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Microstructure and Mechanical Properties of Niobium and 316L Stainless Steel Joints by TU1 Oxygen Free Copper Brazing

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Abstract: A vacuum brazing technique was used to braze reactor grade niobium and 316L stainless steel with oxygen-free copper as filler materials. Microstructure and mechanical properties of both samples and transition joints at different temperatures were investigated. Results demonstrate that brittle intermetallic layer forms and diffusion phenomenon is observed. In spite of the existence of brittle intermetallic, the brazing joints' application in superconducting radio frequency (SRF) cavities is not affected. Mechanical tests including tensile tests and shear tests were conducted both at room temperature (300 K) and liquid nitrogen temperature (77 K). The tensile strengths at liquid nitrogen temperature are higher than at room temperature, while the shear strengths are reduced due to the formation of brittle intermetallic. The transition joints always have higher mechanical strengths than samples when the thickness of the brazing seam is strictly controlled. Leak tests were also performed on the transition joints. The joints' leak rates are all lower than 1.1×10^{-9} Pa·L/s, indicating that the vacuum brazing technology is applicable to high vacuum vessels used at cryogenic temperatures, such as stainless steel helium vessel for SRF cavities.

Key words: brazing; niobium; stainless steel; oxygen free copper; SRF cavities

Superconducting radio frequency (SRF) cavities made of high-purity niobium feature small surface dissipation and large beam apertures. They are widely used by modern accelerators to produce high energy particles for physical research[1,2]. During the operation of SRF cavities, liquid helium with temperature of 2 K or 4 K flows through the space between helium jackets and cavities to cool the SRF cavities, and keeps the niobium material in superconducting state[3]. Currently, titanium is used to make helium jackets since its thermal expansion coefficient is similar to that of niobium[4]. However, titanium has the disadvantages of manufacturing difficulties and high cost, so many laboratories have tried to replace it with austenitic 316L stainless steel[5,6]. SRF cavities and their helium vessels usually operate at liquid helium temperature and undergo vacuum heat treatment at 873 or 1073 K before installation[7]. Therefore, the effectiveness of joints' hermetic seal needs to be ensured between 2 K and 1073 K.

There is few successful fusion welding techniques, including electron beam welding, reported for joining niobium and stainless steel, because fusion welding produces intermetallic compounds (such as Nb_xFe_y) in the welding seam and results in vacuum leak[8,9]. In addition, these compounds cannot withstand heavy thermal load when cooled to cryogenic temperatures and turn fractured[5]. Some laboratories have used explosive bonding to prepare composite material, such as niobium/stainless steel plates[10,11], or titanium/stainless steel/titanium plates[8], in order to fabricate transition joints. No vacuum leak has been detected on this type of joints even after a num-

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ber of wide-range thermal cycles. Saito has developed hot isostatic pressing (HIP) to connect niobium/stainless steel and successfully applied it to the SRF cavities[12]. Some other laboratories have used vacuum brazing to connect niobium and stainless steel with oxygen free copper as fillers. The brazing joints' reliability has been verified by accelerator operation experiences[13-18]. The microstructure study of the previous brazed joints shows that they all have Fe element at the Nb/Cu interface, which signifies the formation of Nb_xFe_y intermetallic compounds. But the operation experiences suggest that the intermetallic compounds do not affect their performance[13]. Meanwhile, some researchers explored a way to minimize the formation of intermetallic compounds by minimizing the brazing holding time, and believed that such procedures can improve the bonding quality[9].

In the past, the microstructure of the brazing interface and transition joints are only roughly reported from the view of engineering applications. In this research, we systematically studied the microstructure, mechanical properties, and brazing holding time of the brazing samples. We also studied the vacuum leak rate, ultimate shear strength of transition joints made by vacuum brazing. The morphology and elemental distribution of the brazing interface were investigated by scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDS). The mechanical properties of the brazing samples and joints were characterized by tensile tests and shear tests with an MTS-SANS CMT5000 universal testing machine at a strain rate of 2 mm/min. Leak rates were tested with a Agilent VSPD03 helium mass spectrometer leak detector.

1 Experiment

1.1 Materials and preparation

Three kinds of raw materials were involved in the vacuum brazing, including reactor-grade niobium (RRR=30), 316L stainless steel, and TU1 oxygen-free copper as fillers. Beside the commercial 316L stainless steel, the chemical compositions of the two materials are shown in Table 1. Wire-shaped fillers were adopted for brazing samples, while ring-shaped fillers were adopted for real joints, which have bigger filler area. The brazing temperature is 1100 °C, with vacuum better than 5×10^{-4} Pa at brazing temperature. Before the brazing, niobium was soaked in a solution of HF, HNO_3, and H_2SO_4 (in the ratio of 1:1:2.5) for 20 s to remove surface oxides.

1.2 Sample preparation

The dimension of niobium and stainless steel pieces used to study the microstructure of the brazing joint was 15 mm×15 mm×3 mm. A piece of brazing wire with 0.8 mm in diameter was placed between the two base materials. After brazing, samples were mechanically polished with sand paper (600# to 3000# grits), then followed by a standard chemical-mechanical polishing with 0.3 μm alumina slurry. SEM was used to analyze the evolution of the structure near the interface; and EDS spectrum was used to measure the element diffusion behavior of the interface.

1.3 Mechanical testing

GB/T 11363-2008 and GB/T 1329-2008 were adopted for testing strength of brazing samples at 300 and 77 K (Fig.1a). The layout of brazing samples was butt joint brazing. Since the sample provided a reference for the brazing of the transition joint, we did not strictly control the brazing gap. Therefore, the brazing seam thickness of samples was 100~200 μm and the thickness of samples was 3 mm. The initial shear test samples were prepared in accordance with GB/T 11363-2008. But, the niobium base metal was broken during the test so that we cannot get the strength of joints. Then, the test was carried out in accordance with the standards GB/T 6396-2008 (Fig.1b). The ultimate shear strength of transition joints was measured with its scheme shown in Fig.1c. The schematic diagram of the brazing of the transition joints is shown in Fig.1d. A plug was inserted in the niobium tube in order to ensure the uniform thickness of transition joints.

2 Results and Discussion

2.1 Microstructure of brazing joints

Fig.2a shows the morphology of the interface of Nb/Cu/316L SS at brazing temperature of 1100 °C for holding time of 90 s. A good alloy bonding forms between the copper brazing and the two base materials, and there are no defects such as cracks and pores. In order to determine the composition and the element distribution in the interface region, EDS line scan was performed on the joint surface, whose path is shown by the straight line in Fig.2a. Moreover, it can be seen from Fig.2a that the joint is divided into three areas. The diffusion layer A where Fe and Cu coexist consists of many gray areas and a small part of white strips. This phenomenon is confirmed by interdiffusion of Fe and Cu in EDS line, as shown in Fig.2b. Layer B is the zone of oxygen-free copper brazing. Layer C is the diffusion layer where Nb/Cu and Fe coexist. We can learn from Fig.2b and Fig.3c that the Fe element diffuses to the Nb/Cu interface, all the way passes through the copper, and forms an intermetallic compound layer. The composition of the diffusion layer C was measured with an EDS point scan at point D, as shown in Fig.2a. The results in Fig.2d reveal that Fe:Nb ratio is close to 2:1. According to the Fe-Nb binary phase diagram [19], the most likely component of the intermetallic compounds is Fe_2Nb. The intermetallic compound is expected to harm the mechanical property of the transition

Table 1 Chemical composition of niobium and TU1 oxygen free copper (wt%)

Niobium	Ta	C	Fe	N	W	Mo	Ni	H	Nb
	0.0762	0.0026	0.0003	0.0006	0.0021	0.001	0.0002	0.0002	Bal.
TU1 oxygen free copper	O	Sb	Fe	Ni	Pb	Zn	S	P	Cu+Ag
	0.002	0.002	0.004	0.002	0.003	0.003	0.004	0.004	Bal.

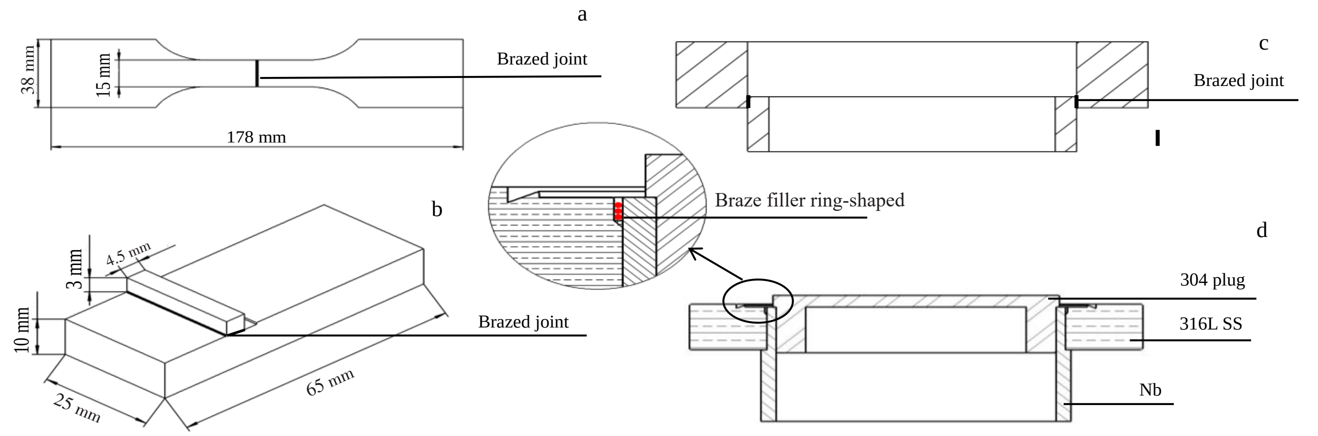

Fig.1 Schematic diagram of tensile test samples (a), shear test samples (b), ultimate shear tests samples (c), and braze joint configuration (d)

joints, so the formation of this compound should be avoided during brazing.

The rugged Nb/Cu interface in Fig.2a indicates that the holding time is too short, resulting in insufficient time for the elements to diffuse. Fig.2c shows the morphology of the brazing surfaces after annealing at 600 °C for 10 h. It can be found that the Nb/Cu interface is flat, indicating that there is sufficient time for the elements to diffuse. In addition, the samples in this research were subjected to heat treatment which meets the heat treatment requirements of SRF cavities, that is, heat treatment can remove hydrogen and release stress before serving.

2.2 Element distribution across the interface under different holding time

In order to investigate the development of intermetallic compounds under different holding time, we kept the brazing temperature at 1100 °C and studied the element distribution and strength of the interface under different holding time. The EDS line scan results of four holding states, namely 15, 30, 45 and 60 s, are shown in Fig.4. It can be seen that elements are diffused at the Nb/Cu interface and Fe/Cu interface during the brazing process, which is a prerequisite for successful brazing of the transition joints. It can be seen from the phase diagrams of Fe-Cu and Nb-Cu that the mutual solubility of Fe and Cu is better than that of Nb and Cu, and the solid solubility of Cu in Nb is only 1.2at% at 1083 °C [19]. Thus, it can be seen from Fig.4 that the diffusion distance of Fe/Cu interface is bigger than that of Nb/Cu interface at four states. We also found that Fe diffuses to interface of Nb/Cu in all states, forming interme-

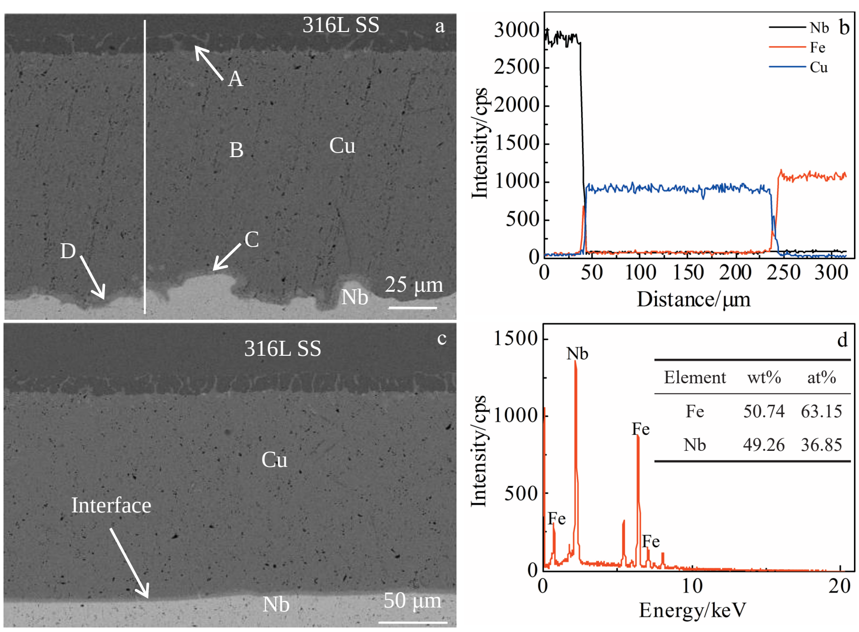

Fig.2 SEM morphologies of brazing surface at 1100 °C for 90 s (a) and 600 °C for 10 h (c); EDS line scan results across interface marked as straight line in Fig.2a (b); EDS results of spot D marked in Fig.2a (d)

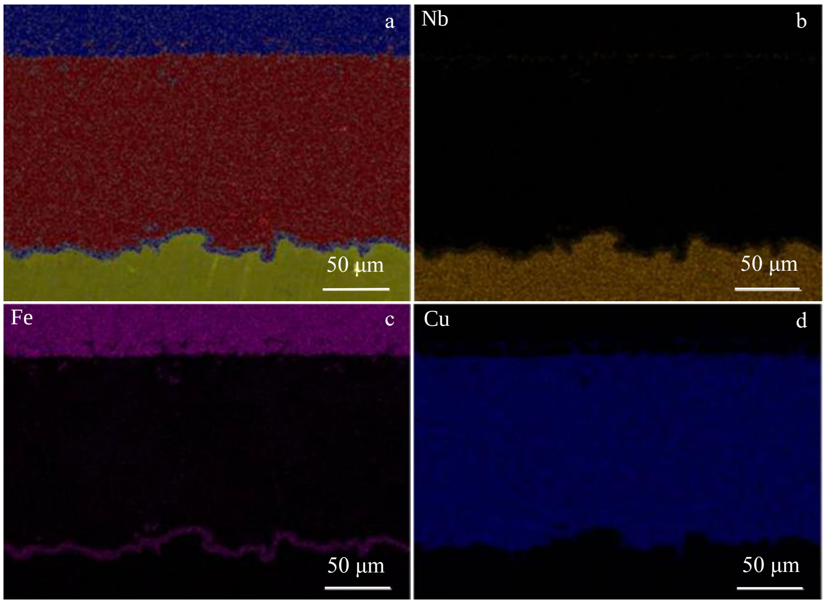

Fig.3 EDS mapping across the whole brazing surface at 1100 °C for 90 s (a): (b) Nb, (c) Fe, and (d) Cu

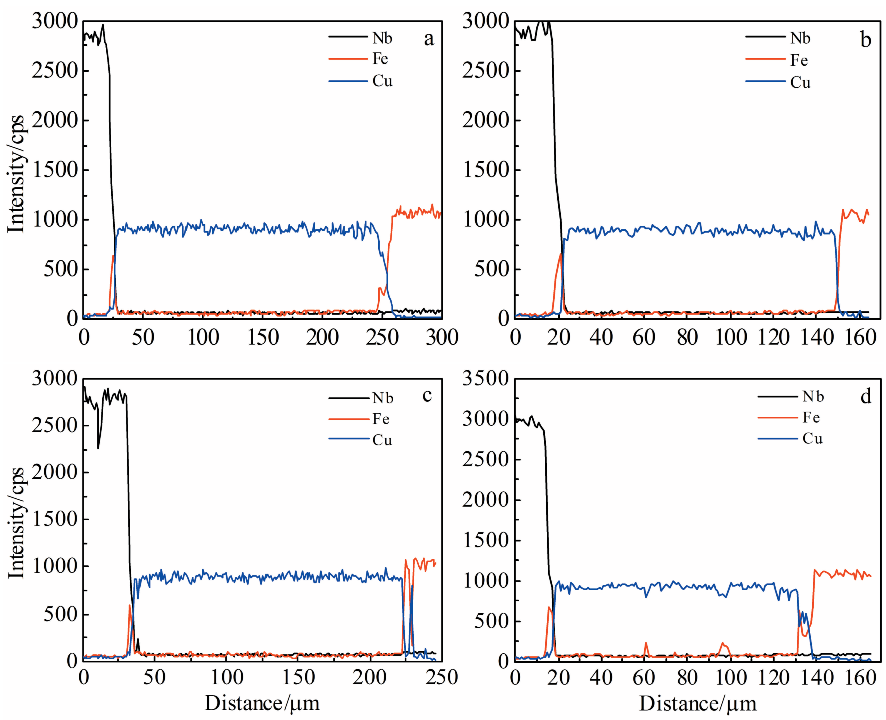

Fig.4 EDS line scan results across interface at 1100 °C for different holding time: (a) 15 s, (b) 30 s, (c) 45 s, and (d) 60 s

tallic compounds at interface, thereby reducing the plasticity and strength of the brazing joint. In particular, the formation of intermetallic compounds is bad for its reliability in low temperature environments. Unfortunately, the formation of intermetallic compounds still exists at 15 s holding time, which is the shortest holding time that we can control by many times of experiment.

2.3 Brazing joint strength

Fig. 5 shows the average tensile strength and average shear strength of the brazed joint under different holding time. The tensile strength test and shear strength test were conducted on three samples in one state. It can be seen from Fig. 5a that the holding time has little effect on tensile strength at 300 K, and tensile strength is in the range of 85~93 MPa, which is consistent with the results in Ref.[16]. Since the base material and brazing filler metals cannot sufficiently diffuse in a short holding time of 15 s, the tensile strength is the minimal. This phenomenon is more obvious at 77 K. At 77 K, the tensile strength is 175 and 247 MPa at holding time of 15 and 30 s, respectively. We can also find that the change in tensile strength is small when the holding time continues to increase.

At 300 K, when the holding time becomes longer, the shear strength increases. It can be seen from Fig.5b that the base material and the brazing filler metal are not sufficiently diffused to cause the minimum shear strength when the holding time is 15 s. When the holding time is longer than 60 s, the change of shear strength is small. The shear strength at 77 K is less than that at 300 K, but is still greater than 100 MPa, which meets the engineering requirements[20].

In short, when the holding time is greater than 60 s, the shear strength and tensile strength are hardly influenced by the holding time. These results provide a reference for the selection of the holding time of the transition joint when the brazing area of the transition joint is large and the holding time is required to be bigger than 120 s.

2.4 Brazing and leak detection of transition joints

The thermal expansion coefficient of stainless steel is close to 2.6 times larger than that of niobium at the brazing temperature, which brings challenges to the uniform thickness of the weld (20~50 μm)[4]. Assuming that the niobium tube expands freely and is thin-walled structure, the outer diameter of the niobium tube is R_{Nb} and the expansion coefficient is α_{Nb};

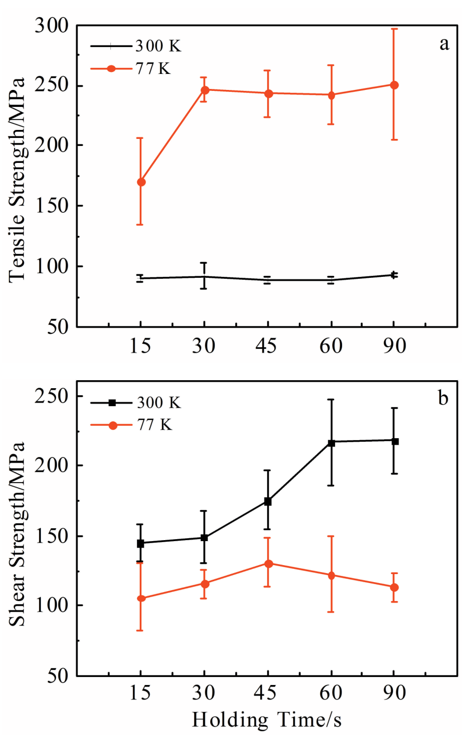

Fig.5 Tensile strength (a) and shear strength (b) of samples

the inner diameter of the stainless steel flange is r_{316L} and the expansion coefficient is α_{316L}; the brazing temperature is ΔT. There is a certain gap between the inner diameter of the stainless steel flange and the outer diameter of the niobium tube, and this gap is the assembly tolerance G_{VB}, and then $r_{316L} = G_{VB} + R_{Nb}$. At the brazing temperature, the expansion of the outer diameter of the niobium tube is $\alpha_{Nb} R_{Nb} \Delta T$[4], the expansion of the inner diameter of the stainless steel flange is $\alpha_{316L} r_{316L} \Delta T$, and then the difference between the expansion of stainless steel and niobium ΔG_{ap} is as follows:

$$\Delta G_{ap} = \alpha_{316L} r_{316L} \Delta T - \alpha_{Nb} R_{Nb} \Delta T \quad (1)$$

Substituting $r_{316L} = G_{VB} + R_{Nb}$ into Eq.(1):

$$\Delta G_{ap} = \alpha_{316L} \Delta T G_{VB} + (\alpha_{316L} - \alpha_{Nb}) R_{Nb} \Delta T \quad (2)$$

Assuming $\alpha_{316L} \approx 2.6\alpha_{Nb}$, then:

$$\Delta G_{ap} = \left(2.6G_{VB} + 1.6R_{Nb}\right)\alpha_{Nb}\Delta T \quad (3)$$

Because the diameter of the niobium tube is much larger than the gap ($R_{Nb} \geqslant G_{VB}$), thus:

$$\Delta G_{ap} = 1.6\alpha_{Nb}\Delta T R_{Nb} \quad (4)$$

The cleaning tube of half-wave resonator (HWR) cavity has the minimum dimensions, whose outer diameter is 46 mm[21]. The brazing temperature of oxygen-free copper brazing is 1100 °C and the coefficient of expansion of niobium is 7.88×10^{-6} K^{-1} [21]. Therefore, the gap is 319 μm which means that the gap of transition joint at the brazing temperature is 319 μm. For larger niobium tubes, this means greater gaps. This clearance can be ensured by inserting a stainless steel plug into the niobium. The role of plug is to force the niobium pipe to yield and follow the expansion of the plug during the brazing process. The schematic configuration is shown in Fig.1d. Fig.6 shows two brazed transition joints both with 90 s holding time. The inner diameter of niobium tube is 60 mm. It can be seen from Fig.6 that the copper brazing on the front and back of the transition joints is complete, indicating that the filler filled up the entire seam. After withstanding ten cold shocks of liquid nitrogen, the joints still show leakage rate below 1.1×10^{-9} Pa·L/s both at room temperature and liquid nitrogen temperature.

2.5 Ultimate shear strength

In our tests, we selected three types of transition joints: CF80 (niobium tube inner diameter 80 mm), CF100 (niobium tube inner diameter 94 mm), and CF150 (niobium tube inner diameter 105 mm). Fig.7 shows the average shear strength of different types of transition joints. Each type was tested three times. It can be seen that the average shear strength is 230 MPa at 300 K and 178 MPa at 77 K. The reason for that lower shear strength at 77 K may be the formation of intermetallic compounds. It is also found from Fig.7 that the consistency of the three types of transition joints is good, indicating good feasibility to prepare transition joints with oxygen-free copper as brazing fillers. In addition, the shear strengths of the transition joints are greater than the samples. The difference is more obvious at 77 K, and such enhancement results from the strictly controlled thickness of the brazing seam. 20~50 μm is carefully maintained when brazing the transition joints.

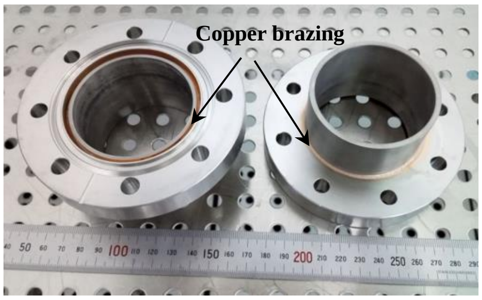

Fig.6 Transition joints after brazing

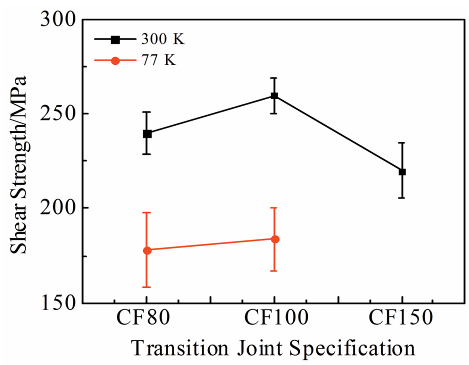

Fig.7 Ultimate shear strength of transition joints

3 Conclusions

1) Niobium-316L stainless steel transition joints can be successfully prepared by vacuum brazing with oxygen-free copper as fillers. Elemental diffusion is observed on both sides of the welding seam while no visible defects such as cracks and pores are seen. The EDS line scan results reveal that the presence of Fe at the Nb/Cu interface leads to the formation of intermetallic compounds, possibly Fe_2Nb.

2) When the holding time is longer than 60 s, increasing holding time cannot significantly affect the tensile strength and shear strength, which provides a good reference for the brazing process of transition joints. Due to the presence of intermetallic compounds, the shear strengths at 77 K are all lower than at 300 K.

3) According to the brazing experience of samples, different types of transition joints can be successfully prepared. After 10 cold shocks of liquid nitrogen, the leak rates are better than 1.1×10^{-9} Pa·L/s. During the brazing process, the thickness of the weld is strictly controlled in order to obtain transition joints with good strengths. In the future, we will try to fabricate the transition joint on the SRF cavities.

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TU1 无氧铜钎料制备铌和316L 不锈钢接头的微观组织和力学性能

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摘　要： 采用TU1无氧铜作为填充材料进行了反应堆级铌与316L不锈钢连接的真空钎焊，研究了样品和过渡接头在不同温度下的显微组织和力学性能。显微组织表明形成了脆的金属间化合物层并观察到结合面有扩散现象发生。虽然在结合面有脆性金属间化合物形成，但并不影响其在超导射频（SRF）腔中的使用。在室温（300 K）和液氮温度（77 K）下进行了拉伸测试和剪切测试。在液氮温度下，抗张强度高于其在室温下的抗张强度，由于脆性金属间化合物的存在导致其在液氮环境下抗剪切强度低于室温环境。由于我们严格控制焊缝厚度，使过渡接头的抗剪切强度高于样品的强度。最后我们对过渡接头进行真空漏率测试。结果显示，其真空漏率均低于1.1×10^{-9} Pa·L/s，这表明真空钎焊技术适用于低温下使用的高真空容器，例如用于SRF腔的不锈钢氦容器。

关键词： 钎焊；铌；不锈钢；无氧铜；超导射频腔

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