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Original article

# A novel high entropy CoFeCrNiCu alloy filler to braze SiC ceramics

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ABSTRACT

In order to reduce intermetallic compound formations in brazed joints, a CoFeCrNiCu high entropy alloy was invented and employed to braze SiC ceramics. Results show that SiC ceramics were tightly and strongly brazed with the CoFeCrNiCu filler. Microstructure, phase and shear strength were systematically studied for joints brazed at different temperature. Main compositions were identified as high-entropy FCC, Cu(s, s), Si(s, s), and $Cr_{23}C_6$ phases, regardless the brazing temperature differences. After being brazed at 1453 K, the joint reached a maximum shear strength of 60 MPa, much higher than those brazed with conventional AgCuTi filler. Thanks to high entropy effect of CoFeCrNiCu filler, random solid solution turned out in the seam and benefitted joint quality. The successful use of CoFeCrNiCu high entropy alloy as fillers can expand the application range of high entropy alloys and provide a new filler system to braze ceramics.

## 1. Introduction

SiC ceramic has been widely applied in nuclear powerplants, semiconductors and machinery due to its outstanding high strength, high hardness, low density, good oxidation resistance, and low coefficient of thermal expansion [1–5]. However, its intrinsic properties of high hardness, brittleness, and low electrical conductivity hinder its formations in large sizes and complex shapes [6]. To extend the SiC application scope, various techniques have been assessed to join the ceramic to other metals and compounds [7–9]. Among them, the brazing technology is a simple, convenient and economical connection method and considered promising to solve problems arisen from the physical properties of the carbide.

Choosing a proper filler is important for brazing [10]. Conventionally, Ag-Cu-Ti-based fillers and Ni-based fillers are used in ceramics brazing [11]. It was found that addition of Zr element in the Ti-Ni eutectic filler facilitated SiC ceramics brazing. The shear strength of the joints was improved from 69 MPa to 112 MPa and a large amount of brittle intermetallic compound $Ti_2Ni$ was generated in the joint [12]. The Ag-Cu-Ti composite filler was also modified with $B_4C$. Due to the presence of the $B_4C$, TiB whiskers and TiC particles were simultaneously formed in the Ag-based and Cu-based solid solutions. While a high shear strength of 140 MPa was reached, a large number of brittle TiCu phases turned out in the joint [13]. Zhong et al. studied microstructure and mechanical strength of SiC joints brazed with a $Cr_3C_2$-particles reinforced Ag-Cu-Ti filler. The carbide at an appropriate proportion in the filler became randomly distributed particulates in the brazed matrix. As a result, the Ag-rich and Cu-rich solid solution phases were refined. However, the $Cu_2Ti$ intermetallic phase was also associated with the solid solution formations [14]. From the above reports, Ni-based fillers and Ag-Cu-Ti-based fillers are good at introducing wetting effect on the ceramic surface., a large amount of brittle intermetallic compounds stayed at the brazed joints and deteriorated the joint qualities due to large negative mixing enthalpies between Cu/Ni and Ti. Consequentially, Cu or Ni can easily react with Ti to reduce the activity of the Ti element and ruin joint performance. In addition, the expensive AgCuTi fillers are easily oxidized and rather soft. The low melting points of brazed products from the AgCu fillers damage the overall stabilities of the composites in high temperature. As a result, the application range of the joint SiC is limited [12]. Therefore, it is urgent to design a new type of filler for reliable self-joining of the SiC ceramic.

As a new kind of alloys, high-entropy alloy has attracted great attention due to its high mechanical properties, and especially the thermal stability at high temperature. In high-entropy alloy, component elements prefer random distributions instead of being alloyed intermetallically. The activity of each element is kept, and solid solutions are formed as the products after high temperature treatments [15]. In addition, slow diffusions of these component elements inhibit excessive

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dissolution of the base material into the brazing seam during the brazing process. Up to date, many high entropy alloys have been developed such as FeCrMnNiCo, AlCoCrFeNiTi, CoCrCuFeNiTi etc [16,17]. However, application of high-entropy alloys has been scarcely reported in brazing. Zhang et al. successfully joined $ZrB_2$-SiC-C ceramic to GH 99 superalloy by using a Ti/FeCoNiCrCu composite filler. Therein, the activities of Ti and Cr were preserved while the solid solution phase was formed in the brazing seam eventually. The (TiB + CrB)/solid solution was well bonded to ZSC and GH99. A maximum shear strength of 71 MPa was achieved [18]. The Ni-Mn-Fe-Co-Cu high entropy alloy brought in superior mechanical performances when employed to brazed metals to Inconel 718. The maximum bending strength reached 140 MPa [19].

In this work, a high entropy alloy of CoFeCrNiCu alloy was prepared and employed as the brazing filler, owing to its simple solid solution structure, low melting point and common elements [20,21]. Comprehensive studies of brazing temperature influences on interfacial structure and joint strength were carried out. The relation between the microstructural evolution and mechanical properties of the joints was assessed. It is found that an active interfacial reaction was reached between SiC and the active element of Cr during the brazing. Solid-solution bulks were formed as the matrices at the brazing seams, leading to mechanical enhancements of the joints. Moreover, a formation mechanism of brazed joint was proposed based on element diffusion schemes.

## 2. Experimental

The SiC ceramic in this study was prepared by pressureless sintering (supplied by Kaifa Special Ceramics Co., Ltd., Beijing, China). As declared by the manufacturer, the sintering additives used in the SiC ceramics were $Al_2O_3$ and $Y_2O_3$. The CoFeCrNiCu alloy was prepared by arc melting of pure elements, and then suction-casted into a rod with a diameter of 6 mm under an argon atmosphere. The SiC ceramics was cut into dimensions of 4 mm × 4 mm × 4 mm and 10 mm × 10 mm × 4 mm for metallographic observation and strength testing, respectively. The CoFeCrNiCu alloy was shaped to a foil with a thickness of 600 μm in an electrical discharge machine. The foil was grounded with the SiC grit paper until to a thickness of ~400 μm. All of the polished samples were ultrasonically cleaned in acetone for 10 min and then dried by an air flow.

Before brazing, the CoFeCrNiCu foil was intercalated in SiC ceramics, as shown in Fig. 1a. The assembly was then pinched by a graphite jig. A nominal load of 0.016 MPa was applied on the top to stabilize the assembly. During the brazing, a rate of 10 K/min was selected to heat up the assembly to 573 K. At this temperature, the assembly was held for 900 s to remove the binder. The brazing tests were performed in a vacuum brazing furnace (JVLF211) with a basic pressure less than 1.3 × $10^{-3}$ Pa. The brazing temperature varied from 1433 K to 1473 K but the holding time fixed to 3600 s.

The melting points of CoFeCrNiCu filler were analyzed by a differential thermal analysis (DTA, DTG-60 H). The interfacial microstructure of the brazed joint was characterized on a scanning electron microscope (SEM, S-8010, Hitach, Japan) coupled with an energy dispersive spectrometer (EDS, TN-8000). X-ray diffraction (XRD, D-MAX Rapid II) analysis was utilized to identify the reaction phases of the brazed joint. To further investigate the micro-morphology and phase structures of the brazed joints, the seams were polished using a focused ion beam (FIB) method on a FEI Helios Nanolab 600 with the source material of Ga. The millings were performed with a voltage of 30 kV and 5 kV- 2 kV, for rough and fine millings. Source current was adjusted within a range of 90 pA - 22 nA during the FIB operation. The FIB samples were then analyzed by a transmission electron microscopy (TEM, JEOL-2200FS EFTEM). To evaluate the mechanical property of the brazed joint, shear tests were carried out on a universal material testing machine (EUTM, MTS CMT4204) with a constant speed of 0.5 mm/min, as shown in Fig. 1b. At least three test results for a joint brazed at one temperature were used to calculate the average shear strength of the brazed joint.

## 3. Results and discussion

The microstructure of the CoCrCuFeNi alloy filler is depicted in Figs. 2(a) and (b). It is composed of a dendritic microstructure (darker phase $\alpha$) and interdendrite microstructure (lighter phase $\beta$). The average primary arm width of dendritic microstructure is about 15 μm. From the EDS results of Table 1, α is determined to the Cu-depleted phase (high-entropy FCC phase), and the Cu rich phase $\beta$ to Cu(s, s). Hereafter, for convenience, $\alpha$ phase is named as HEAF phase for convenience. Cu is reported as an electronegative element. It becomes less stable in the FCC dendrites and can be supplanted into the interdendritic regions and yielded Cu aggregations [22]. Combining XRD results of Fig. 2c, phases $\alpha$ and $\beta$ are identified to Cu solid solutions but varied in Cu contents. The result is in line with these reported from Refs [20–23]. Fig. 2d demonstrates the DTA curve of CoCrCuFeNi filler. The liquid temperature $T_l$ is about 1413 K. The brazing temperature sited in the present work is higher than 1413 K.

Fig. 3 depicts the microstructure and EDS results of a SiC/CoFeCrNiCu/SiC joint brazed at 1453 K for 3600 s. A successful joint of SiC ceramics was reached. Obvious reaction layers appeared at the ceramic-metal interfaces as shown in Fig. 3a. Sufficient element distributions in the brazed joint can be well seen from Fig. 3b to Fig. 3h. According to the distributions, the C, Si and Cr elements mainly locate at the reaction layer based on Figs. 3f-3 h. The Co, Ni, Cu, Cr and Fe elements from the high entropy filler are mainly disorderly distributed in the whole brazing seam. Besides, it is worth noting that Cu from the high entropy alloy filler is distributed in the middle of joint, indicating the formation of Cu-based compound.

Fig. 4a shows a typical microstructure of SiC/CoFeCrNiCu/SiC joint brazed at at 1453 K for 3600 s. In the overview, the joint is about 350

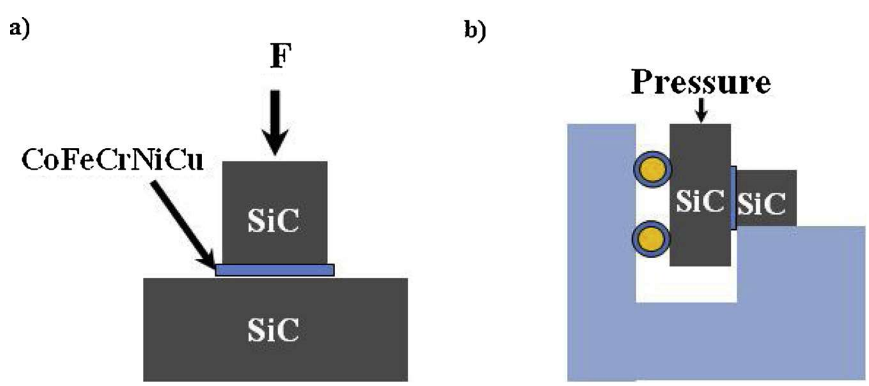


**Fig. 1.** Schematic diagram of a) brazing assembly and b) shear test.

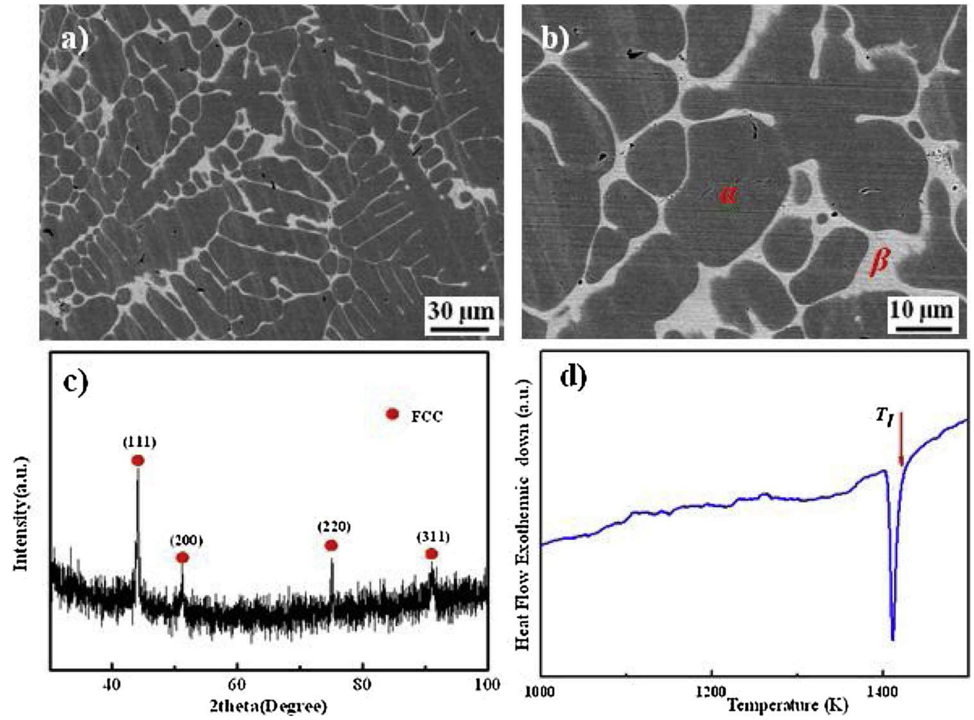


**Fig. 2.** a), b) microstructure; c) XRD pattern and d) DTA curve of CoCrFeNiCu alloy filler.

**Table 1**
EDS results from Fig. 2b.

| Point | Co | Cr | Fe | Cu | Ni | phase |
|---|---|---|---|---|---|---|
| $\alpha$ | 17.85 | 36.05 | 13.91 | 10.46 | 21.73 | HEAF |
| $\beta$ | 12.77 | 14.41 | 11.51 | 50.58 | 10.73 | Cu(s,s) |

µm width without defects. A region of continuous reaction layers adjacent to SiC ceramic was found distinguishing from a region of the brazing seam. They were marked as zone I and zone II. Figs. 4b and 4c are the zoomed images of zones I and II. Zone I has an average width of ~15 µm. Therein three mixed phases are found, and marked as A, B and C. Zone II was the center zone of the joint with width of 300 µm where two phases were identified and marked as D and E.

Chemical compositions of phases A–E in the brazed joint were tabulated in Table 2. The EDS determination identified the Cr and C in the gray phase A at a ratio of ~4:1. It is reported that for Cr, six compounds ($Cr_{23}C_6$, $Cr_7C_3$, $Cr_3C_2$, $Cr_3Si$, CrSi and $Cr_5Si_3C$) could be formed. Among them, the $Cr_{23}C_6$ phase is the most favorable because its formation requires lowest Gibbs free energy [24]. Combined the Cr and C ratio, phase A is inferred as $Cr_{23}C_6$. The main reaction between Cr and C underwent a process of 23Cr +6C = $Cr_{23}C_6$ ($\Delta G$=-309600-77.4 T (J/mol)). Such a Cr-C phase meets the necessary thermodynamic condition and can exist at a high temperature [25]. Moreover, high hardness and good oxidation resistance of $Cr_{23}C_6$ make it as a reinforcing phase in the coating area. Thus, in the present work, the suitable formation of $Cr_{23}C_6$ phase can hinder the propagation of crack, and benefit strength of brazed joints [26,27]. The main elements in the black phase B are Si, which is identified as the Si(s, s), consistent with the previous result where Cr-Si binary eutectic was employed as a filler [28]. Phase C with tiny white structures mainly contains the Cu elements. It is identified as Cu(s, s), corresponding to the previous research [29]. The molar ratio of Co, Cu, Cr, Ni and Fe in the gray phase D are about 1:1:1:1:1, while

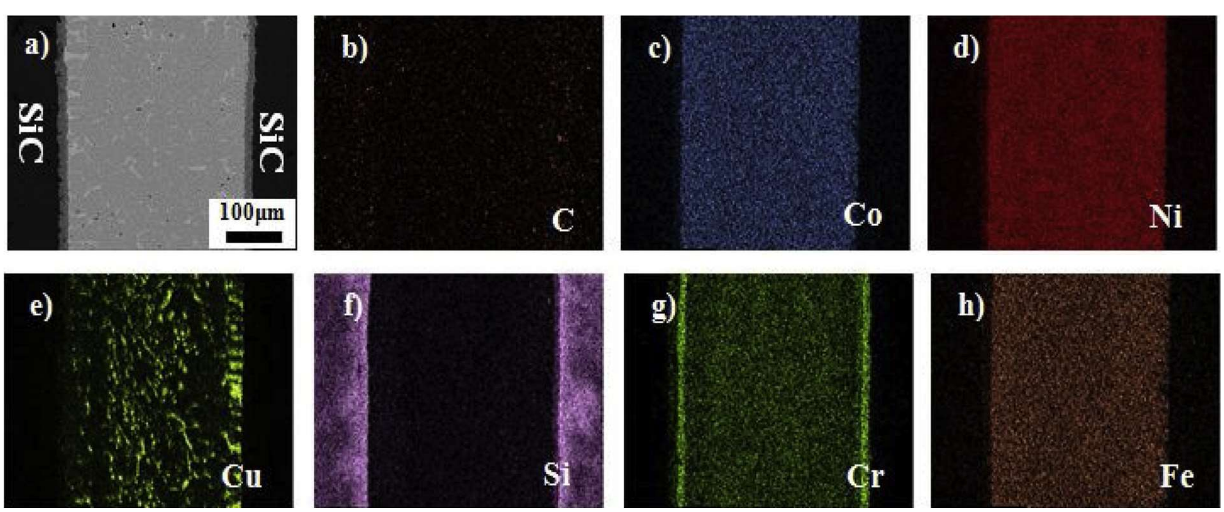


**Fig. 3.** a) Microstructure and b) to h) corresponding EDS results of brazed joint at 1453 K for 3600 s.

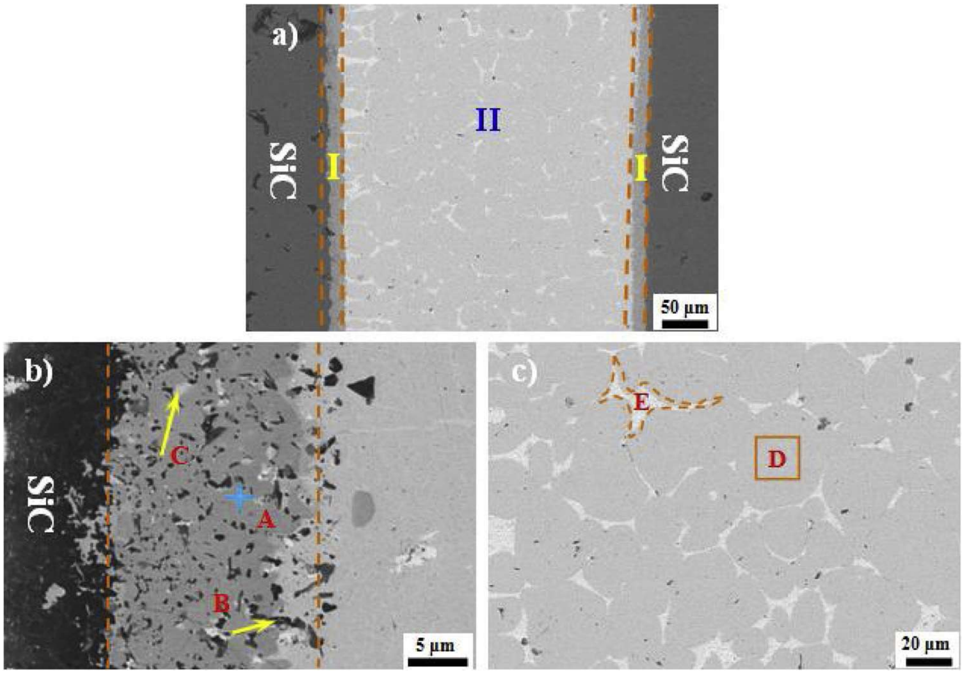


**Fig. 4.** SEM images of typical SiC/SiC brazed joint at 1453 K for 3600 s.

**Table 2**
EDS of each point marked in Fig. 4.

| spot | C | Fe | Co | Ni | Cu | Si | Cr | Possible phase |
|---|---|---|---|---|---|---|---|---|
| A | 14.41 | 1.60 | 0.89 | 1.06 | 6.13 | 4.04 | 71.87 | $Cr_{23}C_6$ |
| B | 10.00 | 0.32 | 2.61 | 7.16 | 1.65 | 50.56 | 27.70 | Si(s, s) |
| C | 11.97 | 0.94 | 0.02 | 5.14 | 77.42 | 1.39 | 3.12 | Cu(s, s) |
| D | 13.09 | 11.75 | 15.55 | 18.29 | 11.23 | 2.56 | 27.53 | FCC(HEAF) |
| E | 11.39 | 0.96 | 0.01 | 5.03 | 79.15 | 0.65 | 2.81 | Cu(s, s) |

phase E is a copper region. Thus, phases D and E are inferred as HEAF phase and Cu (s, s) phase, respectively. However, compared to the results in Fig. 2a, the primary dendrites of as-cast filler alloy are significantly refined and form the equiaxed dendrite in the brazing seam. During brazing process, the solute contents are nearly equal for the Co, Cr, Fe and Ni elements in the HEAF phase. In this context, a solute diffusion-controlled growth determines the dendritic velocity, and the HEAF phase grows in a dendritic path. On the other hand, a larger potential barrier inhibits the Cu solute during the solidification [30].

In order to reveal micro- and phase structures of the product in the joint, TEM and the selected area electron (SEAD) patterns of zone I and zone II were analyzed, as shown in Fig. 5. From Fig. 5a, main phases of $Cr_{23}C_6$, Cu(s,s) and Si(s,s) were well figured out. The corresponding SAED patterns were depicted in Figs. 5b and 5c for the crystals. Spots are identified as diffractions from the [3 4 7] and [10] zone axis for Cu (s, s) and Si(s, s), respectively. Similarly, zone II are mainly Cu(s, s) and FCC HEAF phase, as shown in Fig. 5d. The strong diffraction spots are indexed to diffractions from [224] and [02] zone axis for HEAF phase and Cu(s, s), respectively. Fig. 6 demonstrates the micro-focused XRD pattern obtained from zone I and zone II, respectively. The XRD results are consistent with the analysis of SEM and TEM. From the above analysis, it can be determined that the A–E phases in the brazed joint are HEAF, Cu (s, s), Cu (s, s), Si(s, s), and $Cr_{23}C_6$, respectively.

The formation mechanism of the SiC/CoFeCrNiCu/SiC joint is systematically investigated. In Fig. 7, a physical model is established and the diagram of the brazed joint visualized. At the beginning, the CoFeCrNiCu filler was melt at the melting point of 1413 K based on the DTA result. During the heat process below 1413 K, the plastically deformed filler tightly contacted with ceramics, as shown in Fig. 7a. When the temperature elevates above 1413 K, the molten CoFeCrNiCu filler transformed into liquid and wetted the surface of the base materials. At the same time, partial base materials were dissolved into the molten alloy. The main elements of SiC and filler began to diffuse, as shown in Fig. 7b. When the temperature was elevated to the brazing temperature, SiC dissolved into the brazing alloy and released Si and C atom. The active element of the Cr diffused to the SiC at both sides. Cr element is

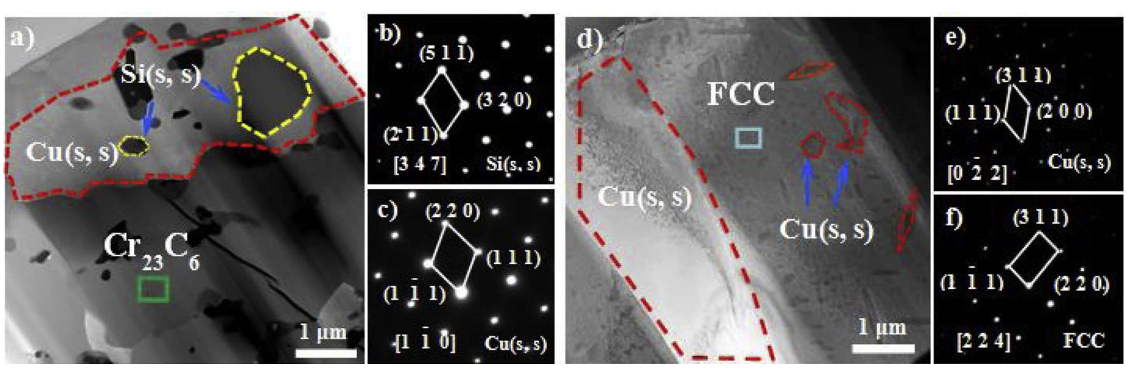


**Fig. 5.** TEM images and corresponding SAED patterns from: a)-c) zone I and d)-f) zone II.

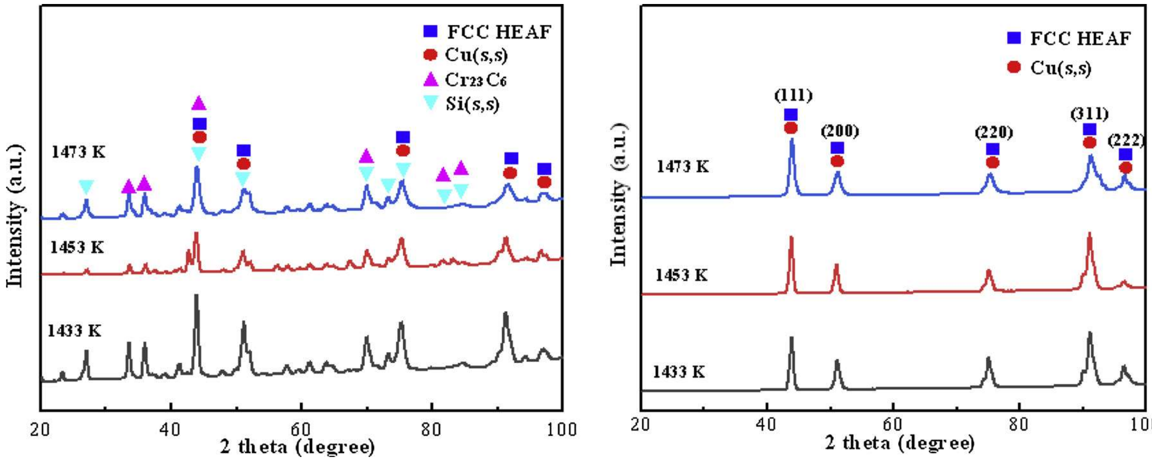


**Fig. 6.** Micro-focused XRD pattern of brazed joint at 1453 K for 3600 s from: a) zone I b) zone II.

more active than other elements in CoFeCrNiCu alloy. The mixing enthalpies between Cu, Fe, Co, Ni, C and Cr are + 12, -1, -4, -7 and −61 kJ/mol, respectively. However, the mixing enthalpies between Fe, Co, Ni and Cu are respectively + 13, + 6, and +4 kJ/mol [31]. Due to different in enthalpies, Cr is capable to react with other elements, especially C. Energetically favorable reactions between the Cr and SiC happened. As a result, the $Cr_{23}C_6$ phases and Si phases were formed. Chemical reaction took place as Cr + SiC → $Cr_{23}C_6$ + Si [29,32], as shown in Fig. 7c., The residual liquid brazing alloy was solidified into a solid solution during the cooling process following the high entropy effect. It further became the matrix of joints. In the last stage, zone I became thicker because of continued reactions between SiC and filler. However, due to the high entropy effect and slow diffusion effect of high entropy alloys, the center of the joint still held a high entropy alloy structure [33]. When the temperature decreased to the melting point of Cu, the Cu-enriched phase started to solidify from the liquid alloy [34]. As reported, mixing enthalpies between Fe, Cr, Co, Ni and Cu are respectively + 13, + 12, + 6, and +4 kJ/mol [31]. Thermodynamically, the Cu is not capable to react with other elements. Alternatively, weak mutual solubilities between Cu and the other elements lead to segregations of Cu rich phase in the joint, resulting in the formation of Cu(s, s), as shown in Fig. 7d. Due to the good plasticity of the copper, the Cu (s, s) in the joint can relieve the coefficient of thermal expansion mismatch of filler and SiC, and decrease residual stress in the joint. Following the further decrease of temperature, no other phase precipitated from the molten and the growth of the primary CoCrFeNiCu FCC solid solution phase continued. Due the diffusion of Cu element and the repulsion from other elements, some Cu was also pushed into reaction layer and formed Cu(s, s) in the interface, as shown in Fig. 7e. Based on the above analysis, it can be found that the Cr element can stabilize the Cu element in CoFeCrNiCu HEA due to the active of Cr, and reaction between Cr and SiC. Thus, in order to obtain metallurgical bonding of joint when using the HEA filler, the active element in the alloy is also necessary to initiate the interfacial reaction. This is a crucial factor to reconsider other HEA filler.

The shear strengths of SiC/SiC brazed joints brazed were plotted following brazing temperature changes at a fixed time of 3600 s, as shown in Fig. 8. All obtained joints own good shear strength despite temperature variations. At 1433 K, 1453 K and 1473 K, the shear strengths are 51 MPa, 60 MPa and 48 MPa, respectively. All values are

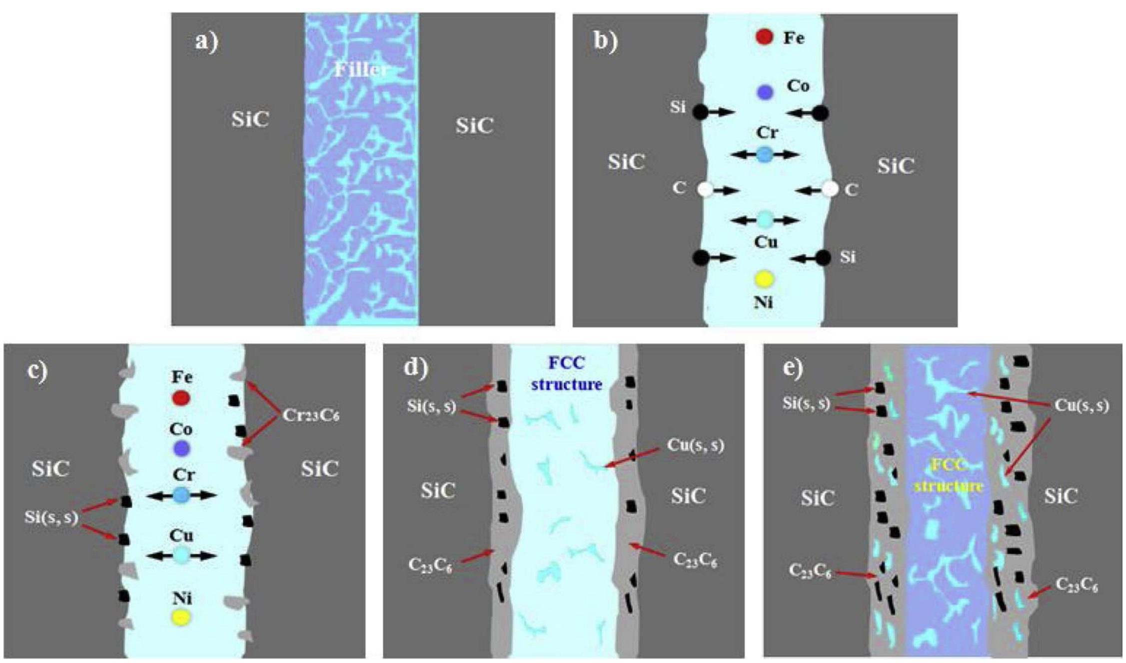


**Fig. 7.** Schematic diagram of microstructural evolution of SiC/SiC brazed joint.

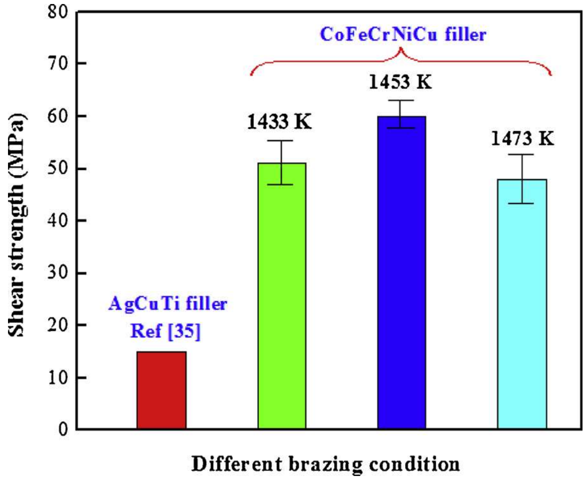


**Fig. 8.** The shear strength of SiC/SiC brazed joints brazed in the present and other works.

higher than theses given by brazing with conventional Ag-Cu-Ti fillers [35]. Thus, it can be concluded that the activity of Cr is kept in the high entropy filler and ensures the interface reaction. At the same time, the FCC solid solutions, such as HEAF phase and Cu (s, s), form the matrix of the bulk of brazing seam. The formation of solid solution in the brazing seam is beneficial to strengthen the joints due to its positive effect on solid solution strengthening of brazed fillers. It is worth noting that there are still many micro- and even nano Cu(s, s) particles in the Zone II, as shown in Fig. 5b. During shear test, it requires extra energy for the dislocations passing the particles, leading to the enhancement of strength. Moreover, generated by the mismatch of coefficients of thermal expansion between ceramic and metal, the residual stress is released thanks to Cu solid solution microstructure in the seam.

Fig. 9 depicts the microstructures of SiC joints brazed at different brazing temperatures. The brazing temperature affects the microstructure slightly. Similar to the case of 1453 K, two obviously zones were found in the resulted joints. Besides, there is no change in the phase type of the brazed joint, and the central region of the joint is an equiaxed dendritic high-entropy alloy solid solution structure, as shown in Figs. 9a, 9d and 9 g. These claims are supported by the XRD results from Fig. 5. However, changes of micro-morphology appeared at individual zone following the temperature increase. In the middle of joints, Cu-rich spherical structures are observed in the brazed joint at a low temperature (1433 K). This indicates an occurrence of the liquid phase separation in the initial liquid prior to the liquid solid transformation. The Cu-rich droplets appeared firstly [36]. Relatively, the molten subjects surrounding the Cu-rich droplets contains copper depletion. As shown in Fig. 9c, typical equiaxed dendrite and interdendritic structures were yielded through the solidification. The former is rich in Co, Cr and Fe elements, and the latter in Cu and Ni elements. In the reaction layers on both sides of SiC, reaction layer increased from 10 μm to 20 μm with the brazing temperature (Figs. 9b, 9f and 9 h).

The formation path affects mechanical properties eventually. The shear strength was low when brazing temperature was below 1453 K as given by results of shear strength in Fig. 8. At these temperatures, atomic diffusions were low, and reactions remained insufficient between the filler alloy and the base materials. At brazing temperatures above 1453 K, the joint strength decreased. The interface became much thicker than before. Both mismatches of thermal expansion coefficients and Young's modulus resulted in large residual stresses between the alloyed filler and the ceramic. The joint is no more homogenous but containing micro-cracks [37,38]. From the aforementioned determinations, the optimized condition of brazing is found as ~15 μm for the filler thickness and brazing at 1453 K for 3600 s.

Fig. 10 shows morphologies of the fracture surfaces of the SiC joint brazed at 1433 K to 1473 K for 3600 s, respectively. In brazing, the filler was well expanded, and reactions at interfaces were well accomplished, as shown in Figs. 10a to 10c. It is worth noting that a small amount of residual SiC ceramic was detected from the fracture surface

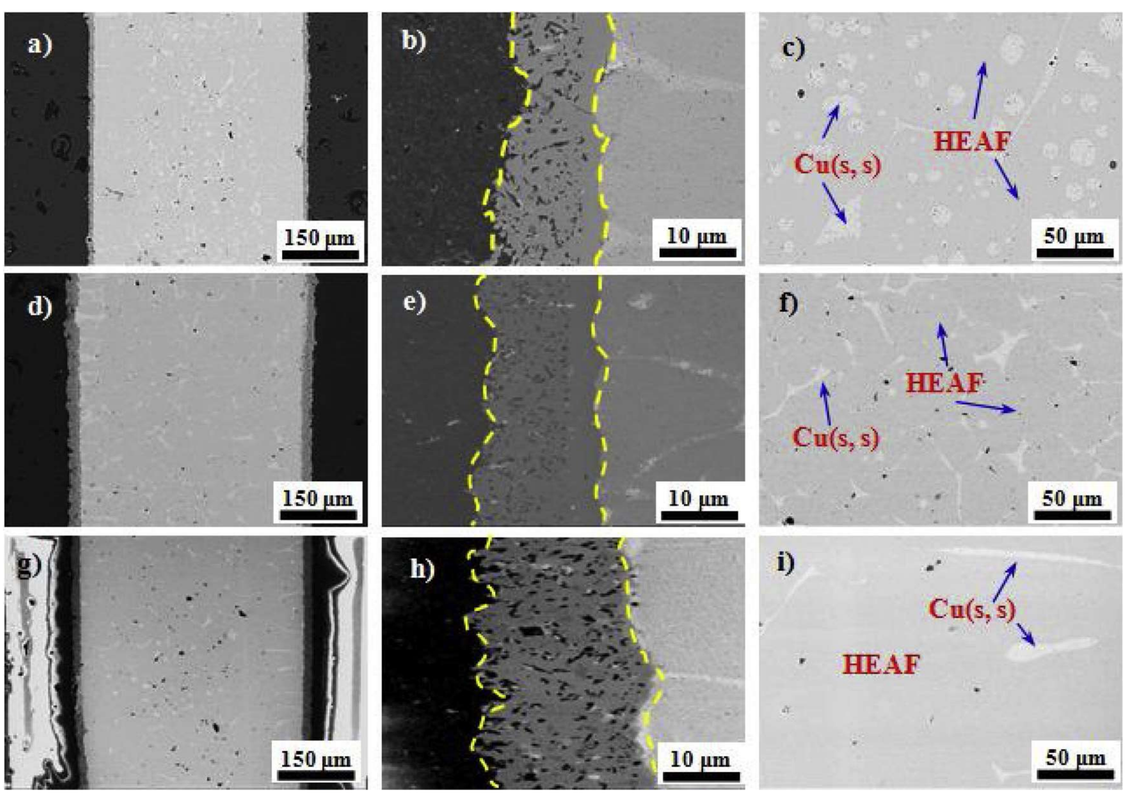


**Fig. 9.** Microstructures of SiC joints brazed at different brazing temperatures: a, b, c) 1433 K, d, e, f) 1453 K and g, h, i) 1473 K.

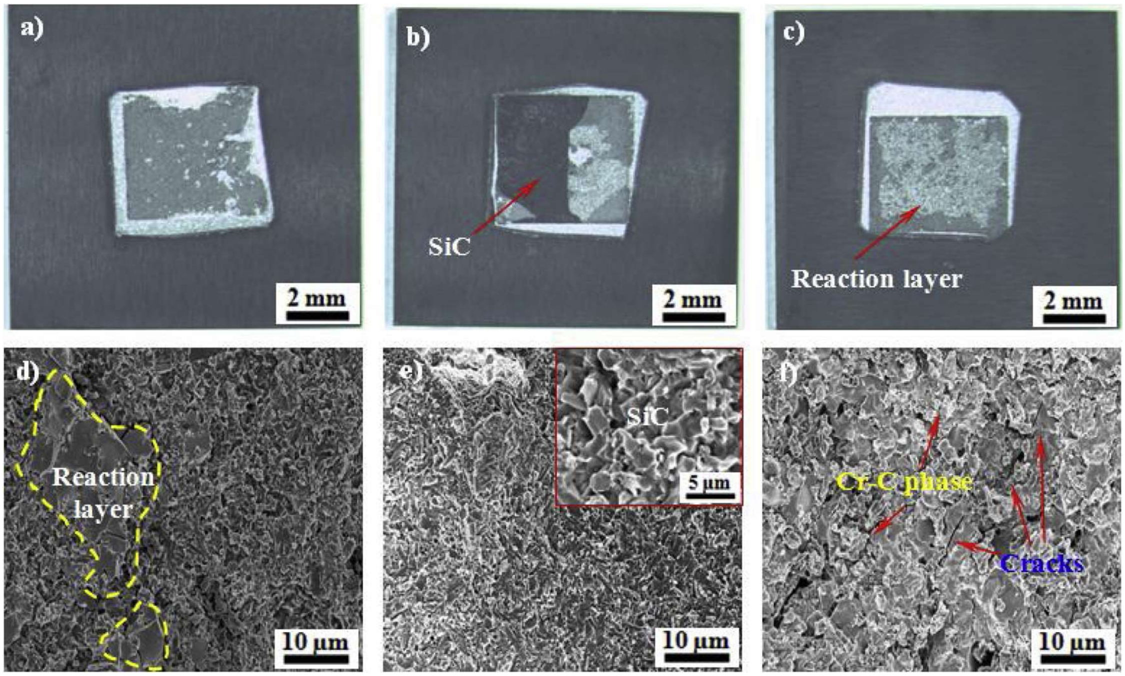


**Fig. 10.** Fracture surface of SiC/SiC brazed joint after shear test at different brazing temperature for 3600 s: a) and d) 1433 K; b) and e) 1453 K; c) and f) 1473 K.

from Fig. 10b. When the brazing temperature is 1433 K, as shown in Fig. 10d, two obvious different layers are formed. Consequentially, the stress concentration is easily induced and a weak joint yielded. When the brazing temperature is 1453 K, due to sufficient interface reaction and FCC solid solution in the brazing seam, the fracture takes place in the SiC ceramics substrate, as shown in Fig. 10e. When the joint brazed at 1473 K, the Cr and C vigorously reacted. This leads to excessive Cr-C phase ($Cr_{23}C_6$) at the joint, inducing the formation of micro-cracks during brazing. Thus, during shear test, fracture can easily occur along these cracks, as shown in Fig. 10f.

## 4. Conclusion

In this present work, a novel CoFeCrNiCu high entropy alloy filler was prepared and introduced to braze SiC. Comprehensive properties of the brazed joints were investigated. The following are the main conclusions:

1) A sound joint was obtained at different brazing temperature for 3600 s using CoFeCrNiCu high entropy alloy filler. Due to the high entropy effect, the filler alloy is prone to form solid solution rather than intermetallic compounds. Variation of the brazing temperature brings slight changes for the microstructure of SiC joint. The typical microstructure of brazed joint is SiC/$Cr_{23}C_6$ + Cu(s, s) + Si(s, s)/ HEAF + Cu(s, s)/ $Cr_{23}C_6$ + Cu(s, s) + Si(s, s)/SiC.
2) When using the high entropy filler, the brazed joints own higher shear strengths than these brazed with common AgCuTi filler, regardless the changes of brazing temperature. The maximum shear strength achieved 60 MPa at 1453 K for 3600 s. Higher or lower brazing temperature is not beneficial for the achieving of good joint quality.
3) A large quantity of FCC solid solution (e.g., HEAF phase and Cu (s, s)) was formed as the matrix of the bulk of brazing seam. It led to the release of the high residual stress of joint. At the same time, the suitable formation of $Cr_{23}C_6$ phase with high hardness can hinder the propagation of crack. Both reasons benefit the strength of brazed joints.
4) During the formation of joint, the loss of Cr elements may indeed influence solid solution structure of original HEA. In the present work, with the increasing of temperature, the solid solution structure in the seaming was changed. Such a question deserves inventions of composite fillers based on the HEA and a dedicated study in the future.

## Declaration of Competing Interest

We declare that we have no conflict of interest.

## Acknowledgement

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