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Interfacial microstructure of diffusion-bonded SiC and Re with Ti interlayer

Joo-Hyung Kim [a], Dong Seok Kim [a], Seong Taek Lim [b], Do Kyung Kim [a, *]

[a] Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea
[b] Agency for Defense Development, Daejeon 305-600, Republic of Korea

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ABSTRACT

SiC plates were diffusion bonded to Re metal using a Ti interlayer by hot-pressing. For the joining, a uniaxial pressure of 25 MPa was applied from 1400 to 1600 °C for 2 h in an argon atmosphere. The interfacial microstructure and elemental composition of the SiC/Ti/Re joints were investigated. The Ti interlayer diffused into the SiC substrate to form carbide intermediate phases that enhance the bonding strength and also that of the layer brazed with Re metal. Multi-component phases (Ti_3SiC_2, $Ti_5Si_3C_x$, and TiC) were formed in the Ti interlayer with different atomic ratios. Each phase had a different coefficient of thermal expansion, causing micro-cracks and pulverization at high temperature. At 1600 °C, the phase ratio and thickness of the detrimental phase $Ti_5Si_3C_x$ were much lower than those at other joining temperatures. For the Re/Ti interfaces, the diffusion of Ti and Si into Re gradually induced the formation of bcc-Ti precipitates, ReTi, and Re-Si alloys depending on the joining temperature. The micro-hardness was measured for the joined SiC/Ti/Re along all the interfaces.

1. Introduction

Rhenium is one of the most promising refractory metals, having a high melting point (3180 °C) and excellent properties such as high thermal shock resistance, high modulus of elasticity (461–471 GPa), superior tensile strength (1000–2500 MPa), high shear modulus (155 GPa), and excellent wear properties. On the basis of these outstanding properties, rhenium and its alloys have been applied in coating form to enhance the heat resistance and endurance of components and also to protect them from ablation and corrosion. It is thus considered an ideal material for application in various fields such as high temperature structural materials, heat exchangers, and heat protectors for space shuttles and missile thrusting systems. The chemical vapor deposition (CVD) method generally has been used for the fabrication of the refractory metal layer [1,2]. Yang et al. reported rhenium coated molybdenum pellets prepared by exposing molybdenum to a stream of chlorine gas in the presence of hydrogen gas in a reaction chamber at the deposition temperature with $ReCl_5$ [3]. However, CVD has some drawbacks such as complexity, high manufacturing cost, and high energy requirements. To develop a novel method for the deposition of rhenium, replacing the conventional CVD is necessary. Diffusion bonding is a solid-state welding technique used in metalworking that is capable of joining similar and dissimilar metals. It operates on the material science principle of solid-state diffusion, wherein the atoms of two solid, metallic surfaces intermingle over time under elevated temperature [4–6]. Diffusion bonding is typically implemented by applying both high pressure and high temperature to the materials to be welded. Depending on the joining materials, a thin interlayer is often introduced to the joining interface [6–8]. In this study, rhenium metal was joined to the SiC substrate by using a Ti interlayer. The microstructural change and phase transformation across the SiC/Ti/Re interfaces with various joining temperatures were investigated by microstructural and elemental analyses. The mechanical properties of the bonded joints were evaluated using a micro-hardness test.

2. Experimental procedure

Rhenium and titanium foil with 99.97% and 99.94% purity, respectively, were purchased from a commercial vendor (Alfa Aesar, South Korea). For the HP joining of Re and SiC, Rhenium foil and SiC were prepared with dimensions of

* Corresponding author. Tel.: +82 42 350 4158.
E-mail address: dkkim@kaist.ac.kr (D.K. Kim).

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10 mm (W) × 20 mm (L) × 100 μm (T) and 10 mm (W) × 20 mm (L) × 3 mm (T), respectively. Titanium foil with dimensions of 10 mm (W) × 20 mm (L) × 25 μm (T) was used for the interlayer material. Titanium foil and SiC were cleaned in ethanol and acetone for 10 min with ultra-sonication. Rhenium foil was etched with dilute acid (30 wt% HCl in de-ionized H_2O) for 5 min with ultra-sonication to remove the surface of the oxidation layer and was subsequently cleaned with the same method. The prepared rhenium foil and SiC were assembled with insertion of Ti foil as an interlayer material in a sandwich shape (SiC-Ti-Re-Ti-SiC). The assembled materials were sintered between two boron nitride (BN) coated graphite plates. Hot press joining was performed at 1400, 1500 and 1600 °C, respectively, with 25 MPa for 2 h under an argon atmosphere in a graphite furnace (ASTRO, Thermal Technology, Santa Barbara, CA). The heating and cooling rate during sintering was 13.3 and 17.7 °C min^{-1}, respectively, which were same in all joined samples. Sintering was conducted under pressure of 20 MPa from 600 °C to the joining temperature because of relaxation time to escape an impurity of surface. The pressure was changed to 25 MPa when the sintering temperature reached the joining temperature. The morphology and atomic composition of the joints were analyzed by scanning electron microscopy (SEM, XL30, Philips, Netherlands) coupled with energy dispersive spectrometry. Micro-hardness across the SiC/Ti/Re interfaces was measured using a nano indentation system (MTS, Nano Indenter XP, USA).

3. Results and discussion

Fig. 1 shows the microstructure of the diffusion bonded interfaces of SiC/Re using a Ti interlayer with different joining temperature from 1400 to 1600 °C. The SiC/Ti/Re joint was pressed under 25 MPa with different joining temperature for 2 h to form a sandwich-like structure, as shown in the schematic drawing in Fig. 1(a). All joints appeared to form a stable interlayer without any micro-cracking, pores, or defects. The titanium interfaces were divided into three different contrast interlayers in Fig. 1(b)(c). In the case of the sample joined at 1600 °C, a dark gray region near the SiC substrate and a bright gray region could be distinguished at the interface. The Ti interlayer, which is situated close to Re metal, had a thickness of 40 μm, as shown in Fig. 1(d), which is greater than that (~35 μm) of the other joined samples. This indicated that the diffusion layer between SiC and Re with the Ti interlayer was intensively bonded at high temperature.

The microstructures and elemental analysis of the joined interface between SiC and Re using a Ti foil with different temperature are shown in Fig. 2. In the case of carbon, it cannot be detected because of its small atomic weight. Mixed phases were observed in the Ti interlayer, showing different contrast in the SEM images according to various discrete physical layers: Ti-rich, Ti-poor, and Ti-gradient layers, denoted as TR, TP, and TG, respectively. The diffusion of Si into the Ti interlayer is uniformly observed from TR to TP in Fig. 2(a). However, the atomic ratio of Si from the SiC/TR interface varied by the joining temperature. As the joining temperature rose, smaller amounts of silicon were observed across the SiC/TR interface. Furthermore, silicon cannot be detected in the TR layer, as shown in Fig. 2(c), indicating the formation of multilayer diffusion phases. The overall concentration of Ti uniformly varied from the TR to TP layer. The elemental ratio of Ti sharply increased in the TP/Re interface, shown in Fig. 2(a), indicating the formation of an inter-lamella structure with Re-Ti alloy. This Re-Ti precipitates were constantly decreased with higher temperature, eventually

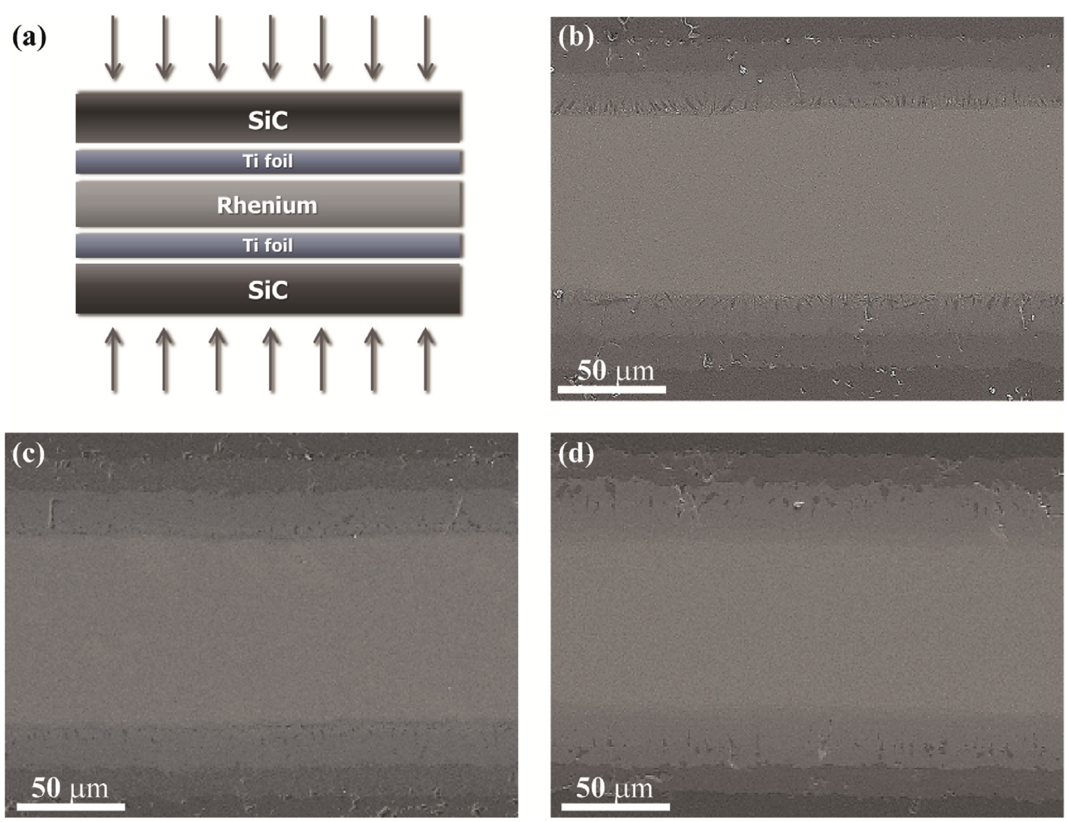

Fig. 1. (a) Schematic illustration of the sandwich shaped SiC/Ti/Re joint, SEM micrographs of interface of the hot-pressed joined sample; the joining temperature was (b) 1400 °C, (c) 1500 °C, (d) 1600 °C, respectively.

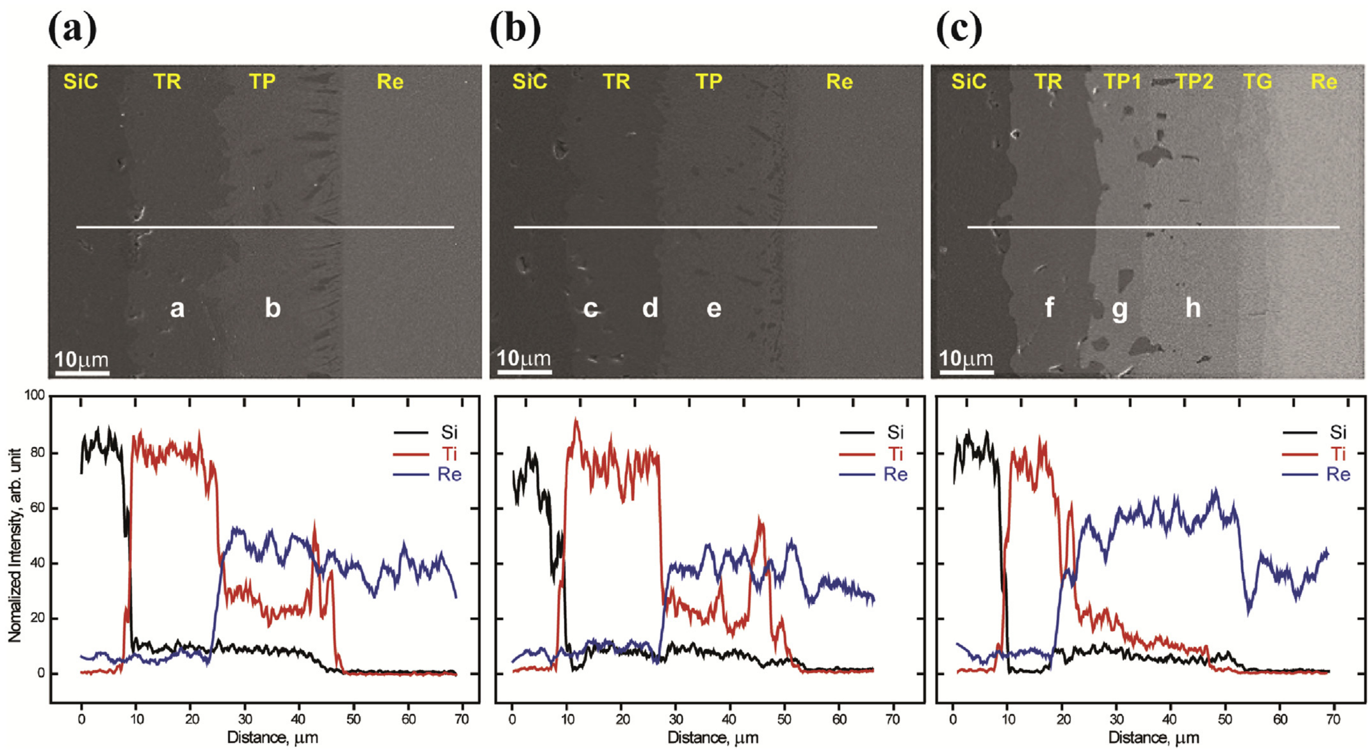

Fig. 2. Elemental distribution of interface of the hot-pressed joined sample with different temperatures (a) 1400 °C (b) 1500 °C, (c) 1600 °C.

changing to a Re/Ti gradient layer (TG). This is consistent with the brightly contrasted layer-by-layer microstructure. Also, the elemental ratio of rhenium was homogeneously distributed from the TR to TP layer, as shown in Fig. 2(c), indicating diffusion bonding at the Ti/Re interface.

To quantitatively show the elemental compositions at each layer, the analyzed positions and expected composition are shown in Table 1. The formation of Ti_3SiC_2, $Ti_5Si_3C_x$, and TiC was reported in the diffusion bonding of a Ti-SiC system [9,10]. Multilayered diffusion phases were observed in all joined samples. The atomic ratio of granular phases ranged from 18.26 to 29.47 at.% for Si, 81.06 to 52.96 at.% for Ti, and 0.66 to 17.57 at.% for Re, respectively. Considering the diffusion rate of carbon to silicon, the atomic concentration of Ti/Si might indicate TiC and $Ti_5Si_3C_x$ are intermediate phases of Ti_3SiC_2. For a parallel location, these regions have an average elemental composition that is consistent with the presence of Ti_3SiC_2 and also possibly Ti_5Si_3 (point markers a, d, and g, Fig. 2). Phase ratios of both TiC and $Ti_5Si_3C_x$ in the TR layer are calculated on the basis of the quantitative elemental composition in Fig. 3(a). The atomic ratio of regions c and f indicated the composition of TiC, which thickened with higher joining temperature. This is also consistent with the EDS line profile in Fig. 2. The thermal stability of the diffusion bonded layer can be evaluated by the distribution of the coefficient of thermal expansion (CTE). $Ti_5Si_3C_2$ has a stable CTE of 9.29×10^{-6} K^{-1} in a temperature range of 25–1400 °C [11]. The intermediate phases $Ti_5Si_3C_x$ and Ti_5Si_3 have an anisotropic CTE along ‘a’ and ‘c’ axes, which are $\alpha_a = 6.1 \times 10^{-6}$ K^{-1} and $\alpha_c = 16.6 \times 10^{-6}$ K^{-1}, respectively [12,13]. The mismatch of CTE along the different axes possibly leads to the formation of micro-cracking in the Ti-contained layer. The phase ratio of $Ti_5Si_3C_x$ with the anisotropic CTE in the TP layer is also calculated and the thickness in both the TP and TR layers is shown in Fig. 3(b). The highly anisotropic expansion properties of $Ti_5Si_3C_x$ and Ti_5Si_3 would be detrimental to the bonding strength of the TP layer. In the case of the joint at 1600 °C, these phases might be formed only in the TP1 layer with thickness of ~10 μm (point markers g, Fig. 2). Other joints contain more of these deleterious phases in both the TR (point markers a, d) and TP layers (point markers b, e) than the joint at 1600 °C, and they increase the propensity for micro-cracking with higher temperature. Therefore, the formation of $Ti_5Si_3C_2$ with a stable CTE of 9.29×10^{-6} K^{-1} in the joint at 1600 °C is qualitatively better than the formation of the deleterious phases: $Ti_5Si_3C_x$, Ti_5Si_3.

Table 1
Quantitative elemental compositions of TR and TP layers with different temperatures for the indicated positions (a-h) in Fig. 2.

Point	Si (at.%)	Ti (at.%)	Re (at.%)	Remark
a	18.26	81.06	0.66	$Ti_5Si_3C_x$ + TiC
b	29.47	52.96	17.57	(Re)-$Ti_5Si_3C_x$ + (Re)-Ti_3SiC_2
c	1.10	97.85	1.05	TiC
d	13.32	85.32	1.35	$Ti_5Si_3C_x$ + TiC
e	28.08	54.34	17.57	(Re)-$Ti_5Si_3C_x$ + (Re)-Ti_3SiC_2
f	0.49	98.34	1.16	TiC
g	28.03	56.03	15.93	(Re)-$Ti_5Si_3C_x$ + (Re)-Ti_3SiC_2
h	25.41	46.83	27.76	(Re)-Ti_3SiC_2 + Re_2Si

Fig. 4 shows that a band containing lenticular precipitates was formed in the interface between Re and Ti. The quantitative elemental composition of each precipitate was also analyzed, as shown in Table 2. According to the Ti-Re phase diagram [14], Ti is largely divided into α and β phases according to solubility of rhenium according to titanium. Depending on the fraction of rhenium in the alloy, the solubility of Re in α-Ti is about 0.1% at 750 °C, up to about 6 at% exists in the α + β phase and thereafter remains in the β phase and the maximum solubility is about 50 at%. As relatively fast cooling rates, the solid solution undergoes a martensitic transformation, which depends on the fraction of rhenium contained in the β phase. Considering the joining

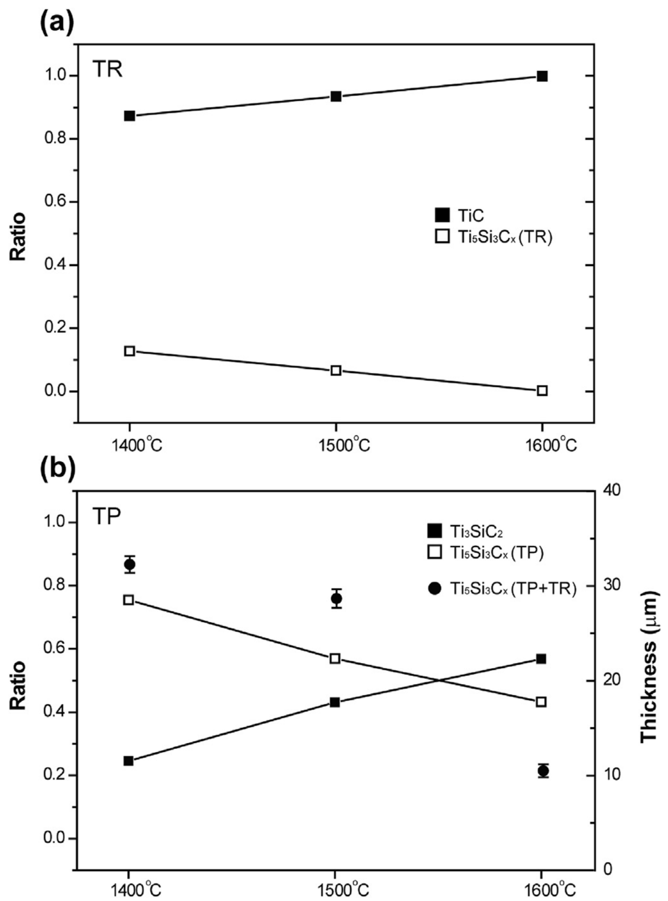

Fig. 3. Phase ratio of interface of the hot-pressed joined sample with different temperatures (a) TR layer (b) TP layer, respectively.

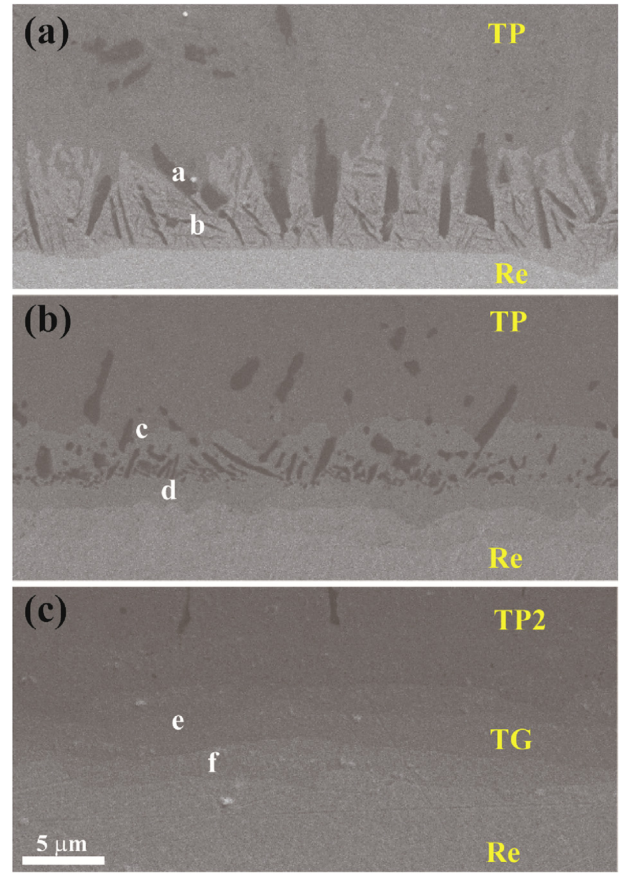

Fig. 4. SEM micrographs of the Ti/Re interface of the hot-pressed joined sample; the joining temperature was (a) 1400 °C, (b) 1500 °C, (c) 1600 °C, respectively.

temperature and the solubility of Re to Ti [15] (Table 2.), the shape of the needle shaped precipitates, which are observed in the Fig. 4(a) and (b), seems to be a martensitic transformation. Dark gray precipitates such as lamella structures (point marker a, Fig. 4(a)) have a composition that is consistent with bcc-Ti, containing 7.32 at.% of Re. The white gray precipitates (point marker b, Fig. 4(a)) were likely formed when liquid Re-Ti alloy was cooled to room temperature, which is consistent with the atomic ratio of ReTi. The interface of TP/Re, joined at 1500 °C, contained similar gray precipitates with different contrast. The dark gray precipitates (point marker c, Fig. 4(b)) were also confirmed as bcc-Ti, containing 14.18 and 10.95 at.% of Re and Si, respectively. A bright gray plate-like precipitate (point marker d, Fig. 4(b)) was formed under the bcc-Ti precipitates. It is likely to be ReTi, which is soluble to Si with 23.28 at.%. This indicated that an alloying reaction between Si and Re occurred and broadened the multiphase diffusion layers near the Re metal. The interface between TP2 and Re consisted of a gray-colored layer with various contrasts, as shown in Fig. 4(c). The atomic ratio of Si and Ti decreased from 37.48 to 6.15 to 29.52 and 0 at.%, respectively, with increasing presence of Re. Considering the phase diagram of Re-Si, several multi-components between Re-Si phases exist in the alloying system: Re_2Si, ReSi, $ReSi_{1.8}$ [16,17]. However, ReSi might have decomposed into Re_2Si and $ReSi_{1.8}$ in the specific temperature range under atmospheric pressure. Considering the atomic ratios of the TG layer (point markers e, f, Fig. 4(c)), the TG layer was confirmed to be multi-phase layers of Re_2Si and $ReSi_{1.8}$, Re and Re_2Si, respectively. In summary, the diffusion of Si increased at the high temperature of 1400–1600 °C, resulting in the

Table 2
Quantitative elemental compositions of the Ti/Re interface with different temperatures for the indicated positions (a-f) in Fig. 4.

Point	Si (at.%)	Ti (at.%)	Re (at.%)	Remark
a	–	92.67	7.32	Ti (Re)
b	–	51.94	48.06	ReTi
c	10.95	72.46	14.18	Ti (Re, Si)
d	23.28	34.43	38.40	ReTi (Si)
e	37.48	06.15	56.37	$Re_2Si + ReSi_{1.8}$
f	29.52	–	70.48	$Re + Re_2Si$

formation of a gradient joined region composed of bimetallic interlayers among Si-Ti-Re without any micro-cracks. It is expected that the gradient region can relieve internal stress caused by the thermal expansion with high temperature.

The micro-hardness was measured for the joined samples with respect to the temperature and interface, as shown in Fig. 5. Each measurement was conducted five times to reduce the average error. The standard deviation of the average hardness was also represented. The SiC substrate showed a highest hardness value of ~48 GPa at the joining temperature of 1600 °C, compared to other interfaces throughout the joining temperature range. The micro-hardness of Re also showed a similar trend with that of SiC, that is, enhanced values with increasing joining temperature. The relatively higher hardness value was attributed to the effect of compression under high temperature. The highest average hardness of the TR interface was ~28 GPa at the joining temperature of 1600 °C. This is consistent with the existence of TiC (point markers

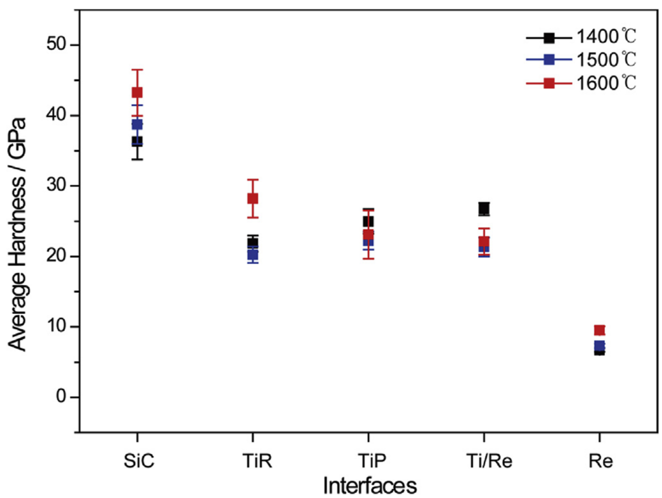

Fig. 5. Variation in average hardness values of each interface for the SiC-Ti-Re joints with different temperatures.

a, c, d, f in Fig. 2.), which has high hardness. Similar hardness was observed at the TP interface, containing $Ti_5Si_3C_x + Ti_3SiC_2$ phases. To sum up, the hardness gradually decreased from ~48 GPa (SiC) to ~9.5 GPa (Re) in the SiC/Ti/Re sample joined at 1600 °C. The gradual variation of hardness values along the interfaces indicates stable joining of disparate interfaces without brittle phases.

4. Conclusions

Re was successfully joined to SiC by hot-pressing with a Ti interlayer under process conditions of 25 MPa at various temperatures from 1400 to 1600 °C for 2 h. The SiC-Ti-Re sandwich-liked joints showed stable interfaces without any micro-cracking, pores, or defects. The composition of Si, Ti, and Re along the interlayers varied with distance and joining temperature. Multi-component phases (TiC, $Ti_5Si_3C_x$, and Ti_3SiC_2) were formed in the Ti interlayer, and they have different coefficients of thermal expansion. A band containing lenticular precipitates (bcc-Ti and ReTi) was formed in the interface between Re and Ti, changing to a gradient interlayer of Re-Ti-Si alloy because of the high joining temperature. The micro-hardness was measured for the joined SiC/Ti/Re along the all interface. In terms of the thickness of the detrimental phase $Ti_5Si_3C_x$, the gradient layer of the Re/Ti interface, and the distribution of average hardness, the SiC/Ti/Re joints exhibited a successful joining structure when joined at 1600 °C.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2017.01.081.

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