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ARTICLE

Intergranular Infiltration of TZM Alloy Joints Brazed Using Ni-Ti Brazing Filler Alloy at High Temperature

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Abstract: The interfacial microstructure and joining properties of titanium-zirconium-molybdenum (TZM) alloy joints were characterized by SEM, EDS, XRD, mechanical tests, etc. The results show that the Ni-Ti brazing filler metal can efficiently realize the high-temperature vacuum brazing of TZM. Mo in the base metal and Ni in the braze filler metal form $MoNi_4$ phase, which is the main reason for the metallurgical bond between the TZM and the Ni-13.7Ti/TZM interface region. Ti in Ni-44Ti braze filler metal dissolves in Mo to form an infinite solid solution in TZM/Ni-44Ti/TZM interface zone, forming a metallurgical bond between the braze filler metal and TZM. However, a serious intergranular infiltration phenomenon is observed when Ni-44Ti braze filler alloy is used to braze TZM alloy. The degree of intergranular infiltration and corrosion of the base material significantly decrease with decreasing the Ti content in the braze filler alloy. The average shear strength of TZM/Ni-13.7T/TZM brazed joints reaches 193 MPa, while that of TZM/Ni-44Ti/TZM brazed joints is 167 MPa. The lower shear strength of TZM/Ni-44Ti/TZM is attributed to the intergranular infiltration due to the higher content of Ti in the brazing filler.

Key words: TZM alloy; brazing; intergranular infiltration; mechanical property

TZM alloys are widely used in the fields of aerospace, nuclear and electronics industries[1-4], owing to their outstanding properties such as high melting point, excellent high temperature mechanical properties and good heat-conduction and electrical conductivity.

Common joining methods for Mo alloys such as TZM include fusion welding[5], electron beam welding[6,7], friction welding[8,9], diffusion welding[10] and brazing[11-15]. However, the fusion welding, electron beam welding and other welding methods have high welding temperature, even exceeding the re-crystallization temperature of TZM alloy, resulting in the rapid growth of grain size during welding, which restricts their application. Brazing currently becomes one of the most reliable methods for connecting Mo alloy such as TZM with Mo alloy, ceramic, and TiAl alloy, at a higher temperature because of its relatively low working temperature. Moreover, brazing has little effect on the properties of base materials.

Braze metal plays an important role in achieving reliable brazing of TZM alloy with TZM alloy or other materials. In the previous studies, commercially available brazing filler alloys for TZM alloy were Ag, Cu, Au and Ti-based alloys. Chan et al[11,12] used 72Ag-28Cu and 95Ag-5Al to join Ti-6Al-4V and TZM alloy. They found that these silver-based fillers cannot wet the TZM substrate effectively at a brazing temperature range of 800~950 °C. Liaw et al[13] achieved infrared brazing of Mo alloy at 1050 °C using 70Au-22Ni-8Pd. Song et al[14] studied the interfacial microstructure and joining properties of TZM alloy joints brazed using Ti-28Ni eutectic brazing filler alloy in the brazing temperature range of 1000~1160 °C, and found that brazing temperature plays an important role in the interfacial microstructure. However, since the working temperature of the braze joint has to be lower than the melting point of brazing filler metal, generally lower than 1200 °C, it is necessary to develop a brazing filler material with a higher brazing temperature to enhancing the application temperature of brazed joints.

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In the present study, Ni-Ti brazing filler alloys were developed to braze TZM alloy at a high temperature by a vacuum brazing method. The effects of Ni-44Ti and Ni-13.7Ti (wt%) brazing filler metals on the intergranular infiltration of the TZM brazed joints were compared.

1 Experiment

The base metal in this study was hot rolled TZM plate with a thickness of 5 mm. The chemical composition of TZM is (0.4 wt%~0.55 wt%) Ti, (0.07 wt%~0.12 wt%) Zr, (0.01 wt%~0.04 wt%) C and the balance Mo. The TZM alloy was cut into blocks with two kinds of dimensions (5 mm×5 mm×5 mm and 20 mm×10 mm×5 mm). Ni-13.7Ti and Ni-44Ti (nominal composition, wt%) brazing filler alloys were prepared by an argon protection arc melting method. According to the Ni-Ti binary phase diagram, the theoretical melting temperatures of Ni-13.7Ti and Ni-44Ti brazing filler metals are 1304 and 1310 °C, respectively. The two as-cast brazing alloys were cut into foils with the thickness of 1 mm by spark cutting. Prior to brazing, the brazing surfaces of TZM blocks were ground by SiC grit papers and then polished using diamond pastes. Both surfaces of foils of Ni-13.7Ti and Ni-44Ti brazing filler alloys were ground by SiC grit papers. The TZM blocks and Ni-13.7Ti and Ni-44Ti foils were cleaned with alcohol and dried by air blowing, and then the samples were etched with H_2O_2 (30 vol%)+$NH_3 \cdot H_2O$ (10 vol%)+H_2O (60 vol%) solution.

Brazing was performed in vacuum atmosphere (2~5×10^{-3} Pa) at a temperature of 1350 °C for 300 s. The brazing filler foils were sandwiched between two TZM blocks, as shown in Fig.1.

The base metal, cross-section of TZM brazed joints, and shear fracture morphology were examined by scanning electron microscope (SEM, Phenom XL). Quantitative componential analyses of joints and fracture were performed using an energy dispersive spectrometer (EDS, SEM, Phenom XL). Phases of brazing seam were analyzed using X-ray diffraction (XRD, Ultima IV). Shear tests were conducted at room temperature at a constant speed of 0.5 mm/min using a universal testing machine (MTS E45.105). For each brazing condition, five shear test specimens were used to average the joint strength.

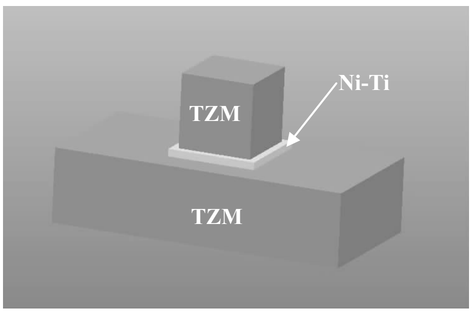

Fig.1 Schematic of the assembling brazing parts

2 Result and Discussion

2.1 Typical interfacial microstructure of TZM/Ni-Ti/TZM brazed joints

Fig.2 shows the microstructures of TZM before and after brazing. The base metal grains grow up when brazing temperature exceeds 1000 °C, which is one of the unavoidable problems of high temperature brazing of Mo alloy. After brazing at 1350 °C for 300 s, recrystallization occurred in the TZM base materials, and the microstructure transformed from deformed band structure (Fig.2a) to equiaxed grains (Fig.2b). The average grain size of TZM is 50 μm after brazing.

Fig.3 and Fig.4 show the interfacial microstructures of TZM/Ni-13.7Ti/TZM and TZM/Ni-44Ti/TZM braze joints, respectively, and corresponding EDS analysis results are shown in Table 1.

It can be seen from Fig.3 and Fig.4 that after vacuum brazing of TZM alloy at 1350 °C for 300 s using two different brazing filler metals of Ni-13.7Ti and Ni-44Ti, two joints with good metallurgical bonding are achieved with no obvious

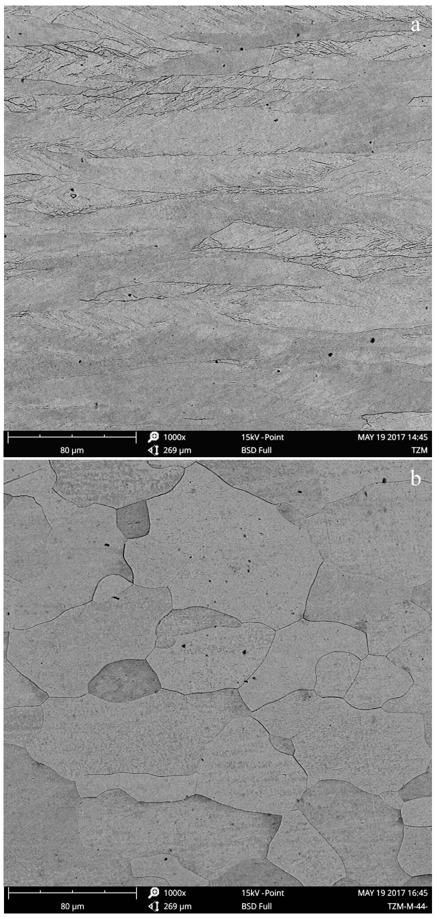

Fig.2 TZM morphologies before (a) and after (b) brazing

holes, inclusions, cracks and other defects. However, even under the same brazing condition, different interfacial microstructures were observed in the two TZM/Ni-Ti/TZM brazed joints, which is attributed to different Ti contents in the two Ni-Ti brazing filler metals.

The TZM/Ni-13.7Ti/TZM brazed joint shown in Fig.3 can be divided into three typical zones, named A, B and C according to contrasts. And the EDS results of A, B and C zones are shown in Table 1. As can be seen from Table 1, zone A near the interface consists of Ni, Ti, Mo and a small amount of Zr. It is presumed that the $MoNi_4$ may form according to atomic ration of Mo/Ni. The main components of micro-zone B are Ni, Ti, and a small amount of Mo and Zr. The atomic ratio of Ni:Ti is about 3:1, so zone B is supposed to be $TiNi_3$. Micro-zone C is supposed to be Mo particles.

From the EDS results in Table 1, zones F and G in the middle of the brazing seam of TZM/Ni-44Ti/TZM brazed joint (Fig.4) present a Ni/Ti atomic ratio of about 1. Therefore, it can be considered as NiTi phase. In addition, in the interface area, a thin layer with bright contrast (zone H) is observed, and a small amount of bright Mo particles are distributed in the center of the brazing seam. The EDS result shows that these two features mainly consist of Mo, Ti and a small amount of Ni and Zr. Considering that Mo and Ti can form a solid solution phase with unlimited mutual solubility, these two features can be considered as Mo-Ti solid solution. Compared with Ni-13.7Ti, Ni-44Ti brazing filler metal contains more Ti, so it can form Mo-Ti solid solution with a matrix material with high content of Mo during brazing at high temperature.

Analyses of the intergranular infiltration of the joints brazed with Ni-13.7Ti and Ni-44Ti brazing filler metals are as follows. Combining the results of EDS analyses of zone D and zone E in Table 1 with the topography and EDS mapping in Fig.3, it can be concluded that the TZM grain boundary (zone D) and intragranular area (zone E) of TZM/Ni-13.7Ti/TZM basically consist of Mo and a trace amount of Ti and Zr. Moreover, there is no distinct composition difference between the two zones D and E, so the diffusion of Ni-13.7Ti brazing filler metal to the crystal is negligible, which illustrates that no obvious intergranular infiltration occurs when TZM is brazed using Ni-13.7Ti. However, corrosion of the base material (at the arrow) occurs at the grain boundaries close to the interface. Because of the dissolution of the parent metal, Mo dissolves in

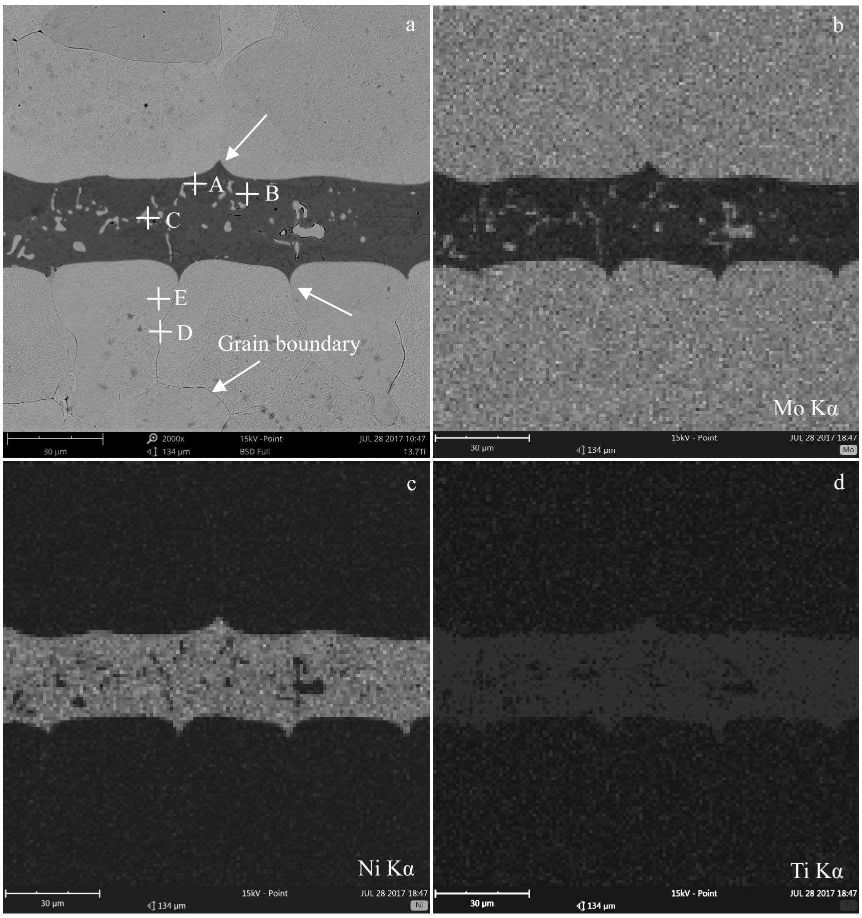

Fig.3 Interfacial microstructure and elemental distribution of TZM joint brazed at 1350 °C for 300 s using Ni-13.7Ti alloy: (a) BEI of the joint and EDS maps of Mo (b), Ni (c), and Ti (d)

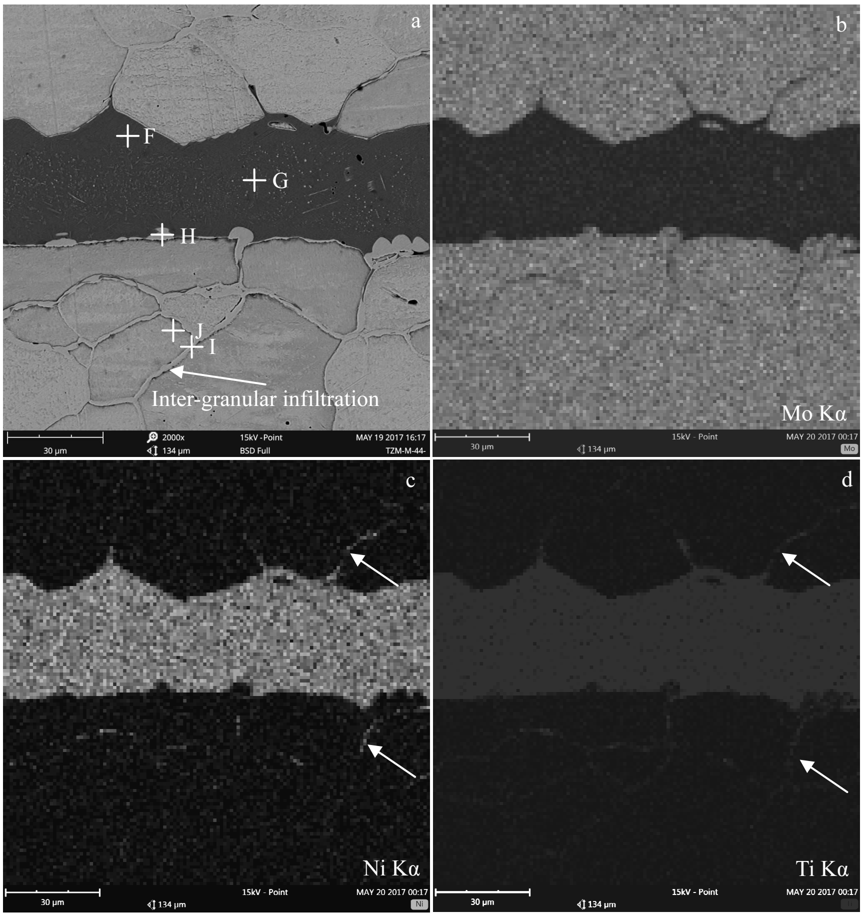

Fig.4 Interfacial microstructure and elemental distribution of TZM joint brazed at 1350 °C for 300 s using Ni-44Ti alloy: (a) BEI of the joint and EDS maps of Mo (b), Ni (c), and Ti (d)

Table 1 Chemical composition (at%) and possible phase of each zone marked in Fig.3 and Fig.4

Filler metal	Micro-zone	Mo	Ni	Ti	Zr	Possible phase
Ni-13.7Ti	A	12.25	71.26	15.23	0.76	$MoNi_4$
	B	4.34	73.58	22.08	-	$TiNi_3$
	C	69.01	23.22	5.77	2.00	Mo
	D	97.02	-	-	2.98	Mo
	E	96.62	-	0.75	2.63	Mo
Ni-44Ti	F	2.86	49.42	47.22	-	NiTi
	G	3.84	47.20	48.95	-	NiTi
	H	74.86	3.59	19.25	2.31	Mo-Ti
	I	81.0	0.40	16.28	2.32	Mo-Ti
	J	96.85	-	0.25	2.77	Mo

the brazing seam and reacts with Ni and Ti in the brazing seam, resulting in the formation of a white phase (region C). For TZM/Ni-44Ti/TZM joint, the results of EDS analyses of zones I and J in Table 1, the topography and EDS mapping in Fig.4 show that the Ti content in the TZM grain boundary (zone I) near the brazing seam and intragranular area (zone J) of TZM/Ni-44Ti/TZM varies greatly. A large amount of Ti and a small amount of Ni are enriched at the grain boundary zone close to the interface, as shown in the EDS mapping in Fig.4, indicating the intergranular infiltration of Ti. The intergranular infiltration of Ti into TZM grain boundaries during brazing leads to the formation of Ti-Mo solid solution at grain boundaries, which decreases the interfacial temperature and grain boundary stability of the base metal grains close to the joints, resulting in the deterioration of the base material's properties.

In addition, XRD analysis was performed on the fracture surface. As shown in Fig.5, $MoNi_4$, $TiNi_3$, TiNi, Ti and Mo phases are detected, corresponding well with the analyses of the interfacial microstructure and phase described above.

2.2 Mechanical properties of brazed joints

The joining properties of the TZM joints brazed with Ni-13.7Ti and Ni-44Ti were evaluated by shear tests at room temperature. The average shear strength of TZM/Ni-13.7Ti/TZM brazed joint is 193 MPa with a standard deviation of 8.12 MPa, while that of TZM/Ni-44Ti/TZM brazed joint is 167 MPa with a standard deviation of 7.27 MPa.

Fig.6 shows the BEI fracture topographies of TZM brazed

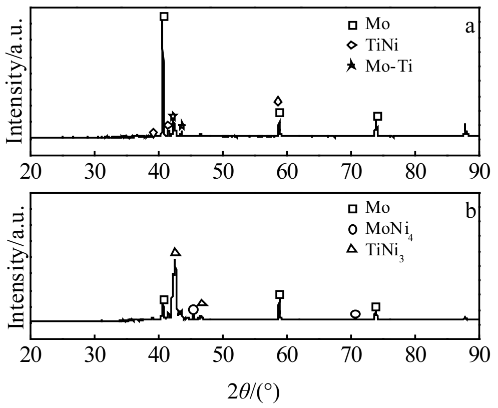

Fig.5 XRD patterns of the fracture surfaces after shear test for specimens brazed at 1350 °C for 300 s: (a) TZM/44Ti/TZM and (b) TZM/13.7Ti/TZM

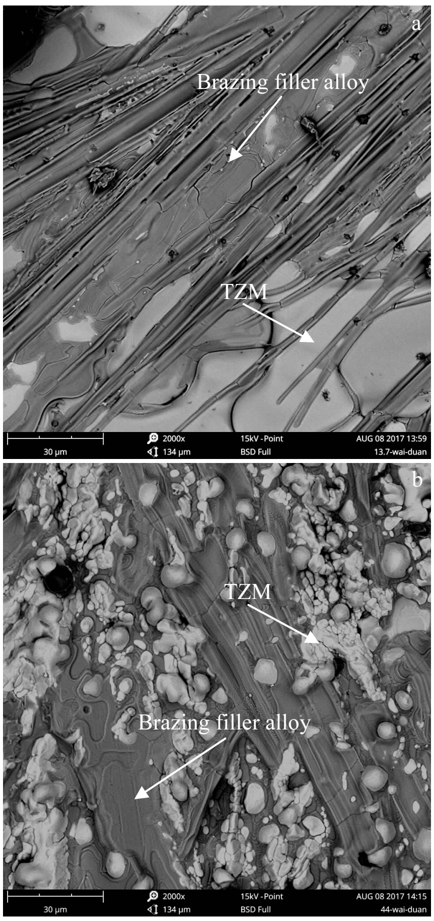

Fig.6 BEI fracture topographies of TZM brazed joints using Ni-13.7Ti (a) and Ni-44Ti (b)

joints using Ni-13.7Ti and Ni-44Ti. It can be clearly seen that the fracture surface of TZM/Ni-13.7Ti/TZM is basically composed of brazing filler metal, and the fracture location is at the brazing seam. In addition, at the fracture surface of TZM/Ni-44Ti/TZM brazed joints, a mixture of brazing filler metal and base metal is observed and the fracture location is at the interface. Due to the intergranular infiltration of Ni-44Ti brazing alloy into TZM, the microstructure of grain boundaries was destroyed, resulting in a sharp decrease in the strength of the joint.

3 Conclusions

1) Vacuum brazing of TZM alloy is achieved using Ni-Ti brazing filler alloy. The brazing seam of TZM/Ni-13.7Ti/TZM brazed joints consists of $MoNi_4$ phase, Ni_3Ti phase and Mo particles, while that of TZM/Ni-44Ti/TZM brazed joints consists of NiTi phase.

2) The formation of $MoNi_4$ phase is due to the dissolution of base material with high content of Mo and the high content of Ni in the brazing filler metal, which is the main reason for the formation of metallurgical bond between the TZM and the Ni-13.7Ti brazing filler metal. Ti in Ni-44Ti dissolves into the base materials to form a Mo-Ti infinite solid solution in the TZM/Ni-44Ti/TZM interface zone, forming a metallurgical bond between the brazing filler metal and TZM.

3) The shear strength of TZM/Ni-44Ti/TZM brazed joint is 167 MPa, lower than that of TZM/Ni-13.7Ti/TZM (193 MPa). When TZM is brazed with Ni-44Ti brazing filler metal, Ti infiltrates into the intergranular area of the base metal TZM, destroying the interfacial strength and decreasing the joint strength.

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Ni-Ti 钎料高温钎焊 TZM 合金的晶间渗入行为

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摘　要：采用 SEM，EDS，XRD 和力学试验机等分析测试方法，研究了 Ni-Ti 钎料对 TZM 合金钎缝组织和性能的影响。结果表明：Ni-Ti 钎料可实现 TZM 的高温真空钎焊连接。Ni-13.7Ti/TZM 界面区，母材中的 Mo 与钎料中的 Ni 形成 MoNi 相，是钎料与 TZM 形成冶金结合的主要原因。在 TZM/Ni-44Ti/TZM 界面区，Ni-44Ti 钎料中的 Ti 与母材中的 Mo 反应形成 Mo-Ti 固溶体，使钎料和 TZM 形成冶金结合。Ni-44Ti 钎料钎焊 TZM 合金产生严重晶间渗入现象。降低钎料中 Ti 的含量，晶间渗入和母材溶蚀现象大幅减弱；TZM/Ni-13.7Ti/TZM 钎焊接头抗剪切强度 193 MPa，TZM/Ni-44Ti/TZM 钎焊接头抗剪切强度 167 MPa；晶间渗入使钎缝强度降低，降低钎料中的 Ti 含量，钎焊接头强度提高。

关键词：TZM 合金；钎焊；晶间渗入；力学性能

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