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ARTICLE

Effect of SiC Nanowires on Microstructures and Properties of Ni-Cr-P Filler Metal and Ni-Cr-P/Q235 Brazed Joints

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Abstract: SiC nanowires with excellent high temperature strength, high thermal conductivity, high wear resistance, and high corrosion resistance were adopted as additive into the Ni-Cr-P filler metal. The microstructures and properties of filler metal/brazed joints were studied. Results show that the microstructure of filler metal is composed of Ni(Cr) solid solution, Ni_3P intermetallic compound phase, and Ni(Cr)+Ni_3P eutectic structure. A small amount of SiC nanowire can refine the matrix microstructure and improve the shear strength of brazed joints by 29.6%. The addition of SiC nanowire can increase the melting temperature of filler metal by about 4 °C and significantly enhance the wettability of filler metals on steel substrate by 12.5%. However, excessive addition of SiC nanowire can significantly coarsen the matrix microstructure, reduce the wettability of filler metal, and decrease the shear strength of brazed joints. Among the Ni-Cr-P filler metals with different SiC contents, Ni-Cr-P-0.1SiC filler metal/brazed joint shows the obvious superiority.

Key words: SiC nanowire; shear strength; wettability; filler metal

Nickel-based superalloy consists of Ni-Cr solid solution as the matrix (Ni content$\geqslant$50wt%) and some alloying elements, such as cobalt, molybdenum, aluminum, niobium, tungsten, boron, and titanium. Therefore, the filler metals composed of nickel-based superalloys have good thermal stability, excellent thermal strength and toughness, fine corrosion resistance and oxidation resistance, and high-temperature microstructure stability[1]. Ni-based alloys are usually used as filler metals to braze high temperature alloys (stainless steel, heat-resistant steel) in the furnace brazing, resistance brazing, and induction brazing processes, and the protective gas or vacuum conditions are required during the brazing[2–4]. The alloying elements directly influence the properties of Ni-based filler metals. Thus, the appropriate selection and addition amount of alloying elements are crucial to the filler metals.

Ni-14Cr-10P filler metal was prepared by vacuum melting and inert gas atomization method, and then an organic binder was added and stirred at high speed to prepare paste[5]. The prepared filler metal could braze the C/C composite smoothly, which reduced the thermal mismatch and enhanced the shear strength of brazed joints. For Ni-Cr-W filler metals, the addition of Zr, B, Y, and Nb alloying elements can increase the sensitivity to crack, whereas the Ti and Mg addition can reduce the crack sensitivity[6]. Rare earth elements can be used as additives to modify the properties of Ni-based filler metals[7–8]. It is found that the addition of 0.1wt% La and 0.05wt% Ce can significantly enhance the wettability and brazing properties of joints and the good interface can be achieved by these filler metals through infiltration brazing method. In addition, C addition can also improve the property and microstructure of Ni-Cr filler metal[9]: 1.0wt% C addition can enhance the joint wettability. The C can react with Cr to form the carbides: Cr_3C_2 nucleates and grows on the diamond surface; Cr_7C_3 forms in brazed joints; the microhardness $HV_{0.2}$ of the brazed joints decreases from 6174 MPa to 5684 MPa. The addition of particles into filler metals is also an effective method. The addition of carbon nanotubes can improve the microstructures and properties of Ni-Cr-P filler metals[10], and the lead-free solders with particles[11–13] have been widely investigated for Ni-based filler metals.

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SiC nanowires are artificial compounds with covalent bonds, and they have been widely used in aerospace, automobile, chemistry, electronics, and other industrial fields due to their excellent high temperature strength, high thermal conductivity, high wear resistance, and fine corrosion resistance. According to Ref. [14 – 15], the properties and microstructure can be improved obviously after SiC nanowires are added into Sn paste. In this research, the SiC nanowires were added into Ni-Cr-P filler metals, and the microstructures and properties of the filler metals and brazed joints were investigated.

1 Experiment

Commercial Ni-Cr-P paste was selected as filler metal, and the commercial SiC nanowires with 5–30 μm in length were used as additives. The morphology of SiC nanowires was observed by scanning electron microscope (SEM), as shown in Fig. 1. The Ni-Cr-P-*x*SiC (*x*=0.0, 0.05, 0.1, 0.2, 0.5, 1.0, wt%) filler metals were prepared by mechanical agitation, and Table 1 shows the detailed composition of Ni-Cr-P-*x*SiC filler metals. The Q235 steel with dimension of 40 mm×40 mm×2 mm was selected as the substrate for tests of wettability and lap mechanical property.

STA449 F3 comprehensive thermal analyzer was used to determine the melting characteristic of Ni-Cr-P-*x*SiC filler metals at 0 – 1000 °C with the heating rate of 10 °C/min. According to GB/T113634-2008 standard, the wettability of Ni-Cr-P-*x*SiC filler metals on the steel surface was evaluated. The oxides on the Q235 steel surface were firstly removed by hydrochloric acid and H_2O solution. Then, the Ni-Cr-P-*x*SiC filler metals were put on the steel surface. The to-be-brazed samples were heated in a vacuum furnace to 945 °C. For the wettability tests, the spreading areas of filler metals were calculated by Image-J software. Each test was conducted six times and the average value was used to analyze the effect of SiC nanowires on the spreading area of Ni-Cr-P filler metals.

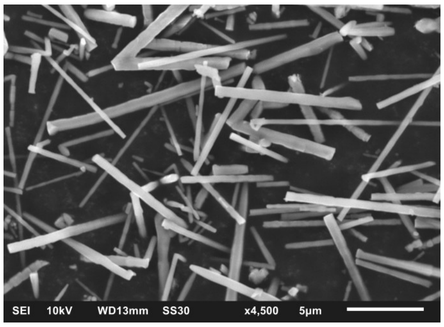

Fig.1 SEM morphology of SiC nanowires

Table 1 Composition of Ni-Cr-P-*x*SiC filler metals (wt%)

Filler metal	SiC	Ni-14Cr-10P
Ni-Cr-P	0.0	100
Ni-Cr-P-0.05SiC	0.05	Bal.
Ni-Cr-P-0.1SiC	0.1	Bal.
Ni-Cr-P-0.2SiC	0.2	Bal.
Ni-Cr-P-0.5SiC	0.5	Bal.
Ni-Cr-P-1.0SiC	1.0	Bal.

According to GB/T 11363-2008 standard, the lap joints of Ni-Cr-P-*x*SiC filler metals formed in vacuum brazing at 945 °C, and the shear strength tests of Ni-Cr-P-*x*SiC brazed joint were conducted. SANS universal testing machine was applied to determine the shear strength of Ni-Cr-P-*x*SiC brazed joints. Each test was conducted six times and the average value was used to investigate the effect of SiC nanowires on brazed joints.

The microstructure evolution was analyzed to determine the mechanical properties of Ni-Cr-P-*x*SiC brazed joints. The specimens were prepared by section, grinding, polishing, and corrosion by $(NH4)_2S_2O_8$+H_2O solution. SEM was used to observe the microstructures of Ni-Cr-P-*x*SiC filler metals and the fracture morphology of brazed joints. The energy dispersive spectrometer (EDS) was also used to determine the element distribution in the Ni-Cr-P-*x*SiC brazed joints.

2 Results and Discussion

2.1 Effect of SiC nanowire addition on microstructures of filler metals

In order to analyze the mechanical properties of Ni-Cr-P-*x*SiC filler metals and brazed joints, the microstructures of Ni-Cr-P-*x*SiC filler metals are observed, as shown in Fig. 2. For the Ni-Cr-P-*x*SiC filler metals, their microstructures consist of Ni(Cr) solid solution, Ni_3P intermetallic compound phase, and Ni(Cr)+Ni_3P eutectic structure, which are similar to the results in Ref. [16]. During the brazing process, the Fe atoms diffuse into the filler metal to form Ni(Cr, Fe) solid solution in Ni-Cr-P-*x*SiC/Q235 brazed joints. The bulk Ni_3P phase with 60 μm in length and 20 μm in width can be observed in the matrix microstructure. The existence of massive Ni_3P intermetallic compounds is harmful to the mechanical properties of filler metals and brazed joints. With the addition of 0.05wt% SiC nanowires, the microstructure and Ni_3P intermetallic compounds can be refined obviously, particularly the Ni_3P phase. When the addition amount of SiC nanowire is 0.1wt%, the eutectic microstructure becomes more uniform and finer, compared with that in the original Ni-Cr-P and Ni-Cr-P-0.05SiC filler metals. Besides, the size of Ni_3P intermetallic compounds decreases obviously. This is because SiC nanowires with high melting temperatures can act as the heterogeneous sites for nucleation, promoting the high nucleation density of Ni_3P phase and eutectic particles during solidification. However, when the addition amount of SiC nanowires is 0.2wt%, the matrix microstructure, Ni_3P phase, and eutectic particles are coarsened, compared with those in the Ni-Cr-P-0.1SiC filler metals. The bulk Ni_3P phase with 30 μm in length and 8 μm in width is precipitated in the matrix microstructure. With further increasing the addition amount of SiC nanowires to 0.5wt% and 1.0wt%, the microstructures of Ni-Cr-P-*x*SiC filler metals are further coarsened, and the size of Ni_3P phase is 50 μm×10 μm and 60 μm×15 μm,

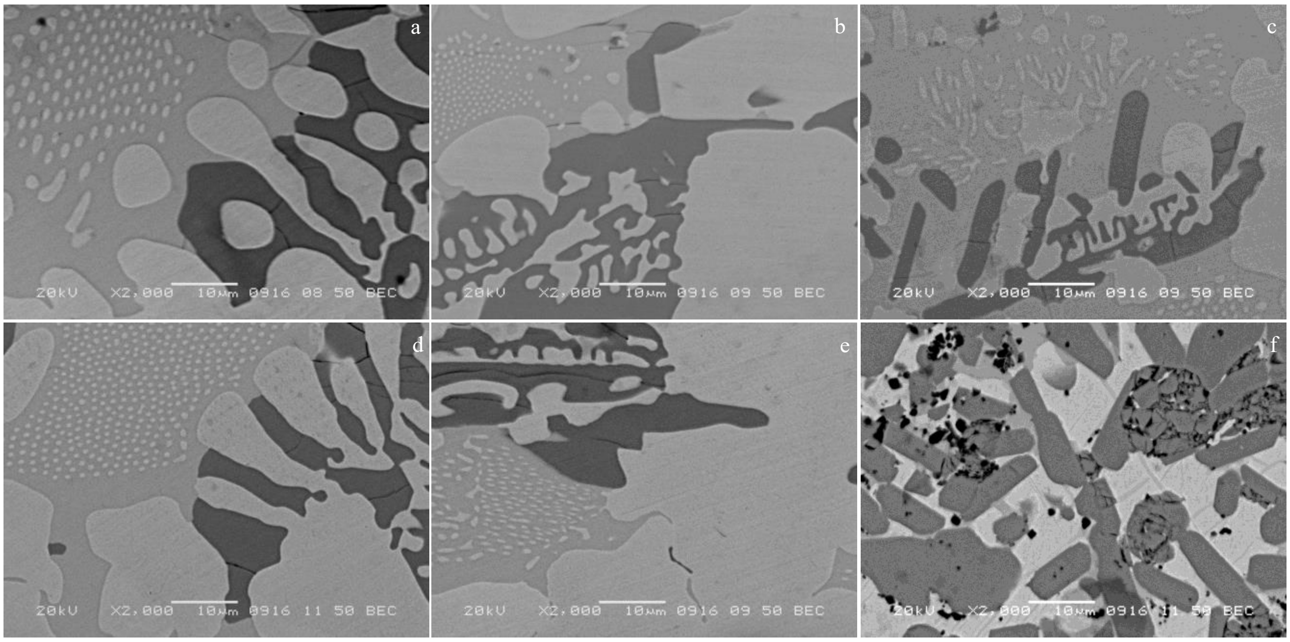

Fig.2 SEM microstructures of Ni-Cr-P-xSiC filler metals: (a) x=0; (b) x=0.05; (c) x=0.1; (d) x=0.2; (e) x=0.5; (f) x=1.0

respectively. Moreover, for Ni-Cr-P-1.0SiC filler metal, the cracks can be clearly observed in Ni_3P phase. The excessive SiC nanowire addition results in the agglomeration of SiC nanowires, and thereby induces the coarsening of microstructures, which can degrade the positive influence of SiC nanowires and is harmful to the mechanical properties of filler metals and brazed joints.

2.2 Effect of SiC nanowire addition on melting temperature

The melting temperature of the Ni-Cr-P-xSiC filler metals is an important index, because it directly determines the brazing process parameters and the microstructures of brazed joint, and even affects the reliability of the Ni-Cr-P-xSiC brazed joints in service. Fig.3 shows the melting temperatures of different Ni-Cr-P-xSiC filler metals. After the addition of SiC nanowires, the solid temperature and liquidus temperature of the Ni-Cr-P-xSiC filler metals is increased slightly within 4 °C. Because SiC does not react with filler metal, the trace addition of SiC nanowires cannot greatly increase the melting temperature. As for the lead-free solders[17–18], the particle additive has a slight effect on the melting temperature. Similarly, for the Ni-Cr-P filler metal, trace addition of SiC nanowire has slight influence on the melting temperature.

2.3 Effect of SiC nanowire addition on wettability

Wettability is a crucial index for Ni-Cr-P filler metal, because the spreading behavior of filler metal directly determines the shape of brazed joints. The spreading areas of Ni-Cr-P-xSiC filler metals on Q235 steel substrate are shown in Fig. 4. The results indicate that the Ni-Cr-P filler metals with SiC nanowire addition present better wettability than the original Ni-Cr-P filler metal does. It is found that the addition of SiC nanowires (≤0.1wt%) can enhance the wettability of Ni-Cr-P filler metal. The spreading area of filler metal increases by 12.5% when the addition amount of SiC nanowire is 0.1wt%. This is because SiC nanowires can decrease the surface tension of liquid filler metal and increase

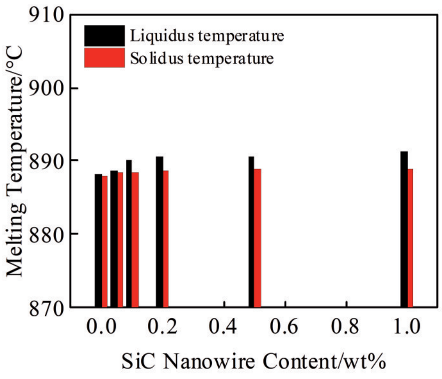

Fig.3 Effect of SiC nanowire content on melting temperature of Ni-Cr-P-xSiC filler metals

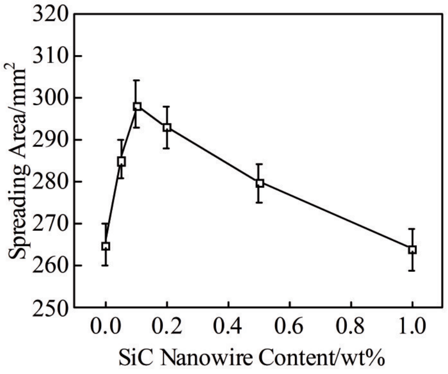

Fig.4 Effect of SiC nanowire addition on spreading area of Ni-Cr-P-xSiC filler metals

the wettability of the filler metal on the steel substrate. However, when excess SiC nanowire (>0.1wt%) is added, the spreading area of filler metals decreases obviously. The spreading area of Ni-Cr-P-1.0SiC filler metal is the lowest among those of the Ni-Cr-P-*x*SiC filler metals, but it is still higher than that of the original Ni-Cr-P filler metal by 3.5%. Excess SiC nanowires result in the agglomeration, which degrades the wettability of filler metals.

2.4 Effect of SiC nanowire addition on shear strength

Fig.5 shows the shear strength of Ni-Cr-P-*x*SiC/Q235 steel brazed joints. It is found the shear strength has a certain relationship with the SiC content. When the addition amount of SiC nanowires is 0.05wt%, the shear strength of brazed joints is enhanced obviously. When the addition amount of SiC nanowires increases to 0.1wt%, the shear strength of brazed joints is further improved, and the maximum shear strength is achieved, which increases by 29.6% compared with that of the original Ni-Cr-P brazed joints. When the addition amount of SiC nanowires increases to 0.2wt%, 0.5wt%, and 1.0wt%, the shear strength of Ni-Cr-P-*x*SiC/Q235 steel brazed joints is reduced obviously. For Ni-Cr-P-1.0SiC/Q235 steel brazed joints, the shear strength decreases by 8.7%, compared with that of the original Ni-Cr-P/Q235 steel brazed joint. This result demonstrates that the optimal shear strength can be obtained with 0.1wt% SiC nanowire addition.

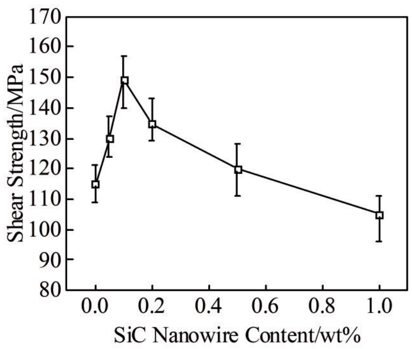

Fig.5 Effect of SiC nanowire addition on shear strength of Ni-Cr-P-*x*SiC/Q235 steel brazed joints

It is concluded that the addition of SiC nanowires can refine the matrix microstructure and reduce the sizes of intermetallic compound particles. According to Hall-Petch equation, the yield strength has a relationship with the grain size, as shown in Eq.(1), as follows:

$$\sigma_s = \sigma_i + k_y d^{-1/2} \qquad (1)$$

where σ_s is the yield stress, σ_i is the frictional resistance, k_y is the pinning constant to measure the contribution of grain boundary to strengthening, and *d* is the average diameter of grains.

With decreasing the *d* value, the yield stress is enhanced obviously. Moreover, the small intermetallic compound particles can also influence the mechanical properties of brazed joints. The relationship between the critical shear stress and the particle movement around the dislocation can be expressed by Eq.(2), as follows:

$$\Delta\tau \propto \frac{G|\boldsymbol{b}|f^{\frac{1}{2}}}{r}\ln\left(\frac{2r}{r_0}\right) \approx af^{\frac{1}{2}}r^{-1} \qquad (2)$$

where $\Delta\tau$ is critical shear stress, $\boldsymbol{b}$ is the Burgers vector, *f* is volume fraction of particles, *r* is the radius of particles, *a* is the constant, r_0 is the dislocation core radius, and *G* is the shear elastic modulus. With decreasing the *r* value, the critical shear stress is increased obviously and the strengthening effect can be greatly improved. Therefore, it can be concluded that the refinement of matrix structure and intermetallic compound particles after the addition of SiC nanowires can improve the mechanical properties of brazed joints.

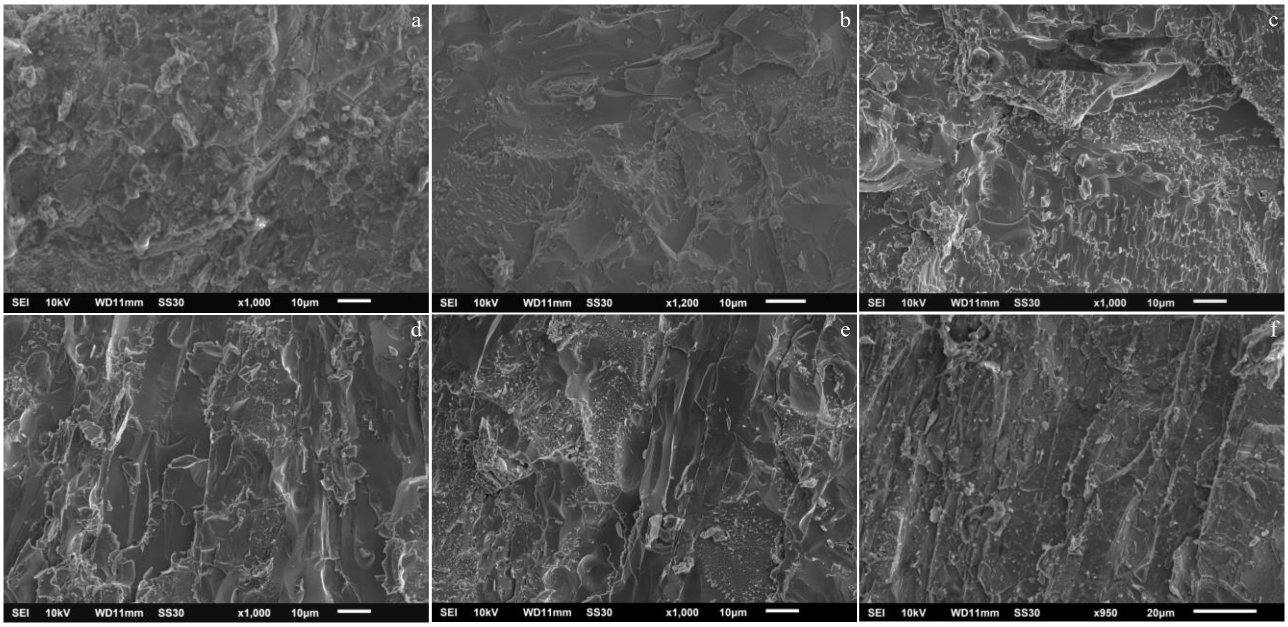

Fig.6 SEM fracture morphologies of Ni-Cr-P-*x*SiC/Q235 steel brazed joints: (a) *x*=0; (b) *x*=0.05; (c) *x*=0.1; (d) *x*=0.2; (e) *x*=0.5; (f) *x*=1.0

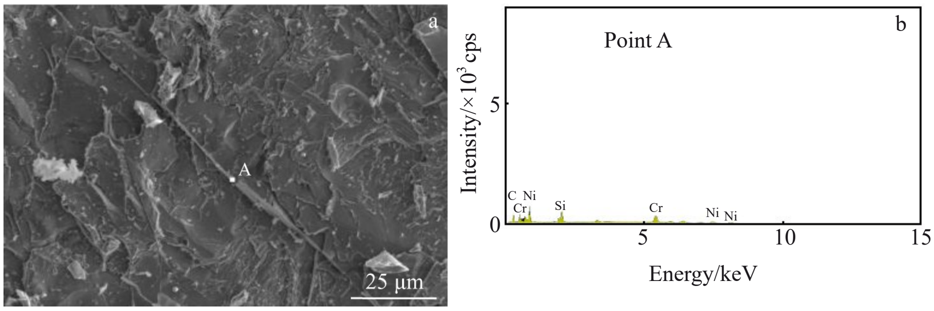

Fig.7 Fracture morphology of Ni-Cr-P-0.5SiC/Q235 steel brazed joint (a); EDS spectrum of point A in Fig.7a (b)

Fig. 6 shows the fracture morphologies of Ni-Cr-P-xSiC/Q235 steel brazed joints after shear tests. It can be seen that the fracture mode is mainly the brittle fracture in Ni-Cu-P/Q235 steel brazed joint, and the intermetallic compound particles can be observed on the fracture surface. A few dimples exist in partial area and some intermetallic compound particles exist in the dimples. When the addition amount of SiC nanowires is 0.05wt%, the fracture mode is similar to that of Ni-Cr-P/Q235 brazed joints. Tiny dot-shape particles can be observed on the fracture surface. With the addition of 0.1wt% SiC nanowires, a large number of laceration marks form during the shear test, and many tiny dot-shape particles are precipitated on the fracture surface, which indicates that the ductile mode is the main fracture pattern. This result also explains why Ni-Cr-P-0.1SiC/Q235 steel brazed joint has the highest shear strength. But when the addition of SiC nanowires is more than 0.1wt%, the number of laceration marks and tiny dot-shape particles is reduced significantly. Moreover, the secondary cracks can be found in the Ni-Cr-P-0.5SiC/Q235 steel brazed joints. When the addition amount of SiC nanowires is 1.0wt%, the mixed fracture mode with ductile and brittle fracture is in the dominant position. The fracture morphologies of Ni-Cr-P-xSiC/Q235 steel (x=0.2, 0.5, 1.0) brazed joints show that the excess addition of SiC nanowires can degrade the mechanical properties of brazed joints. In addition, the agglomeration of SiC nanowires occurs due to the excessive addition of SiC nanowires, as shown in Fig. 7a. The agglomeration of SiC nanowires, as verified by Fig.7b, negatively affects the refinement of microstructure and intermetallic compounds, therefore reducing the mechanical properties of brazed joints. In Sn-58Bi alloy[19], with excess addition of graphene, the properties of solder joints are decreased. Thus, the addition of nanoparticles or nanowires should be carefully controlled. The similar phenomena can also be found in Ag-Cu-Ti filler metals with SiC nanowires[20].

3 Conclusions

1) The addition of SiC nanowires can refine the microstructure of Ni-Cr-P filler metals and intermetallic compound particles.

2) The addition of 0.1wt% SiC nanowire can enhance the wettability and shear strength by 12.5% and 29.6%, respectively, compared with those of the original Ni-Cr-P filler metals.

3) The solid temperature and liquidus temperature of the Ni-Cr-P filler metals increases slightly within 4 °C after the SiC nanowire addition.

4) Excessive SiC nanowire addition (>0.1wt%) results in the SiC agglomeration, which decreases wettability and shear strength of filler metals and brazed joints.

References

1 Fu Yucan, Xu Jiuhua, Ding Wenfeng *et al. Efficient Grinding Theory and Technology of Brazing Super-Abrasive Wheel*[M]. Beijing: Science Press, 2016 (in Chinese)

2 Zhang Qiyun, Zhuang Hongshou. *Handbook of Brazing and Soldering*[M]. Beijing: China Machine Press, 2008 (in Chinese)

3 Zhang L. *Journal of Manufacturing Processes*[J], 2021, 66: 651

4 Rong Wan, Cao Qigao, Zheng Jing *et al. Precious Metals*[J], 2020, 41(S1): 43 (in Chinese)

5 Yi Zhenhua, Ran Liping, Yi Maozhong. *Journal of Materials Engineering*[J], 2020, 48(5): 127 (in Chinese)

6 Kurata Y, Saito T, Tsuji H *et al. JMSE International Journal Series A*[J], 2002, 45(1): 104

7 Xiong M Y, Zhang L. *Journal of Materials Science*[J], 2019, 54(2): 1741

8 Yang Yanyan, Yan Jianwu, Liu Guoliang *et al. Journal of Nanchang Institute of Technology*[J], 2014, 33(6): 27 (in Chinese)

9 Lu Jinbin, Zhang Wangxi, Zhang Lei *et al. Journal of Mechanical Engineering*[J], 2014, 50(4): 80 (in Chinese)

10 Zhang L, Long W M, Zhong S J *et al. Materials Transactions*[J], 2022, 63(10): 1375

11 Zhang L, Liu Z Q. *Journal of Materials Science: Materials in Electronics*[J], 2020, 31(3): 2466

12 Xu K K, Zhang L, Jiang N. *Journal of Materials Science: Materials in Electronics*[J], 2021, 32(3): 2655

13 Xu K K, Zhang L, Sun L *et al. Materials Transactions*[J], 2020, 61(4): 718

14 Li M L, Zhang L, Jiang N *et al. Journal of Materials Science: Materials in Electronics*[J], 2021, 31: 18 067

15 Jiang N, Zhang L, Xu K K *et al. International Journal of Modern Physics B*[J], 2021, 35(1): 2 150 007

16 Shi Haichuan, Yu Zhishui, Zhang Peiliang *et al. Chinese Journal of Vacuum Science and Technology*[J], 2015, 35(3): 367 (in Chinese)

17 Zhang L, Tu K N. *Materials Science and Engineering R*[J], 2014, 82: 1

18 Jiang N, Zhang L, Xu K K *et al. Rare Metal Materials and Engineering*[J], 2021, 50(7): 2293

19 Qiu Xiliang, Hao Chengli, Xiu Ziyang *et al*. *Transactions of the China Welding Institution*[J], 2017, 38(4): 63 (in Chinese)

20 Zhang L, Long W M, Jiang N *et al. International Journal of Modern Physics B*[J], 2022, 36(5): 2 250 046

SiC纳米线对Ni-Cr-P钎料及Ni-Cr-P/Q235焊点组织与性能影响

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摘　要：采用具有优良高温强度、高热导率、高耐磨性能和耐腐蚀性能的SiC纳米线为Ni-Cr-P钎料的添加物，研究了钎料/焊点的组织与性能。结果表明，钎料的组织由Ni(Cr)固溶体、Ni_3P固溶体以及Ni(Cr)和Ni_3P共晶组织组成，微量的SiC纳米线可以显著细化基体组织，使焊点抗剪切强度提高29.6%。SiC纳米线的添加使钎料的熔化温度提高约4 ℃，显著促进钎料在Q235基板表面的润湿性，增幅达到12.5%。然而，过量添加SiC纳米线会显著粗化基体组织，降低钎料的润湿性和焊点的抗剪切强度。在不同SiC含量的Ni-Cr-P钎料中，Ni-Cr-P-0.1SiC钎料/焊点具有明显的优越性。

关键词：SiC纳米线；抗剪切强度；润湿性；钎料

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