC phases at liquid-solid interface. The formation of TiB_2 and TiC phases at the interface between B_4C substrate and Ni-Ti alloys was different from those (TiB and TiC phases) in this research. The conventional thermodynamics was an effective criterion to determine whether chemical reaction could occur or not. And the chemical reaction with the lowest ΔG^0 value possessed the greatest tendency among all possible chemical reactions. In terms of the Ti/B_4C system, the following chemical reactions might occur during the brazing process.

$3Ti+B_4C=2TiB_2+TiC$

$\Delta G^0(kJ/mol)=0.01T-160.55$ (3)

$TiB_2+Ti=2TiB$

$\Delta G^0(kJ/mol)=0.002T-10.49$ (4)

The ΔG^0 value for reaction (3) was about -151.05 kJ/mol at 950 °C, which was higher than that of reaction (2). It could be indicated that TiB and TiC phases were energetically easier to form than TiB_2 and TiC phases. Moreover, because the ΔG^0 value of reaction (4) was -8.59 kJ/mol at 950 °C, TiB_2 phase could react with Ti to form TiB phase. The atomic ratio of Ti to B_4C in the composite filler was 5.6 : 1. Therefore, TiB whiskers would be favorably formed in the brazing seam due to the presence of sufficient Ti around the B_4C particles. Fan et al. [29] indicated that the growth rate of TiB whisker along the needle direction was more than 6 times higher than that of TiB_2 phase. The estimated diffusion coefficient for B in TiB whisker along the needle direction was about 45 times larger than that in TiB_2 phase at the brazing temperature, despite the fact that the activation energies for B diffusion in both TiB whisker and TiB_2 phase were effectively the same. Therefore, TiB_2 phase was just a transitional phase and would change to TiB whisker by consuming Ti, because TiB whisker was thermodynamically more stable.

3.3 Mechanism of microstructure evolution of the joints

Based on the above analysis, the addition of B_4C particles in composite filler has an enormous effect on the microstructure evolution of the joints. The microstructure evolution and formation mechanism of related phases of the joints are proposed in Fig. 6. During the brazing process, when the temperature reached 780 °C, the Ag-Cu eutectic parts in the filler firstly melted and Ti began to dissolve in the liquid. When the joint assembly was heated to the brazing temperature of 950 °C in Fig. 6 (a), the active Ti diffused and enriched the region next to the SiC ceramic and B_4C particles. At the interface, Ti reacted with SiC ceramic and a Ti_3SiC_2+Ti_5Si_3 layer was formed along the ceramic. Ti_3SiC_2+Ti_5Si_3 layers were formed by the following reaction [30]:

$$14Ti+6SiC=3Ti_3SiC_2+Ti_5Si_3 \quad (5)$$

Meanwhile, Ti also reacted with B_4C particles resulting in the precipitation of TiB whiskers and TiC particles in the brazing seam, as shown in Fig. 6(b). Compared to the joints without B_4C addition, the average thickness of Ti_3SiC_2+Ti_5Si_3 layers in the joints brazed by composite filler decreased dramatically. The B_4C particles in molten filler consumed large amounts of Ti, therefore the concentration of Ti at the SiC ceramic surface was reduced, which resulted in thinner Ti_3SiC_2+Ti_5Si_3 layers. As the brazing process proceeded, Ti was continuously consumed by the reaction with SiC ceramic substrates and B_4C particles. Therefore, a concentration gradient was formed in the brazing seam which in turn promoted the diffusion of Ti toward SiC ceramic and B_4C particles. With the

prolongation of holding time in Fig. 6(c), the total thickness of Ti_3SiC_2+Ti_5Si_3 layers adjacent to SiC ceramic increased gradually. Also, the increase of holding time favored reaction (3) and reaction between Ti and B_4C particles are more sufficient. Thus, the fraction of TiB whiskers and TiC particles reinforcements in the brazing seam were increased. In addition, when the process temperature dropped, the joints began to solidify and Ag-based and Cu-based solid solutions were formed in the brazing seam as illustrated in Fig. 6(d).

3.4 Effect of holding time on the mechanical properties of the joints brazed with composite filler

Fig. 7 shows the bending strength of the joints brazed at 950 °C for different holding time. For comparison, the bending strength of the joints brazed using pure Ag-Cu-Ti filler at 950 °C for 10 min was also given in this figure. The results revealed that the bending strength of the joints firstly increased and then decreased with the prolongation of holding time. The maximum bending strength of 140 MPa was obtained when the brazing process was performed at 950 °C for 10 min, which was 52% higher than the joints brazed without B_4C particles. The bending strength of the joints brazed by Ag-Cu-Ti filler at 950 °C for 10 min was 92 MPa, which was lower than the result reported by Liu et al. [31]. It was mainly due to the different sintering additives and synthesis process of SiC ceramic substrate. The improvement of bending strength was well dependent on the microstructure evolution of the joints. As analyzed in Section 3.1, a desirable microstructure similar to the metal-based composite reinforced by TiB and TiC reinforcements could be obtained in the brazing seam when brazed at 950 °C for 10 min. Not only the reinforcements with lower CTE in the brazing seam would refine the Ag-based and Cu-based solid solution, but also reduce the thermal mismatch between SiC ceramic and the brazing seam. That was why the bending strength of the joints was improved significantly with the presence of B_4C addition. Variation of the holding time influenced the bending strength of the joints, which could be attributed to two reasons. Firstly, the holding time affected the thickness of Ti_3SiC_2+Ti_5Si_3 layers next to SiC ceramic. It was essential to maintain certain thickness of Ti_3SiC_2+Ti_5Si_3 layers because it played a critical role in decreasing the thermal residual stress gradient between SiC ceramic and the brazing seam. At a shorter holding time of 5 min, the reaction between Ti and SiC ceramic was insufficient resulting in thinner or discontinuous Ti_3SiC_2+Ti_5Si_3 layers along the SiC ceramic. When Ti_3SiC_2+Ti_5Si_3 layers were thin, they could not transfer enough load and lead to lower bending strength. When the holding time was increased to 15 min, thicker but brittle Ti_3SiC_2+Ti_5Si_3 layers were formed which consequently deteriorated the bending strength of the joint.

Secondly, the holding time also affected the reaction between Ti and B_4C particles. Longer holding time could result in adequate reaction between Ti and B_4C particles, leading to an increased amount of TiB and TiC reinforcements in the brazing seam.

Typical fracture surfaces of the joints are observed after bending tests by SEM, as shown in Fig. 8. The EDS results of each region are listed in Table 1. The fractographic analysis was in excellent agreement with the microstructure analysis in Fig. 1. When the holding time was 5 min, the reaction between active Ti and SiC ceramic was inadequate to form a reliable interfacial bonding. The fracture mainly propagated along the Ti_3SiC_2+Ti_5Si_3 layers adjacent to SiC ceramic as shown in Fig. 8(a). The EDS analysis of region A also indicated that Ti_3SiC_2 phase mainly dominated the fracture surface. For the holding time of 10 min, almost all the B_4C particles reacted with active Ti forming in situ synthesized TiB and TiC reinforcements in the brazing seam. The fracture started at the SiC ceramic and then expanded across the brazing seam into the other SiC ceramic, as shown in Fig. 8(b). When the holding time increased to 15 min in Fig. 8(c), the thickness of Ti_3SiC_2+Ti_5Si_3 layers reached 2.7 μm and thus the load-carrying ability dropped during the bending tests.

3.5 Strengthening mechanism of the joints brazed by composite filler

Based on the above analysis, compared with the bending strength of the joints brazed with pure Ag-Cu-Ti filler, the joint strength was evidently improved using Ag-Cu-Ti+B_4C composite filler. The interfacial microstructure of the joints, the mechanical properties (hardness and elastic modulus) and the CTE of the brazing seam were analyzed to elucidate the strengthening mechanism.

Firstly, the interfacial Ti_3SiC_2+Ti_5Si_3 layers with an appropriate thickness were achieved using the composite filler. Iwamoto et al. [14] reported that interfacial Ti_3SiC_2+Ti_5Si_3 layers were new phases and exhibited different CTE. Too thick Ti_3SiC_2+Ti_5Si_3 layers could reduce the joint strength due to the brittleness of Ti_3SiC_2+Ti_5Si_3 layers. The overall thickness of Ti_3SiC_2+Ti_5Si_3 layers became thinner as some active Ti was consumed by the addition of B_4C particles, which might be in favor of a higher joint strength. Conversely, the load-carrying ability of Ti_3SiC_2+Ti_5Si_3 layers could be weakened when extremely thin Ti_3SiC_2+Ti_5Si_3 layers were formed. Hence, a suitable thickness of interfacial Ti_3SiC_2+Ti_5Si_3 layers was essential to achieve high mechanical properties of the brazed joints.

Secondly, the brazing seam was enhanced by in situ synthesized TiB whiskers and TiC particles produced by the reaction between B_4C and Ti in composite filler. Nano-indentation test was employed to study the mechanical behavior of the brazing seam of the joints brazed with and without the B_4C

addition. The hardness and elastic modulus of Ag-based solid solution were 2.22 GPa and 126.5 GPa respectively, while the hardness and elastic modulus of particle-reinforced brazing seam were 4.03 GPa and 191.8 GPa respectively. It could be indicated that the hardness and elastic modulus of particle-reinforced brazing seam were higher than those of the Ag-based solid solution due to the hardening effect by the TiB whiskers and TiC particles. To some extent, the strengthening of the brazing seam was beneficial for the brazed joints. Fig. 9 depicts the load-displacement curves of Ag-based solid solution and particle-reinforced Ag-based solid solution. The deformation behavior could be divided into elastic-plastic loading and purely elastic unloading. The Ag-based solid solution recovered 44 nm of the total 296 nm indentation depth corresponding to an elastic recovery of 14.9%, while the elastic recovery was 18.5% for particle-reinforced Ag-based solid solution. The results revealed that the plastic deformation of the brazing seam became smaller by incorporating B_4C particles into the joint, which was certainly detrimental to the relief of the thermal residual stresses. However, the adverse effect was not crucial because the hardness and elastic modulus of particle-reinforced brazing seam were still lower than those of the substrates due to the low content of B_4C in the composite filler.

Thirdly, the CTE reduction of the brazing seam also released the thermal mismatch existing between it and SiC ceramic, which could improve the joint strength. For joining SiC ceramic, the large CTE mismatch existing between SiC ceramic and Ag-Cu-Ti filler could cause high residual stresses in the joint, which deteriorated the joint strength. For this reason, in situ synthesized TiB whiskers and TiC particles with lower CTE values in Ag-based and Cu-based solid solutions could reduce the residual stresses in the brazing seam. The CTE reduction in the brazing seam could be estimated according to the formula (6), as reported in Ref. [23]:

$$\alpha_c=\alpha_m(1-\Sigma V_r)+\Sigma\alpha_r V_r \quad (6)$$

where α_c was the CTE of the particle-reinforced brazing seam, α_m and α_r were the CTE of the matrix of the brazing seam and reinforcing particles respectively, V_r was the volume fraction of reinforcing particles, which consisted of in situ synthesized TiB whiskers and TiC particles. The effect of B_4C particles addition on the CTE of the brazing seam is shown in Fig. 10. As mentioned above, the CTE of the brazing seam was reduced by 14.6% with the addition of 1.5 wt.% of B_4C particles, which was beneficial for improving the joint strength.

4 Conclusions

In this study, Ag-Cu-Ti+ B_4C composite filler was employed to braze SiC ceramic. The effect of holding time on the microstructure and mechanical properties of the joints was systematically investigated. The main conclusions could be drawn as follows:

(1) The microstructure of the joints brazed with Ag-Cu-Ti+B_4C composite filler mainly consisted of two regions: the Ti_3SiC_2+Ti_5Si_3 layers adjacent to SiC ceramic and Ag-based and Cu-based solid solutions reinforced by TiB whiskers and TiC particles.

(2) Holding time had a strong influence on the microstructure evolution and bending strength of the joints. As the holding time increased, the thickness of Ti_3SiC_2+Ti_5Si_3 layers adjacent to SiC ceramic increased gradually. In addition, longer holding time resulted in adequate reaction between Ti and B_4C particles, leading to an increase of TiB and TiC reinforcements in the brazing seam.

(3) The bending strength of the joints brazed by Ag-Cu-Ti+B_4C composite filler firstly increased with holding time but thereafter decreased dramatically. The maximum bending strength was 140 MPa when the joints were brazed at 950 °C for 10 min, which was 48 MPa (~52%) higher than that of the joints brazed using pure Ag-Cu-Ti filler.

(4) The in situ formation of TiB whiskers and TiC particles resulted in the decrease of the CTE mismatch between SiC ceramics and brazing seam, which was beneficial for reducing the residual stresses in the joint, improving the joint strength.

Acknowledgments

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China under Grant nos. 51275133 and U1537206. This work is also supported by “the Fundamental Research Funds for the Central University” (Grant No. HIT.BERTIII.201508).

References

[1] Ding SQ, Zeng YP, Jiang DL. In situ reaction bonding of porous SiC ceramics. Mater Charact 2008;59:140-143.

[2] Bai CY, Deng XY, Li JB, Jing YN, Jiang WK. Preparation and properties of mullite-bonded porous SiC ceramics using porous alumina as oxide. Mater Charact 2014;90:81-87.

[3] Xiong HP, Li XH, Mao W, Cheng YY. Wetting behavior of Co based active brazing alloys on SiC and the interfacial reactions. Mater Lett 2003;57:3417-3421.

[4] Mao YW, Li SJ, Yan LS. Joining of SiC ceramic to graphite using Ni–Cr–SiC powders as filler. Mater Sci Eng A 2008;491:304-308.

[5] Chen XG, Yan JC, Ren SC, Wang Q, Wei JH, Fan GH. Microstructure, mechanical properties, and bonding mechanism of ultrasonic-assisted brazed joints of SiC ceramics with ZnAlMg filler metals in air. Ceram Int 2014;40:683-689.

[6] Nicholas MG. Materials Science and Technology. Wiley Online Library; 2006.

[7] Feng JC, Dai XY, Wang D, Li R, Cao J. Microstructure evolution and mechanical properties of ZrO_2/TiAl joints vacuum brazed by Ag–Cu filler metal. Mater Sci Eng A 2015;639:739-746.

[8] Liu JK, Cao J, Song XG, Wang YF, Feng JC. Evaluation on diffusion bonded joints of TiAl alloy to Ti_3SiC_2 ceramic with and without Ni interlayer: Interfacial microstructure and mechanical properties. Mater Des 2014;57:592-597.

[9] Zhang PF, Fang J, Fu RL, Gu XG, Fei M. Bonding of Al to Al_2O_3 via Al–Cu eutectic method. Mater Des 2015;87:619-624.

[10] Jin YJ, Khan TI. Effect of bonding time on microstructure and mechanical properties of transient liquid phase bonded magnesium AZ31 alloy. Mater Des 2012;38:32-37.

[11] Halbig MC, Asthana R, Singh M. Diffusion bonding of SiC fiber-bonded ceramics using Ti/Mo and Ti/Cu interlayers. Ceram Int 2015;41:2140-2149.

[12] Qin YQ, Yu ZH. Joining of C/C composite to TC4 using SiC particle-reinforced brazing alloy. Mater Charact 2010;61:635-639.

[13] Dai XY, Cao J, Liu JK, Su S, Feng JC. Effect of holding time on microstructure and mechanical properties of ZrO_2/TiAl joints brazed by Ag–Cu filler metal. Mater Des 2015;87:53-59.

[14] Iwamoto C, Tanaka SI. Reactive wetting of Ag-Cu-Ti on SiC in HRTEM. Acta Mater 1998;46:2381-2386.

[15] Cao J, Song XG, Li C, Zhao LY, Feng JC. Brazing ZrO_2 ceramic to Ti–6Al–4V alloy using NiCrSiB amorphous filler foil: Interfacial microstructure and joint properties. Mater Charact 2013;81:85-91.

[16] Lee MK, Kim KH, Lee JG, Rhee CK. Growth of isothermally-solidified titanium joints using a multi-component Zr–Ti–Cu–Ni–Be amorphous alloy as a brazing filler. Mater Charact 2013;80:98-104.

[17] Zhao YX, Wang MR, Cao J, Song XG, Tang DY, Feng JC. Brazing TC4 alloy to Si_3N_4 ceramic using nano-Si_3N_4 reinforced AgCu composite filler. Mater Des 2015;76:40-46.

[18] Wang TP, Liu CF, Leinenbach C, Zhang J. Microstructure and strengthening mechanism of Si_3N_4/Invar joint brazed with TiNp-doped filler. Mater Sci Eng A 2016;650:469-477.

[19] He YM, Zhang J, Wang X, Sun Y. Effect of brazing temperature on microstructure and mechanical properties of Si_3N_4/Si_3N_4 joints brazed with Ag-Cu-Ti+Mo composite filler. J Mater Sci 2011;46:2796-2804.

[20] Wang TP, Zhang J, Liu CF, Wang GC. Microstructure and mechanical properties of Si_3N_4/42CrMo joints brazed with TiN_p modified active filler. Ceram Int 2014;40:6881-6890.

[21] Lin TS, Yang MX, He P, Huang C, Pan F, Huang YD. Effect of in situ synthesized TiB whisker on microstructure and mechanical properties of carbon-carbon composite and TiBw/Ti-6Al-4V composite joint. Mater Des 2011;32:4553-4558.

[22] Halbig MC, Coddington BP, Asthana R, Singh M. Characterization of silicon carbide joints fabricated using SiC particulate-reinforced Ag-Cu-Ti alloys. Ceram Int 2013;39:4151-4162.

[23] Yang ZW, Zhang LX, Ren W, Lei M, Feng JC. Interfacial microstructure and strengthening mechanism of BN-doped metal brazed Ti/SiO_2-BN joints. J Eur Ceram Soc 2013;33:759-768.

[24] Zhu MG, Chung DDL. Improving the strength of brazed joints to alumina by adding carbon fibres. J Mater Sci 1997;32:5321–5333.

[25] Qiu QW, Wang Y, Yang ZW, Wang DP. Microstructure and mechanical properties of Al_2O_3 ceramic and Ti6Al4V alloy joint brazed with inactive Ag–Cu and Ag–Cu+B. J Eur Ceram Soc 2016;36:2067-2074.

[26] Dai XY, Cao J, Chen Z, Song XG, Feng JC. Brazing SiC ceramic using novel B_4C reinforced Ag-Cu-Ti composite filler. Ceram Int 2016;42:6319-6328.

[27] Zhao L, Li XH, Hou JB, Sun Q, Zhang FL. Bonding of C_f/SiC composite to Invar alloy using an active cement, Ag–Cu eutectic and Cu interlayer. Appl Surf Sci 2012;258:10053-10057.

[28] Lin QL, Sui R. Wetting of B_4C by molten Ni–Ti alloys at 1753 K. J Alloy Compd 2013;577:37-43.

[29] Fan Z, Guo ZX, Cantor B. The kinetics and mechanism of interfacial reaction in sigma fibre-reinforced Ti MMCs. Compos Part A: Appl Sci Manufact 1997;28:131-140.

[30] Zhang J, He YM, Sun Y, Liu CF. Microstructure evolution of Si_3N_4/Si_3N_4 joint brazed with Ag-Cu-Ti+SiC_p composite filler. Ceram Int 2010;36:1397-1404.

[31] Liu Y, Huang ZR, Liu XJ. Joining of sintered silicon carbide using ternary Ag-Cu-Ti active brazing alloy. Ceram Int 2009;35:3479-3484.

Figures Captions

Fig. 1 Microstructure in BSE mode of the joints brazed at 950 °C for different holding time: (a) 5 min; (b) 10 min; (c) 15 min

Fig. 2 High magnification BSE images of the microstructure of the joints brazed at 950 ℃ for different holding time: (a) 5 min; (b) 10 min; (c) 15 min

Fig. 3 (a) Microstructure around B_4C particles in the joint brazed with composite filler at 950 ℃ for 10 min; (b-d) corresponding element distribution for Ag, Cu and Ti

Fig. 4 XRD patterns of the brazing seam of the joint

Fig. 5 (a) TEM bright field image of the microstructure of the brazing seam; SAED patterns of (b) TiB; (c) TiC

Fig. 6 Physical model of the microstructure evolution: (a) aggregation of Ti around B_4C particles and near SiC ceramic substrates; (b) formation of reaction products around B_4C particles and near SiC ceramic substrates; (c) growth of reaction products (d) solidification of the joint

Fig. 7 Effect of holding time on bending strength of the joints

Fig. 8 Fractographs of the joints brazed at 950 °C for: (a) 5 min; (b) 10 min; (c) 15 min

Fig. 9 Load-depth curves for the brazing seam

Fig. 10 Effect of B_4C particles addition on the CTE of the brazing seam

Tables Captions

Table 1 EDS elemental analysis (at.%) of different regions in Fig. 8

Table(1)

	B	C	Si	Ti	Ag	Cu	Possible phase
A	-	30.5	16.2	48.8	2.4	2.1	Ti_3SiC_2
B	-	43.6	16.8	36.4	1.3	1.9	Ti_3SiC_2
C	14.5	12.4	5.5	20.0	44.9	2.7	TiB, TiC, Ag(s,s)

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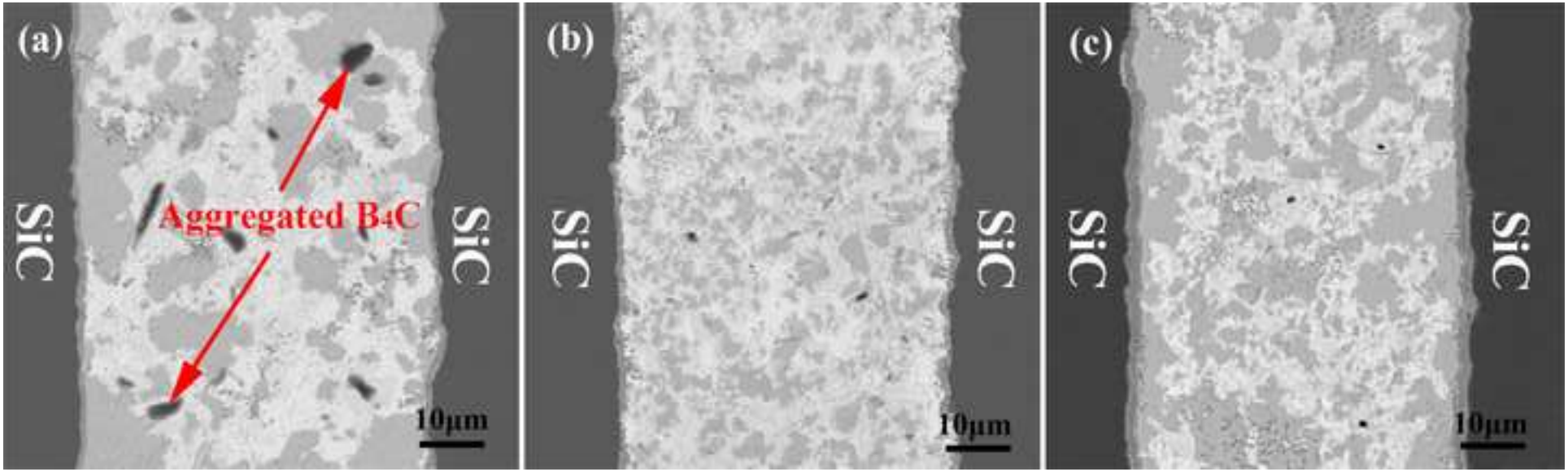

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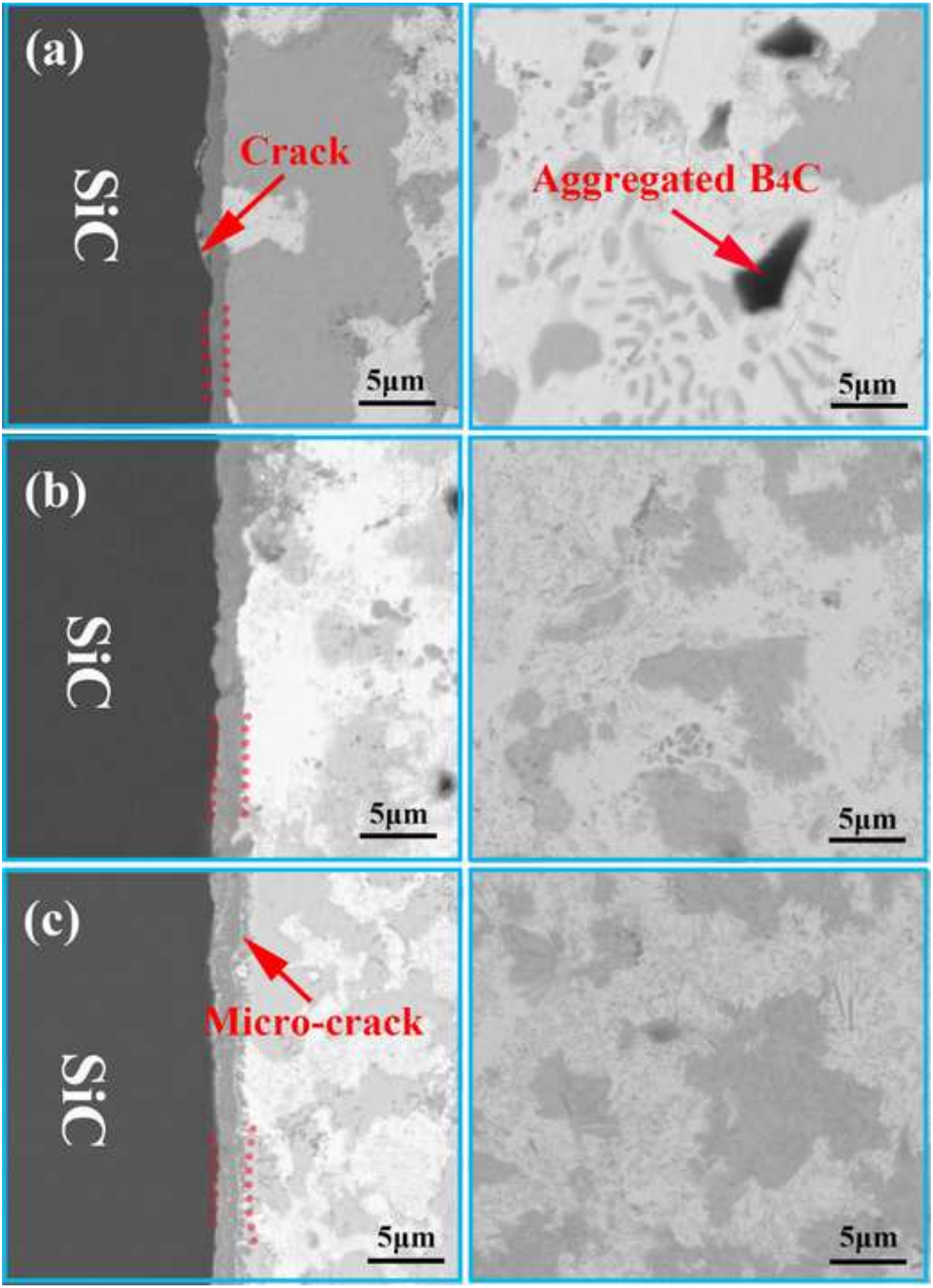

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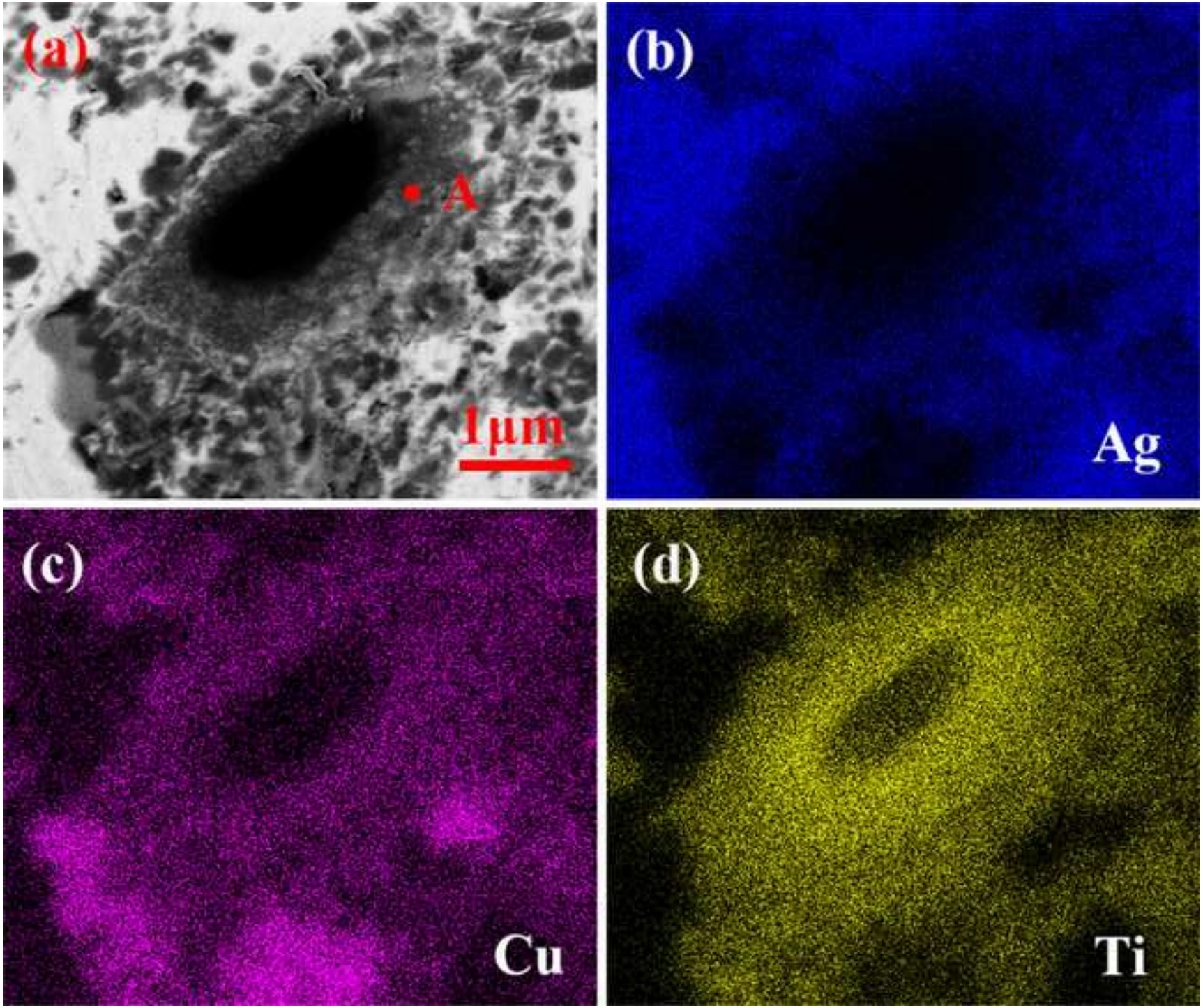

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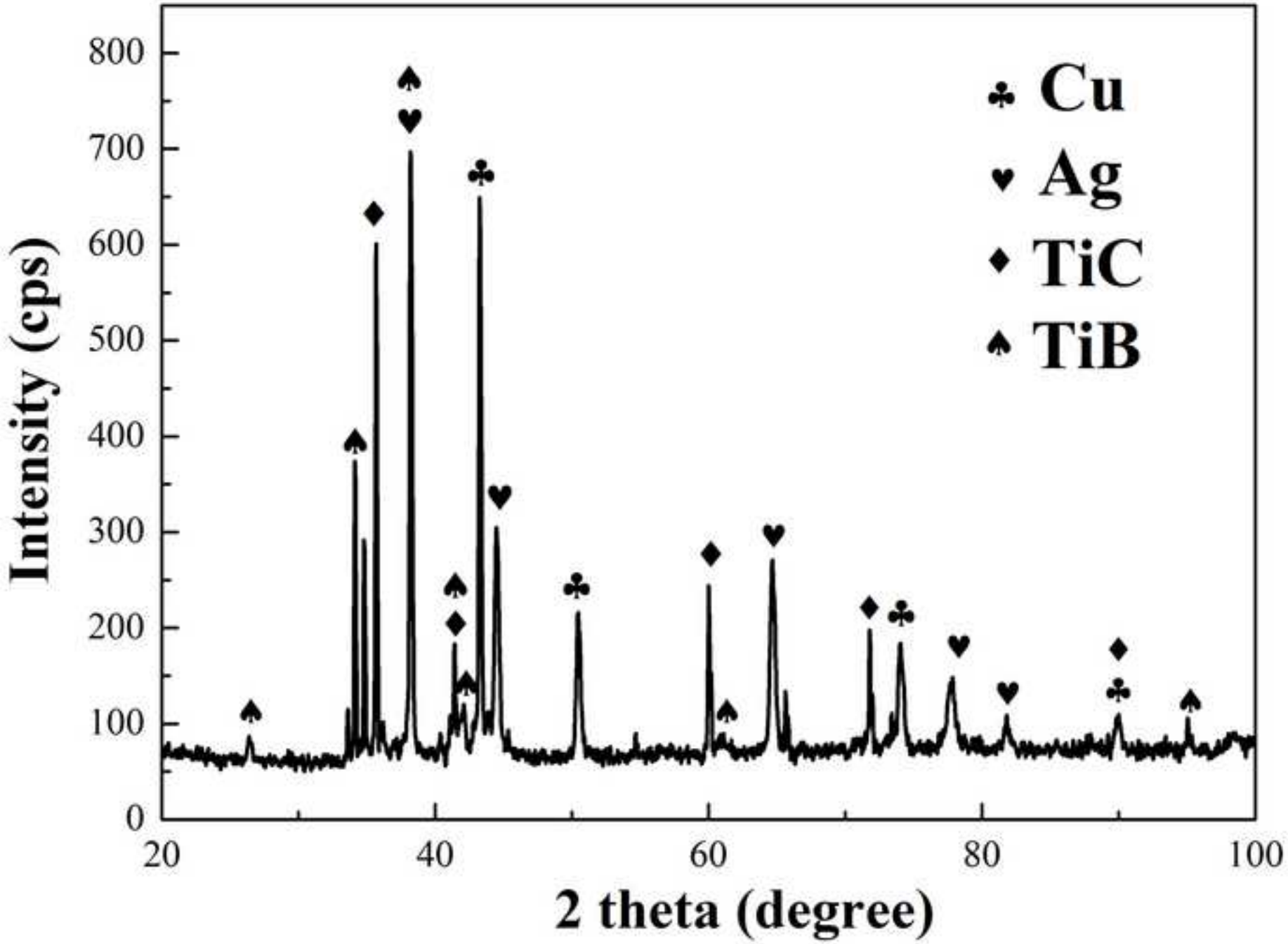

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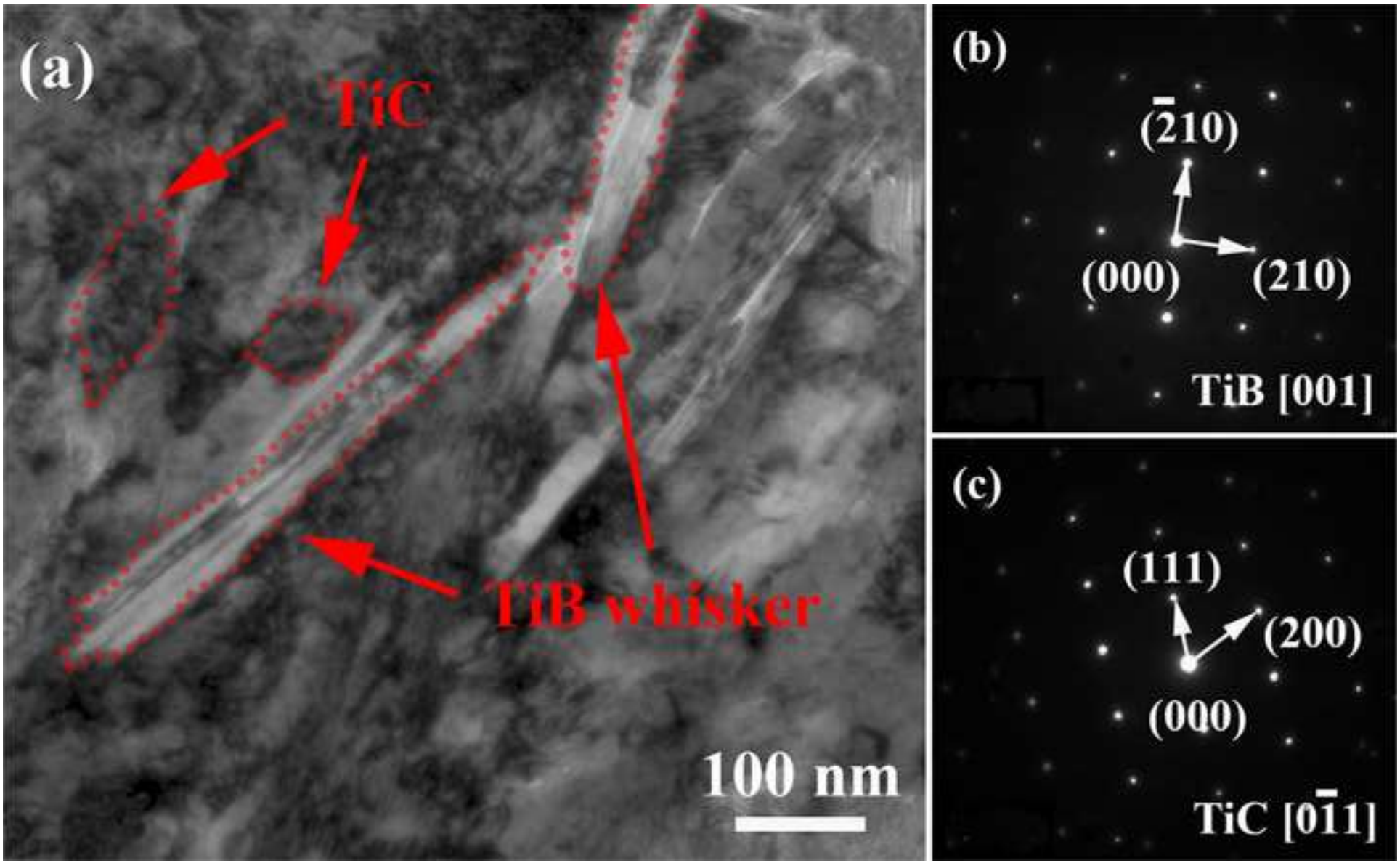

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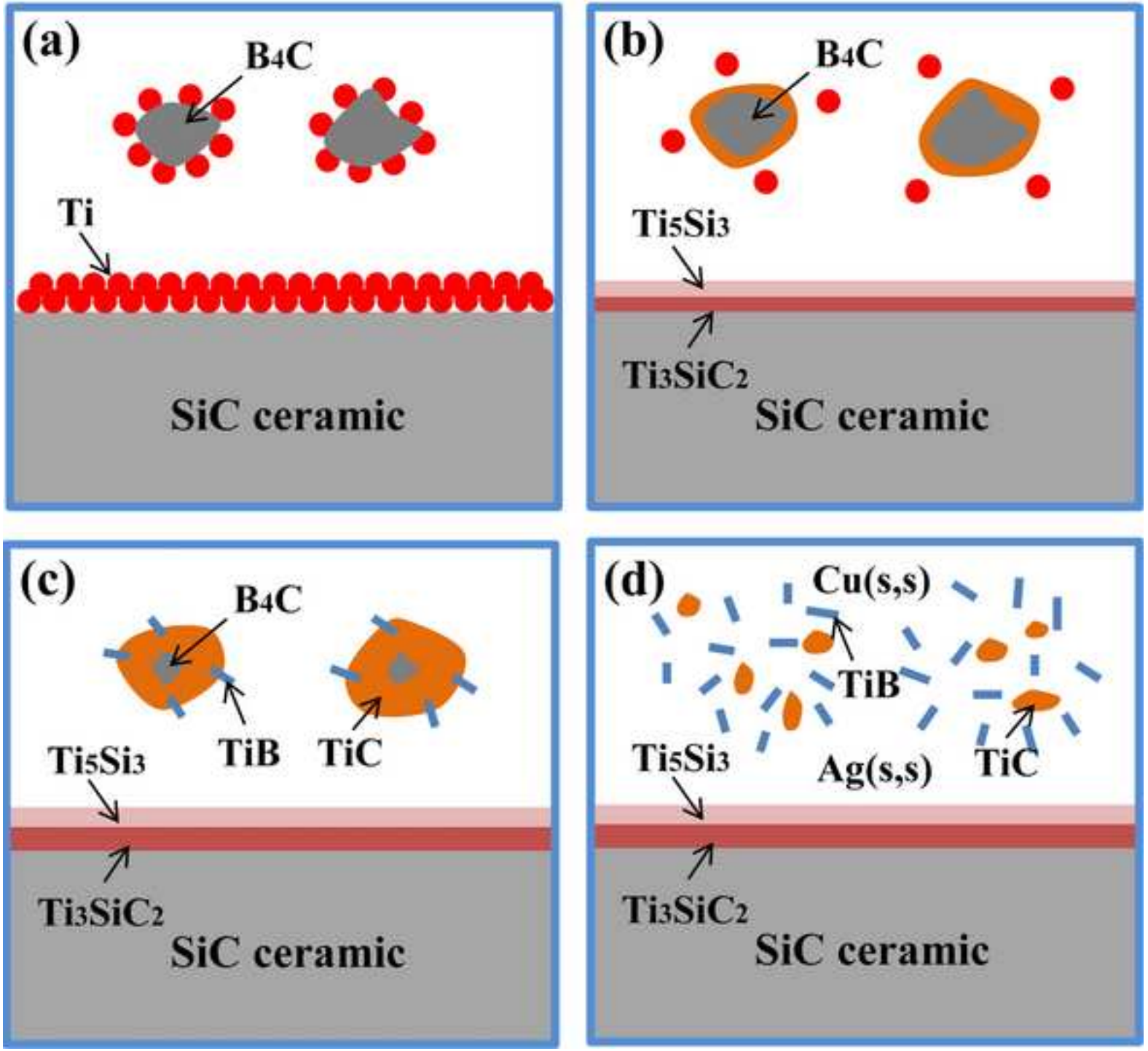

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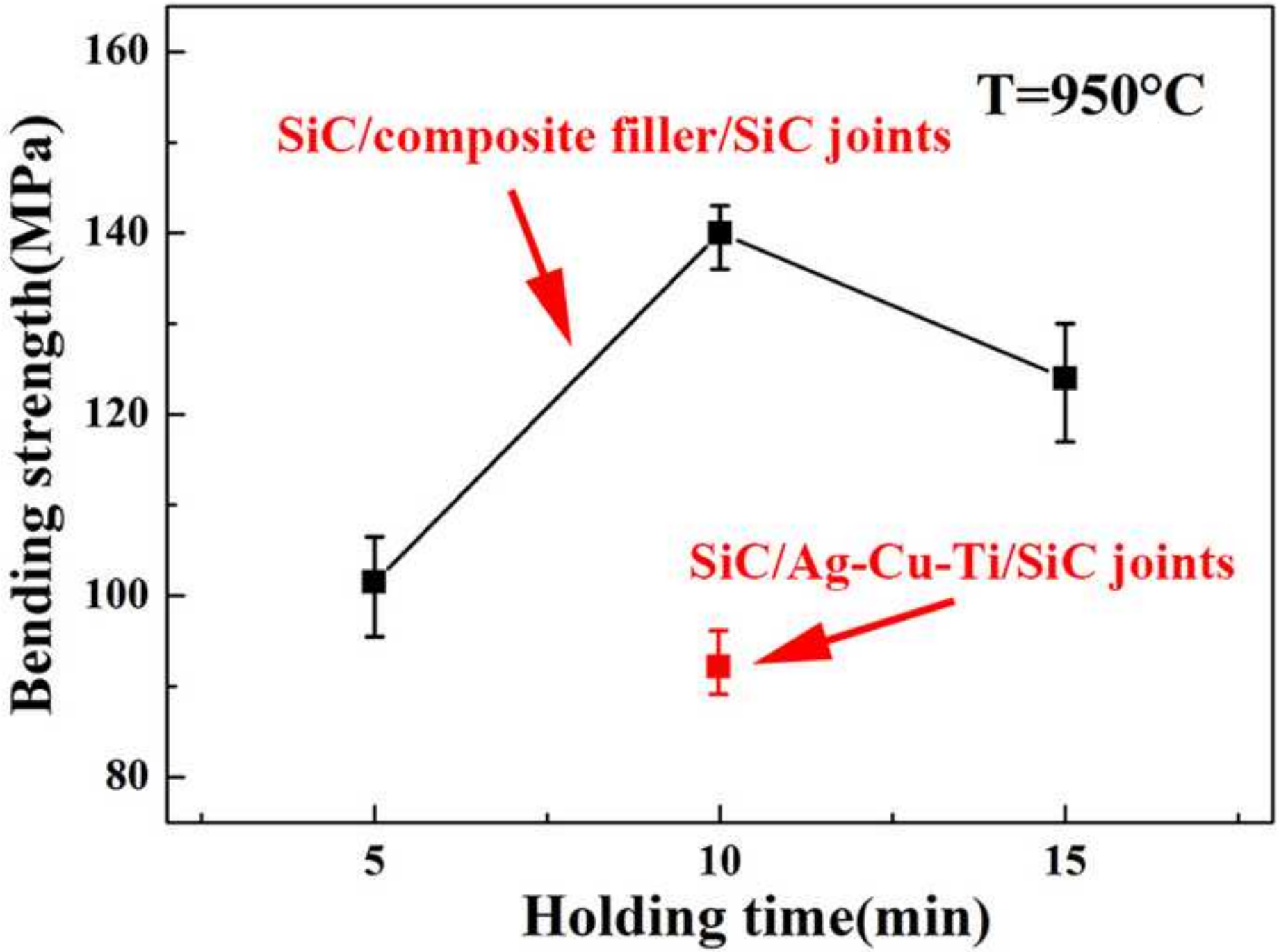

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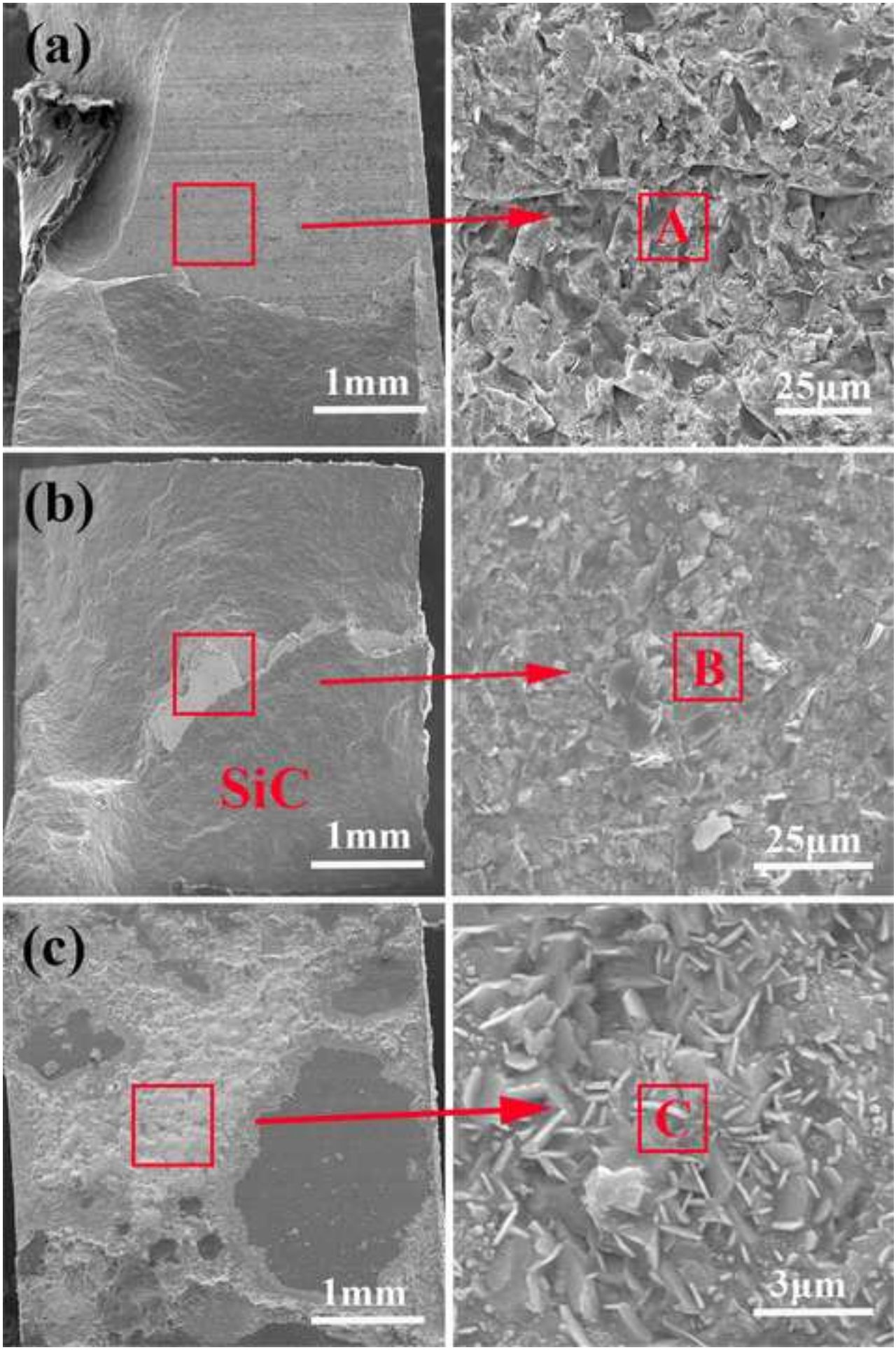

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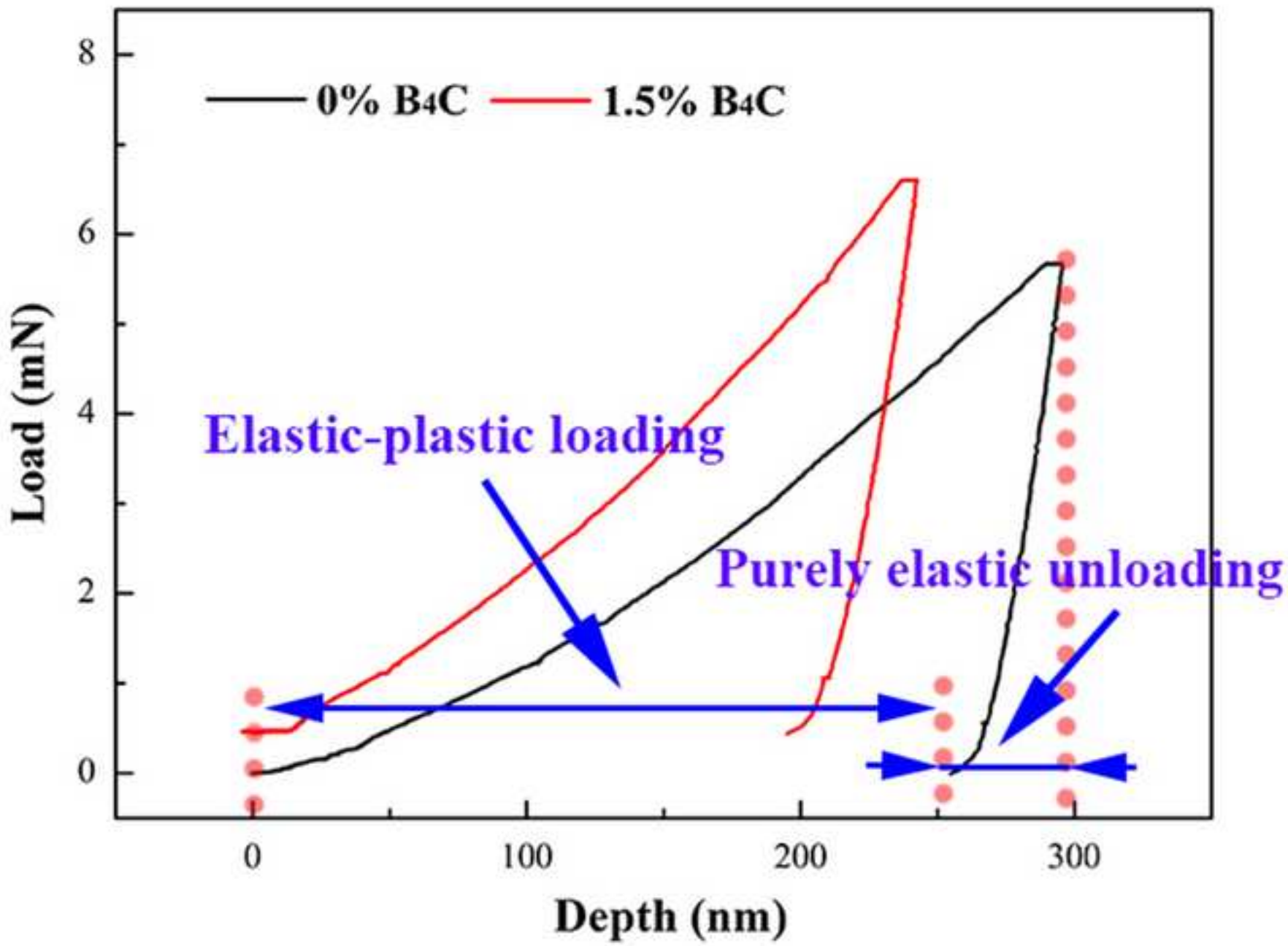

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