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Effect of Silicon on the Microstructure and Performance of the New Binary Deep Eutectic Ti–Cu–Zr–Ni-Based Filler Metal

He Gao, Fuxiang Wei *, Yanwei Sui, Jiqui Qi, Yezeng He and Qingkun Meng

School of Materials Science & Engineering, China University of Mining and Technology, Xuzhou 221116, China; gaohe_1108@163.com (H.G.); suiyanwei163@163.com (Y.S.); qijiqui_hit@163.com (J.Q.); heyezeng@cumt.edu.cn (Y.H.); qkmeng@cumt.edu.cn (Q.M.)

* Correspondence: weifuxiang2001@163.com; Tel.: +86-139-5218-7949

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Abstract: This study designed $(\text{Ti}_{0.55}\text{Cu}_{0.20}\text{Zr}_{0.15}\text{Ni}_{0.10})_{1-x}\text{Si}_x$ amorphous alloys based on binary deep eutectics and examined the effect of silicon (Si) on the amorphous forming ability of the filler alloys. The results show that a certain amount of Si added to the filler metals could improve the amorphous forming ability of the alloys. Under the same experimental conditions, the $\text{Ti}_{0.55}\text{Cu}_{0.20}\text{Zr}_{0.15}\text{Ni}_{0.10}$ filler metal with 0.5 wt % Si had the strongest amorphous forming ability compared to the other filler alloys containing different amounts of Si; its reduced glass transition temperature (T_{rg}) was 0.5554, and its supercooled liquid phase region width (ΔT_x) reached 60 °C. The $(\text{Ti}_{0.55}\text{Cu}_{0.20}\text{Zr}_{0.15}\text{Ni}_{0.10})_{99.5\%}\text{Si}_{0.5\%}$ filler metal designed in these experiments presented good amorphous forming ability and wettability. The brazed joint of SiC and TC4 obtained with this amorphous filler metal showed a shear strength of 102 MPa, indicating an increase of 122% compared to the brazed joint obtained with the filler metal without Si.

Keywords: amorphous materials; binary deep eutectics; $\text{Ti}_{0.55}\text{Cu}_{0.20}\text{Zr}_{0.15}\text{Ni}_{0.10}$ alloy; Si content; amorphous forming ability; microstructure

1. Introduction

The SiC ceramic is widely used in high-temperature service structures, offering such advantages as superior high-temperature properties and excellent wear and oxidation resistance. Therefore, it has a wide range of application prospects in aviation and aerospace. However, it shows disadvantages, such as poor impact toughness, ductility, and machining properties [1–3]. Titanium alloys are another type of material widely used in aviation and aerospace, with their light weight, high strength, machinability, and comprehensive mechanical properties [4,5]. Furthermore, it is often necessary to connect SiC ceramics and titanium alloys in various application to make full use of their separate properties. Some problems occur in the connection processing due to the large differences in their thermal expansion coefficients, wettability, and other physicochemical properties [6]. Brazing, because of its unique connecting principle, lower cost, and simple operation, becomes one of the most useful techniques applied for joining dissimilar materials [7]. Studies on filler metals have been performed by many researchers. Both titanium alloys and SiC ceramics are regarded as important support materials for filler metals, with the rapid development of aviation and aerospace. Therefore, titanium alloy and SiC ceramic brazing technology has also grown with the studies on filler metals. Zhao et al. achieved the connection between a titanium alloy and other materials using an Ag-based filler metal, which, however, presented poor high-temperature performance [8,9]. Song et al. achieved the successful connection of a titanium alloy with other materials using binary, ternary, and multi-element alloys of a

titanium-based filler metal [10,11]. However, the common filler metals present poor wettability and low bonding strength between the filler metal and the base metals [12]. Li et al. found that amorphous filler metals had better wettability and excellent mechanical properties as base metals [13,14].

Amorphous alloys, also called metallic glass, present excellent mechanical properties. Metallic glass had been increasingly studied by researchers in recent years [15–17] because of the scientific and commercial interests in Ti–Cu-based metallic glasses with a high specific strength [18,19], and their glass-forming ability has attracted much attention [7,20]. In order to identify metallic glasses with a higher glass-forming ability, Ti–Cu-based alloy systems with different compositions were designed. The Ti–Cu–Zr–Ni system was known to form amorphous alloys (or metallic glasses) [21]. Many materials scientists established various rules in order to improve the amorphous forming ability of the Ti–Cu–Zr–Ni system [22]. Zhai et al. reported that the addition of Sn into the Ti–Cu–Zr–Ni system could promote the amorphous forming ability of the composite alloys [23]. Huang et al. developed a novel composite filler metal by incorporating Sn and Cu into the conventional Ti–Cu–Zr–Ni based system, and such new composite alloy showed a higher glass-forming ability [24]. Li et al. created a composite filler by adding Hf into the Ti–Cu–Zr–Ni alloy and found that the metallic glasses exhibited favorable mechanical properties and the forming ability of the composite filler increased significantly [25]. Li et al. showed that the addition of Co into the Ti–Cu–Zr–Ni alloy could improve the amorphous forming ability of the filler metal, and the brazing joints had higher mechanical properties than the Co-free filler metal [26]. Moreover, by using calculations of formation enthalpies, King et al. confirmed that an amorphous solid solution was more stable than a body-centered solid solution of the elements [27]. Reyes-Retana et al. previously developed the method of Si addition to an alloy system, reporting the improvement of the amorphous forming ability of the alloy [28], and Gargarella et al. investigated the effect of the addition of Si to a Ti–Cu-based bulk, indicating that both glass-forming ability and plasticity were improved [29]. Figueroa et al. concluded that the addition of 0.5% Si to a Ti–Cu–Hf alloy could enhance the glass-forming ability and increase the critical casting diameter of the Ti–Cu–Hf alloy [30]. These researchers demonstrated that the effect of Si was clear on some alloys, but there was no effect of Si on Ti–Cu–Zr–Ni-based alloys. Similarly, a method of “proportionally mixing binary eutectics”, also called binary deep eutectic, was reported to increase the glass-forming ability of metallic glasses [21]. According to a report, Yang et al. designed a Cu–Ti–Zr–Ni system composition of metallic glasses by proportionally mixing the binary deep eutectic composition and obtained a multi-component alloy that was close to deep eutectics. Their method could result in a higher amorphous forming ability of metallic glasses [31]. In addition, Li et al. prepared a Ti–Cu–Zr–Ni amorphous alloy by proportionally mixing eutectic phases, finding that a higher amorphous forming ability of the Ti–Cu–Zr–Ni alloy could be obtained by this method [20]. These researchers demonstrated that the addition of Si could affect the glass forming ability, but there was no effect of Si on the amorphous forming ability of Ti–Cu–Zr–Ni-based alloys and the amorphous filler metal designed on the basis of binary deep eutectics.

In this paper, a $\text{Ti}_{0.55}\text{Cu}_{0.20}\text{Zr}_{0.15}\text{Ni}_{0.10}$ alloy was obtained by the binary eutectic mixing method, and the effect of Si on the amorphous forming ability and mechanical properties of the filler metal was studied by adding Si to the filler metal.

2. Materials and Methods

The $(\text{Ti}_{0.55}\text{Cu}_{0.20}\text{Zr}_{0.15}\text{Ni}_{0.10})_{1-x}\text{Si}_x$ (wt %) composite filler metal was prepared by mixing four different weight percentages (0, 0.5, 1.0, and 2.0 wt %) of Si (Aladdin-e, Shanghai, China) into the filler metal matrix, and the mixed material was melted in a vacuum furnace using an electric arc at 1600 °C for 2.5 h. The filler metal was melted in a crucible and chill-cast in a water-cooled copper mold to form cuboid ingots of 8 mm × 10 mm × 20 mm (L × W × H). The $(\text{Ti}_{0.55}\text{Cu}_{0.20}\text{Zr}_{0.15}\text{Ni}_{0.10})_{1-x}\text{Si}_x$ is indicated as TA-Si_x, where $x = 0, 0.5, 1.0$, and 2.0 wt %. In the process of electric arc melting, the vacuum degree was 5×10^{-3} Pa, and each ingot was repeatedly melted four times in order to obtain its chemical uniformity. The amorphous filler metal foil was prepared in a high-vacuum melt-spun furnace, and

the alloy foil was cut into strips. The physical phases, microstructures, and thermodynamic parameters of the filler metal were analyzed using X-ray diffraction (XRD, Bruker D-8 with Cu K α radiation, Germany), energy dispersive spectrometry (EDS), scanning electron microscopy (SEM, JSM-6610, JEOL, Tokyo, Japan), and differential scanning calorimetry (DSC, Q-100, TA Instruments, New Castle, DE, USA) under continuous argon flow and a heating rate of 4 K s⁻¹. Both SiC and TC4 (Changfeng factory, Lanzhou, China) were brazed with the TA-Si_x amorphous filler metal and cooled in the furnace. As the TA-Si_x ($x = 0, 0.5, 1.0$, and 2.0 wt %) filler metal was a Ti-based alloy, the wettability could be figured out by the coordinate paper spreading area of the filler metal on SiC. The surface of the SiC was successively ground to grit sizes of 220, 400, 600, 800, 1000, 1500, and 2000 using silicon carbide paper (HX factory, Wuhan, China), cooled with flowing water, then polished with 0.5 μ m Al₂O₃ powders (HX factory, Wuhan, China). The polished SiC was placed into an ultrasonic cleaner to remove the polishing agent and impurities, washed with deionized water, and cleaned with methanol. Finally, it was dried in air. The same method was used to treat TC4 and SiC in the brazing; the filler metal strips were treated in a 5 vol % water solution of HCl (Kejia Chemical Company, Ningbo, China), degreased in a 2% vol water solution of NaOH (Kejia Chemical Company, Ningbo, China), and subjected to ultrasonic cleaning in ethanol and drying in air. Both the filler metal wettability test and the brazing experiment were done in high-vacuum conditions, at a brazing temperature of 1030 °C for 20 min; the temperature rising speed was 10 °C min⁻¹, and the vacuum degree was not lower than 5×10^{-3} Pa. The shear strength test was done for the brazed joint in the electronic universal testing machine (Instron-3366, Instron corporation, Canton, MA, USA) with an extension rate of 0.3 mm s⁻¹ at a temperature of 25 °C. Lastly, four samples were tested for the matrix and composite filler metal joints with varying weight proportions of Si. The shear strength of each component of the filler metal joint was obtained by averaging the test data. The temperature of the samples was controlled within ± 2 °C.

3. Results and Discussion

3.1. Composition

Figure 1 shows the XRD patterns of the TA-Si_x brazing filler metals. It can be seen that the three filler metals TA-Si_{0.5%}, TA-Si_{1.0%}, and TA-Si_{2.0%} have a diffraction peak at an angle of 40° or so in the XRD diffraction patterns of amorphous alloy, without any corresponding sharper diffraction peak. They all show the typical diffraction patterns of an amorphous alloy. The XRD patterns of the TA-Si_{0%} filler metal present several sharper peaks. By calibrating the XRD pattern diffraction peaks, it was found that the crystalline phases were Cu₁₀Zr₇, Ni₁₁Zr₉, and β -Ni, respectively. Figure 2 shows the microstructure of the TA-Si_x ($x = 0, 0.5, 1.0$, and 2.0 wt %) filler metals at low magnification. As can be seen from Figure 2a (point 1), the patterns in Figure 2e are low-magnification SEM images of Figure 2a (point 1) with the corresponding EDS analysis, where the light crystalline phase is Cu₁₀Zr₇, Ni₁₁Zr₉, and β -Ni. Because amorphous Ti exists in crystal phase, it cannot be tested by XRD but can be analyzed by EDS. This observations are in agreement with Sun's results [15]. It was found that large crystals with a diameter of 1 μ m are dissolved in the dark grey base of TA-Si_{0%}, and small crystals are dissolved in the dark grey base of TA-Si_{2.0%}. However, there was no crystalline precipitated phase for TA-Si_{0.5%} and TA-Si_{1.0%}. The test results showed that the TA-Si_{0%} filler metal contained many crystal microstructures. From the above analyses, the brazing filler metal supplemented with Si could improve its amorphous forming ability.

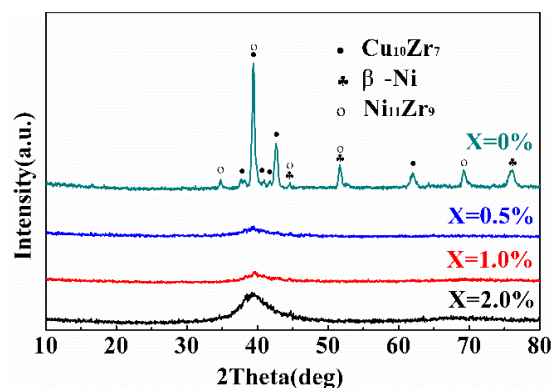


Figure 1. X-ray diffraction (XRD) pattern of the TA-Si_x filler metals; $x = 0, 0.5, 1.0$, and 2.0% .

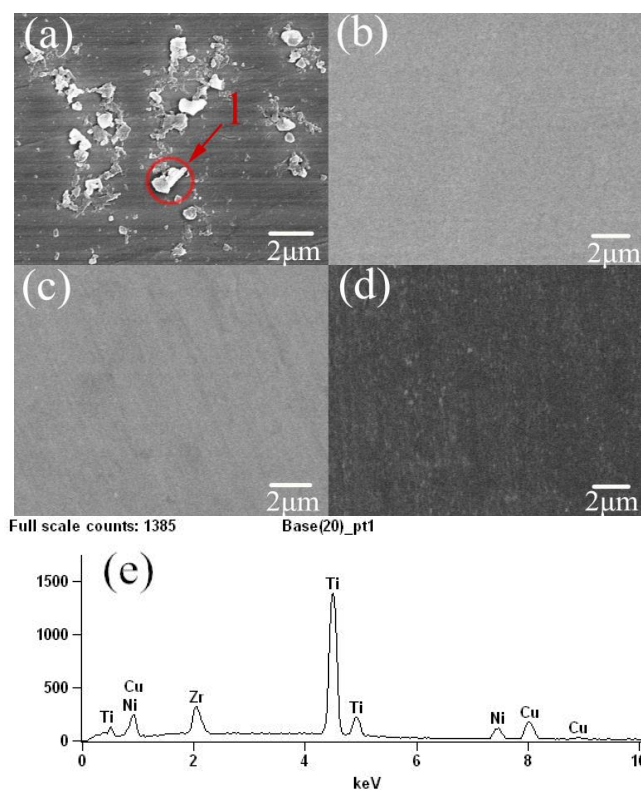


Figure 2. Microstructures at low magnification of the TA-Si_x filler metals (a) $x = 0\%$; (b) $x = 0.5\%$; (c) $x = 1.0\%$; (d) $x = 2.0\%$; (e) energy dispersive spectrometry (EDS) of the highlighted region (point 1) in Figure 2a.

3.2. Thermodynamic Characteristics

Figures 3 and 4 show the differential scanning calorimetry (DSC) curves of the crystallizing and melting processes of the metal fillers TA-Si_x ($x = 0, 0.5, 1.0$, and 2.0%). Table 1 gives the thermodynamic parameters of TA-Si_x. The DSC traces exhibit the typical shape of amorphous alloys. With the increase of Si content from 0 to 2.0% , the glass transition temperature of the filler metal varied from 304 to 355 °C. These data clearly show that the addition of Si could improve the glass transition temperature of the filler metal. The addition of $0.5, 1.0$, and 2.0% of Si increased the glass transition temperature of the filler metal by 12.17% , 15.13% , and 16.78% , respectively. In particular, for the addition of $0, 0.5, 1.0$, and 2.0% of Si into the $\text{Ti}_{0.55}\text{Cu}_{0.20}\text{Zr}_{0.15}\text{Ni}_{0.10}$ alloy, the melting points of the composite filler metal were $946, 932, 943$, and 951 °C, respectively. These results indicated that the melting point of

the composite filler decreased firstly and then increased slightly with the increase of Si content. The melting point decreased from 964 to 932 °C for the composite filler metal with 0.5% Si content and followed a rising trend for the other filler metals, increasing to 943 °C and 951 °C for the 1.0% and 2.0% composites, respectively. It was found that the temperature difference between the maximum width (TA-Si_{0.5%}) and the minimum width (TA-Si_{0%}) of the supercooled liquid phase region (ΔT_x) was 22 °C. The filler metal TA-Si_{0.5%} is considered better in the supercooled liquid phase region (ΔT_x) in comparisons described in previous reports [32]. The narrower strait supercooled phase region means that a smaller solid–liquid interface energy of the alloy system and the nucleation and growth of the alloy were promoted. As a result, the amorphous forming ability of the alloy became poorer.

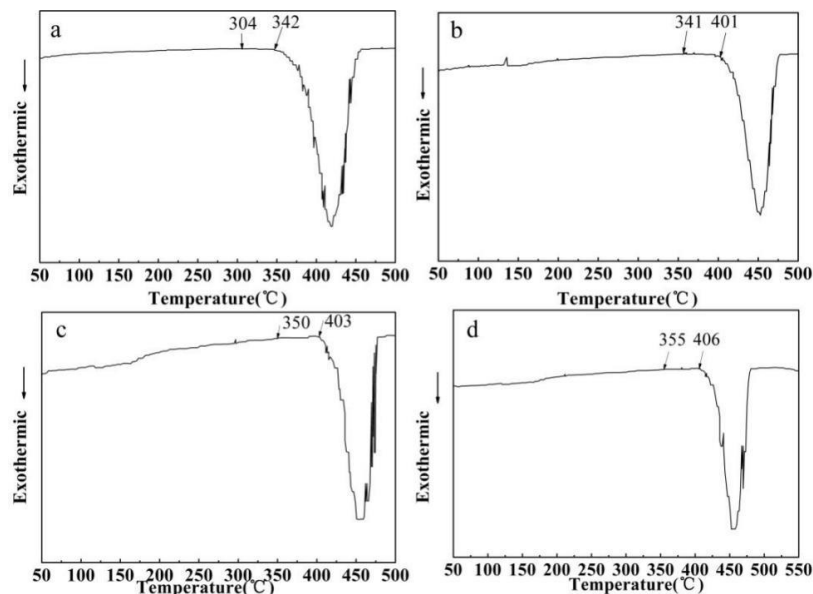


Figure 3. Differential scanning calorimetry (DSC) of the TA-Si_x filler metals during the crystallization process: (a) $x = 0\%$; (b) $x = 0.5\%$; (c) $x = 1.0\%$; (d) $x = 2.0\%$.

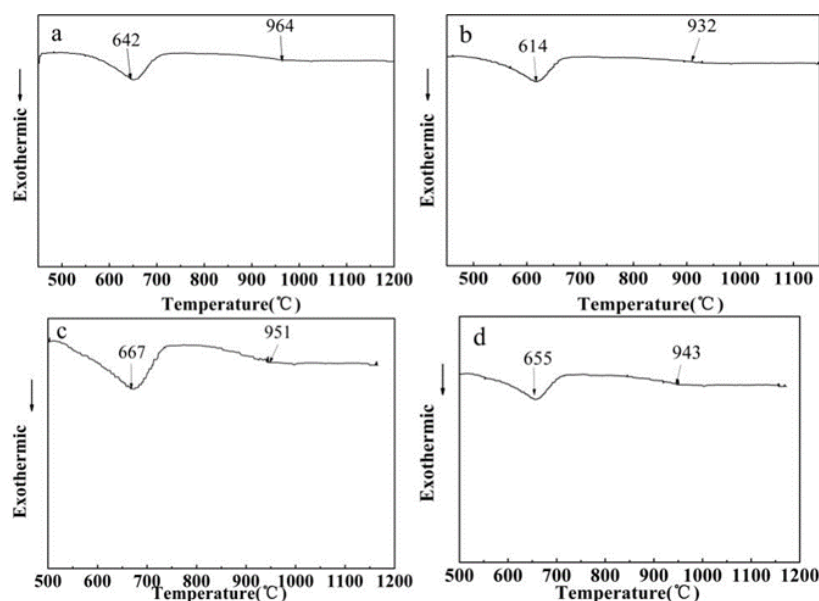


Figure 4. Differential scanning calorimetry (DSC) of the TA-Si_x filler metals during the melting process: (a) $x = 0\%$; (b) $x = 0.5\%$; (c) $x = 1.0\%$; (d) $x = 2.0\%$.

Table 1. Thermodynamic parameters of the TA-Si_x filler metals.

Alloy	T_g (°C)	T_x (°C)	T_m (°C)	T_l (°C)	ΔT_x (°C)	T_{rg}	δ	γ
$x = 0\%$	304	342	642	964	38	0.4735	0.5182	0.2697
$x = 0.5\%$	341	401	614	932	60	0.5554	0.6785	0.3150
$x = 1.0\%$	350	403	655	943	53	0.5344	0.6796	0.3116
$x = 2.0\%$	355	406	667	951	51	0.5322	0.6812	0.3109

3.3. Amorphous Forming Ability

On the basis of the classical nuclear theory, Turnbull proposed an evaluation on the amorphous forming ability of metallic glasses of alloys systems in glass transition temperature [33]. The glass transition temperature (T_{rg}) can be expressed by:

$$T_{rg} = \frac{T_g}{T_m} \quad (1)$$

In Chen et al. [34], the glass forming ability (GFA) of amorphous alloys is called δ and can be expressed as shown in the following equation:

$$\delta = \frac{T_x}{T_l - T_g} \quad (2)$$

In addition, Lu et al. reported a new glass forming ability criterion for metallic glasses [35], where a new parameter γ was defined as follows for inferring the relative glass forming ability of amorphous alloys:

$$\gamma = \frac{T_x}{T_g + T_l} \quad (3)$$

Table 1 lists the measured thermal parameters γ , δ , and T_{rg} for four alloys. It is noteworthy that the glass transition temperature (T_{rg}) increased to the maximum value with the addition of 0.5% Si. With a further increase of Si content, the glass transition temperature (T_{rg}) decreased slightly but still remained greater than that of the Si-free filler metal. The difference between the maximum glass transition temperature (T_{rg}) (TA-Si_{0.5%}) and the minimum one (TA-Si_{0%}) was 8.19%. Compared with other researches, the filler metal TA-Si_{0.5%} showed the best glass transition temperature [36] and presented a high amorphous forming ability. It was also found that the parameter δ can be used to evaluate the glass forming ability of the alloys; δ was enhanced by 30.9–31.5% for the Si-containing composite filler metal alloys compared with the Si-free non-composite filler metals. This means that a certain amount of Si added to the filler metal could improve the amorphous forming ability of the alloy. Similarly the parameter γ can be used to infer the relative glass forming ability of amorphous alloys; the value of the parameter γ increased with the increase of Si content, and a rising trend was maintained until the weight of Si approached about 0.5%. Beyond this amount, γ increased only slightly but still remained higher than that of the Si-free non-composite filler metal matrix. This suggests that addition of Si could improve the amorphous forming ability of the filler metal. The above results indicate that the amorphous forming ability of the filler metal could be improved with the addition of Si to the TA-Si_x ($x = 0, 0.5, 1.0$, and 2.0%) filler metals, and the effect of Si on the amorphous forming ability of the filler alloys was most remarkable when the Si content was increased to about 0.5%. Beyond this amount, the amorphous forming ability of the alloy was only slightly improved.

3.4. Wettability

The wettability of a filler metal is one of the important indexes to evaluate the brazing performance. Figure 5 shows the wettability test results of filler metals in SiC ceramics. The results show that the spreading area of the filler metal was 3.24 cm² in TA-Si_{0%}, compared with 4.46, 3.53, and 2.89 cm² in

TA-Si_{0.5%}, TA-Si_{1.0%}, and TA-Si_{2.0%} composite filler metals, respectively. However, for higher amounts (1.0%) of Si in the composite filler metal, the spreading area decreased compared with the TA-Si_{0.5%} filler metal. The spreading area of the composite filler metal with 2.0% Si was lower than that of the pristine filler metal. We found that the TA-Si_x ($x = 0, 0.5, 1.0$, and 2.0%) filler metal spreading areas could be arranged in the following descending order: TA-Si_{2.0%}, TA-Si_{0%}, TA-Si_{1.0%} and TA-Si_{0.5%}. This is because the filler metal with 0.5% Si had the strongest amorphous forming ability, the lowest liquidus temperature, uniform components, and the strongest spreading ability. On the other hand, the fluidity of the molten filler metal decreased with the increase of Si content, and its spreading area was reduced as well.

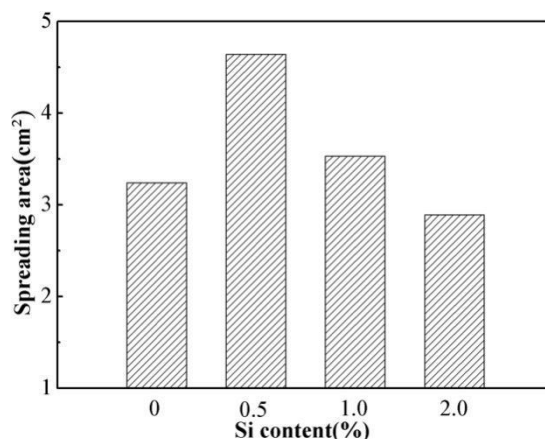


Figure 5. Spreading areas of the filler metals.

3.5. Mechanical Properties

With the same brazing technology, the shear strengths of the brazed joints ranged in the following ascending order: TA-Si_{0%} (46 MPa), TA-Si_{2.0%} (55 MPa), TA-Si_{1.0%} (78 MPa), and TA-Si_{0.5%} (102 MPa). Therefore, the testing data demonstrated that the shear strength of the studied composite filler metals increased with the addition of Si. In addition, the shear strengths of the TA-Si_x ($x = 1.0$ and 2.0%) filler metal joints were slightly lower than that of the TA-Si_{0.5%} filler metal joint by about 23.53% and 46.08%, respectively. Noteworthy, the improvement in shear strength of the composite filler metal joints (especially, TA-Si_{0.5%}) can also be explained in terms of changes of wettability and melting points. The maximum spreading area and the lowest melting point were reached when the Si content was 0.5%. This means that the filler metal diffusion into the base metal by capillarity can be improved in the same brazing conditions and is beneficial to the connection between filler metal and substrate. The TA-Si_{0.5%} filler metal joint displayed the maximum shear strength. The TC4-TA-Si_{0.5%}-SiC joint with additive Si had a certain shear intensity, which was 122% higher than that of the TC4-TA-Si_{0%}-SiC joint without additive Si. In light of these experimental results, it can be concluded that Si addition could strengthen the brazing joint of composite filler metals.

4. Conclusions

In this research, the effect of silicon on the microstructure and performance of a new binary deep eutectic Ti-Cu-Zr-Ni-based filler metal was studied. The results are summarized as follows:

1. The design based on binary deep eutectic or proportionally mixing binary eutectics composites can enhance the glass-forming ability of the filler metal.
2. The amorphous forming ability of the filler metal can be improved with the addition of silicon (Si) to TA-Si_x ($x = 0, 0.5, 1.0$ and 2.0%) filler metals.
3. The filler metal presents the strongest amorphous forming ability when the content of Si is up to 0.5%.

4. The supercooled phase region width ($\Delta T_{x \max} = 60 \text{ }^{\circ}\text{C}$), the reduced glass transition temperature ($T_{\text{rg} \max} = 0.5554$), the parameter γ ($\gamma_{\max} = 0.3150$) for inferring the relative glass-forming ability of the amorphous alloys, and the wetting area (4.64 cm^2), reach their maximum values, and the liquidus temperature ($T_{\text{l} \min} = 932 \text{ }^{\circ}\text{C}$) reach its minimum value when the Si content is up to 0.5%.
5. In the same brazing technology conditions, the shear intensity of the brazing joints is the highest when using the filler metal TA-Si_{0.5%} (102 MPa), being 122% higher than that obtained when using the filler metal TA-Si_{0%} (46 MPa).

Author Contributions: H.G. and F.W. conceived and designed the experiments; H.G. performed the experiments; H.G., F.W. performed the data analysis and drafted the manuscript. Y.S., J.Q., Y.H., Q.M. participated in the data analysis, experimental discussion, and interpretation. H.G. and F.W. completed the paper.

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References

1. Stein, R.S.; Kuwata, M. Microstructure and mechanical properties of Mg-5Nb metal-metal composite reinforced with nano SiC ceramic particles. *Metals* **2012**, *2*, 178–194.
2. Cai, S.; Chen, T.; Zhang, X. Effect of remelting duration on microstructure and properties of SiCp/Al composite fabricated by powder-thixoforming for electronic packaging. *Metals* **2016**, *6*, 311. [[CrossRef](#)]
3. Tang, C.; He, Z.; He, X.; Huang, J.; Yi, Y.; Wang, H.; Wang, T. Preparation and characterization of SiC hollow microspheres. *Mater. Lett.* **2017**, *207*, 104–108. [[CrossRef](#)]
4. Shi, J.M.; Feng, J.C.; Liu, H.; Tian, X.Y.; Zhang, L.X. Vacuum brazing of the Gr/2024Al composite and TC4 alloy using AgCuTi filler alloy with Ni–Al interlayer as auxiliary heat source. *J. Alloys Compd.* **2017**, *694*, 672–681. [[CrossRef](#)]
5. Cao, X.; Xu, X.; Wang, C.; Pyoun, Y.; Wang, Q. Effect of ultrasonic surface impact on the fatigue behavior of Ti-6Al-4V subject to simulated body fluid. *Metals* **2017**, *7*, 440. [[CrossRef](#)]
6. Song, X.R.; Li, H.J.; Zeng, X. Brazing of C/C composites to Ti6Al4V using multiwall carbon nanotubes reinforced TiCuZrNi brazing alloy. *J. Alloys Compd.* **2016**, *664*, 175–180. [[CrossRef](#)]
7. Ba, J.; Wang, Y.; Liu, Y.; Lin, J.; Qi, J.; Wang, G.; Zhong, Z.; Ma, Q.; Wang, Z.; Feng, J. In situ consume excessive Ti element and form fine Ti based compounds as reinforcements for strengthening C/C-TC4 joints. *Vacuum* **2017**, *143*, 303–311. [[CrossRef](#)]
8. Zhao, Y.; Song, X.; Hu, S.; Zhang, J.; Cao, J.; Fu, W.; Feng, J. Interfacial microstructure and mechanical properties of porous-Si₃N₄ ceramic and TiAl alloy joints vacuum brazed with AgCu filler. *Ceram. Int.* **2017**, *43*, 9738–9745. [[CrossRef](#)]
9. Xiong, J.H.; Huang, J.H.; Zhang, H.; Zhao, X.K. Brazing of carbon fiber reinforced SiC composite and TC4 using Ag–Cu–Ti active brazing alloy. *Mater. Sci. Eng. A* **2010**, *527*, 1096–1101. [[CrossRef](#)]
10. Song, X.R.; Li, H.J.; Zeng, X.; Zhang, L. Brazing of C/C composites to Ti6Al4V using graphene nanoplatelets reinforced TiCuZrNi brazing alloy. *Mater. Lett.* **2016**, *183*, 232–235. [[CrossRef](#)]
11. Komolafe, B.; Mostafa, A. Wetting and spreading behavior of Ti-based brazing filler on Ti64 substrate. *Mater. Res. Express* **2017**, *4*, 066503. [[CrossRef](#)]
12. Cai, Y.S.; Liu, R.C.; Zhu, Z.W.; Cui, Y.Y.; Yang, R. Effect of brazing temperature and brazing time on the microstructure and tensile strength of TiAl-based alloy joints with Ti–Zr–Cu–Ni amorphous alloy as filler metal. *Intermetallics* **2017**, *91*, 35–44. [[CrossRef](#)]
13. Zhao, S.; Wang, H.; Xiao, L.; Guo, N.; Zhao, D.; Yao, K.; Chen, N. High strain rate sensitivity of hardness in quinary Ti–Zr–Hf–Cu–Ni high entropy metallic glass thin films. *Physica E* **2017**, *94*, 100–105. [[CrossRef](#)]
14. Li, Q.; Liu, S.S.; Wang, X.H.; Yang, T.; Dong, C.; Hu, J.T.; Jiang, Y.Q. Mechanical and corrosion properties of Ti–Ni–Cu–Zr metallic glass matrix composites. *J. Alloys Compd.* **2017**, *727*, 1344–1350. [[CrossRef](#)]
15. Sun, Y.J.; Qu, D.D.; Huang, Y.J.; Liss, K.D.; Wei, X.S.; Xing, D.W.; Shen, J. Zr–Cu–Ni–Al bulk metallic glasses with superhigh glass-forming ability. *Acta Mater.* **2009**, *57*, 1290–1299. [[CrossRef](#)]
16. Sun, H.C.; Ning, Z.L.; Wang, G.; Liang, W.Z.; Shen, H.X.; Sun, J.F.; Xue, X. Tensile strength reliability analysis of Cu₄₈Zr₄₈Al₄ amorphous microwires. *Metals* **2016**, *6*, 296. [[CrossRef](#)]

17. Madge, S.V.; Louzguineluzgin, D.V.; Inoue, A.; Greer, A.L. Large compressive plasticity in a La-based glass-crystal composite. *Metals* **2012**, *3*, 41–48. [[CrossRef](#)]
18. Bu, F.; Wang, J.; Li, L.; Kou, H.; Xue, X.; Li, J. The effect of thermal cycling treatments on the thermal stability and mechanical properties of a Ti-based bulk metallic glass composite. *Metals* **2016**, *6*, 274. [[CrossRef](#)]
19. Hsu, C.; Lin, H.; Lee, P. Wear behavior of mechanically alloyed Ti-based bulk metallic glass composites containing carbon nanotubes. *Metals* **2009**, *6*, 289. [[CrossRef](#)]
20. Li, P.; Wang, G.; Ding, D.; Shen, J. Glass forming ability and thermodynamics of new Ti–Cu–Ni–Zr bulk metallic glasses. *J. Non-Cryst. Solids* **2012**, *358*, 3200–3204. [[CrossRef](#)]
21. Lee, D.M.; Sun, J.H.; Kang, D.H.; Shin, S.Y.; Welsch, G.; Lee, C.H. A deep eutectic point in quaternary Zr–Ti–Ni–Cu system and bulk metallic glass formation near the eutectic point. *Intermetallics* **2012**, *21*, 67–74. [[CrossRef](#)]
22. Lee, P.Y.; Cheng, Y.M.; Chen, J.Y.; Hu, C.J. Formation and corrosion behavior of mechanically-alloyed Cu–Zr–Ti bulk metallic glasses. *Metals* **2017**, *7*, 148. [[CrossRef](#)]
23. Zhai, H.; Wang, H.; Liu, F. Effects of Sn addition on mechanical properties of Ti-based bulk metallic glass composites. *Mater. Des.* **2016**, *110*, 782–789. [[CrossRef](#)]
24. Huang, Y.J.; Shen, J.; Sun, J.F.; Yu, X.B. A new Ti–Zr–Hf–Cu–Ni–Si–Sn bulk amorphous alloy with high glass-forming ability. *J. Alloys Compd.* **2007**, *427*, 171–175. [[CrossRef](#)]
25. Li, P.; Wang, G.; Ding, D.; Shen, J. Glass forming ability, thermodynamics and mechanical properties of novel Ti–Cu–Ni–Zr–Hf bulk metallic glasses. *Mater. Des.* **2014**, *53*, 145–151. [[CrossRef](#)]
26. Li, X.; Li, L.; Hu, K.; Qu, S. Vacuum brazing of TiAl-based intermetallics with Ti–Zr–Cu–Ni–Co amorphous alloy as filler metal. *Intermetallics* **2015**, *57*, 7–16. [[CrossRef](#)]
27. King, D.J.M.; Middleburgh, S.C.; Liu, A.C.Y.; Tahini, H.A.; Lumpkin, G.R.; Cortie, M.B. Formation and structure of V–Zr amorphous alloy thin films. *Acta Mater.* **2015**, *83*, 269–275. [[CrossRef](#)]
28. Reyes-Retana, J.A.; Naumis, G.G. The effects of Si substitution on the glass forming ability of Ni–Pd–P system, a DFT study on crystalline related clusters. *J. Non-Cryst. Solids* **2014**, *387*, 117–123. [[CrossRef](#)]
29. Gargarella, P.; Pauly, S.; Khoshkhoo, M.S.; Kiminami, C.S.; Kühn, U.; Eckert, J. Improving the glass-forming ability and plasticity of a TiCu-based bulk metallic glass composite by minor additions of Si. *J. Alloys Compd.* **2016**, *663*, 531–539. [[CrossRef](#)]
30. Figueroa, I.A.; Davies, H.A.; Todd, I. High glass formability for Cu–Hf–Ti alloys with small additions of Y and Si. *Philos. Mag.* **2009**, *89*, 2355–2368. [[CrossRef](#)]
31. Yang, Y.J.; Xing, D.W.; Li, C.P.; Wei, S.D.; Sun, J.K.; Shen, Q.K. A new way of designing bulk metallic glasses in Cu–Ti–Zr–Ni system. *Mater. Sci. Eng. A* **2007**, *448*, 15–19. [[CrossRef](#)]
32. Gargarella, P.; Pauly, S.; Khoshkhoo, M.S.; Kühn, U.; Eckert, J. Phase formation and mechanical properties of Ti–Cu–Ni–Zr bulk metallic glass composites. *Acta Mater.* **2014**, *65*, 259–269. [[CrossRef](#)]
33. Turnbull, D. Under What Conditions can a Glass be Formed. *Contemp. Phys.* **1969**, *10*, 473–488. [[CrossRef](#)]
34. Chen, Q.; Shen, J.; Zhang, D.; Fan, H.; Sun, J.; McCartney, D.G. A new criterion for evaluating the glass-forming ability of bulk metallic glasses. *Mater. Sci. Eng. A* **2006**, *433*, 155–160. [[CrossRef](#)]
35. Lu, Z.P.; Liu, C.T. A new glass-forming ability criterion for bulk metallic glasses. *Acta Mater.* **2002**, *50*, 3501–3512. [[CrossRef](#)]
36. Xie, K.F.; Yao, K.F.; Huang, T.Y. Preparation of $(\text{Ti}_{0.45}\text{Cu}_{0.378}\text{Zr}_{0.10}\text{Ni}_{0.072})_{100-x}\text{Sn}_x$ bulk metallic glasses. *J. Alloys Compd.* **2010**, *504*, S22–S26. [[CrossRef](#)]

