Graphical Abstract

Control of residual stresses in 2Si-B-3C-N and Nb joints by the Ag-Cu-Ti + Mo composite interlayer

Rui Pan^{a,f}, Sasa Kovacevic^e, Tiesong Lin^{a,*}, Peng He^{a,*}, Dusan P. Sekulic^{a,b,*}, Sinisa Dj. Mesarovic^{e,*}, Zhihua Yang^c, Yanxu Shen^d, Hongmei Wei^a

^aState Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China;

^bDepartment of Mechanical Engineering, College of Engineering, University of Kentucky, Lexington, KY 40506, USA;

^cInstitute for Advanced Ceramics, Harbin Institute of Technology, Harbin 150001, China;

^dHuawei Technologies Co., Ltd., Beijing 110000, China

^eSchool of Mechanical and Materials Engineering, Washington State University, Pullman 99164, USA

^fDepartment of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Abstract

2Si-B-3C-N ceramic was successfully vacuum brazed to Nb. Brazing was executed at 850 °C for 10 min using Ag-Cu-Ti/Mo/Ag-Cu-Ti composite interlayer. Effects of the Mo interlayer thickness within the composite interlayer on the microstructure of the joint and its shear strength were investigated. In joints brazed without Mo and with 50 µm Mo interlayer a continuous through cracks propagated within the ceramic during cooling. However, no cracks were found in joints when Mo interlayers thicker than 100 µm were used. The improvement of the shear strength with an increase in the thickness of Mo interlayer within the composite interlayer was achieved. To explain the effects of the Mo layer thickness, detailed FEM simulations of the cooling process were performed. The analysis of the residual stress is consistent with the observed joint strengthening and crack propagation.

Keywords: Brazing, Si-B-C-N ceramic, Composite interlayer, Mo, Residual stress

1. Introduction

Si-B-C-N is a ceramic with low density, good mechanical properties, excellent stability and resistance to oxidation at high temperatures, which all make it a promising candidate for applications in a harsh environment, such as hypersonic aircraft thermal structures, advanced rocket propulsion thrust chambers, high temperature membranes and other space systems [1-8]. It has been established that an incorporation of B and N into SiC, hence a formation of systems like Si-B-C-N, offers a substantial improvement in high-temperature anti-oxidation performance over pure SiC [9, 10]. However, as for other ceramics, its application for large, complex components is restricted by its poor formability [11]. Therefore, it is necessary to perform effective joining of Si-B-C-N with other ceramics or metals, such as Nb. Such methods are suited for components

* Corresponding authors: hitjoining@hit.edu.cn; hithepeng@hit.edu.cn; sekulicd@engr.uky.edu; smesarovic@wsu.edu

required to operate as a high-temperature, for a prolonged period of time [12, 13].

We have found no reports about joining of Si-B-C-N ceramic in literature. However, various studies of joining of SiC based ceramics, the major components of Si-B-C-N, have been reported. The most common joining method is brazing [14-18]. One of the major issues in brazing ceramics, including SiC, to metals has been an appearance of an excessive residual stress in the joint after cooling, as a result of large differences in the coefficients of thermal expansion (CTEs). Typical solution for this problem would be a use of either ductile interlayers or composite filler metals. Liu et al. [19] have reported an improvement in the flexural strength of SiC/SiC brazed joint by using a mixture of SiC particles and Ag-Cu-Ti powders as an interlayer. The reduction of the CTE mismatch between the filler metal and SiC, resulted in a decrease of residual stresses. The same approach has been adopted by Halbig [20]. By adding SiC particles into Ag-Cu-Ti filler metal (45 vol. %), the CTE of the braze was reduced significantly, up to 45-60%. An Ag-Cu-Ti+Mo particles composite filler metal was used by He et al, to braze Si_3N_4 to itself [21], as well as to 42CrMo steel [22]. The same study presented a FEM simulation in an attempt to evaluate a reduction of the residual stress within the joint [23]. However, a disadvantage of using a particle-reinforced composite filler is a possible (and likely) nonhomogeneous distribution of the constituents, hence a deleterious impact of the nonhomogeneous distribution when a large fraction of the reinforcement is incorporated [20]. A ductile metal interlayer with a low CTE would be yet another option for a residual stress relief. Tian et al [24], have used Ag-Cu-Ti/Cu mesh/Ag-Cu-Ti composite interlayers to braze ZrB_2 -SiC-C ceramic with the GH99 super alloy. A great improvement in the shear strength of the joint was observed.

In this study, 2Si-B-3C-N and Nb were selected as base materials. Ag-Cu-Ti/Mo/Ag-Cu-Ti sandwich structure was selected as the composite interlayer. The main objective of the study is to identify the effect of the thickness of the Mo interlayer on the joint microstructure and to confirm, unambiguously, an improvement of the shear strength of a joint featuring this system. The FEM simulation accompanies the empirical study with an objective to predict the mechanical behavior of the structured joint. The simulation results are consistent with the experimental data.

2. Experimental procedure

The 2Si-B-3C-N powder was prepared by mechanically assisted alloying, and subsequently hot pressed into a ceramic bulk, as described in [25]. The ceramic density and the corresponding relative density were $2.52 \times 10^3 \text{ kg/m}^3$ and 97.9%, respectively. The raw ceramic and the Nb sheet were cut into $5 \times 5 \times 4 \text{ mm}$ and $10 \times 20 \times 3 \text{ mm}$ pieces, respectively. The brazing filler material was prepared as follows. First, 5 wt.% TiH_2 powder ($D_{90} \approx 10 \text{ }\mu\text{m}$; purity 99.95%; commercially available) was added into a Ag-Cu braze (Ag-28 wt.% Cu, $D_{90} \approx 15 \text{ }\mu\text{m}$; purity 99.94%; commercially available) powder. Subsequently, the mixed powders were ball-milled for 12 hours in pure ethanol in an agate bottle. The planetary ball mill operated with a rotational speed of 600 rpm. After dried in vacuum for 3 h at $50 \text{ }^\circ\text{C}$, the mixed powder was compacted with a 10 bar pressure at room temperature to obtain the 0.4 mm thick Ag-Cu-Ti sheet. The so formed brazing sheet and 50 μm , 100 μm , 150 μm , 200 μm , and 250 μm thick Mo foils (termed “Mo interlayers”), respectively, were sliced into $5 \text{ mm} \times 5 \text{ mm}$ pieces. The vacuum brazing method was applied to join 2Si-B-3C-N ceramics to Nb. Prior to brazing, all 2Si-B-3C-N ceramic surfaces to be brazed were polished with diamond grinding disks with up to 1000 grit and ultrasonically cleaned in acetone for 15 min. The Ag-Cu-Ti/Mo/Ag-Cu-Ti composite interlayer was placed between

2Si-B-3C-N and Nb, as shown in Fig. 1a. The assembly was brazed in a vacuum furnace at 5×10^{-3} Pa and 850 °C and held for 10 min at that peak temperature. The heating and cooling rates were both at the 10 °C/min level.

The cross sections of joints formed during brazing were polished for scanning electron microscopy (SEM) testing. The scanning electron microscopy (Hitachi S-4700) equipped with the energy dispersive spectrometer (EDS, TN-4700X) has been used. The interface plane of the joint was subsequently polished, layer by layer, and the X-ray diffractometry (XRD, Bruker D8 ADVANCE) was used to examine the phase state and composition at the joint interface. The shear strength of the joint was measured with a universal mechanical testing machine (Instron-1186) equipped with a shear test fixture. Tests were performed with a constant displacement rate of 0.5 mm/min. The fixture schematic is shown in Fig. 1b. The shear strength was calculated by dividing the maximum load by the brazed interface area. At least five specimens were used to determine the average strength value for each condition. Large cracks were observed after cooling for the cases with no Mo interlayer and with the 50 μ m thick Mo interlayer, Fig. 2.

The temperature at the peak is nearly homogenous within the brazing sample. The verification of this hypothesis has been performed by calculating Biot number by a lumped-capacitance transient heat transfer model. The calculated Biot number is $Bi = 0.034 < 0.1$, so that the spatial distribution can be considered uniform.

Fig. 1. Schematic diagram of the (a) brazed assembly; (b) shear test configuration.

Fig. 2. The macrocrack in the Si-B-C-N ceramic joints using Mo as the interlayer: (a) Without Mo interlayer, (b) With 50 μ m thick Mo interlayer. (c) Fracture surface of the specimen with the 100 μ m thick Mo interlayer.

Table 1

Basic materials properties at different temperatures.

Material	Temperature (°C)	Thermal conductivity (W/(m·°C))	Specific heat capacity (J/(kg·°C))	CTE ($\times 10^{-6}/^{\circ}\text{C}$)	Elastic modulus (GPa)	Yield Stress (MPa)	Poisson's ratio	References
Ag-Cu-Ti	20	90	290	19.0	93.6	230	0.35	[23]

	200	---	---	19.7	85	170		
	400	---	---	20.2	79.4	98		
	600	---	---	20.5	70.2	25		
	800	---	---	21	58.1	20		
	20	147	239	5.44	329	543		
	200	133	264	5.98	320	477		
Mo	400	117	271	6.22	312	409	0.31	[26, 27]
	600	115	286	6.29	304	347		
	800	108	299	6.62	295	255		
	20	9.4	750	2.4	139.4	---		
	200	7.4	920	4.2	---	---		
2Si-B-3C-N	400	8.2	1150	4.4	---	---	0.16	[25]
	600	8.4	1230	4.7	---	---		
	800	8.0	1300	4.9	---	---		
	20	52.3	265	7.21	123	248		
	200	56.5	276	7.67	121	189		
Nb	400	60.7	284	7.89	118	156	0.38	[28, 29]
	600	65.5	293	8.12	115	87		
	800	68.3	302	8.64	111	62		

3. Results and Discussion

3.1. Microstructure characterization of the joint

Typical morphology of a 2Si-B-3C-N/Nb joint domain brazed with the composite interlayer is shown in Fig. 3a. The thickness of the Mo interlayer in this case was 250 μm . No detrimental reaction occurs at the Ag-Cu-Ti/Mo interface, except for some dissolution of Mo due to the interaction between Mo and Ti in the filler metal [22]. Similarly, no intermetallic compounds were produced between Ag-Cu-Ti and Nb (in spite of the complete miscibility between Ti and Nb [13]). The interface structures on the 2Si-B-3C-N side are shown in Fig. 3b. Two reaction layers, namely (i) a continuous dark reaction layer and (ii) a two-phase layer composed of distributed gray particles, were formed. Each layer is approximately 1-3 μm thick. These are formed at the interface in the direction from the base ceramic toward the braze. These two reaction layers are composed of a Ti-C compound and two Ti-Si compounds, respectively (see the EDS results in Table 2, corresponding to the points marked in Fig. 3b). In the latter layer, the content of Si in the particles adjacent to the Ti-C compound layer appears to be higher than in the particles near the braze. These Ti-C and Ti-Si compounds are identified as TiC, TiSi₂ and TiSi (as confirmed by the XRD pattern shown in Fig. 4). The reaction layers with a moderate thickness are essential for good integrity between 2Si-B-3C-N and the braze.

Fig. 3. SEM BSE images of typical 2Si-B-3C-N/composite interlayer/Nb joint: (a) morphology of the entire joint and (b) a higher magnification view of the 2Si-B-3C-N/Ag-Cu-Ti interface.

Table 2

EDS analysis results of the points in Fig. 3b.

Points	Si	C	Ag	Cu	Ti	Possible phase
A	7.2	41.3	2.1	3.5	45.9	TiC
B	51.9	---	5.8	7.2	35.1	TiSi _x
C	45.4	---	7.7	5.2	41.7	TiSi _y
D	---	---	20.3	78.2	1.5	Cu-rich
E	---	---	85.4	12.2	2.4	Ag-rich

Fig. 4. Comparison of XRD patterns of the base ceramic and the reaction layer at 2Si-B-3C-N/Ag-Cu-Ti interface.

The interfacial reaction products are different from the products in SiC/Ag-Cu-Ti joints, the latter typically composed of TiC and Ti₅Si₃ [19]. It is hypothesized that the reason for that should be the consumption of active Ti atoms reacting with excessive C atoms, hence reducing the amount of Ti available to react with Si atoms. As a result, different Ti-Si compounds with less Ti content are produced at the interface.

3.2. Effect of the Mo interlayer's thickness on the microstructure and shear strength of the joints

The microstructure of 2Si-B-3C-N/Nb joints brazed with Mo interlayer with different thicknesses is shown in Fig. 5. In the joints brazed without Mo interlayer, as well as with 50 μm thick Mo interlayer, continuous cracks were formed in the base ceramic near the interface without any external stress, while no cracks are observed in the joints brazed with Mo interlayers thicker than 100 μm. Obviously, the cracks were caused by the residual stress upon cooling due to large difference in CTE. The distribution of the residual stress is controlled by Mo interlayer addition. As for interfacial microstructure, no changes are observed in the joints with Mo interlayers with

various thicknesses, if brazing temperature and holding time are kept constant.

The control of the residual stress by an application of composite interlayer is well reflected in the shear strength of the joints, as shown in Fig. 6. When brazed without Mo interlayer or with 50 μm thick Mo interlayer, the joints fail in the base ceramic even before the shear test is administrated. With the increase of thickness of Mo interlayer, no microcracks appear during cooling, and the shear strength rapidly increases at first and then remains constant when the thickness of Mo interlayer exceeds 200 μm . All the specimens without cracks failed within the 2Si-B-3C-N ceramic domain. The strength of the joint is expressed by the nominal shear strength, i.e. the result of the maximum load divided by the joining interface area. In spite of the location of the failure, the increase in the maximum load is still an indicator of the relief or redistribution of the residual stress in the base ceramic near the interface.

Fig. 5. SEM BSE images of 2Si-B-3C-N/Nb joint brazed without Mo (a) or with composite interlayer containing 50 μm (b), 100 μm (c) and 150 μm (d) thick Mo interlayer.

Fig. 6. Variation of 2Si-B-3C-N/Nb joint shear strength with the thickness of Mo interlayer used. Continuous cracks were found in all the joints brazed with 0 and 50 μm thick Mo interlayers after cooling. These specimens did not go through the mechanical test procedure, and the shear strengths were all considered to be 0 MPa.

3.3. The results of FEM simulations

To understand the effects of the increasing thickness of Mo layer, we perform finite element

(FE) stress analysis of the cooling process after the bonding of the surfaces. The initial stresses at the peak bonding temperature are assumed to be zero. The metals are considered elastic – ideally plastic with the temperature dependent (Mises) yield stress. The ceramic is considered elastic. Temperature dependence of elastic constants, yield stresses and thermal expansion coefficients is shown in Table 1. Details of the FE analysis are given in Appendix A.

As illustrated in Fig. 2, the mechanisms of failure in all cases are the fracture in the ceramic, close to the interface. The specimens without Mo interlayer and with the 50 μm thick Mo layer accumulate high residual stresses so that they fracture without any additional load in the shear apparatus (Fig. 2 a, b). The specimens with thicker molybdenum layer require additional shear load, but still fracture in the ceramic, with the crack getting closer to the interface as the Mo layer becomes thicker (Fig. 2 c).

Fracture of ceramics in the present configuration (with a ductile film sandwiched between ceramics and another hard substrate) has not been analyzed in literature. However, a similar problem of a ductile thin film on the surface of a brittle substrate has been analyzed in some detail, notably by Suo & Hutchinson [30], for the overview, see and Freund & Suresh monograph [31]. Full analysis of the fracture process is beyond scope of this paper. Nevertheless, with our finite element analysis of the residual stresses in uncracked elastic-plastic specimens (details in the Appendix A) and general understanding of the fracture based on Griffith criterion, the effect of increasing Mo layer thickness on the shear strength of the specimen can be explained qualitatively.

The interface tractions between thin film (free on one side) and the substrate can be represented by the equivalent force shear force T_0 and the equivalent moment M_0 (Fig. 7). The shear force is the resultant of shear tractions. The normal tractions have no resultant but produce the moment. In the case of a thin ductile film the forces are transmitted in the small region ($\approx 4\bar{h}$) [31].

Fig. 7 The forces transmitted from the metal layers to the ceramic, and the notation used.

Shear and normal tractions obtained by our finite element analysis are shown in Fig. 8. The normal tractions are still confined to a small region near the edge. However, the shear tractions, while somewhat concentrated near the edge, at larger distances decay almost linearly to zero at the symmetry line.

The edge of the contact (the singularity in linear analysis) is subject to an extremely high normal stress concentration (see inset in Fig. 8a). We expect that a microcrack will nucleate in all cases considered, at the interface or in its vicinity. The normal stresses can drive the microcrack to

the length of about 2-3 microns (inset in Fig. 8a). Both the moment and shear force decrease with increasing thickness of Mo layer (Fig. 9). By comparing the magnitudes of the normalized moment $2M_0/L$ and the shear force, we conclude that apart from driving the crack initiation, the normal tractions (and thus the moment) play negligible role in the remainder of the crack growth process.

Fig. 8. Traction at the metal-ceramic interface for different thicknesses of the Mo layer: (a) Distribution of normal tractions. Inset: Magnified high stress concentrations at the edge. (b) Distribution of shear tractions.

Fig. 9. Dependence of the total shear force and the normalized moment on the thickness of Mo layer.

The crack of a given length propagates in certain direction so that the energy release rate G is maximized and is (in ideally brittle material and with quasistatic growth) equal to the critical energy release rate G_c :

$$G_{\max} = G_c. \quad (1)$$

For the loading consisting of the thermal mismatch and without external forces the energy released for cracking is the strain energy, stored initially and finite. In contrast to the simpler problem of thin film on a substrate, [30], where the energy release rate decreases with increasing crack length, the energy release rate $G_{\max}(a)$ in the present case may be increasing or decreasing function of the crack length a for different ranges of crack lengths. Experimental results indicate that for Mo layer of 50 microns or less, the strain energy stored during the cooling process is sufficient to drive the crack through the specimen, while with Mo layer of 100 microns or thicker, the crack propagates only a certain length. Then, an additional loading in the shear apparatus propagates the crack further.

The decreasing shear force and softening of the shear stress concentration explain the general trend observed in Fig. 6. However, the apparent discontinuity in the initial crack length between the cases with 50 and 100 micron Mo layers cannot be explained without detailed analysis of the

crack propagation process. We note that the problem of the initial crack growth is a nonlinear stability problem whereby small differences in geometry, and hence stress distribution, may imply the difference between a stable finite crack and a dynamically propagating runaway crack. To illustrate the point, we outline a possible scenario for crack propagation in Appendix B, on the basis of estimated lengths of initial cracks.

In summary, the finite element residual stress analysis of uncracked specimens with varying thicknesses of Mo layer, indicate that the size of the initial crack decreases with the increasing Mo thickness, but it does not quantitatively explain the threshold Mo thickness below which the crack propagates through the specimen without additional load.

4. Conclusions

Ag-Cu-Ti/Mo/Ag-Cu-Ti composite interlayer braze was used to bond the 2Si-B-3C-N ceramic. The influence of the Mo interlayer thickness on the morphology and shear strength of the joint was investigated. The main conclusions are summarized as follows.

(1) In the joints brazed without Mo interlayer or with 50 μm thick Mo interlayer, through cracks appear in 2Si-B-3C-N ceramic near the interface of 2Si-B-3C-N/TiC during cooling. No microcracks are found in joints brazed with Mo interlayer thicker than 100 μm .

(2) The shear strength increased with the increasing thickness of the Mo interlayer and then remained constant for Mo interlayer thicker than 200 μm . The maximum shear strength reached is 48 MPa in case of 250 μm thick Mo interlayer.

(3) The finite element residual stress analysis of uncracked specimens with varying thicknesses of Mo layer, indicate that the size of the initial crack decreases with the increasing Mo thickness. The full explanation of the threshold Mo thickness below which the crack propagates through the specimen without additional load requires detailed analysis of the fracture process. Nevertheless, the distribution of residual stresses indicates a possible mechanism.

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Appendix A. Finite element analysis of residual stresses

The main challenges in the numerical analysis of this class of problems are the edges of interfaces, i.e., the corners of material domains. In linear analysis, the solutions exhibit singularities. Numerically, nonlinear analysis performed here softens the singularities into high stress concentration points. Nevertheless, a high resolution (dense meshing) is needed to avoid propagation of numerical instabilities in to the bulk.

We consider a 2D problem consisting of a slice of unit thickness shown in Fig. 7. Allowing for the thermal expansion orthogonal to the plane of the problem, the problem is formulated as

generalized plane strain (uniform displacements normal to the plane of the problem are allowed). Commercial FE software ABAQUS [32] is used with quadratic triangular elements. The mesh consisting of 400,000 elements is shown in Fig. A.1. The load is the temperature change from 850°C to 20°C. The contours of the strain energy density in the ceramic are shown in Fig. A.2. Relaxation of the ceramic with increasing Mo layer is evident. In Appendix B, we argue that the corner at the edge of the metal-ceramic contact (0.5×0.5 mm) is particularly relevant for crack propagation.

Fig. A.1. Variable density FE Mesh. The size of the largest elements is 0.25 mm, the size of the smallest element is 0.1 μ m.

Fig. A.2. Strain energy density: (a) Half of the ceramic piece, Left: $H=0$ μ m; Right: $H=250$ μ m; (b) Corner near the edge of metal-ceramic interface (0.5×0.5 mm), Left: $H=0$ μ m; Right: $H=250$ μ m.

Appendix B. Possible crack growth mechanisms for different thicknesses of Mo layer

While a quasi-static crack arrests as soon as the available energy release rate falls below the critical value, the dynamically propagating crack possesses inertia and will propagate beyond the

quasi-static arrest point. One criterion for deciding if the crack is a dynamic runaway crack or a quasi-static crack is the length which is available for the crack tip acceleration. To estimate such lengths in the present problem, we estimate the length of initial cracks for the cases where Mo layer is 100 microns or more. The stress intensity factor at the tip of the preexisting crack of length a , under nominal shear load (in shear apparatus) τ , can be expressed as:

$$K = \alpha \tau \sqrt{a}, \quad (\text{B.1})$$

where α is a constant of order 1. The critical stress intensity factor is

$$K_c = \sqrt{G_c E}, \quad (\text{B.2})$$

So that

$$a = \frac{G_c E}{\alpha^2 \tau^2}. \quad (\text{B.3})$$

For the order of magnitude estimate, assuming the surface energy of the ceramics to be O (1 J/m²), the Griffith toughness would be $G_c = 2$ J/m². With the Young's modulus $E = 140$ GPa, and $\alpha = 1$, we compute the initial crack lengths for cases $H = 100 - 250$ μm , and include them on the shear tractions plot (Fig. B.1). There appears to be the residual shear traction threshold of about 75 MPa, and we hypothesize that the crack accelerates through the region where shear tractions are higher than this value for the cases $H = 0$ and 50 μm . It accelerates up to 600 and 400 microns in length respectively, by which point it has reached sufficient velocity to propagate through the specimen. For the cases with thicker Mo layer, the crack accelerates for a much shorter distance (100-200 microns), acquiring insufficient velocity to run away before arresting.

Fig. B.1. Detail of residual shear tractions (from Fig. 8b) with estimated initial crack lengths (dots) and possible shear traction threshold (grey dashed line).

In the present problem, the energy released in crack propagation is supplied by the strain energy $U(\epsilon)$:

$$G = -\frac{\partial U}{\partial a} \quad (\text{B.4})$$

Thus, the available strain energy is an indicator of the driving force for crack growth. If a crack is small compared to the dimensions of the whole structure, the strain energy is relaxed locally, so that a concentration of strain energy is indicative of the crack driving force. In Fig. B.2,

we show the average strain energy density for the whole ceramics and for the corner at the edge of the metal-ceramic interface with dimensions ($500\text{ }\mu\text{m}$) corresponding to the estimated crack acceleration distance for $H = 0$ and $50\text{ }\mu\text{m}$. Concentration of strain energy in this region is noticeable (cf. Fig. A.2). Also noticeable is the sharper decrease with Mo thickness of the strain energy in this corner then of the overall strain energy. The threshold of 0.36 mJ/mm^3 is analogous to the shear tractions threshold shown in Fig. B.1. It is the energy density required to drive a crack through the entire region.

Fig. B.2. Average strain energy density for the whole ceramic and for the corner $0.5 \times 0.5\text{ mm}$ at the edge of the metal-ceramic interface.

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