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Journal of the European Ceramic Society 30 (2010) 3245–3251

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Microstructure and mechanical properties of the Si_3N_4/42CrMo steel joints brazed with Ag–Cu–Ti + Mo composite filler

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Received 21 March 2010; received in revised form 16 June 2010; accepted 1 July 2010

Abstract

The Si_3N_4 ceramic was joined to 42CrMo steel using Ag–Cu–Ti + Mo composite filler. Effect of Mo particles content on the microstructure and mechanical properties of the joints were investigated. Defect-free joints were received when the Si_3N_4/42CrMo steel joints were brazed with Ag–Cu–Ti + Mo composite filler. The results show that a continuous reaction layer which is composed of TiN and Ti_5Si_3 was formed near the Si_3N_4 ceramic. A double reaction layer which consists of Fe_2Ti and FeTi was also formed adjacent to 42CrMo steel, with Fe_2Ti being located near the steel. The central part of the joint is composed of Ag based solid solution, Cu based solid solution, Mo particles and some Cu–Ti intermetallic compounds. The maximal bending strength reached 587.3 MPa with 10 vol.% Mo particles in the joint, at which the joint strength was 414.3% higher than the average strength for the case without Mo particles addition.

Keywords: Si_3N_4; Joining; Ag–Cu–Ti + Mo composite filler; Microstructure; Mechanical properties

1. Introduction

Silicon nitride ceramics are considered one of the most promising structural materials for harsh environment applications due to its unique properties – high strength, oxidation and corrosion resistance, thermal stability and resistance to thermal shock.[1] However, the natural brittleness of ceramic materials limits their applications greatly. Metals and alloys usually possess lots of excellent performance, such as easy workability, excellent electrical conductivity, low cost, but they generally lack the durability and corrosion resistance of ceramics. To take advantage of respective superiorities of ceramics and metals, it is necessary to join the ceramics with metallic parts. There are many applications in which both ceramics and metals can be employed to maximize the performance and minimize the respective shortcomings, such as parts of engines, heat exchangers, cutting tools and so on.[2]

So far, the research on the bonding technologies of ceramics to metals has been well documented, such as fusion welding, brazing, diffusion bonding, glass sealing or glazing, adhesive bonding. Among the joining techniques, brazing is receiving extensive attention due to its simplicity and cost-effectiveness.[3] However, there are two main problems when brazing ceramics to metals: the first is poor wettability of ceramics by most metals and alloys. The problem can be overcome by use of an activated brazing alloy. The addition of an active element (Ti, Zr, V, Cr) in the brazing alloy induces a considerable improvement in the wettability due to its chemical reactivity with the ceramic surface, which gives rise to a modification of the metal–ceramic interface chemistry. The second problem is the significant differences in physical and mechanical properties between ceramics and metals, such as coefficients of thermal expansion (α) and Young's moduli (E). These differences can lead to high residual stresses in the joint when cooling from the brazing temperature, resulting in decrease of the joint strength.[4–7] The problem may be alleviated through addition of a low CTE material (particles or fibers) to the brazing alloy. The addition of ceramic particles or fibers, such as carbon fibers,[8,9] SiC[10–12] and WC[4] into brazing alloy has been shown significant improvement in the joint flexural strength. Zhu et al.[9] reported that the addition of 12 vol.% short carbon fibers to 63Ag–34Cu–2Ti–1Sn (wt.%) brazing alloy resulted in up to 30% improvement in the shear/tensile joint strength of the stainless steel and alumina joints. We have used the SiC particles-

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doi:10.1016/j.jeurceramsoc.2010.07.005

reinforced active brazing alloy to joining silicon nitride ceramics to themselves successfully and the joint strength was improved greatly.[13]

Unfortunately, scant researches have been done on the brazing Si_3N_4 ceramic to 42CrMo steel using the composite filler. In this investigation, a commercially available Ag–Cu–Ti brazing alloy accompanying with Mo particles was evaluated for the joining Si_3N_4 ceramic to 42CrMo steel. Mo particles, whose CTE is only $5.1 \times 10^{-6}\,K^{-1}$, serves to decrease the CTE of the brazing alloy. Effect of Mo particles content on the microstructure and mechanical properties of the joints were investigated.

2. Materials and experimental procedures

The Si_3N_4 ceramic used in this investigation was hot pressed with MgO and Al_2O_3 additives. The metallic partner was 42CrMo steel with the chemical compositions Fe–0.42C–1.0Cr–0.7Mn–0.3Si–0.5Mo (mass fraction, %). The ceramic and steel were machined to form rectangular specimens $3 \times 4 \times 17\,mm^3$ in size. The bonding surfaces (3 mm × 4 mm) of the samples were coarsely ground on SiC sand papers and then polished with 0.5 μm diamond paste. The composite filler were composed of 69.12Ag–26.88Cu–4Ti (wt.%) alloy powder with an average particle size of 50 μm and Mo particles with an average diameter of 10 μm. The volume fraction of Mo particles in the composite filler was designed as 0%, 5%, 10% and 15%. The initial powders were weighed in the scheduled composition and then the powder mixture were high-power ball milled for 1 hour with a ball to powder mass ratio of 10:1. Afterwards, a small amount of cellulose nitrate and octylacetate were added to the powder mixture for making a composite brazing paste. Before assembling, the Si_3N_4 ceramic and 42CrMo steel were cleaned with acetone in an ultrasonic bath for 30 minutes. The composite brazing paste was placed between Si_3N_4 ceramic and 42CrMo steel and a normal load of 0.015 MPa was applied on the assembly to hold them together. Brazing experiments were carried out at 1173 K for 10 min in a vacuum furnace with a vacuum of 1×10^{-3} Pa.

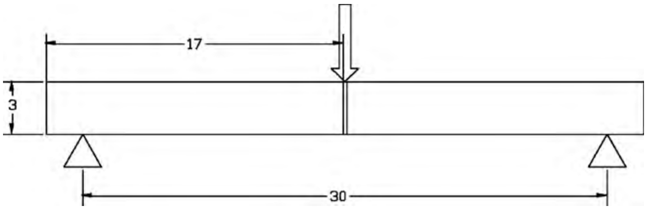

Fig. 1. Configuration for joint strength testing.

The strength of the butt joint was measured by a three-point bending test with a cross-head speed of 0.5 mm/min. Joint-strength testing was performed using the following configuration, which was shown in Fig. 1 schematically. At least five samples were used to determine the bending strength of joint for each joining condition. The cross-sections of the Si_3N_4 ceramic/steel joints were cut perpendicular to the bonded interface and the samples for microstructure analysis were prepared by standard polishing techniques. The joint morphology and chemistry were investigated using a Scanning Electron Microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS).

3. Results and discussion

Fig. 2 shows microstructure and corresponding elements' area distribution images of a Si_3N_4/42CrMo joint brazed with Ag–Cu–Ti + 15 vol.% Mo at 1173 K for 10 min. A defect-free Si_3N_4 ceramic/Ag–Cu–Ti + Mo/42CrMo joint revealed good

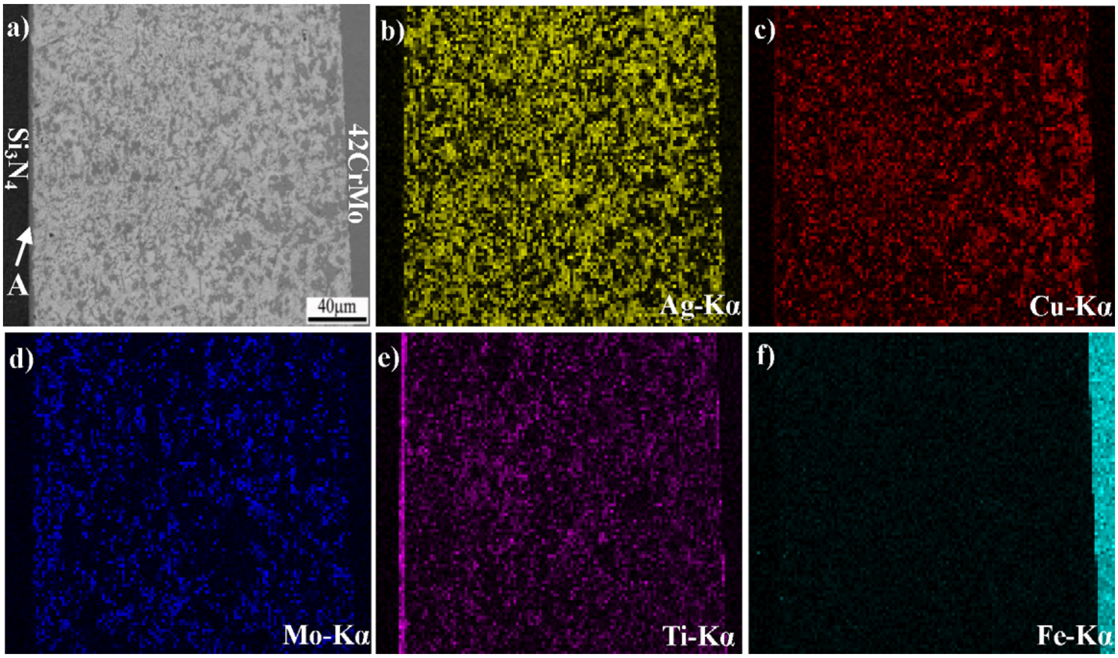

Fig. 2. Morphology and elemental analysis results of the Si_3N_4/42CrMo steel joint brazed using $(Ag_{72}Cu_{28})_{96}Ti_4$ + 15 vol.% Mo composite filler at 1173 K for 10 min.

wetting and intimate contact was formed between the substrates and the composite filler. It is clear that a continuous reaction layer with an average thickness of 1.8 μm was formed at the Si_3N_4 ceramic/braze interface (zone A in Fig. 2(a)). This reaction layer is mainly composed of Ti element, as shown in Fig. 2(e), indicating that Ti was concentrated near the Si_3N_4/braze interface. According to composition analysis, the reaction layer was composed of 15.57 at.% Si, 71.16 at.% Ti and 13.27 at.% N. It should consist of a bi-layer system of TiN and Ti_5Si_3 phases, which correspond to the lowest free energy of formation for the reaction products.[14] According to the Ag–Cu binary phase diagram,[15] Ag–Cu eutectic temperature is 1053 K (the eutectic composition of Ag–Cu is $Ag_{72}Cu_{28}$ (wt.%)). During the heating process, Ag–Cu brazing alloy melted at 1053 K. Then, Ti began to be dissolved in the liquid. Ti, as an active element, will diffuse towards the Si_3N_4 ceramic and react with them to form TiN layer at the Si_3N_4 ceramic/braze interface by the following reaction[16–19]:

$$Si_3N_4\,(s) + 4Ti\,(l) = 4TiN\,(s) + 3Si\,(s) \qquad (1)$$

$$\Delta G^0\,(\mathrm{KJ/mol}) = -1356 + 0.199T$$

Due to the negative free energy of the reaction (1), the reaction will proceed continuously until a certain thickness of TiN reaction layer has been received. Further reaction between Ti and Si_3N_4 ceramic will be hindered since the previous TiN layer impedes Ti diffusing towards Si_3N_4 ceramic further. During the formation of TiN reaction layer, Si was released and diffused into the molten braze. Combining with the higher concentration of Ti elements near the Si_3N_4 ceramic/braze interface, Ti_5Si_3 phases were formed adjacent to TiN reaction layer according to the following reaction[16–19]:

$$5Ti\,(s) + 3Si\,(s) = Ti_5Si_3\,(s) \qquad (2)$$

$$\Delta G^0\,(\mathrm{KJ/mol}) = -194.14 + 0.0167T$$

Thermodynamic calculations from the free energy of formation for Ti_5Si_3 confirm its stability. As can be seen from Fig. 2(a), a thin reaction layer also exist at the 42CrMo steel/braze interface. Fig. 3 presents SEM-BSE images of the reaction layer at the 42CrMo steel/braze interface and the concentration profiles of the corresponding elements across the reaction zone. It appears that a double reaction layer was also formed at the 42CrMo steel/braze interface.[20] As shown in the picture, a thin reaction layer, which is made up of 71.89 at.% Fe, 21.39 at.% Ti and a small amount of Ag and Cu, was detected adjacent to 42CrMo steel. This region is presumably Fe_2Ti intermetallic compounds layer. Next to Fe_2Ti, a wide region which consists of 43.41 at.% Ti, 45.17 at.% Fe, 10.38 at.% Cu and 1.04 at.% Ag has been observed. The stoichiometric ratio between Fe and Ti of the layer indicates it is almost a FeTi intermetallic compound. The central part of the joint was composed of bright Ag based solid solution, grey Cu based solid solution, Mo particles together with some reaction phases. Mo particles, which appear to be grey in Fig. 2(a), uniformly distributed in the brazing layer of the well-bonded joint.

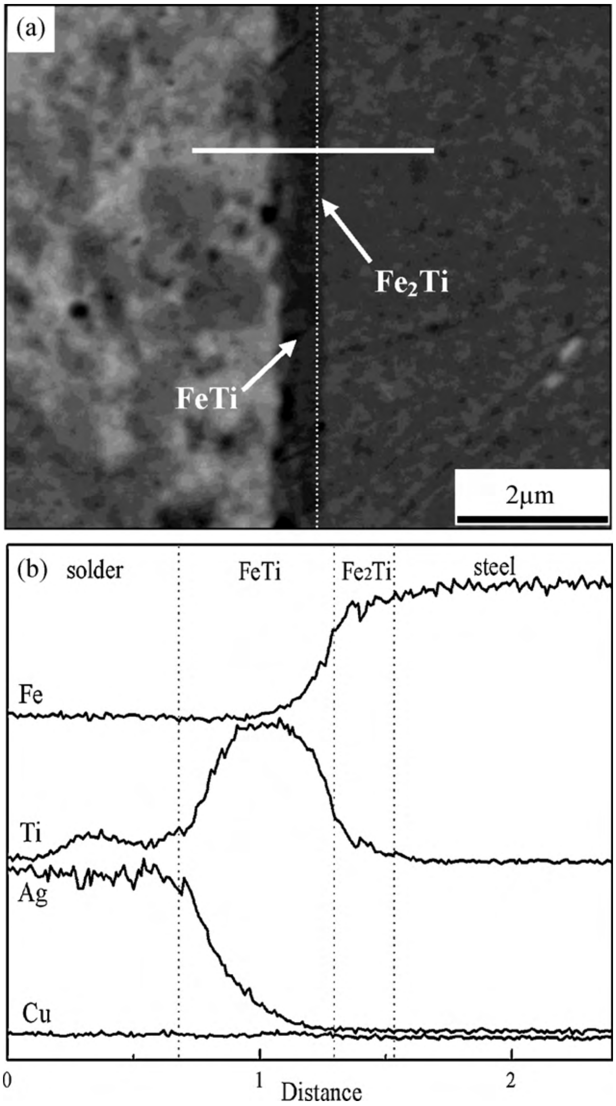

Fig. 3. SEM-BSE images of the reaction layer at 42CrMo steel/braze interface and the concentration profiles of corresponding elements across the reaction zone.

As Ag–Cu–Ti brazing alloy melted, Mo particles kept in a solid state during brazing. The interaction between Ag–Cu–Ti and Mo particles has an impact on the composite filler mitigating residual stresses, which will eventually affect the joint strength. It is necessary to investigate the interaction between the brazing alloy and Mo particles.

Fig. 4 presents back-scattered micrograph of the reaction products in the joint and corresponding elements' concentration profiles across Mo particles. Interfaces between the brazing alloy and Mo particles show intimate physical bonding. No cracks or pores are found. The grey part across the scanning line is rich in Mo and simultaneously no other elements are detected. They are determined to be Mo particles. Ti concentration fluctuates where Mo particles contact the matrix, as shown in Fig. 4(b), which will be elucidated in the following chapter.

As can be seen from Fig. 2(e), Ti elements not only concentrate at the substrates/braze interface, but also distribute in the joint randomly. It is necessary to clarify the existence form

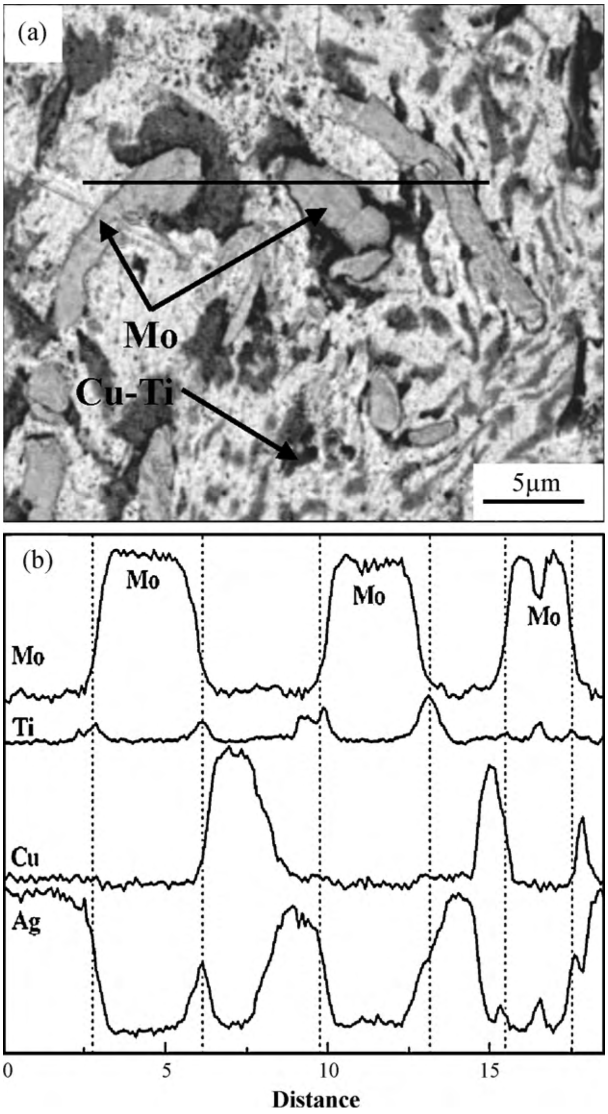

Fig. 4. Morphology of the joint (a) and elemental distributions (b) of Mo, Ag, Cu and Ti elements along the black line in (a).

of Ti element in the joint. Fig. 5 shows back-scattered micrograph of the reaction products in the joint and corresponding elements' area distribution images. It is clear that Cu elements concentrate where Ti elements exist, indicating that Ti may react with Cu to form Cu–Ti intermetallic compounds owing to their strong mutual affinity.[21] As shown in Fig. 5, tiny precipitates are randomly distributed in the joint. The precipitate, such as A, is enriched with Ti (~39.03 at.%), Cu (~36.14 at.%) and a definite amount of Ag. The stoichiometric ratio between Cu and Ti of the precipitate indicates that it is close to be a Cu–Ti intermetallic compound. It is worth noting that there are also Cu_2Ti, Cu_3Ti_2 and Cu_4Ti_3 intermetallic compounds detected in the joint. Formation mechanism of Cu–Ti intermetallic compound in the joint can be clarified as following: Ti possesses two typical allotropic structures, existing in the form of α-Ti at low temperatures and transforming to β-Ti when the allotropic transformation occurs at 1155.5 K. Based on the Mo–Ti binary phase diagram, β-Ti and Mo are infinitely miscible in the temperature range of β-Ti. However, the maximal solubility of Mo in α-Ti is less than 1 wt.%, at which level α-Ti cannot be dissolved in Mo. Hence, whole Ti elements in the joint were β-Ti at the brazing temperature (1173 K). They diffused towards and reacted with substrates (Si_3N_4 ceramic and 42CrMo steel) continuously. Besides, partial Ti elements were absorbed by Mo particles and they began to be dissolved mutually. The transformation of β-Ti → α-Ti occurred when the temperature was cooled to 1155.5 K. Thus, those Ti elements that were dissolved in Mo particles must be precipitated in subsequent cooling due to the lower solubility between α-Ti and Mo. They reacted with Cu to form Cu–Ti intermetallic compounds as the temperature decreased. The varieties of Cu–Ti intermetallic compounds in the joint depend upon the composition ratio of the two elements during reaction.

Table 1
Effect of Mo particles content in the composite filler on the reaction layer thickness.

		Mo particles content (vol.%)			
		0	5	10	15
Average reaction layer thickness (μm)	$Ti_5Si_3 + TiN$	7 ± 0.5	5.3 ± 0.5	2.4 ± 0.5	1.8 ± 0.5

Fig. 6 shows SEM micrographs of the cross-sections of the Si_3N_4 ceramic/42CrMo joints for uniformly distributed Mo particles in the brazing material: (a) 0 vol.%, (b) 5 vol.%, (c) 10 vol.% and (d) 15 vol.%. As can be seen from the picture, more fine Cu–Ti intermetallic compounds occur in the joint as the content of Mo particles in the composite filler rises, as comparing Fig. 6(b–d). With increasing Mo particles addition in the joint, more Ti elements and Mo particles were dissolved due to the interaction between Ti and Mo during brazing, resulting in more Ti elements were expelled into the molten braze during solidification. These Ti elements can react with Cu, leading to more Cu–Ti intermetallic compounds were precipitated in the cooling stage. Furthermore, the thickness of reaction layer at the Si_3N_4/braze interface decreases as the content of Mo particles in the joint increases, as demonstrated in Table 1. It was attributed to insufficient Ti concentration at the Si_3N_4 ceramic/braze interface due to trapping of Ti by excessive Cu–Ti intermetallic compounds present in the joint. However, the thickness of reaction layer at the 42CrMo/braze interface varies less with variation of Mo particles addition in the joint.

Fig. 7 presents the three-point bending test results of the Si_3N_4/42CrMo joints brazed with different Mo particles addition. The bending strength of joint increases as Mo particles content in the joint increases up to 10 vol%, at which the average strength is maximal (587.3 MPa), corresponding to a 414.3% increase from the value at 0 vol.% Mo particles. The joint strength decreases from the maximal value above 10 vol.% Mo. When the Si_3N_4/42CrMo joints were brazed by Ag–Cu–Ti brazing alloy, a CTE mismatch among the joining materials (the CTE of Si_3N_4 is $3 \times 10^{-6}\,K^{-1}$ and that of 42CrMo steel is $11.1 \times 10^{-6}\,K^{-1}$, but the CTE of Ag–Cu–Ti brazing alloy is $18 \times 10^{-6}\,K^{-1}$) can result in large residual stresses near the joint interface, appreciably lowering the joint strength. Thus, the joint

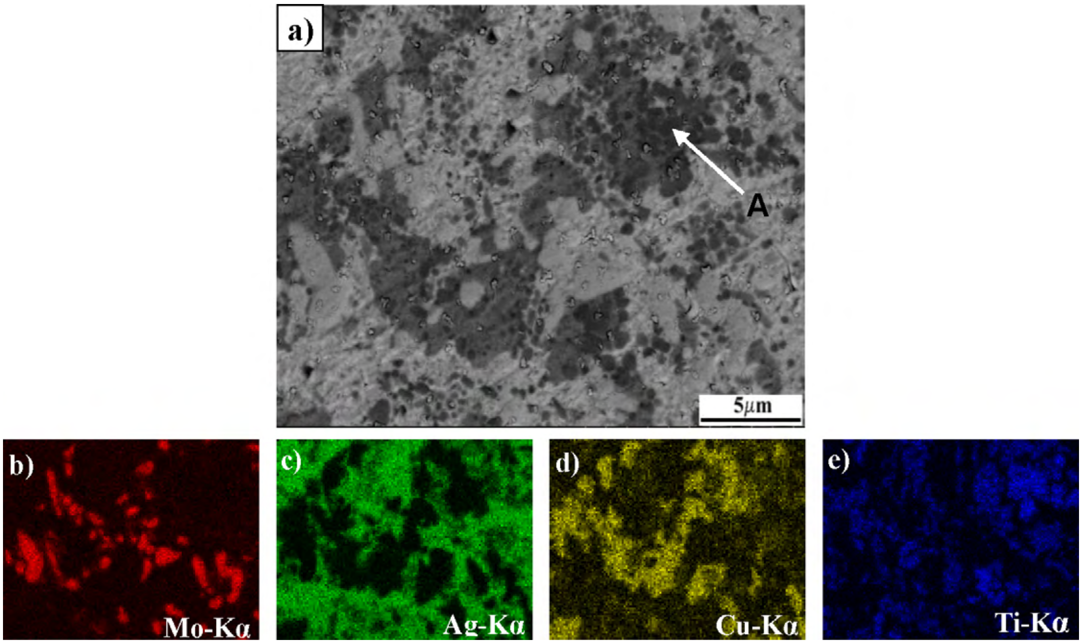

Fig. 5. Cross-sectional view (a) of a Si_3N_4/42CrMo steel joint brazed with $(Ag_{72}Cu_{28})_{96}Ti_4$ + 15 vol.%Mo and the Mo-Kα (b), Ag-Kα (c), Cu-Kα (d) and Ti-Kα (e) map showing the Mo, Ag, Cu and Ti distributions in (a).

strength is only 114.2 MPa. By adding 5 vol.% Mo particles into the Ag–Cu–Ti brazing alloy, the CTE reduction of the composite filler (Ag–Cu–Ti + Mo) could be achieved to a certain extent due to Mo particles addition whose CTE is only $5.1 \times 10^{-6}\,K^{-1}$. It can result in a stronger, higher quality joint since the CTE mismatch between the substrates and the brazing alloy was lowered. Hence, the joint strength is elevated to 162.8 MPa. However, the lower the Mo particles content in the joint is, the less the CTE

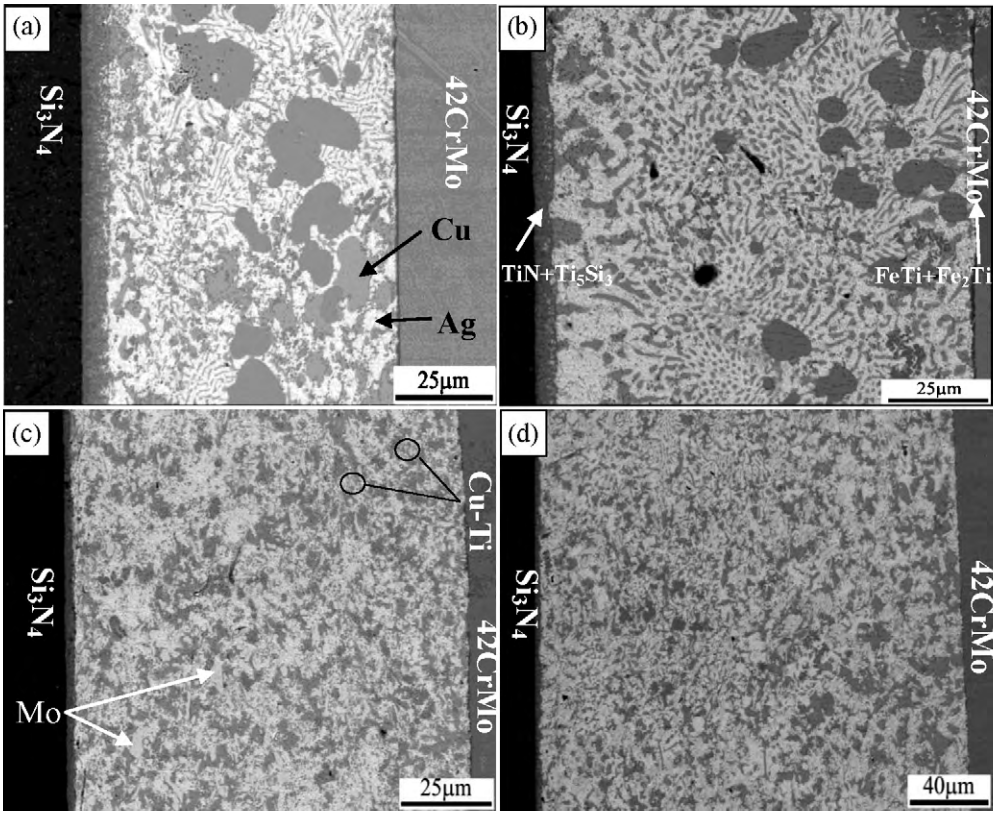

Fig. 6. SEM micrographs of the cross-sections of the Si_3N_4/42CrMo steel joints for uniformly distributed Mo particles in the brazing material: (a) 0 vol.%, (b) 5 vol.%, (c) 10 vol.%, (d) 15 vol.%.

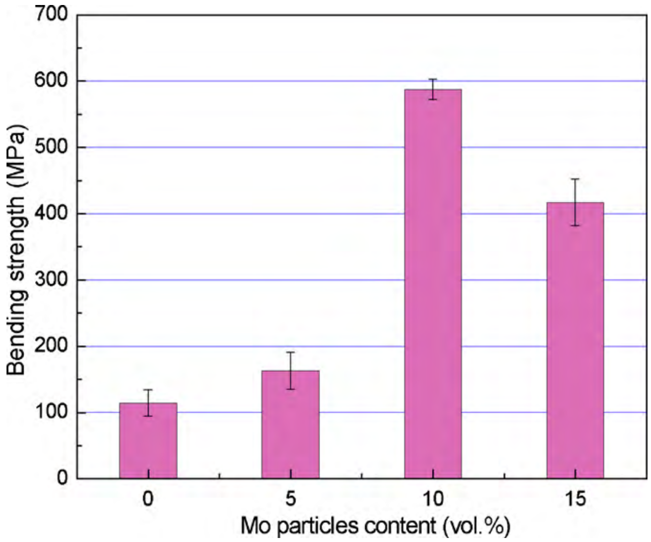

Fig. 7. Effect of Mo particles content on bending strength of the joint.

reduction will be, so the relatively lower content of Mo particles addition (5 vol.%Mo) in the joint was not sufficient in reducing the CTE of the brazing alloy and hence was not effective in reducing the CTE mismatch and correspondingly residual thermal stresses during the joining process.

The maximal flexural strength of 587.3 MPa could be received when the ceramic-to-steel joints were brazed with Ag–Cu–Ti + 10 vol.% Mo. This maximal joint strength can be contributed to following reasons. Firstly, formation of Cu–Ti intermetallic compounds in the joint would consume a certain amount of Ti element and thus decrease Ti element diffusing towards Si_3N_4 ceramic, resulting in the thickness of reaction layer at the Si_3N_4 ceramic/braze interface was diminished from 7 μm at 0 vol.% Mo particles to 2.4 μm at 10 vol.% Mo particles. It is essential that a suitable thickness of interfacial reaction layer is formed at the interface because the reaction layer can decrease the thermal residual stresses gradient between Si_3N_4 ceramic and braze.[22] A thin reaction layer at the interface can not transfer enough load and lead to lower joint strength. The joint strength will also be deteriorated when the thickness of reaction layer exceeds a certain value. Interfacial reaction products are new phases (TiN and Ti_5Si_3) to the substrates, and have different thermal expansion coefficients. A thick reaction layer could also cause great stress in the joint due to their brittleness nature. The optimum thickness of the reaction layer at Si_3N_4 ceramic/brazing alloy interface is 2.4 μm when the maximal joint strength was achieved in this research. Secondly, the CTE of the brazing alloy was reduced by 7.1% by using the Rule of Mixtures (ROM) when 10 vol.% Mo particles were added into the brazing alloy. The brazing alloy's CTE reduction due to Mo particles addition appears to play an important role in the enhancement of the joint strength because CTE mismatch is proportional to the thermal strain and therefore proportional to the thermal stress.[23,24] Thirdly, A certain amount of Cu–Ti intermetallic compounds were precipitated in the joint during brazing. Intermetallic compounds generally possess high corrosion resistance, high heat resistance, especially high strength and high rigidity. Homogeneous distribution of intermetallic compounds in the matrix makes the joint appear as a metal matrix reinforced by particles. Besides, these intermetallic compounds were formed in situ, resulting in strong interfacial bonding between the matrix and the intermetallic compounds.[25] At the same time, it is also beneficial to the joint strength that a certain amount of Cu–Ti intermetallic compounds exist in the joint owing to their lower coefficient of thermal expansion (CTE), which would lower the CTE mismatch between the substrates and the brazing alloy further, accommodating the residual stresses.

The joint strength decreases to 416.9 MPa when Mo particles addition reaches 15 vol.% in the joint. Finite element analysis indicates that the introduction of the highly stiff particles into Ag–Cu–Ti actually results in an increase in residual stresses. The plastic strain of the brazing alloy to release thermal residual stresses is effectively hindered in the joint due to stiffening effect of the stiff particles.[26–30] When the content of stiff particles exceeds a certain value in the composite filler, this lowering of the plastic strain has a greater effect than any reduction of the CTE of the brazing alloy. Consequently, when the Si_3N_4/42CrMo joints were brazed by Ag–Cu–Ti + 15 vol.% Mo composite filler, an abundant presence of Cu–Ti brittle intermetallics and Mo particles in the joints limited the ability of Ag and Cu based solid solution to plastic deformation, which was detrimental to relax the thermal residual stresses during brazing, resulting in degradation of the joint strength.

4. Conclusion

The Si_3N_4 ceramic was successfully brazed to 42CrMo steel using Ag–Cu–Ti + Mo composite filler at 1173 K for 10 minutes. The following conclusions can be drawn.

(1) The reaction layer beside Si_3N_4 ceramic was composed of an inner TiN layer near the ceramic and an outer Ti_5Si_3 layer adjacent to the brazing alloy. A double reaction layer consisting of Fe_2Ti and FeTi were also formed adjacent to 42CrMo steel, with Fe_2Ti being located near the steel. The central part of the joint was composed of Ag based solid solution, Cu based solid solution, Mo particles together with some Cu–Ti intermetallic compounds.

(2) As Mo particles addition increased in the joint, the reaction layer at Si_3N_4 ceramic/braze interface was gradually thinned. However, the thickness of reaction layer at 42CrMo/braze interface varied less. Besides, more fine Cu–Ti intermetallic compounds were precipitated in the joint with the higher Mo particles content in the joint.

(3) The optimum Mo particles addition for receiving the highest bending strength (587.3 MPa) was 10 vol.%, at which the joint strength was 414.3% higher than that of 0 vol.% Mo. The appropriate thickness of reaction layer at the substrates/braze interface and suitable amount of Mo particles and Cu–Ti intermetallic compounds in the joint contributed the maximal strength.

Acknowledgments

This work was supported by the National Nature Science Foundation of China under the number of 50975064 and Harbin Special Funds for Technological Innovation Research Projects under the number of 2009RFXXG036.

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