crystals

MDPI

Review

Carbon–Carbon Composite Metallic Alloy Joints and Corresponding Nanoscale Interfaces, a Short Review: Challenges, Strategies, and Prospects

Chenyu Wang [1,2], Yingguo Yang [1,3,*], Guangli Zeng [1,2], Xingtai Zhou [1,2], Hefei Huang [1,2] and Shanglei Feng [1,2,*]

[1] Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China
[2] University of Chinese Academy of Sciences, Beijing 100049, China
[3] School of Microelectronics, Fudan University, Shanghai 200433, China
* Correspondence: yangyingguo@sinap.ac.cn (Y.Y.); fengshanglei@sinap.ac.cn (S.F.)

Abstract: Brazing of carbon–carbon (C/C) composites with metallic materials currently faces a series of difficulties, such as the poor wettability of metallic materials on the surface, the nanoscale interface bonding of C/C composites and metallic materials, thermal stress problems for these different materials, etc. Especially, the practical problems, including the low joint strength and insufficient reliability, still limit the large-scale practical application of brazing technology for C/C composites and metal materials. Herein, in order to guide the fabrication of high-quality joints, we present a brief discussion on the latest research progress in the joints of C/C composites and metallic materials, including current challenges, solution methods, mechanisms, and future prospects. More importantly, the nanoscale interface in the carbon–carbon composites and metallic alloys is paid very little attention, which has been critically discussed for the first time. Then, we further outline the possible solutions in joint problems of C/C composites and metallic materials, proposing feasible strategies to control the reaction in the brazing process, such as surface treatments, the addition of reinforcing phases, a transition layer sandwiched between the base material and the intermediate layer, etc. These strategies are being envisioned for the first time and further contribute to promoting the converged applications of C/C composites and metallic materials.

Keywords: carbon–carbon composites; alloy; joint; nanoscale interfaces

Citation: Wang, C.; Yang, Y.; Zeng, G.; Zhou, X.; Huang, H.; Feng, S. Carbon–Carbon Composite Metallic Alloy Joints and Corresponding Nanoscale Interfaces, a Short Review: Challenges, Strategies, and Prospects. *Crystals* **2023**, *13*, 1444. https://doi.org/10.3390/cryst13101444

Academic Editor: Tomasz Sadowski

Received: 9 August 2023
Revised: 24 September 2023
Accepted: 25 September 2023
Published: 28 September 2023

1. Introduction

Carbon–carbon (C/C) composite material is a new type of composite material, with carbon fiber or graphite fiber as the reinforcement material and carbonized or graphitized resin or carbon, made by chemical vapor deposition, as the matrix. It has a series of excellent properties, such as lightweight, high strength, an outstanding modulus, a low coefficient value of thermal expansion, a high resistance temperature, corrosion resistance, a high fracture toughness, a low creep property, etc. C/C composite material is considered a novel material, which has simultaneous structural and functional properties [1–4].

The density of C/C composites is low (<2.2 g/cm^3), only 1/4 that of nickel-based superalloys and 1/2 that of ceramic materials [3]. The C/C composite is an ultra-high temperature composite that can be used at temperatures higher than 3000 °C. As the temperature increases, its strength not only does not decrease, but is even higher than that at room temperature [3]. Therefore, C/C composites are widely used in aerospace, marine, nuclear energy systems, biomedical, and other high-tech fields, such as space shuttle engines, aircraft brake discs, the International Thermonuclear Experimental Reactor (ITER) divertor, artificial joints, etc. [4–7]. It is worth mentioning that China plans to develop C/C composites for the Thorium Molten Salt Reactor Nuclear Energy System (TMSR) during the 15th Five-Year Plan [8]. However, the expensive preparation process and long production cycle of C/C composites make it difficult to prepare large and complex components. At the same time, C/C composites are susceptible to oxidation and have weaker mechanical properties than metallic materials at high temperatures. The individual use of C/C composites is almost impossible and usually requires a composite structure with other materials (especially metallic materials) to be used. In order to exploit their respective advantages, high-quality joining between C/C composites and metallic materials needs to be achieved. This is one of the key technologies that must be solved to promote the application of C/C composites.

To date, the joining methods of C/C composites mainly include mechanical joining [9,10], adhesive bonding [11–14], brazing [15–19], diffusion joining [20,21], and high-temperature self-propagation reactions. There are two problems with forming mechanical joints by using the difference in roughness between the C/C composite and the material to be joined. The first is the low interface strength of the mechanical joint, and the second is that the notch and tip effects caused by the notches and cracks introduced by the mechanical joint can greatly weaken the C/C composite and the joint. It is also possible to join C/C composites using adhesive joining, but the physical bond between the interfaces is weak. It is difficult to guarantee the quality of the joint. Meanwhile, the adhesive is usually a high polymer, which faces the aging problem when joining C/C composites. C/C composites are often used in extreme environments, such as high-temperature environments or friction fields, and the aging rate will seriously limit the service life of the joints. Due to the high melting point of C/C composites (3600~3800 °C), they cannot be joined by traditional methods of fusion welding. Brazing, as an economical and reliable material joining method, is one of the most researched, mature, and widely used methods for joining C/C composites to metals in recent decades.

2. Difficulties in Brazing C/C Composites and Metals

In order to obtain high-quality brazed joints of C/C composites and metals, it is crucial to solve the following problems: improving the wetting of the brazing material with the joined material, eliminating the thermal stresses due to the coefficient mismatch of thermal expansion for the matrix, and therefore, suppressing the generation of brittle phases in the process of their joining [18,22,23].

2.1. Improving the Wettability

The behavior of a non-reactive liquid wetting a solid can be described by the classical Young's equation [4]:

$$\theta = \arccos\left(\frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}}\right) \tag{1}$$

where σ_{sv}, σ_{sl}, and σ_{lv} denote the surface tension between a solid and gas, solid and liquid, and gas and liquid. The angle of θ is called the wetting angle and is a physical quantity used to characterize the wettability of two materials. The correspondence between its size and wettability is shown in Table 1.

Table 1. Correspondence between the wetting angle and the wettability.

θ	$\cos\theta$	Wettability
$\theta = 0$	1	completely wettable
$0 < \theta < 90°$	$0 < \cos\theta < 1$	wettable
$90° \le \theta \le 180°$	$-1 \le \cos\theta \le 0$	non-wettable

C/C composites greatly differ from metals in terms of the crystal structure and physical–chemical properties, and it is difficult to wet metals and to not wet C/C composites. Meanwhile, some active metallic elements, such as Ti, Cr, Mo, and W, can form carbides with C in a liquid state. Based on this, many scholars have carried out a lot of research in improving the wettability of metal and C/C composites [24–29], and there are mainly two methods, as follows:

(1) The surface of the C/C composites is pre-treated with a layer of active metallic elements' powder by plating, sintering, or deposition, and then conventionally brazed. Kong [27] introduced a simple ammonium dichromate solution immersion method to synthesize copper wettable Cr_3C_2 coatings on and inside C/C preforms. The wetting angle of molten copper with C/C decreased from 140° to 60°, indicating a significant improvement in the wettability. Wenyan Zhou et al. [28] fabricated Mo_2C layers on the entire inner surface of C/C preforms in molten salt (NaCl-KCl) with the addition of ammonium paramolybdate. An approximately 1 µm-thick Mo_2C layer that uniformly covered the inner surface of the C/C preforms was obtained. The formation of the Mo_2C layer shows a transformation from the non-wettable interface of Cu/C into the wettable interfaces Mo_2C/C and Cu/Mo_2C, respectively. Good interface bonding was observed between Mo_2C/C and Cu/Mo_2C.

(2) An appropriate amount of the active metal element is added to the brazing material to make an active brazing material. The most commonly used active metallic element is titanium (Ti). This method is called active metal brazing. Huang Wu et al. [29] investigated the effect of Ti on improving the wettability of liquid Cu with C/C composites by using the sessile drop method. The wetting angle of Cu–10 wt% Ti dropped on the C/C composite at 1300 °C for 60 min was measured as ~70°, which was smaller than that of a Cu drop on the composite. This indicates that the addition of Ti can effectively improve the wettability of liquid Cu on a C/C composite.

There are three types of active metal brazing: (1) brazing by placing titanium or zirconium directly between C/C composites in the form of shims, (2) pre-coating the surfaces to be joined with titanium or zirconium fine powder or titanium or zirconium hydride, and then brazing with brazing material, and (3) brazing directly with an active brazing material containing titanium and zirconium. Titanium-containing brazing materials are brittle and difficult to process and shape and are often made into double- or multi-layer brazing materials. For example, Cu-Ti brazing materials are made into bimetallic sheets, and Ag-Cu-Ti brazing materials are made into wires with titanium as the core and covered with silver-copper alloy. Titanium-containing brazing materials are also often used in powder form.

In recent years, scholars have reported some Fe-based and high-entropy alloy brazing materials that can be used for the brazing of C/C composites. However, the related studies are relatively few and need to be further developed [30,31].

2.2. Eliminating the Thermal Stresses

In addition to the wettability, how to relieve the thermal stress due to the coefficient mismatch in thermal expansion for the current composite materials is also a key issue to be solved in brazing. The coefficient of thermal expansion of 2D C/C composites is generally around: (2~3) × 10^{-6}/K, and that of 3D C/C composites is generally around: (7~8) × 10^{-6}/K, depending on the temperature range and tissue shape. The coefficient of thermal expansion of most metals and alloys is generally larger than 1 × 10^{-5}/K depending on the temperature range and tissue shape, which results in a large amount of thermal stress in the joint during cooling. He Peng et al. [32,33] used finite element analysis to analyze the fracture of the joint and found that most of the residual thermal stresses in the joint are concentrated between the material with a smaller coefficient of thermal expansion and the joint layer. The authors further proposed the concepts of a residual stress factor in the connection layer, R_f, and a thickness factor in the connection layer, T_f:

$$R_f = \Delta\alpha \cdot E \cdot \sigma_{0.2} \cdot \omega \tag{2}$$

$$T_f = E \cdot \sigma_{0.2} \cdot \omega \cdot \sqrt{\Delta\alpha_1 \cdot \Delta\alpha_2} \tag{3}$$

In Equations (2) and (3), $\Delta\alpha$ represents the difference in the coefficients of thermal expansion between the intermediate layer material and the base material with a smaller coefficient of thermal expansion. E is the modulus of elasticity of the material, $\sigma_{0.2}$ is the yield limit of the material, ω is the coefficient of work hardening of the material, and $\Delta\alpha_{1,2}$ are the differences in the coefficients of thermal expansion between the intermediate layer and the two base materials.

After data simulation by the computer, the authors concluded that the connection layer should be selected as small as possible for T_f and R_f. Moreover, the thickness of the connecting layer should be as small as possible under the premise of ensuring sufficient physical contact.

2.3. Suppressing the Generation of Brittle Phases

The active element added to the brazing material can improve the wetting of the brazing material on the C/C composite. However, excessive active elements can form brittle carbides with C/C composites, which in turn reduce the joint strength [34]. At the same time, the active brazing material also forms some brittle intermetallic compounds with the metal base material, leading to a reduction in joint strength [35]. In order to reduce the formation of brittle phases, it is not advisable to add large amounts of reactive elements to the brazing material. For example, the mass fraction of Ti in the commonly used AgCuTi brazing materials is usually below 15 wt% [25,36,37].

In recent years, research to improve the brazing performance of C/C composites with metals has focused on both surface modification and the study of composite brazing materials. The more representative studies are shown in Figure 1.

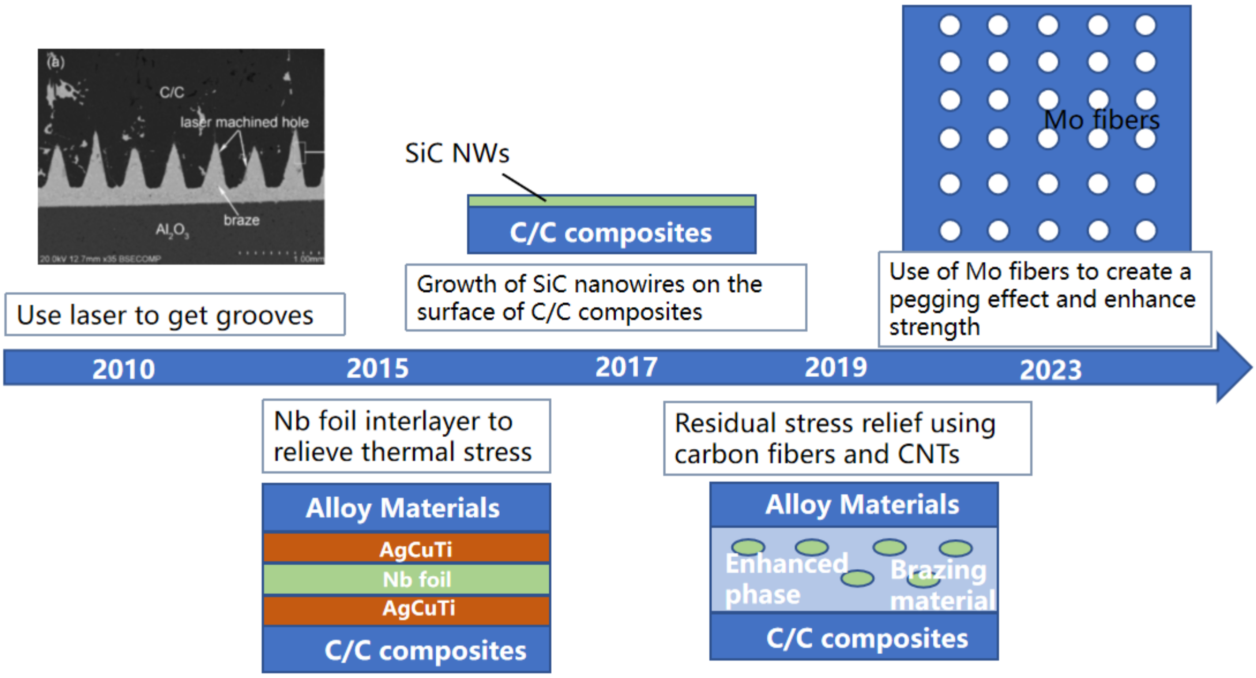

Figure 1. Strategies for improving the brazing performance of C/C composites with metals [35–37].

3. Brazing of C/C Composites and Metals

Many studies have been conducted on the brazing between C/C composites and metals or non-metals. The brazing system of C/C composites and metals mainly includes C/C composites with copper and copper alloys (pure copper, oxygen-free Cu, CuZrCr alloy, CuW alloy, etc.), titanium and titanium alloys (TC4 alloy, TC17 alloy, Ti600 alloy, etc.), nickel-based superalloys (GH3044 alloy, GH3128 alloy, GH99 alloy, etc.), intermetallic compounds (TiAl alloy, Ti_3Al alloy), stainless steel, Nb, W, TZM alloy, and so on (as shown in Figure 2).

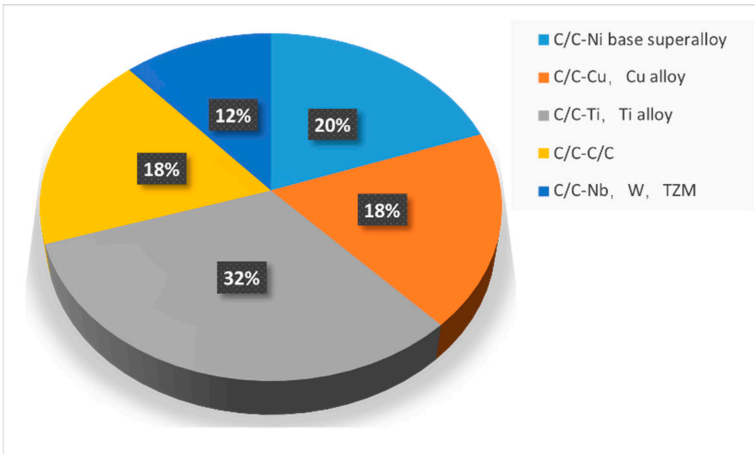

Figure 2. Brazing systems of C/C composites.

3.1. Brazing of C/C Composites with Copper and Copper Alloys

Since 1998, C/C composites have been selected as the first-wall protection material for the internal copper alloy cooling tubes in the cooling system protecting the vertical target of the International Thermonuclear Experimental Reactor (ITER) deflector due to their excellent overall performance, which are showed in Table 2 [38–45]. The ITER's engineering team achieved a reliable connection between the C/C composite and OF-Cu by brazing.

Table 2. Summary of the brazing of C/C composites to copper alloys.

Base Materials	Composition of Brazing Filler Metal (wt%)	Brazing Temperature (°C)/ Holding Time (min)	Strength (MPa)	References
C/C-OF Cu	Cu-28Ag-2Ti	850/10	22 (Shear)	[38]
C/C-OF Cu	Cu-2Al-3Si-2.3Ti	1030 ± 2	20.2 (Tensile)	[39]
C/C-Cu	Cu-50Pb	1150/40	1.5 (Shear)	[40]
C/C-Cu	Ti-15Cu-15Ni	1008/10	24 (Shear)	[41]
C/C-Cu	Ag-68.8Cu-4.5Ti	910/10	Bending: 14 (Flat), 52 (Conical interface)	[42]
C/C-Cu	Cu-30Ti	930	7 (Shear)	[43]
C/C-Cu	Ni-33Cr-24Pd-4Si	1210	6 (Shear)	[43]
C/C-Cu	Ni-11Cr-10P	935	7 (Shear)	[43]
C/C-CuCr	AgCu-2Ti	850/10	16 (Shear)	[43]
C/C-CuW	AgCu-2Ti	850/10	13 (Shear)	[43]
C/C-CuMoCu	68.8Ag-26.7Cu-4.5Ti	(915–920)/5	/	[44,45]
C/C-CuMoCu	63Ag-34.3Cu-1Sn-1.75Ti	(821–826)/5	/	[44]
C/C-CuMoCu	92.8Cu-3Si-2Al-2.25Ti	(1040–1045)/5	/	[44]
C/C-CuMoCu	70Ti-15Cu-15Ni	(975–980)/5	/	[44]
C/C-CuMoCu	63Ag-35.3Cu-1.75Ti	(830–835)/5	/	[45]

Appendino et al. [41] brazed C/C composites and copper with Ti/15Cu/15Ni brazing material and performed mechanical shear tests on the joined specimens, which are showed in Figure 3A. The results show that the best results were for the brazing process at ~1008 °C for 10 min (1 kPa, Ar flow). The average shear strength of the six specimens was 24 MPa, and the dispersion of the mechanical results was small. The analysis of the fracture surfaces revealed that the cracks propagated through the joint region, while the TiCuNi/Cu, C/C/TiCuNi, and their interfaces did not fail, indicating a strong adhesion of the brazing alloy for these two materials (composite and the copper). It is well known that brazing the carbon-fiber-reinforced C/C composite and copper has gained increasing interest because of its important application in thermal management systems in nuclear fusion reactors and in the aerospace industry [42]. Figure 3B shows the high-resolution TEM images, revealing the microstructure and interfacial micro-chemistry of C/C composite/AgCuTi/Cu brazed joints [42]. Milena Salvo used a slurry technique to deposit metallic Cr on the surface of C/C composites. C/C/Cu and Cu/CuCrZr were joined using Gemco brazing material (87.75 wt% Cu, 12 wt% Ge, and 0.25 wt% Ni) (Figure 3C) [46]. This study achieved brazing of C/C composites with CuCrZr alloys by using a braze without reactive elements and prevented interfacial cracking and debonding by modulating the thermal stresses through the large ductility of the braze and pure copper. The presence of Ge_xCr_y intermetallic phases was not confirmed by XRD analysis or the Cr diffusion pattern. It was confirmed that the Cu interlayer can prevent the brittle intermetallic compounds' formation, and then improve the joint strength.

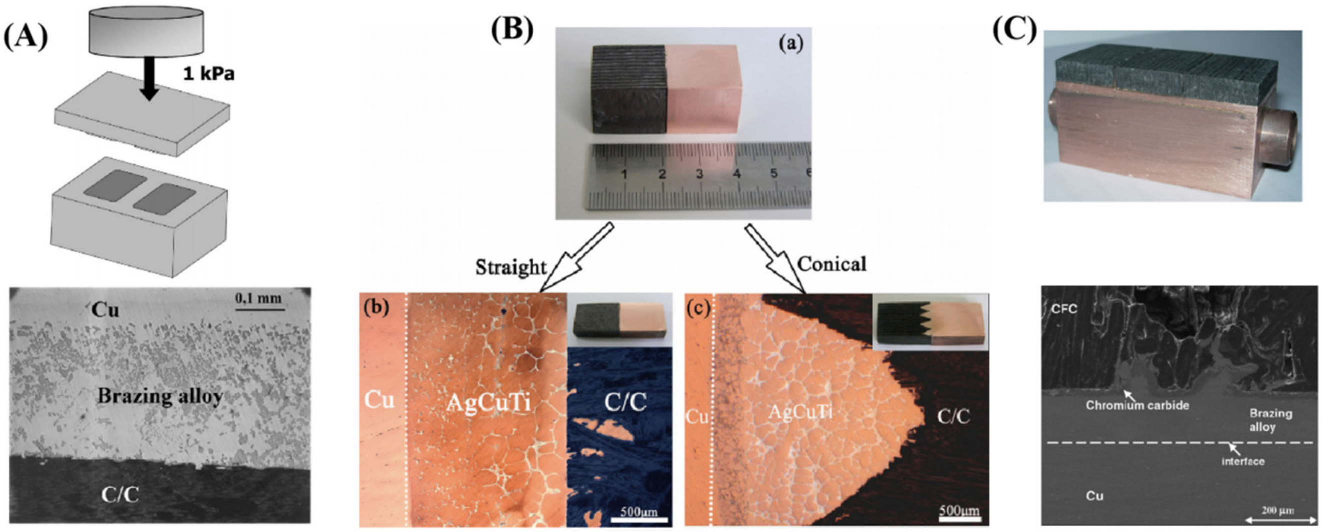

Figure 3. (**A**) Graphite sample holder for the preparation of the joints. Cross-section of C/C/Cu brazed at 1008 °C for 10 min [41]. (**B**): (**a**) Macroscopic appearance of the brazed C/C composite/AgCuTi/Cu joints. There was no difference on the outside surface between straight and conical interface brazed joints. (**b**,**c**) OM views of straight and conical interface joints, respectively. Insets show that the interface for the straight interface joint is flat, while the conical interface shows a zigzag structure due to the conical design [42]. (**C**) Experimental setup for the CFC/pure copper/CuCrZr one-step brazing process [46].

3.2. Brazing of C/C Composites to Titanium and Titanium Alloys

Titanium alloy is a vital material in the aerospace field because of its high specific strength, good corrosion resistance, and excellent overall mechanical properties. Joining titanium alloys with C/C composites with excellent high-temperature properties can obtain a lightweight, high-temperature performance and meet certain structural strength requirements of the joint, showing a large number of applications in rocket, aerospace, and other fields. The titanium- and silver-based brazing materials are commonly used for brazing C/C composites to titanium alloys, which are shown in Table 3 clearly [47–55]. M. Singh et al. [53] used three brazing materials, Cu-ABA, TiCuNi, and TiCuSi, in the form of a foil with a thickness of about 50 μm, to braze C/C composites to pure titanium. The analysis revealed that metallurgical bonding due to redistribution and diffusion of solutes during the brazing process ensures the wetting of the brazing material to the substrate. The best joint performance was achieved with the Cu-ABA brazing material. The orientation of the C fiber bundles in the C/C composite affects the joint properties. The highest joint load capacity was obtained with the carbon fiber bundles oriented perpendicular to the Ti tube axis, and the lowest was obtained with the C fiber bundles oriented parallel to the Ti tube axis. Youqiong Qin et al. [47,48] brazed C/C composites and the TC4 titanium alloy by using a TiZrCuNi amorphous alloy braze, and they investigated the effect of the brazing process parameters on the microstructure of the joints. The Cu and Mo interlayers are added between the C/C composite and the TC4 titanium alloy to form the foil titanium-based brazing material. On the one hand, it relieves the residual stresses at the joint due to the differences in the thermal expansion coefficients between the base material and the brazing material; on the other hand, it avoids the formation of a large number of brittle intermetallic compounds, such as Ti_xCu_y and Ti_xNi_y, between the brazing material and the TC4 titanium alloy base material. The results demonstrate that this method can be used for brazing of C/C composite materials and TC4 titanium alloys. At lower brazing temperatures, the interface structure of this joint is: $Cu/Cu_{51}Zr_{14}/Ti_2(Cu,Ni)$ + Ti(Cu,Ni) + TiCu + Cu_2TiZr/TiC/C/C composites. As the temperature increases, the Cu in the layer dissolves into the brazing material, forming $Ti(Cu,Ni)_2$ and Cu(s.s), and then the TiC reaction layer changes from intermittent to continuous. The end products in the center of the joint are $Ti(Cu,Ni)_2$ and Cu(s.s).

Table 3. Summary of the brazing of C/C composites to titanium alloys.

Base Materials	Composition of Brazing Filler Metal (wt%)	Brazing Temperature (°C)/Holding Time (min)	Strength (MPa)	References
C/C-TC4	Ag-26.7Cu-4.6Ti	910/10	25 (Shear)	[47,48]
C/C-Graphite foam-Ti tube	63Ag-32.25Cu-1.75Ti	820/5	12.4 (Shear)	[49]
C/C-TiAl	Ag-26.7Cu-4.6Ti	900/10	12.9 (Shear)	[50]
C/C-TiAl	Ti-Ni-Cu (1:1:1)	980/10	18 (Shear)	[51]
C/C-Ti	68.8Ag-26.7Cu-4.5Ti	910/5	0.24 ± 0.09 (Tensile)	[52,53]
C/C-Ti	92.8Cu-3Si-2Al-2.2Ti	1040/5	0.27 ± 0.12 (Tensile)	[52,53]
C/C-Ti	70Ti15Cu15Ni	975/5	0.33 ± 0.13 (Tensile)	[52,53]
C/C-Ti	Ag-32.25Cu-1.75Ti	830/5	24 (Shear)	[54]
C/C-Ti	MBF-20 Amorphous (Ni-6.48Cr-3.13Fe-4.38Si-3.13B)	1045/8	/	[55]
C/C-Ti	MBF-30 Amorphous (Ni-4.61Si-2.8B-0.02Fe)	1080/8	/	[55]

Guo Wei et al. [35] studied the brazing of C/C composites and the TC4 titanium alloy using the AgCu brazing material (72Ag-28Cu, mass fraction, %), with a brazing temperature of 820~940 °C and a holding time of 3~30 min. It was demonstrated that the Ti in the TC4 titanium alloy diffused into the brazing material and the C/C composite during brazing to chemically react with the base and brazing materials, enhancing the wettability of the brazing material to the C/C composite. The interface structure of this joint is: $TC4/Ti_2Cu$ + Ti(s.s)/Ti_2Cu/TiCu/Ag(s.s) + Ti_3Cu_4/TiC/C/C composites. The shear strength of the obtained joint is 33 MPa at 880 °C for 10 min.

Duo Liu and Kehan Zhao et al. introduced carbon fibers in the AgCuTi brazing material to braze C/C composites and the TC4 alloy [15,19,56]. It was demonstrated that the interfacial structure of the brazed joint obtained by using the AgCuTiC composite brazing material, with a CNTs content of 0.2% at a brazing temperature of 880 °C and a holding time of 20 min, was: TC4/diffusion layer/Ti_2Cu/TiCu/Ti_3Cu_4/$TiCu_4$/TiC + $TiCu_2$ + Ag(s.s) + Cu(s.s)/Ti_3Cu_4/$TiCu_4$/TiC/C/C composites. A moderate amount of CNTs can reduce the formation of brittle compounds at the interface and refine the interfacial organization, as well as alleviate the mismatch of thermal expansion coefficients between parent materials and reduce residual stresses. A high content of CNTs consumes a large amount of Ti in the brazing material, which weakens the bonding on one side of the C/C composite and reduces the shear strength of the joint. A maximum joint strength of 44 MPa was obtained at a 0.4% mass fraction of carbon fiber.

3.3. Brazing of C/C Composites to Nickel-Based Alloys

Nickel-based high-temperature alloys have good oxidation resistance, excellent thermal corrosion resistance, a high working temperature, stable organization, and less harmful phases, and can work under high-temperature and high-stress environments. They are widely used in high-tech fields, such as in aerospace and marine industries and nuclear energy systems. C/C composites are joined to nickel-based high-temperature alloys with a low mass, high load-bearing capacity, and a long high-temperature life. The nickel-based braze is the most commonly used braze for brazing C/C composites to nickel-based high-temperature alloys, which are shown in Table 4 clearly [57–67]. As shown in Figure 4A, Guo L. et al. [60] used the Ni-Ti powder to fabricate a thin intermediate layer diffusion connection between C/C composites and the GH3128 high-temperature alloy, with a welding temperature of 1050~1250 °C, pressurization of 8~20 MPa, and a holding time of 60 min. The results show that for the group of C/C composite surfaces without treatment, the shear strength of the joints was almost 0. For the group of C/C composite surfaces coated with the SiC coating, the shear strength of the joints was 23 Mpa at a heating temperature of 1170 °C. The authors found that coating SiC on the C/C surface can improve the wettability of Ti, Ni, and other elements on the C/C surface, on the one hand, and alleviate the thermal stress due to the different thermal expansion coefficients of C/C composites and the GH3128 high-temperature alloy on the other hand.

Table 4. Summary of the brazing of C/C composites to nickel-based alloys.

Base Materials	Composition of Brazing Filler Metal (wt%)	Brazing Temperature (°C)/Holding Time (min)	Strength (MPa)	References
C/C-K24	Ag26Cu2Ti	880/10	16 (Shear)	[57]
C/C-GH3044	Ag-(10,20,30,40)Ti	(990~1080)/(10~90)	45.8 (Shear)	[58]
C/C-GH3044	80Ni-20Ti PTLP	1030/30	9.78 (Shear)	[59]
C/C-GH3044	Ni71CrSi	1080/30	35.08 (Shear)	[60]
C/C-GH3044	Ni71CrSi	1080/30	54.4 (Shear)	[61]
C/C-GH3044	Ti/Ni/Cu/Ni (1:1:20:1)	1030/30	32.09 (Shear)	[62]
C/C-GH3128	Ni-Si	1160	12.6 (Shear)	[63]
C/C-GH3128	BNi-2 (Ni-7.0Cr-3.0Fe-4.5Si-3.1B)	1170/60	Shear: 35.4 (RT), 15.3 (800 °C), 8.6 (1000 °C)	[64]
C/C-GH3128	Ni-Ti	1170	22.5 (Shear)	[65]
C/C-GH99	BNi-2 Ni-(6~8)Cr-(2.5~3.5)Fe-(4~5)Si-(2.75~3.5)B	1170/60	16 (Shear)	[34]
C/C-GH600	BNi68CrWB	1150~1200/10	Shear: 49.9 (RT), 21.6 (800 °C)	[66]
C/C-Ni-based superalloy	NiCrSiBFe Amorphous	1170/60	Shear: 35 (RT), 15 (800 °C), 9 (1000 °C)	[67]

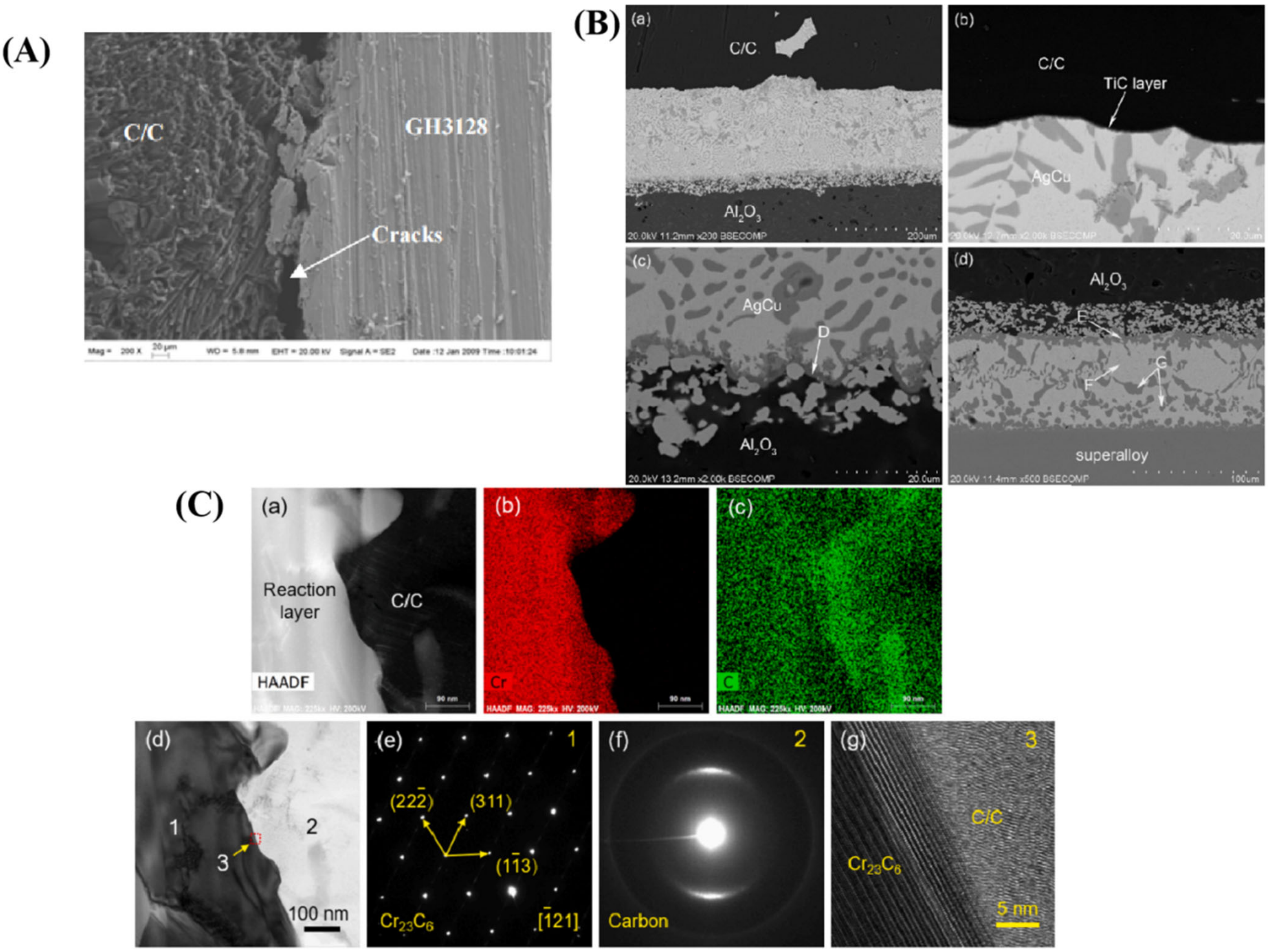

Figure 4. (**A**) SEM image of the C/C and GH3128 joint at 1500 °C [65]. (**B**) SEM micrograph of the: (**a**) C/C-Al_2O_3 joint in mode 2, (**b**) C/C–braze interface, (**c**) braze/Al_2O_3 interface, and (**d**) Al_2O_3-superalloy joint [68]. (**C**) TEM results of the interface: (**a**) HADDF image, elemental mapping of (**b**) Cr and (**c**) C, (**d**) corresponding bright-field image, received SAED patterns in (**e**) region 1 and (**f**) region 2, and (**g**) HRTEM observation of region 3 [69].

Tian et al. [34] brazed C/C composites and GH99 high-temperature alloys by adding TiH_2 to BNi_2 powder brazing material. The welding parameters were 1170 °C, vacuum < 10^{-3} Pa, and a holding time of 60 min. Brazing was performed using brazing materials containing TiH_2 at 1%, 3%, and 8%, and it was found that the best joint performance was obtained with 3% TiH_2 in the brazing material. The shear strength of the joints was 40 MPa at room temperature and 19 MPa and 10 MPa at 800 °C and 1000 °C, which showed a significant increase in strength compared to the pure BNi_2 brazing material. The authors found that Ti in TiH_2 can promote the diffusion of C/C composites into the brazing seam, produce diffuse MC particles, reduce the mismatch between the C/C composite matrix and the brazing seam, and then relieve the residual stresses.

However, excessive TiH_2 will produce a large amount of flaky TiC in the brazing seam and reduce the plastic deformation capacity of the joint. Zhang Xin et al. [60] used BNi5 to braze material vacuum brazing C/C composites with the GH3044 high-temperature alloy, with a welding temperature of 1160 °C, vacuum < 10^{-2} Pa, and a holding time of 30 min. They obtained joints with a shear strength of 38.5 MPa at room temperature. As shown in Figure 4B, Shen Yuanxun et al. [68] concluded that the Al_2O_3 interlayer can effectively prevent the diffusion and reaction of Ni and Ti and reduce the residual stresses in the joints. Guo et al. [69] have reported the brazing of C/C composites and the DD3 alloy using the

AgCr reactive brazing material. The maximum value of the C/C-AgCr-DD3 joint shear strength reaches 27 MPa at 1040 °C by adopting the Ag-10 wt% Cr braze. The joint shear strength shows a trend of first increasing and then decreasing along with the Cr content in the braze and the brazing temperature. The joint fracture analysis indicates the failure along the C/C substrate, mainly attributed to significant residual stress. These mechanisms are deduced from the TEM results of these interfaces shown in Figure 4C. Junliang Xue et al. [70] used different nickel-based fillers to match the high-temperature properties of the C/C composites and the In738LC superalloy. Experimental findings showed that the maximum shear strength of 28 MPa was obtained when the joint was brazed at 1100 °C. The brazed joints fractured at the C/C composite side close to the isothermal solidification zone (ISZ), which was related to the residual stress concentration at the C/C composite interface.

4. Summary

This paper summarized the current status of brazing C/C composites with metallic materials, introduced the problems faced by brazing C/C composites with metallic materials, and sorted out the related research progress. The problem of the poor wettability of metallic materials on the surface of C/C composites has been largely solved, and the thermal stress problem can be alleviated by a suitable brazing system design. However, a series of practical problems, such as low joint strength and insufficient reliability, still limit the large-scale practical application of brazing technology for C/C composites and metal materials. For the surface and nanoscale interface bonding of C/C composites and metallic materials, it has been concluded that the microstructure and cracks play a key role in the welding process of the two types of materials, and how to accurately control the surface and nanoscale interface puts forward a new direction for our future research.

To obtain high-quality joints, it is crucial to control the reaction during the brazing process to ensure that high-strength joint tissue is obtained [71–73]. Possible solutions are proposed as follows:

(1) Surface treatment of C/C composites, such as coating, sintering, perforating, depositing SiC, etc., can improve the wettability of the base and brazing materials, and form a transition layer at the interface of the joint to prevent uneven thermal expansion and cracking.
(2) The addition of some reinforcing phases, such as active elements and CNTs, to the brazing material can promote the diffusion of C/C composites into the brazing seam, produce diffuse particles, reduce the mismatch between the matrix and brazing seam of C/C composites, and relieve the residual stress.
(3) A transition layer can be sandwiched between the base material and the intermediate layer to alleviate the difference in the degree of thermal expansion between the base material and the brazed seam.
(4) New brazing materials can be developed, with promising applications, such as Fe-based brazing materials and high-entropy alloy brazing materials.

Author Contributions: Formal analysis, C.W.; writing—original draft preparation, C.W., S.F. and Y.Y.; writing—review and editing, S.F., G.Z., X.Z., H.H. and Y.Y.; funding acquisition, S.F. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by the National Natural Science Foundation of China (Grant No. 12075309), a research grant (No. 17YF1423700) from the Shanghai Sailing Program.

Acknowledgments: We thank the Shanghai United Energy Technology Co., Ltd. for the help and support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Krenkel, W. *Ceramic Matrix Composites: Fiber Reinforced Ceramics and Their Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2008.
2. Fitzer, E.; Manocha, L.M. *Carbon Fibers and Carbon/Carbon Composites*; Springer: Berlin/Heidelberg, Germany, 1998.
3. Wang, X.; Wang, X.; Liu, K.; Cao, H.; Su, Y. Effect of the CNTs into SiCp-Al interfacial micro-zones on ageing precipitation behavior, microstructure and mechanical properties of SiCp(CNT)/Al–Zn–Mg–Cu composites. *Compos. Part B Eng.* **2023**, *259*, 110708. [CrossRef]
4. Liu, J.; Liu, C.; Cai, H.; Zhang, C.; Dan, C.; Shi, Q.; Wang, H.; Chen, Z. Enhanced precipitate strengthening in particulates reinforced Al–Zn–Mg–Cu composites via bimodal structure design and optimum aging strategy. *Compos. Part B Eng.* **2023**, *260*, 110772. [CrossRef]
5. Wang, J.; Xu, L.; Li, W. Research Progress on C/C Composites for Aerospace Applications. *Aerosp. Mater. Technol.* **2022**, *52*, 1–12.
6. Wang, F.; Chen, J.; Cui, H. Overview of C/C Composites Application for Nuclear Energy System. *Nucl. Sci. Eng.* **2020**, *40*, 1092–1103.
7. Lan, F.T.; Li, K.Z.; Li, H.J.; He, Y.G.; Shen, X.T.; Cao, W.F. Joining of carbon/carbon composites for nuclear applications. *J. Mater. Sci.* **2009**, *44*, 3747–3750. [CrossRef]
8. Zhou, X.; Li, Z.; Lu, Y.; Huang, H.; He, Z.; Dai, Z.; Xu, H. Development Strategy for Thorium Molten Salt Reactor Materials. *Strateg. Study CAE* **2019**, *21*, 29–38. [CrossRef]
9. Warren, K.C.; Lopez-Anido, R.A.; Goering, J. Behavior of three-dimensional woven carbon composites in single-bolt bearing. *Compos. Struct.* **2015**, *127*, 175–184. [CrossRef]
10. Kweon, J.H.; Jung, J.W.; Kim, T.H.; Choi, J.H.; Kim, D.H. Failure of carbon composite-to-aluminum joints with combined mechanical fastening and adhesive bonding. *Compos. Struct.* **2006**, *75*, 192–198. [CrossRef]
11. Yang, G. *Research on High-Temperature Adhesion Process and Mechanism of Carbon Materials*; Harbin Institute of Technology: Harbin, China, 2014.
12. Rakesh, P.; Davim, J.P. *Joining Processes for Dissimilar and Advanced Materials*; Elsevier: Amsterdam, The Netherlands, 2021.
13. Zhang, J.; Luo, R.; Yang, C. A multi-wall carbon nanotube-reinforced high-temperature resistant adhesive for bonding carbon/carbon composites. *Carbon* **2012**, *50*, 4922–4925. [CrossRef]
14. Baldan, A. Adhesion phenomena in bonded joints. *Int. J. Adhes. Adhes.* **2012**, *38*, 95–116. [CrossRef]
15. Zhao, K. *Research on Mechanism of Brzaing TC_4 and C/C Composite with Carbon Fiber Reinforced Composite Filler*; Harbin Institute of Technology: Harbin, China, 2020.
16. Niu, H.; Zhao, Y.; Liu, D. Development of metalbrazing and carbon fiber reinforced composites. *J. Chang. Univ. Technol.* **2016**, *37*, 442–448.
17. Shirvanimoghaddam, K.; Hamim, S.U.; Akbari, M.K.; Fakhrhoseini, S.M.; Khayyam, H.; Pakseresht, A.H.; Naebe, M. Carbon fiber reinforced metal matrix composites: Fabrication processes and properties. *Compos. Part A Appl. Sci. Manuf.* **2017**, *92*, 70–96. [CrossRef]
18. Guo, C.; Guo, L.; Li, H. Hot Pressing Joining of Carbon/Carbon Composites to Metal. *Carbon Technol.* **2009**, *28*, 27–30.
19. Liu, D.; Zhao, K.; Song, Y.; Zhang, L.; Song, X.; Long, W. Effect of introducing carbon fiber into AgCuTi filler on interfacial microstructure and mechanical property of C/C-TC_4 brazed joints. *Mater. Charact.* **2019**, *157*, 109890.
20. Dadras, P.; Ngai, T.T.; Mehrotra, G.M. Joining of Carbon—Carbon Composites Using Boron and Titanium Disilicide Interlayers. *J. Am. Ceram. Soc.* **1997**, *80*, 125–132. [CrossRef]
21. Xue, L.A.; Narasimhan, D. Joining of Rough Carbon-Carbon Composites with High Joint Strength. US5972157A, 26 October 1999.
22. Zhang, Q. *Research on Process of Brazing TC_4 and C/C Composite with CNTs Reinforced Composite Filler*; Harbin Institute of Technology: Harbin, China, 2019.
23. Durodola, J.F.; Fellows, N.; Winfield, P.; Gerguri, S.; Maruyama, B. Continuously Reinforced Metal Matrix Composites. In *Comprehensive Composite Materials*; Elsevier: Amsterdam, The Netherlands, 2017; Volume 3, pp. 717–739.
24. Chen, B.; Xiong, H.; Mao, W.; Li, X.H. Wettability of Several High-temperature Brazing Fillers on C/C Composites. *J. Mater. Eng.* **2008**, *1*, 25–29+37.
25. Yu, Q.; Zhang, F.; Zhang, X.; Xia, L.H.; Zhou, X.G. Effect of the Ti content of Cu-Ti alloy on the wettability of C/C composites. *Mater. Sci. Eng. Powder Metall.* **2013**, *18*, 224–229.
26. Fang, H.; Yu, G.; Xiao, P.; Xiong, X. Effect of active element on interface wettability and microstructure of NiAl-modified C/C composites prepared by infiltration. *Rare Met. Mater. Eng.* **2016**, *45*, 997–1002.
27. Kong, B.; Ru, J.; Zhang, H.; Fan, T. Enhanced wetting and properties of carbon/carbon-Cu composites with Cr_3C_2 coatings by Cr-solution immersion method. *J. Mater. Sci. Technol.* **2018**, *34*, 458–465. [CrossRef]
28. Zhou, W.; Yi, M.; Peng, K.; Ran, L.; Ge, Y. Preparation of a C/C–Cu composite with Mo_2C coatings as a modification interlayer. *Mater. Lett.* **2015**, *145*, 264–268. [CrossRef]
29. Wu, H.; Yi, M.; Ran, L. Improving the wettability between liquid Cu and carbon/carbon composite by addition of Ti. *Mater. Res. Express* **2019**, *6*, 125610. [CrossRef]
30. Zhang, G.; Zhang, Y.; Bao, J.; Yang, G. A novel active braze composition design route for C/C composite using Fe as active element. *Carbon* **2021**, *181*, 177–192. [CrossRef]

31. Xu, H.; Shi, L.; Lu, C.; Li, H.; He, Y.; Chen, W.; Gao, Z. A novel joining of Cf/C composites using AlCoCrFeNi2.1 high-entropy brazing filler alloys. *Mater. Charact.* **2021**, *179*, 111368. [CrossRef]
32. He, P.; Feng, J.; Qian, Y. Distributions of Residual Stresses in Diffusion Bond of Dissimilar Materials and Effect of Interlayer. *Trans. China Weld. Inst.* **2002**, *23*, 76–80.
33. Levano Blanch, O.; Pope, J.; Violatos, I.; Rahimi, S.; Jackson, M. Residual Stress Distributions in Dissimilar Titanium Alloy Diffusion Bonds Produced from Powder Using Field-Assisted Sintering Technology (FAST-DB). *Metall. Mater. Trans. A* **2023**, *54*, 3578–3593. [CrossRef]
34. Tian, X.; Qi, J.; Zhang, L.; Liang, Y. Brazing of C/C composite and GH99 superalloy Using BNi_2 + TiH_2 composite filler powder. *Trans. China Weld. Inst.* **2014**, *35*, 35–38+114–115.
35. Guo, W.; Wang, L.; Zhu, Y.; Chu, P.K. Microstructure and mechanical properties of C/C composite/TC_4 joint with inactive AgCu filler metal. *Ceram. Int.* **2015**, *41*, 7021–7027. [CrossRef]
36. Yu, G.; Xiao, P.; Fang, H. Influence of adding Ti on molten NiAl intermetallic infiltration into C/C composites. *Chin. J. Nonferrous Met.* **2013**, *23*, 3316–3322.
37. Yang, L.; Yi, M.; Ran, L. Joining of carbon/carbon composite using AgCuTi braze. *Mater. Sci. Eng. Powder Metall.* **2015**, *20*, 765–770.
38. Gotoh, Y.; Okamura, H.; Kajiura, S.; Kumagai, M.; Ando, T.; Akiba, M.; Suzuki, T. Development and material testing of OF-Cu /DS-Cu/OF-Cu triplex tube (dispersion strengthened copper clad with oxygen free-copper) and trial fabrication of a vertical target mock-up for ITER divertor. *J. Nucl. Mater.* **1998**, *258*, 271–274. [CrossRef]
39. Trester, P.W.; Valentine, P.G.; Johnson, W.R.; Chin, E.; Reis, E.E.; Colleraine, A.P. Tensile fracture characterization of braze joined copper-to-CFC coupon assemblies. *J. Nucl. Mater.* **1996**, *233*, 906–912. [CrossRef]
40. Hussain, M.Z.; Xiong, J.; Li, J.; Siddique, F.; Zhang, L.J.; Raza, M.A.; Rathore, M.F. Structural characterization of a composite joint prepared during laser welding of Ti–22Al–27Nb intermetallic alloy with an interlayer of Cu-Hf-Ni-Ti-Zr high entropy bulk metallic glass. *Compos. Part B Eng.* **2022**, *243*, 110167. [CrossRef]
41. Appendino, P.; Casalegno, V.; Ferraris, M.; Grattarola, M.; Merola, M.; Salvo, M. Joining of C/C composites to copper. *Fusion Eng. Des.* **2003**, *66*, 225–229. [CrossRef]
42. Zhang, K.; Xia, L.; Zhang, F.; He, L. Active Brazing of C/C Composite to Copper by AgCuTi Filler Metal. *Metall. Mater. Trans. A* **2016**, *47*, 2162–2176. [CrossRef]
43. Okamura, H.; Kajiura, S.J.; Akiba, M. Bonding between carbon fiber/carbon composite and copper alloy. *Q. J. Jpn. Weld. Soc.* **1996**, *14*, 39–46. [CrossRef]
44. Singh, M.; Asthana, R.; Shpargel, T.P. Brazing of carbon–carbon composites to Cu-clad molybdenum for thermal management applications. *Mater. Sci. Eng. A* **2007**, *452*, 699–704. [CrossRef]
45. Singh, M.; Asthana, R. Characterization of brazed joints of CC composite to Cu-clad-Molybdenum. *Compos. Sci. Technol.* **2008**, *68*, 3010–3019. [CrossRef]
46. Salvo, M.; Casalegno, V.; Rizzo, S.; Smeacetto, F.; Ferraris, M.; Merola, M. One-step brazing process to join CFC composites to copper and copper alloy. *J. Nucl. Mater.* **2008**, *374*, 69–74. [CrossRef]
47. Qin, Y.; Yu, Z. Effects of Brazing Parameters on Microstructures of C/C Composite/Cu/Mo/TC_4 Brazed Joints. *J. Mater. Eng.* **2012**, *2*, 78–82.
48. Qin, Y.; Feng, J. Active brazing carbon/carbon composite to TC_4 with Cu and Mo composite interlayers. *Mater. Sci. Eng. A* **2009**, *525*, 181–185. [CrossRef]
49. Singh, M.; Morscher, G.N.; Shpargel, T.P.; Asthana, R. Active metal brazing of titanium to high-conductivity carbon-based sandwich structures. *Mater. Sci. Eng. A* **2008**, *498*, 31–36. [CrossRef]
50. Wang, H.; Cao, J.; Feng, J. Brazing mechanism and infiltration strengthening of CC composites to TiAl alloys joint. *Scr. Mater.* **2010**, *63*, 859–862. [CrossRef]
51. Cao, J.; He, Z.; Qi, J.; Wang, H.; Feng, J. Brazing of C/C Composite to TiAl Alloy Using (Ti/Ni/Cu)f Multi-foil Filler. *J. Mech. Eng.* **2018**, *54*, 108–114. [CrossRef]
52. Morscher, G.N.; Singh, M.; Shpargel, T.; Asthana, R. A simple test to determine the effectiveness of different braze compositions for joining Ti-tubes to C/C composite plates. *Mater. Sci. Eng. A* **2006**, *418*, 19–24. [CrossRef]
53. Singh, M.; Shpargel, T.P.; Morscher, G.N.; Asthana, R. Active metal brazing and characterization of brazed joints in titanium to carbon–carbon composites. *Mater. Sci. Eng. A* **2005**, *412*, 123–128. [CrossRef]
54. Ikeshoji, T.T.; Amanuma, T.; Suzumura, A.; Yamazaki, T. Shear Strength of Brazed Joint Between Titanium and C/C Composites with Various Cross-Ply Angles. *J. Solid Mech. Mater. Eng.* **2011**, *5*, 1022–1028. [CrossRef]
55. Singh, M.; Asthana, R.; Shpargel, T.P. Brazing of ceramic-matrix composites to Ti and Hastealloy using Ni-base metallic glass interlayers. *Mater. Sci. Eng. A* **2008**, *498*, 19–30. [CrossRef]
56. Liu, D.; Li, X.; Zhao, K.; Song, Y.; Zhang, S.; Song, X. Effect of CNTs on microstructure and mechanical properties of TC_4 and C/C composites brazed joint. *Trans. China Weld. Inst.* **2020**, *41*, 1–5+97.
57. Jiao, J.; Zou, Q.; Ye, Y.; Xu, Z.; Sheng, L. Carbon fiber reinforced thermoplastic composites and TC_4 alloy laser assisted joining with the metal surface laser plastic-covered method. *Compos. Part B Eng.* **2021**, *213*, 108738. [CrossRef]
58. Wang, Y.; Wang, W.; Huang, J.; Yu, R.; Yang, J.; Chen, S. Reactive composite brazing of C/C composite and GH3044 with Ag–Ti mixed powder filler material. *Mater. Sci. Eng. A* **2019**, *759*, 303–312. [CrossRef]

59. Zhang, S.; Li, K.; Wang, J.; Song, X.R.; Guo, L.J. PTLP bonding C/C composites to super-alloy GH3044 with Ni/Ti interlayer. *J. Solid Rocket. Technol.* **2012**, *35*, 414–418.
60. Zhang, X.; Shi, X.; Wang, J.; Li, H.J.; Li, K.Z. Brazing of C/C Composites and GH3044 Ni-Based Superalloy Using $Ni_{71}CrSi$ as the Interlayer. *Mater. China* **2013**, *32*, 665–675.
61. Shi, X.; Jin, X.; Lin, H.; Jing, J.; Li, L.; Wang, C. Joining of SiC nanowires-toughened SiC coated C/C composites and nickel based superalloy (GH3044) using $Ni_{71}CrSi$ interlayer. *J. Alloys Compd.* **2017**, *693*, 837–842. [CrossRef]
62. Shi, X.; Jin, X.; Yan, N.; Yang, L. Influence of micro-oxidation on joints of C/C composites and GH3044 for large-size aerospace parts. *Acta Astronaut.* **2017**, *140*, 478–484. [CrossRef]
63. Guo, L.; Guo, C.; Li, H.; Kezhi, L. Mechanical Properties and Microstructure of the Joints between Carbon-Carbon Composites and Ni Based High Temperature Alloys. *Rare Met. Mater. Eng.* **2011**, *40*, 111–114.
64. Feng, Z.; Gao, T.; Shao, T.; Guo, W.; Zhu, Y.; Qu, P. Brazing of C/C composite and Ni-based high temperature alloy GH3128. *Trans. China Weld. Inst.* **2015**, *36*, 105–108+118.
65. Lingjun, G.; Hejun, L.; Chen, G.; Kezhi, L.; Tao, F. Joining of C/C Composites and GH3128 Ni-based Superalloy with Ni-Ti Mixed Powder as an Interlayer. *Rare Met. Mater. Eng.* **2011**, *40*, 2088–2091. [CrossRef]
66. Wu, Y.; Li, H.; Ning, L. Microstructure and Property Analysis of the Vacuum Brazed Carbon-Carbon Composites and High Temperature Alloys Joint. *Aerosp. Mater. Technol.* **2015**, *45*, 69–72.
67. Shi, J.M.; Zhang, L.X.; Tian, X.Y.; Li, H.W.; Feng, J.C. Vacuum brazing of the Cf/C composite and Ni base superalloy using MBF 20 filler. *Vacuum* **2018**, *156*, 427–433. [CrossRef]
68. Shen, Y.; Li, Z.; Hao, C.; Zhang, J. A novel approach to brazing C/C composite to Ni-based superalloy using alumina interlayer. *J. Eur. Ceram. Soc.* **2012**, *32*, 1769–1774. [CrossRef]
69. Guo, X.; Si, X.; Li, C.; Zhao, S.; Yang, B.; Qi, J.; Cao, J. Brazing C/C composites to DD3 alloy with a novel Ag–Cr active braze. *Ceram. Int.* **2022**, *48*, 15090–15097. [CrossRef]
70. Xue, J.; Zhang, H.; Guo, W.; Zhu, Y.; Cheng, Z.; Zhang, L.; Long, W. Microstructure and properties of the C/C-superalloy brazed joint by ni-based filler. *Ceram. Int.* **2022**, *48*, 12549–12558. [CrossRef]
71. Zhou, D.; Zhang, X.; Tehranchi, A.; Hou, J.; Lu, W.; Hickel, T.; Zhang, D. Stacking faults in a mechanically strong Al(Mg)–Al_3Mg_2 composite. *Compos. Part B Eng.* **2022**, *245*, 110211. [CrossRef]
72. Peng, X.; Peng, X.; Zhen, H.; Tian, L.; Wang, X.; Wang, K.; Xie, Y. A novel strategy to apply metallic nanoparticles to manufacture NiCrAl composite coatings smartly growing chromia and alumina. *Compos. Part B Eng.* **2022**, *234*, 109721. [CrossRef]
73. Gilli, N.; Watts, J.; Fahrenholtz, W.G.; Sciti, D.; Silvestroni, L. Design of ultra-high temperature ceramic nano-composites from multi-scale length microstructure approach. *Compos. Part B Eng.* **2021**, *226*, 109344. [CrossRef]