Brazing Si₃N₄ Ceramic to Molybdenum Using an Ag-Cu-Ti Filler

The microstructure and interface formation mechanism of the Si₃N₄/Mo joint was analyzed

BY T. ZHAO, D. F. MO, L. Q. YU, Y. Y. WANG, J. LI, X. LI, D. F. LIU, X. K. WANG, AND H. M. GONG

ABSTRACT

A Si₃N₄ ceramic was successfully joined to molybdenum (Mo) using an Ag-Cu-Ti filler alloy. The interfacial microstructure of the Si₃N₄/Ag-Cu-Ti/Mo joint was investigated by scanning an electron microscopy, energy dispersive spectrometer, and x-ray diffraction. The results showed the joint brazed at 900 °C for 10 min was smooth, and there were no holes and cracks at the interface. A continuous reaction layer, which is composed of TiN and TiSi₂, was formed near the Si₃N₄ ceramic, with TiN being located near the ceramic. The central part of the joint was composed of Ag- and Cu-based solid solutions. At the side near the Mo metal, there was a formation of the MoTi solid solution. The typical structure of the Si₃N₄/Mo joint was Si₃N₄/TiN + TiSi₂ reaction layer/Ag(s,s) + Cu(s,s)/MoTi/Mo. Because TiN and TiSi₂ compounds are generated on the ceramic side, the microhardness of the reaction layer on the ceramic side was decreased but still much higher than the hardness of the brazing seam and the Mo base material. The shear strength of the brazed joint was 204 MPa at room temperature.

KEYWORDS
• Si₃N₄ Ceramic • Molybdenum • Brazing • Interfacial Microstructure • Formation Mechanism

Introduction

Si₃N₄ ceramic has attracted considerable interest in recent years primarily due to its high thermal conductivity, low dielectric loss, good thermal shock resistance, high bending strength, and fracture toughness, so it is considered a potential high-power heat dissipation and packaging material (Ref. 1). However, the hardness and brittleness make it difficult to obtain large-sized and complex components. Therefore, joining Si₃N₄ to metallic materials is important to satisfy its application.

There have been some methods, such as diffusion bonding (Ref. 2), transient liquid phase (Ref. 3), and brazing bonding (Ref. 4), proposed for ceramic metal or joining. Among these methods, brazing bonding has attracted extensive attention due to its simplicity and cost effectiveness (Ref. 5) and has become the most commonly used reliable method to connect ceramics and metals. It has been reported that Si₃N₄ ceramic has successfully brazed together with copper (Ref. 6), TC4 alloy (Refs. 7, 8), TiAl alloy (Refs. 9–11), Invar alloy (Refs. 12–14), and 42CrMo steel (Refs. 15–17).

Molybdenum (Mo) has good thermal conductivity and low coefficient of thermal expansion (CTE). Hadian et al. (Ref. 18) used two Ni-based brazing alloys to braze Mo and Si₃N₄. Mo, Si, and N diffused from the parent materials. Mo compounds were formed at the Si₃N₄/filler metal interface, resulting in brazing joints in the ceramic/filler degumming at the interface. Peteves and Nicholas (Ref. 19) used Mo as a middle layer to braze Si₃N₄ ceramics. Mo was more successful as an interlayer than Cu or Nb, with its CTE matching the ceramic and affecting less the reactive route for the joint formation. Recently, research has focused on adding Mo particles as a reinforcing phase to the brazing filler metal to reduce the CTE mismatch between the ceramic base material and brazing filler metal (Ref. 20), improving the joint strength. However, there are few reports on the joining of Mo/ceramic assemblies using an Ag-Cu-Ti filler. Therefore, it is of great significance to study the brazing process and connection mechanism of Mo and Si₃N₄ ceramics.

In this work, Si₃N₄ was joined to Mo using the traditional Ag-Cu-Ti brazing filler. The microstructure of the Si₃N₄/Mo brazed joint was studied by means of metallographic observation, scanning electron microscopy (SEM), and x-ray diffraction (XRD). At the same time, microhardness tests were performed. The interface formation mechanism brazing parameters on the interfacial microstructure and mechanical properties were also analyzed.

Experimental Procedure

Materials

The materials used in this study were a Mo block and Si₃N₄ pieces. Both Mo, with a purity of 99.9 wt-%, and
Si3N4 with a density of 3.2 g/cm³, were supplied by Shanghai Institute of Ceramics, Chinese Academy of Sciences. The Si3N4 and Mo samples gave the dimensions of 6 × 6 × 1 and 9 × 6 × 6 mm³, respectively. The filler metal of 100 μm Ag-27Cu-3.3Ti wt-% foil was processed into a square sheet with a side length of 6 × 6 mm² as the faying surface of the joint. The properties and performance of the base materials and filler are shown in Tables 1 and 2.

### Joining Process

The joining surfaces of the Mo and Si3N4 samples were treated by polishing with a #400 sandpaper followed by ultrasonic cleaning in acetone for 8 min.

The schematic diagram of the brazed joint is shown in Fig. 1. Vacuum brazing of Mo to Si3N4 was carried out in a MOV-443-type furnace under a vacuum of 2.0 × 10⁻⁴ Pa. The
temperature curve is shown in Fig. 2. The assemblies were heated from room temperature to 300°C at a rate of 20°C/min and held for 10 min. Subsequently, they were heated up to 900°C at a rate of 10°C/min. After holding for 10 min at the brazing temperature of 900°C, the assemblies were forced to cool to 300°C at a rate of 5°C/min with argon. Finally, the joint cooled with the furnace-to-room temperature in vacuum. During brazing, a self-made fixture was used to apply a certain pressure to prevent the sample from moving when the brazing material melted.

Microstructural Characterization

After brazing, the sample was first embedded by a cold inlay method. Then, the connection surface was polished with different grades of metallographic sandpaper, and the brazed joint was etched by mixed acid (HCl: HNO₃: H₂O = 2:1:3) to facilitate the observation of the metallographic structure under a VHX-500F digital microscope. Before observation, the surface of the joint was wiped with absolute ethanol. Metal salt produced during the etching process can be dissolved in water without introducing other impurities.

Results and Discussion

Brazing Joint Morphology

Figure 4 shows the metallographic microstructure of the Si₃N₄/Mo joint brazed with the Ag-Cu-Ti filler at 900°C for 10 min. It can be seen that the filler had good contact with the base materials on both sides, and there were no obvious cracks or holes in the joint. Between Si₃N₄ and the Ag-Cu-Ti filler, there is a gray interfacial reaction Layer I with a thickness of about 3.8 μm, indicating that the filler reacted with Si₃N₄. Layer II is part of the Ag-Cu-Ti filler, mainly composed of a dark and large, light-colored phase. At a high temperature, the filler melted and overflowed to both sides, making the thickness of the intermediate layer slightly lower than the original thickness of the filler. Layer III is the interface layer of the Ag-Cu-Ti/Mo.

Typical Interfacial Microstructure of Mo/Ag-Cu-Ti/Si₃N₄ Brazed Joints

Figure 5 is the secondary electron imaging diagram of the Si₃N₄/Mo joint brazed with the Ag-Cu-Ti filler at 900°C for 10 min. It can be seen that the filler had good contact with the base materials on both sides, and there were no obvious cracks or holes in the joint. Between Si₃N₄ and the Ag-Cu-Ti filler, there is a gray interfacial reaction Layer I with a thickness of about 3.8 μm, indicating that the filler reacted with Si₃N₄. Layer II is part of the Ag-Cu-Ti filler, mainly composed of a dark and large, light-colored phase. At a high temperature, the filler melted and overflowed to both sides, making the thickness of the intermediate layer slightly lower than the original thickness of the filler. Layer III is the interface layer of the Ag-Cu-Ti/Mo.
flat bonding interface between filler and Mo. To obtain the elemental compositions of regions 1–3, microareas A–F were measured by an EDS, and the results are given in Table 3.

According to the literature (Refs. 21–23), in the microstructure of the Si₃N₄/Si₃N₄ or Si₃N₄/metal joint brazed with the Ag-Cu-Ti filler, a thin Ti-N layer will be formed on the Si₃N₄ ceramic side and the Ti-Si phase will be formed next to the Ti-N layer. The light gray microarea B in region 1 contained N (41.21 at.-%), Ti (31.97 at.-%), and Si (22.47 at.-%), inferred as TiN and Si. The microarea C located in region 1 consisted of Si (47.61 at.-%) and Ti (22.31 at.-%), corresponding to TiSi₂. The light gray microareas D and E in region 2 gave elemental compositions of Ag (86.97 at.-%) and Cu (64.77 at.-%), respectively, determined as Cu solid solution (Cu[sub s,s]) and Ag solid solution (Ag[sub s,s]). The microarea F in region 3 contained Mo (17.63 at.-%), Ti (21.93 at.-%), Ag (35.16 at.-%), and Cu (25.29 at.-%), inferred as MoTi and AgCu(sub s,s).

Figure 6 presents a back-scattered electron image of the Si₃N₄/Mo joint brazed with the AgCuTi alloy at 900°C for 10 min and the corresponding element distribution maps throughout the joint. It can be seen that during the brazing process, the active element Ti diffused from the middle of the filler to the base materials on both sides, and the Ti content on the Si₃N₄ side was higher than that on the Mo side, indicating that the Ti element diffused toward the Si₃N₄ side. Mo did not diffuse from the base material to the filler and ceramic side.

The phase identification of the interfacial zone in the
Si₃N₄/Mo joint was performed by an XRD, and the results are shown in Fig. 7. It can be seen that there were TiN, Ti₅Si₂, and MoTi solid solutions in the brazing joint. Combined with the analysis of the XRD and EDS results, the interface structure of the brazed joint was indicated as Si₃N₄/TiN + Ti₅Si₂/Ag(s,s) + Cu(s,s)/MoTi/Mo.

The microhardness distribution along the Si₃N₄/Mo joint brazed with Ag-Cu-Ti is depicted in Fig. 8. It can be seen from the figure that the microhardness of Mo after brazing was about 300 HV. The average hardness values of the filler layer were lower than those of base materials. However, the microhardness of Si₃N₄ ceramics was very high, about 1800 HV. During the brazing process, the TiN + Ti₅Si₂ compound was formed due to the reaction between Ti and Si₃N₄ ceramic, which reduced the hardness of the reaction layer on the ceramic side, about 1500 ~ 1800 HV, but was still much higher than the microhardness at the brazing seam and Mo. Then, the shear strength of the joint brazed with AgCuTi was 204 MPa at room temperature.

**Interface Formation Mechanism of Joint**

According to the above analysis, the microstructure formation process of Si₃N₄ ceramics and Mo joints brazed with Ag-Cu-Ti filler can be summarized into several stages, as shown in Fig. 9.

1) During the brazing process, when the heating temperature reached the melting point of the filler, the filler melted into a liquid phase, the active Ti element diffused to the base materials on both sides under the driving force of the chemical potential difference, and the Mo element in the metal dissolved into the filler, as shown in Fig. 9A.

2) As shown in Fig. 9B, as brazing proceeded, the Ti element diffused to the ceramic side reacted with the Si₃N₄ ceramic matrix as follows (Ref. 24):

\[
\frac{1}{4}Si_3N_4 + Ti = TiN + 3/4Si
\]

\[
\Delta G^0 (J/mol) = -613000 + 40.8T
\]

When the temperature reached 900°C (1173 K), TiN began to nucleate in the local region of the ceramic surface, and the generated Si element diffused into the filler under the driving of a concentration gradient. While at the Mo interface, the dissolved Mo element formed a solid solution with the Ti element diffused to the interface.

3) As shown in Fig. 9C, the microstructure of the joint evolved further with the interfacial reaction between the filler and the base materials. At the Si₃N₄/Ag-Cu-Ti interface, the initially formed TiN grains gradually grew and connected to each other, eventually forming a continuous TiN interfacial reaction layer on the ceramic surface. At the same time, the Si element released by the reaction gradually diffused into the liquid filler, and the filler region near the TiN interface reaction layer reacted with the Ti enriched in the interface region as follows (Ref. 24):

\[
Ti + 2Si = TiSi_2
\]

\[
\Delta G^0 (J/mol) = -140200 + 5.44T
\]

4) In the cooling process after brazing, the high melting point Cu precipitated first, the low melting point Ag precipitated and dissolved certain Ti elements, and finally formed Cu- and Ag-based solid solutions, as shown in Fig. 9D. The microstructure of the joint was Si₃N₄/TiN + Ti₅Si₂/Ag(s, s) + Cu(s,s)/MoTi/Mo.

**Conclusion**

Reliable brazing of Mo and Si₃N₄ ceramic was achieved by using an Ag-Cu-Ti filler. The brazed joints obtained by
holding 10 min at 900˚C were well connected, and there were no holes and cracks at the interface. The interfacial microstructure and joining properties of the Si₃N₄/Ag-Cu-Ti/Mo brazed joint were investigated in this study. Primary conclusions are summarized as follows:

1) The whole brazing joint is mainly comprised of three parts: the interface reaction layer near the ceramic side is composed of TiN and TiSi₂, the middle of the brazing joint is Cu-based and Ag-based solid solution, and the formation of MoTi solid solution is near the Mo side. The typical structure of the Si₃N₄/Mo joint is Si₃N₄/TiN + TiSi₂ reaction layer/Ag(s,s) + Cu(s,s)/MoTi/Mo.

2) In combination with the composition distribution and data analysis, TiN and TiSi₂ compounds are generated on the ceramic side, so the microhardness of the reaction layer on the ceramic side is decreased but still much higher than the hardness of the brazing joint and the Mo base material.

3) The shear strength of the joint brazed at 900˚C for 10 min was 204 MPa at room temperature.

Acknowledgments

This work was supported by Key Project of CAS (No. ZDRW-CN-2019-3) and the Youth Innovation Promotion Association, Chinese Academy of Science (No. 2018274). Many thanks to Xiaosong Jiang and Yali Zhang at Southwest Jiaotong University, China, for microhardness testing.

References

1. Wu, Q. W., Hu, F., and Xie, Z. P. 2018. New progress in the preparation and application of high performance silicon nitride ceramics. Journal of Ceramics 39(001): 13–19.
2. Krajewski, A. 1995. Joining of Si₃N₄ to wear-resistant steel by direct diffusion bonding. Journal of Materials Processing Technology 54(1–4): 103–108. DOI: 10.1016/0924-0136(95)01927-8
3. Kim, J. J., Park, J. W., and Eagar, T. W. 2003. Interfacial mi-
crostructure of partial transient liquid phase bonded Si₃N₄-to-Inconel 718 joints. Materials Science and Engineering: A 344 (1–2): 240–244. DOI: 10.1016/S0921-5093(02)00402-1
4. Xu, X. P., Wang, Y., Zou, J. S., and Xia, C. Z. 2018. Interfacial microstructure and properties of Si₃N₄ ceramics/Cu/304 stainless steel brazed by Ti₄O₂Zr₂SBO.2Cu amorphous solder. Materials 11(11): 2226. DOI: 10.3390/ma11112226
5. Liu, C. F., Zhang, J., Zhou, Y., Yi, H. L., and Naka, M. 2009. Effect of holding time on the self-joining of silicon nitride. Journal of Alloys and Compounds 471(1–2): 217–221. DOI: 10.1016/j.jallcom.2008.03.059
6. ElSawy, A. H., and Fahmy, M. F. 1998. Brazing of Si₃N₄ ceramic to copper. Journal of Materials Processing Technology 77(1–3): 266–272. DOI: 10.1016/s0924-0136(97)00427-5
7. Zhao, Y. X., Wang, M. R., Cao, J., Song, X. G., Tang, D. Y., and Feng, J. C. 2015. Brazing TC4 alloy to Si₃N₄ ceramic using nano-Si₃N₄ reinforced AgCu composite filler. Materials & Design 64: 40–46. DOI: 10.1016/j.matdes.2015.03.046
8. Zhao, Y. X., Song, X. G., Tan, C. W., Hu, S. P., Cao, J., and Feng, J. C. 2017. Microstructural evolution of Si₃N₄/Ti₆Al₁₄V joints brazed with nano-Si₃N₄ reinforced AgCuTi composite filler. Vacuum 142: 58–65. DOI: 10.1016/j.vacuum.2017.05.005
9. Song, X., Zhao, Y. H., Song, X. G., and Feng, J. C. 2018. Wetting of AgCu-Ti filler on porous Si₃N₄ ceramic and brazing of the ceramic to TiAl alloy. Ceramics International 44(5): 4622-4629. DOI: 10.1016/j.ceramint.2017.11.212
10. Song, X. G., Cao, J., Li, C., and Feng, J. C. 2011. Interfacial microstructure and joining properties of TiAl/Si₃N₄ brazed joints. Materials Science and Engineering: A 528(22): 7030-7035. DOI: 10.1016/j.msea.2011.05.079
11. Song, X. G., Cao, J., Wang, Y. F., and Feng, J. C. 2011. Effect of Si₃N₄-particles addition in Ag–Cu–Ti filler alloy on Si₃N₄/TiAl brazed joints. Material Science and Engineering: A 528(15): 5135–5140. DOI: 10.1016/j.msea.2011.03.032
12. Zhang, J., Liu, J. Y., and Wang, T. P. 2018. Microstructure and brazing mechanism of porous Si₃N₄/Invar joint brazed with Ag–Cu–Ti/Cu/Ag–Cu multi-layered filler. Journal of Materials Science & Technology 34(4): 713–719. DOI: 10.1016/j.jmst.2017.07.001
13. Wang, T., Liu, C., Leinenbach, C., and Zhang, J. 2016. Microstructure and strengthening mechanism of Si₃N₄/Invar joint brazed with TiNp-doped filler. Materials Science and Engineering: A 650: 469–477. DOI: 10.1016/j.msea.2015.10.038
14. Wang, T., Ivas, T., Lee, W., Leinenbach, C., and Zhang, J. 2016. Relief of the residual stresses in Si₃N₄/Invar joints by multi-layered braze structure — Experiments and simulation. Ceramics International 42(6): 7080-7087. DOI: 10.1016/j.ceramint.2016.01.096
15. Wang, T., Zhang, J., Lee, W., Ivas, T., and Leinenbach, C. 2019. Numerical analysis on the residual stress distribution and its influence factor analysis for Si₃N₄/42CrMo brazed joint. Simulation Modelling Practice and Theory 95: 49–59. DOI: 10.1016/j.simpat.2019.04.007
16. Wang, T., Zhang, J., Liu, C., and Wang, G. 2014. Microstructure and mechanical properties of Si₃N₄/42CrMo joints brazed with TiNp modified active filler. Ceramics International 40(5): 6881–6890. DOI: 10.1016/j.ceramint.2013.12.008
17. Wang, T., Ivas, T., Leinenbach, C., and Zhang, J. 2015. Microstructural characterization of Si₃N₄/42CrMo joint brazed with Ag–Cu–Ti + TiNp composite filler. Journal of Alloys and Compounds 651: 623–630. DOI: 10.1016/j.jallcom.2015.08.138
18. Hadian, A. M., and Drew, R. A. L. 1999. Distribution and chemistry of phases developed in the brazing of silicon nitride to molybdenum. Journal of the European Ceramic Society 19(8): 1623–1629. DOI: 10.1016/S0955-2219(98)00259-3
19. Petvees, S. D., and Nicholas, M. G. 1996. Evaluation of brazed silicon nitride joints: Microstructure and mechanical properties. Journal of the American Ceramic Society 79(6): 1553–1562.
20. He, Y. M., Wang, X., Wang, G. C., and Wang, T. P. 2013. Brazing Si₃N₄ ceramic with Ag-Cu-Ti+Mo composite filler. Transactions of The China Welding Institution 34(08): 59–62+116
21. Nomura, M., Iwamoto, C., and Tanaka, S. I. 1999. Nanosstructure of wetting triple line in a Ag-Cu-Ti/Si₃N₄ reactive system. Acta Materialia 47(2): 407–413. DOI: 10.1016/s1359-6454(98)00375-9
22. Iwamoto, C., and Tanaka, S. 1998. Interface nanostructure of brazed silicon nitride. Journal of the American Ceramic Society 81(2): 363–368. DOI: 10.1111/1.151-2916.1998.tb02342.x
23. Klein, R., Desmaison-Brut, M., Ginet, P., Bellosi, A., and Desmaison, J. 2005. Wettability of silicon nitride ceramic composites by silver, copper and silver copper titanium alloys. Journal of the European Ceramic Society 25(10): 1757–1763. DOI: 10.1016/j.jeurceramsoc.2004.12.005
24. Tunckan, O., Yurdakul, H., and Turan, S. 2013. Identification and quantification of reaction phases at Si₃N₄-Ti interfaces by using analytical transmission electron microscopy techniques. Ceramics International 39(2): 1087-1095. DOI: 10.1016/j.ceramint.2012.07.031
TONG ZHAO, DE FENG MO (dfmo@mail.sitp.ac.cn), LI QUAN YU, YU YU WANG, JUN LI, XUE LI, DA FU LIU, XIAO KUN WANG, and HAI MEI GONG (hmongon@mail.sitp.ac.cn) are with the Key Laboratory of Infrared Imaging Materials and Detectors, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai, China. ZHAO, MO, X. LI, LIU, WANG, J. LI, and GONG are also with the University of Chinese Academy of Sciences, Beijing, China.