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ARTICLE

Effect of Si on the Microstructure and Performance of Ti-Cu-Zr-Ni-based Amorphous Filler Metal

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Abstract: ($Ti_{0.46}Cu_{0.14}Zr_{0.27}Ni_{0.13}$)-$x$Si ($x$=0, 0.5, 1, 2, wt%) amorphous filler metal was prepared by arc melting and fast-cooling melt-spinning techniques, and the effect of a certain amount of Si added to the filler metal on its amorphous forming ability was studied. The results show that the filler metal has the strongest amorphous forming ability when the content of Si reaches 0.5%; its wetting area is 3.06 cm^2, its supercooled liquid phase region width ΔT_x=56 ºC, its reduced glass transition temperature T_{rg}=0.5387, and its liquidus temperature (T_l) is 949 ºC. The vacuum brazing was done for SiC and TC4 using this amorphous alloy as the filler metal, and the shear strength of brazed joint is 80 MPa. The amorphous forming ability of filler metal is improved with addition of Si to the filler metal.

Key words: Ti-Cu-Zr-Ni amorphous filler metal; additive Si; amorphous forming ability

Brazing is an important method for materials welding and joining, and the brazing filler metal plays a crucial role in the brazing process. Researchers develop many kinds of filler metals to satisfy the requirements for the brazing of different materials. Ti alloy as a filler metal is widely used in aviation and aerospace. The study of Ti-based brazing filler metal is always a hot topic in the material field in the brazing as an important joining method. B. Komolafe, S. Pang and F. Ji et al. performed plenty of studies on Ti-based filler metals[1-3].

H. S. Ren, D. Fan, A. Kocjan, and X. Yue conducted the brazing for Ti-based alloy materials using the Ti-Cu-Zr-Ni filler metal, finding the poor wettability between filler metal and base metal[4-7]. W. Yu et al[8]. completed the brazing of Ti alloy using Ti-Cu-Zr-Ni amorphous filler metal obtained by the fast-cooling way. They found the amorphous filler metal could improve the wettability of filler metal, and possesses the advantages that common brazing filler metals do not have. Moreover, it could improve the mechanical properties of brazed joint. However, it is found through studies that Ti-Cu-Zr-Ni amorphous filler metal has strict requirements for its preparation conditions and technological parameters. In addition, this amorphous filler metal has weak amorphous forming ability. It is always a hot issue discussed by researchers how to improve its amorphous forming ability. P. H. Tsai, J. A. Reyes-Retana, and T. Wang et al. prepared amorphous alloy by adding a certain amount of Si to other alloy systems, and the results showed the amorphous forming ability of the alloy is improved with the addition of Si[9-11].

J. S. Zou et al. realized the brazing of Si_3N_4 using $Ti_{0.40}Zr_{0.25}Ni_{0.15}Cu_{0.20}$ amorphous filler metal[12], but the poor wettability and intensity occurred between filler metal and ceramics in the side of Si_3N_4. Y. Jing and D. Fan et al. found that the addition of a proper amount of Ti and Zr could effectively improve the wettability and intensity of brazed joint[13, 14]. So, the Ti-based brazing filler metal used in this experiment was $Ti_{0.46}Cu_{0.14}Zr_{0.27}Ni_{0.13}$, and it was added with Si to improve its amorphous forming ability. By this way, the effect of Si on microstructure and performances of $Ti_{0.46}Cu_{0.14}Zr_{0.27}Ni_{0.13}$ filler metal was studied.

1 Experiment

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The filler metal for this experiment was prepared by arc melting and fast-cooling melt-spinning. At first, all experiment substances were melted together by arc melting, and they were blended evenly by the arc melting four times. Before the arc melting, the oxidation film on the surface of the substances should be removed first, and then they were cleaned two or three times with acetone and ethanol. The vacuum degree came to 5×10^{-3} Pa in the process of melting. The fast-cooling melt-spinning was completed in the high vacuum single-roll melt-spun furnace, and the alloy foil was cut into strips. $(Ti_{0.46}Cu_{0.14}Zr_{0.27}Ni_{0.13})$-$x$Si (wt%) is used to represent the prepared amorphous filler metal, where, x stands for the mass fraction of additive Si; $(Ti_{0.46}Cu_{0.14}Zr_{0.27}Ni_{0.13})$-$x$Si (wt%) can be written as TA-xSi (wt%) for short; x=0wt%，0.5wt%, 1wt% and 2wt% in the experiment. The filler metal strip was tested by X-ray diffraction (XRD) and differential scanning calorimetry (DSC) after it was polished. The DSC test was done in highly-purified nitrogen (N_2) at a flow rate of 300 mL·min^{-1} and a temperature rising speed of 10 ºC·min^{-1}. Both SiC and TC4 were brazed at 1030 ºC for 20 min using TA-xSi(x=0%, 0.5%, 1%, 2%) amorphous brazing filler metal; the temperature rising speed was 10 ºC·min^{-1}, and the vacuum degree was not lower than 5×10^{-3} Pa in the brazing process. The brazed position was cooled with furnace temperature after the heat keeping ended. As the filler metal was Ti-based alloy, the wettability of filler metal was tested only for SiC in this experiment. The SiC should be polished before the test, and then was cleaned with acetone and alcohol ultrasonically. The filler metal foil was cut into a small square piece; the square piece was folded on SiC and put into the brazing furnace. The test for the wettability of filler metal was done in the condition consistent with the brazing heating curves, and the spreading area of the filler metal on SiC was figured out by the plotting paper.

2 Results and Discussion

2.1 Composition

Fig.1 shows the XRD patterns of TA-xSi (x=0%, 0.5%, 1%, 2%) brazing filler metal. It is known from the figure that the three filler metals TA-0.5%Si, TA-1.0%Si and TA-2.0%Si are featured by the typical XRD patterns of amorphous alloy; a wide diffraction peak with a weak intensity occurs at a diffraction angle of 40° or so, while no sharp and high-intensity crystal diffraction peak occurs at other diffraction angles. Such a broad diffraction peak corresponding to crystalline phase, called non-Bragg scattering in X-ray diffraction, doesn't comply with the Bragg equation. That is to say, the atoms in this crystal microstructure are arranged in disorder, indicating TA-0.5%Si, TA-1.0%Si and TA-2%Si are typical amorphous brazing filler metals. The XRD patterns of

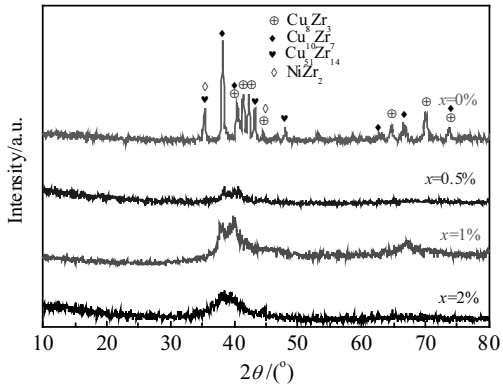

Fig.1 XRD patterns of the TA-xSi (x=0%, 0.5%, 1%, 2%) filler metal

TA-0%Si filler metal without Si addition present several sharp peaks of high intensity. It is found by calibrating XRD pattern diffraction peak of TA-0%Si that the crystalline phases are Cu_8Zr_3, $Cu_{10}Zr_7$, $Cu_{51}Zr_{14}$ and $NiZr_2$. According to the XRD patterns, the brazing filler metal added with Si can significantly improve its amorphous forming ability.

The microstructure morphology of TA-xSi (x=0%, 0.5%, 1%, 2%) filler metal at low magnification is shown in Fig.2. It is known from the figure that the crystalline with a diameter of 1 μm is dissolved out in the dark grey base of TA-0%Si, and the crystalline is dissolved out in the dark grey base of TA-2%Si, but there is no significant crystalline precipitated phase for TA-0.5%Si and TA-1%Si, and both filler metals present a typical non-feature state of amorphous alloy, without such lattice defects as crystal boundary and dislocation.

Fig.3 shows the DSC curves of crystallization process of TA-xSi (x=0%, 0.5%, 1%, 2%) tested in nitrogen (N_2). It is seen from the DSC test curves that four samples of DSC curves present similar features. After the glass transformation occurs in samples, a wide transition zone exits with further heating, followed by a significant crystallization exothermic peak. The TA-0%Si filler metal contains a great many crystalline textures based on its XRD analyses.

2.2 Melting characteristics

Fig.4 shows DSC melting curves of TA-xSi (x=0%, 0.5%, 1%, 2%) at a heating rate of 10 K·min^{-1}, and Table 1 shows the thermodynamic parameters of TA-xSi (x=0%, 0.5%, 1%, 2%). It is found the TA-0.5%Si has the maximum width (ΔT_x) of supercooled liquid phase region, and TA-0%Si has the minimum width; the difference between them is 22 ºC. The wider supercooled phase region indicates the bigger solid-liquid interface energy of the alloy system, so that the nucleation and growth of the alloy system are restrained, and the alloy has a bigger amorphous forming ability. In addition, TA-0.5%Si has the maximum reduced glass transition temperature (T_{rg}), and TA-0%Si has the minimum one; the difference between them is 8.7%.

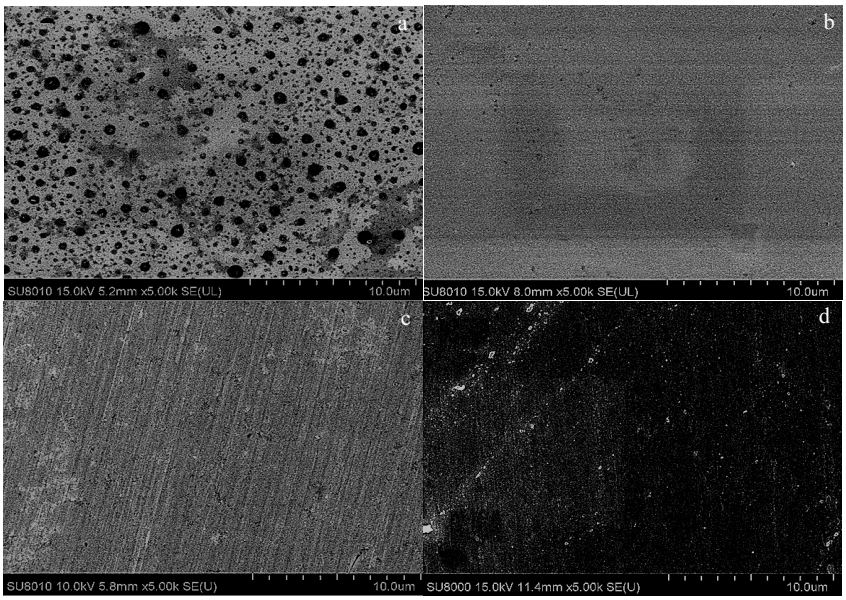

Fig.2 Microstructures of TA-*x*Si filler metal at low magnification: (a) *x*=0%, (b) *x*=0.5%, (c) *x*=1%, and (d) *x*=2%

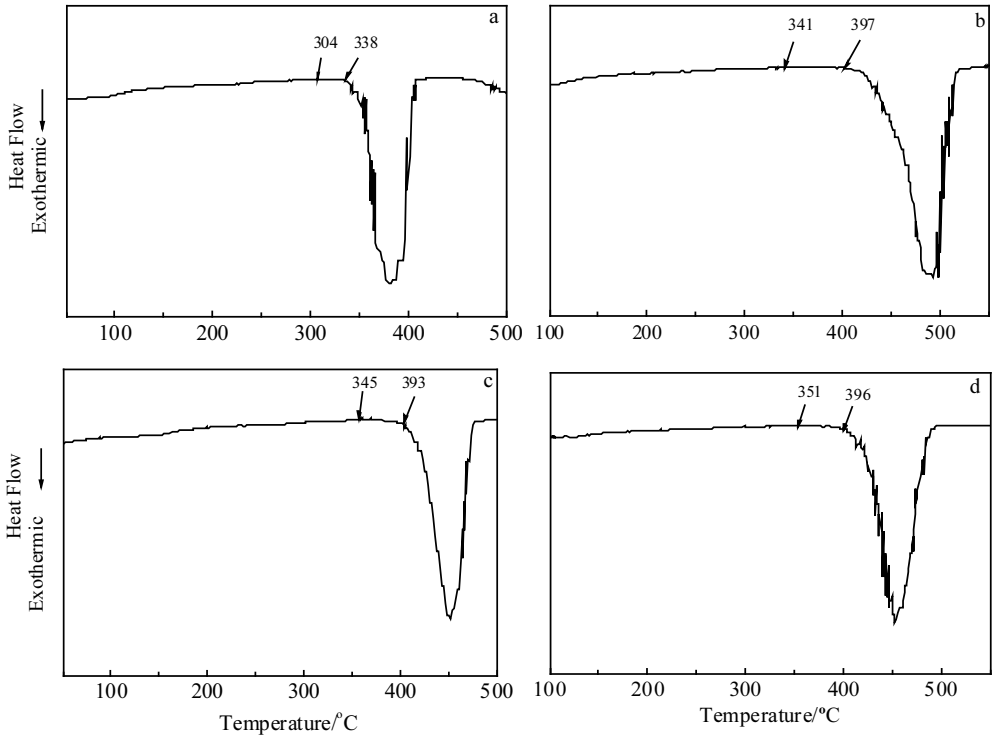

Fig.3 DSC curves of TA-*x*Si filler metal during crystallization process: (a) *x*=0%, (b) *x*=0.5%, (c) *x*=1%, and (d) *x*=2%

2.3 Wettability of filler metal

The wettability of filler metal is one of important criteria to judge the brazing performances of filler metal. As for brazing filler metal, its good wetting with base metal is a key to decide the quality of brazing filler metal[15]. The wettability of filler metal can be measured by the spreading test of filler metal. The spreading test should be done on SiC ceramics before the brazing test. The test results for the spreading area of TA-*x*Si (*x*=0%, 0.5%, 1%, 2%) filler metal are shown in Fig.5. The filler metal with a Si content of 0.5% has the maximum spreading area. On the one hand, the filler metal foil with a Si content of 0.5% has the highest amorphous degree and the lowest liquidus temperature. It contains uniform components, and its spreading area is naturally higher than that of the filler metal without additive Si. On the other hand, too high Si

content can increase can viscosity and lower the fluidity of molten filler metal. When 0.5% Si is added, the filler metal presents the strongest wetting spread capacity; the wetting spread capacity decreases gradually with the continuous increase of Si content.

2.4 Mechanical properties

In the condition of the same brazing technique, the shear test was done for soldered joint, and the shear strengths from high to low were TA-0.5%Si, TA-1.0%Si, TA-0%Si and TA-2.0%Si of 80 MPa, 65 MPa, 56 MPa and 37 MPa, respectively. The TC4/TA-0.5%Si/SiC joint has the maximum shear strength, 116% higher than the minimum shear strength of TC4/TA-2.0%Si/SiC; the TC4/TA-0.5%Si/SiC joint with additive Si has a shear intensity, 43% higher than that of TC4/TA-0%Si/SiC joint without additive Si.

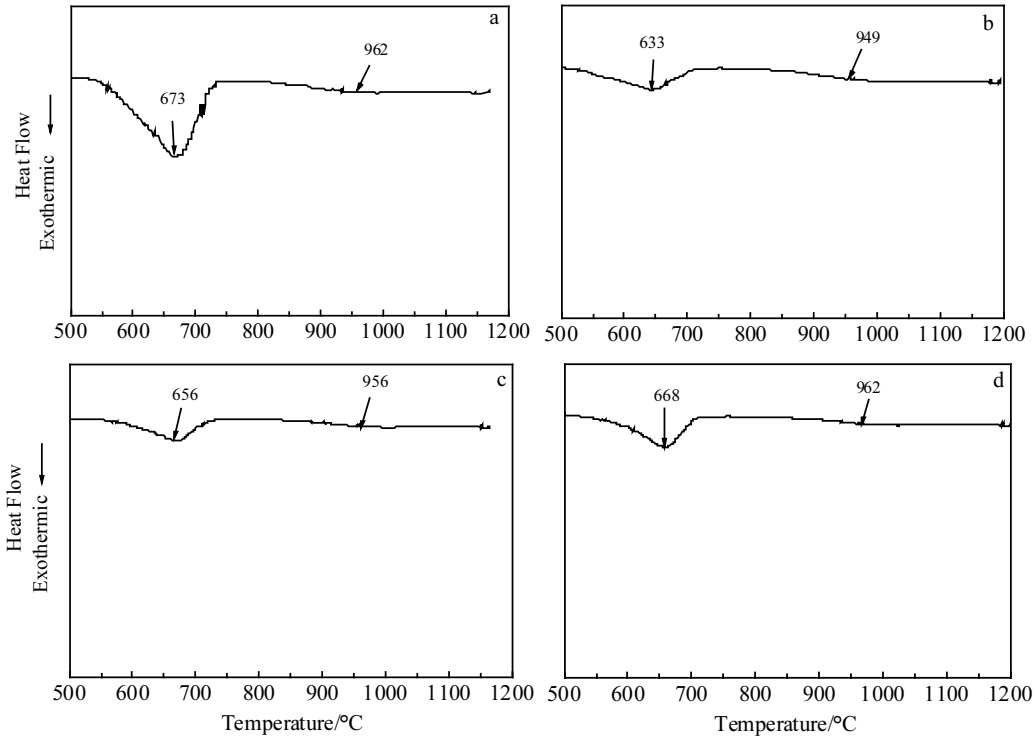

Fig.4 DSC curves of TA-*x*Si filler metal during melting process: (a) *x*=0%, (b) *x*=0.5%, (c) *x*=1%, and (d) *x*=2%

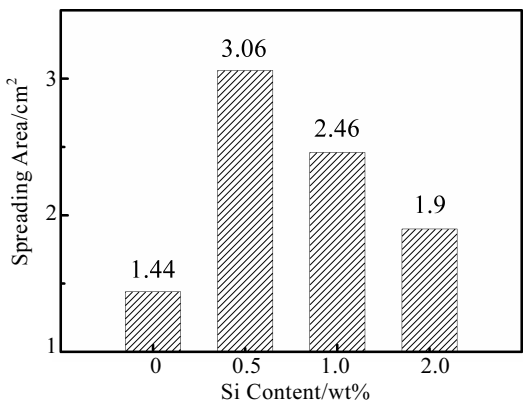

Fig.5 Spreading area of the filler metal

Table 1 Thermodynamic parameters of TA-*x*Si filler metal

x/wt%	T_g/℃	T_x/℃	T_m/℃	T_l/℃	ΔT_x/℃	T_{rg}
0	304	338	673	962	34	0.4517
0.5	341	397	633	949	56	0.5387
1	345	393	656	956	48	0.5259
2	351	396	668	962	45	0.5254

3 Conclusions

1) The amorphous forming ability of filler metal can be improved with an appropriate amount of Si added to TA-*x*Si (*x*=0%, 0.5%, 1%, 2%) filler metal. The filler metal presents the strongest amorphous forming ability when 0.5% Si is added to the filler metal.

2) The filler metal has the maximum supercooled phase region width $\Delta T_{x\ max}$=56 ºC, the reduced glass transition

temperature $T_{rg\ max}$=0.5387, and the lowest liquidus temperature (T_l) of 949 ºC when 0.5% Si is added to the filler metal.

3) At the brazing temperature of 1030 ºC, the shear intensity of the soldered joint reaches 80 MPa when the component of the filler metal is TA-0.5%Si. The shear intensity of the joint welded with the filler metal added with 0.5% Si is 43% higher that of the filler metal without Si addition.

References

1 Komolafe B, Mostafa A. *Materials Research Express*[J], 2017, 4(6): 066 503

2 Pang S, Sun L, Xiong H *et al*. *Scripta Materialia*[J], 2016, 117: 55

3 Ji F, Xue S B, Dai W. *Rare Metal Materials and Engineering*[J], 2013, 42(12): 2453

4 Ren H S, Xiong H P, Pang S J *et al*. *Metallurgical & Materials Transactions A*[J], 2016, 47(4): 1668

5 Fan D Y, Huang J H, Cui B *et al*. *Journal of Materials Engineering & Performance*[J], 2017, 26(3): 1114

6 Kocjan A, Mcguiness P J, Rečnik A *et al*. *Journal of Non-Crystalline Solids*[J], 2010, 356(50-51): 2769

7 Yue X J, Xie Z H, Jing Y J. *Applied Physics A*[J], 2017, 123(7): 471

8 Yu W Y, Lu W J, Xia T D. *Rare Metal Materials and Engineering*[J], 2013, 42(4): 688

9 Tsai P H, Hsu K T, Ke J H *et al*. *Materials & Processing Report*[J], 2016, 30(S3): 161

10 Reyes-Retana J A, Naumis G G. *Journal of Non-Crystalline Solids*[J], 2014, 387(1): 117

11 Wang T, Wu Y D, Si J J *et al*. *Metallurgical & Materials Transactions A*[J], 2015, 46(6): 2381

12 Zou J S, Jiang Z G, Zhao Q Z *et al*. *Materials Science & Engineering A*[J], 2009, 507(1-2): 155

13 Fan D Y, Huang J H, Zhao X P *et al*. *Ceramics International*[J], 2017, 43(5): 4151

14 Jing Y J, Yue X S, Gao X Q *et al*. *Materials Science & Engineering A*[J], 2016, 678: 190

15 Fu W, Hu S P, Song X G *et al*. *Carbon*[J], 2017, 121: 536

Si 元素对 Ti-Cu-Zr-Ni 基非晶钎料微观组织和性能的影响

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摘　要：采用电弧熔炼和快冷甩带工艺制备了 Si 质量分数 x=0%, 0.5%, 1%, 2%的 $(Ti_{0.46}Cu_{0.14}Zr_{0.27}Ni_{0.13})$-$x$Si 非晶钎料，研究了添加一定量的 Si 对钎料非晶形成能力的影响。结果表明，当 Si 的含量达到 0.5%时钎料的非晶形成能力最强，钎料的润湿面积为 3.06 cm^2，过冷液相区宽度ΔT_x=56 ℃，约化玻璃转变温度 T_{rg}=0.5387，液相线温度 (T_l) 为 949 ℃。以此非晶合金作为钎料对 SiC 和 TC4 进行真空钎焊，所得钎焊接头剪切强度为 80 MPa。Si 元素的加入显著提高了钎料的非晶形成能力。

关键词：Ti-Cu-Zr-Ni非晶钎料；添加剂Si；非晶形成能力

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