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Brazing of Al_2O_3 to Ti–6Al–4V alloy with in situ synthesized TiB-whisker-reinforced active brazing alloy

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Abstract

65.9Cu–24.4Ti–9.7TiB_2 (wt.%) composite filler was used to join Al_2O_3 and Ti–6Al–4V alloy. 30 vol.% TiB whiskers were in situ synthesized as reinforcements in joints. Brazing temperature was 890 °C, 910 °C, 930 °C, 950 °C and 970 °C, and the holding time was 0, 5, 10, 20, and 30 min. The microstructure and mechanical properties of brazed joints were analyzed by scanning electron microscope equipped with energy dispersive spectrometer, shear test and nano-indentation test. Results show that reaction layer $Ti_4(Cu,Al)_2O$ forms at Al_2O_3/brazing alloy interface. The reaction between TiB_2 powders and Ti atoms in brazing alloy brings on in situ synthesizing TiB whiskers in $(Ti,Al)_2Cu$ and $AlCu_2Ti$ intermetallics. Formation of TiB whiskers minimizes the mismatch of thermal expansion coefficient between Al_2O_3 and brazing alloy, and makes the ductile–rigid–ductile multiple layer present in joints, which reduces residual stress of joints. The maximum shear strength of joints can reach 143.3 MPa when the brazing temperature is 930 °C, and holding time is 10 min.

Keywords: A. Joining; B. Whiskers; C. Mechanical properties; D. Al_2O_3

1. Introduction

The reliable joining of ceramics and metals will be helpful for extending their applications, particularly in aerospace and automotive [1–3]. Active brazing has been developed to be a main method for joining ceramics to metals. However, mismatch of thermal expansion coefficient (CTE) and modulus of elasticity between ceramics and brazing alloy or metals, will cause high residual stress at ceramic/brazing alloy interfaces or within ceramics [4].

To minimize the magnitude of residual stress as well as to establish adequate compatibility with two different substrates, one of the solution is the introduction of low CTE materials (SiC [5–7], Al_2O_3 [8], TiC [5,9,10]) into brazing filler metals. Lin et al. [11] incorporated (2–6 μm in diameter) tungsten particles into Ag–26.4Cu–6Ti brazing alloy, which resulted in the improvement of the shear strength of C_f/SiC composite/Ti alloy joint. Blugan et al. [6] and Galli et al. [7] used a combination, where reinforcements were used in layered structures, for ceramic-metal joining with strength increasing by more than 20%. However, this method still has its intrinsic defects: reinforcements distribute unevenly and have bad wetting ability with intermetallics, as well as reinforcement/brazing alloy interface is hard to control [12]. Liu et al. improved the mechanical strength of Si_3N_4/Si_3N_4 joint remarkably by forming Ni–Ti intermetallics during brazing [15]. It was reported that in situ synthesized reinforcements originated from brazing process have greater reinforcing effects due to their fine size, uniform distribution, relative stableness and impurity-free interfaces with matrix [13,14].

The microstructure of Al_2O_3/Ti–6Al–4V alloy joint reinforced by in situ synthesized TiB whiskers, has been studied and the components of the composite fillers have been optimized in previous work of the authors. This research was to comprehensively investigate the joining of Al_2O_3 and Ti–6Al–4V alloy with 65.9Cu–24.4Ti–9.7TiB_2 (wt.%) composite filler at different brazing parameters. It was necessary to examine the effects of brazing temperature and holding time on the joints microstructure and the joints

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shear strength, because the brazing temperature and holding time had a great influence on the interfacial reaction. Meanwhile, the microstructure and properties of TiB whiskers were analyzed and obtained.

2. Experimental procedure

Al_2O_3 was sawn by diamond discs into samples with size of 5.0 mm × 5.0 mm × 3.0 mm for interfacial characterization and 4.0 mm × 4.0 mm × 3.0 mm for shear test. Ti–6Al–4V alloy was cut into samples with size of 10.0 mm × 8.0 mm × 1.2 mm by wire electro-discharge machining. The brazed surfaces were ground by 800 grit SiC paper. Then all specimens ultrasonically cleaned in acetone for 30 min.

The composite filler was fabricated from the mixing of pure Cu, Ti (purity ≥ 99.5%) with the powder size of 50 μm and TiB_2 (purity ≥ 95%) with the powder size of 5 μm by mechanical milling. The rotation speed 300 rpm and milling time 200 min were applied, in order to obtain uniform composite filler. The composition of mixed powders was 65.9Cu–24.4Ti–9.7TiB_2 (wt.%), which can in situ synthesize 30 vol.% TiB whiskers in joint during brazing. Then this composite filler mixed uniformly with binder was applied between Al_2O_3 and Ti–6Al–4V alloy. The assembled specimen was placed in vacuum furnace with a pressure of 3.0×10^{-4} Pa. Brazing temperature employed in present study was 890 °C, 910 °C, 930 °C, 950 °C and 970 °C, and the holding time is 0, 5, 10, 20, and 30 min. The thermal cycling curve of brazing process is shown in Fig. 1.

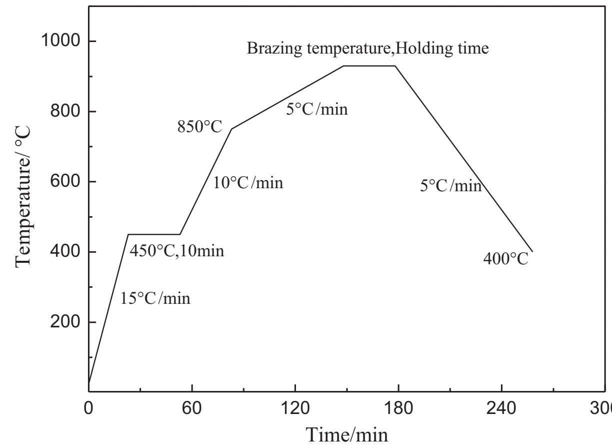

Fig. 1. The thermal cycling curve of brazing.

The microstructure and fracture surfaces of brazed joints were characterized by scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). Instron-1186 universal testing machine was used for the shear strength testing with a displacement rate of 0.5 mm/min. The shear strength of brazed joints was an average value of five measurements at each brazing parameter. The hardness and elastic modulus of each layer in joint were identified by Nano-

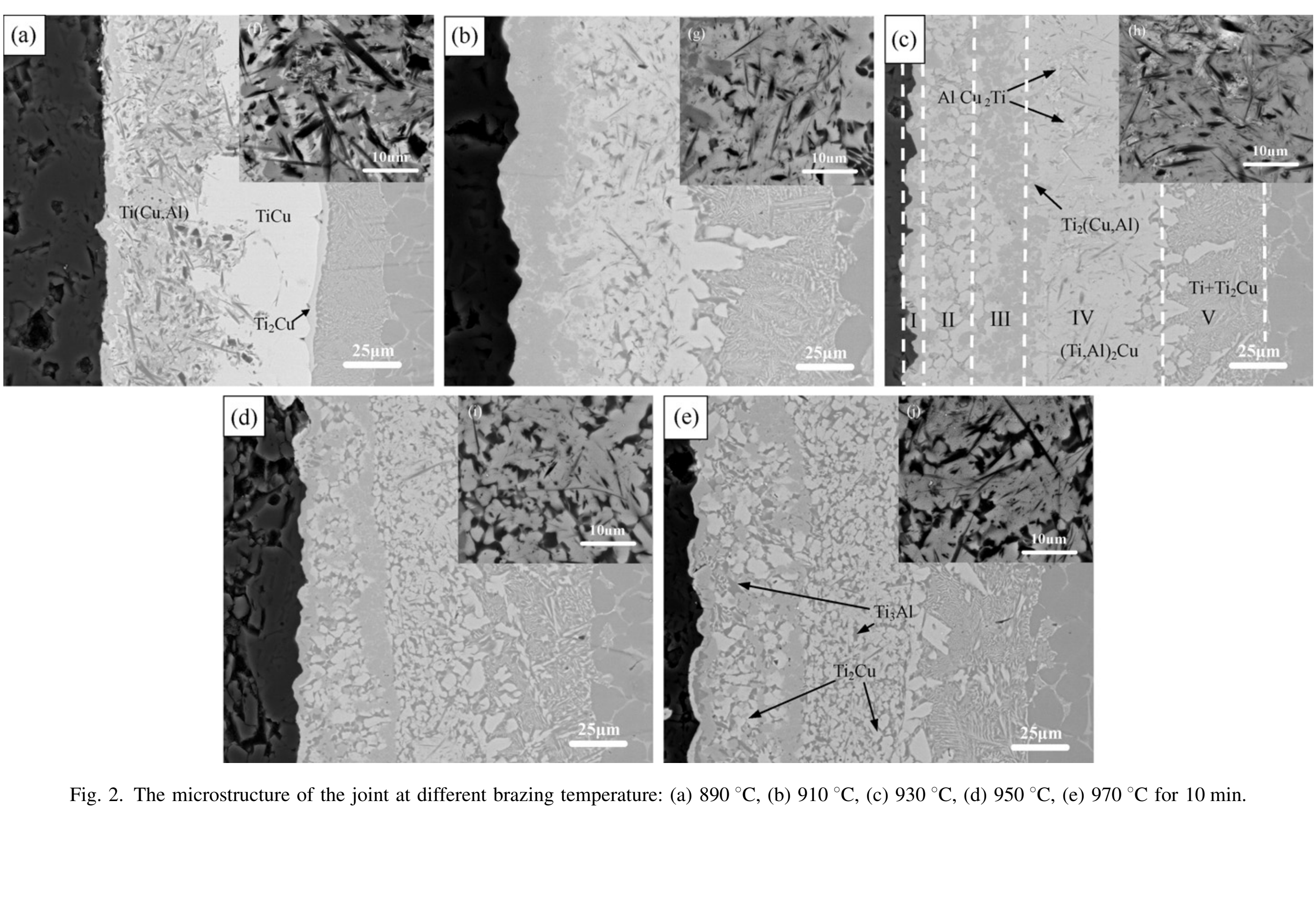

Fig. 2. The microstructure of the joint at different brazing temperature: (a) 890 °C, (b) 910 °C, (c) 930 °C, (d) 950 °C, (e) 970 °C for 10 min.

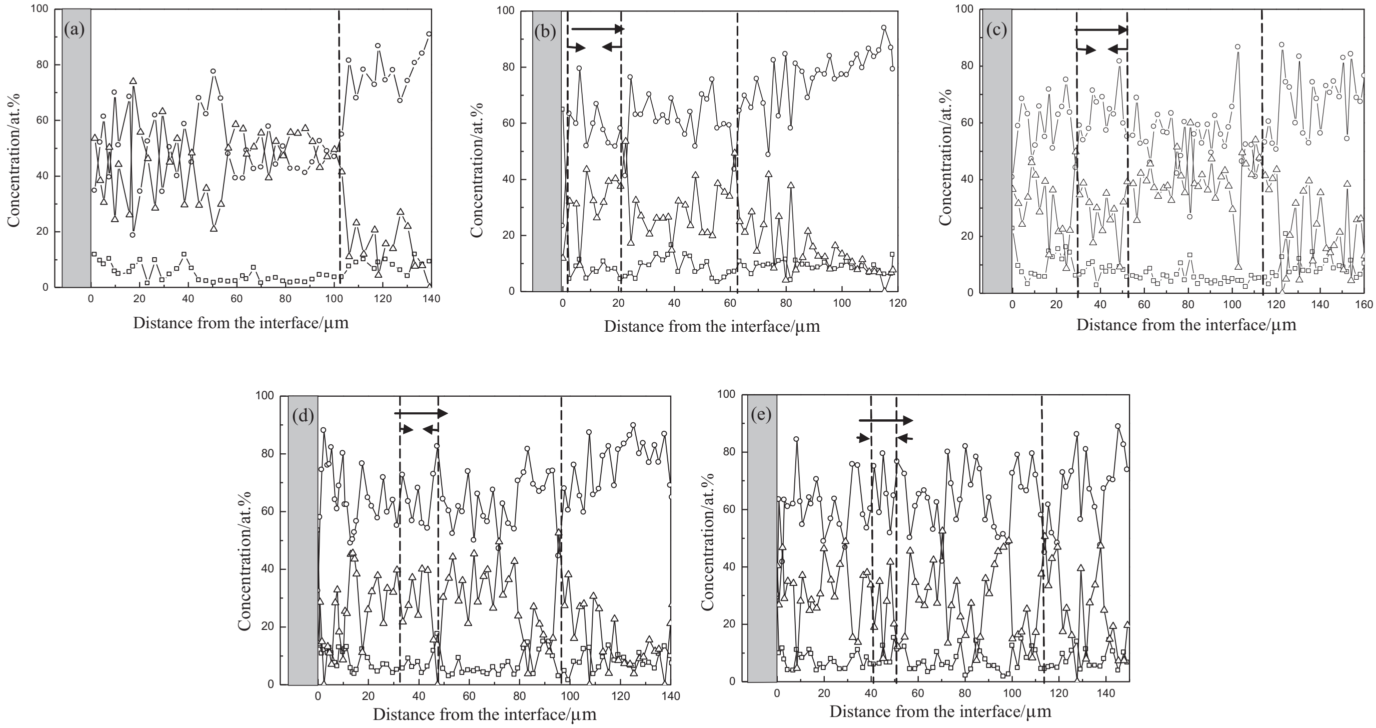

Fig. 3. Quantitative EDS elemental profiles across joint interfacial region corresponding to Fig. 3, joints were bonded at different brazing temperature of (a) 890 °C, (b) 910 °C, (c) 930 °C, (d) 950 °C, (e) 970 °C for 10 min (○, Ti; △, Cu; □, Al).

Indenter XP instrument, and the value was determined from three tests of each layer.

3. Results and discussion

3.1. Effect of brazing temperature on the microstructure of brazed joints

Fig. 2 shows the SEM backscattered electron images of Al_2O_3/Ti–6Al–4V alloy joints brazed at 890 °C, 910 °C, 930 °C, 950 °C and 970 °C with a holding time of 10 min, respectively. The line-scanning of Ti, Cu, and Al elements across the interface of corresponding joints is shown in Fig. 3. It indicates that with the increasing of brazing temperature, Ti content increases and the atoms distribute more uniformly in brazing layer.

One noteworthy phenomenon is that microstructure of the brazed joint changes significantly at 890 °C (Fig. 2(a)), compared with that of joints at other brazing temperature (Fig. 2(b)–(e)). At 890 °C, Ti_2(Cu,Al) intermetallics almost does not appear, TiB whiskers and a few remaining TiB_2 particles distribute in Ti(Cu,Al) intermetallics. Ti_2Cu layer forms between Ti(Cu,Al) and Ti + Ti_2Cu hypereutectoid organization. It can be attributed to the decreasing dissolution of Ti atoms from Ti–6Al–4V alloy. Moreover, the hypereutectoid organization is much more fine and uniform than that at other brazing temperature, because the content of Cu atoms dissolved into Ti–6Al–4V alloy drops. With the increasing of temperature, Ti_2(Cu,Al) forms near Al_2O_3, and then becomes gradually compact and away from Al_2O_3. The arrows shown in Fig. 3 indicate the migration direction of Ti_2(Cu,Al).

Fig. 4 indicates the distribution of Ti, Cu and Al atoms on joint. Al atoms dissolve into brazing layer from Al_2O_3 and Ti–6Al–4V alloy, where they mainly concentrate on Al_2O_3 and Ti–6Al–4V alloy side, as shown in Fig. 4(d). Some region also containing Al is Ti_3Al or $AlCu_2Ti$, based on the analysis of EDS. It proves that Al not only interdissolves in Cu or Ti, but also reacts with brazing filler metals. Combining with Fig. 2(d)–(e), $(Ti,Al)_2Cu$ and $AlCu_2Ti$ change to Ti_2Cu and Ti_3Al intermetallics, as well as much more Ti_3Al intermetallics form in joints, when brazing temperature is more than 950 °C. On the one hand, the content of Al atoms dissolved from Al_2O_3 or Ti–6Al–4V alloy increases when brazing temperature rise. On the other hand, Al solubilizes in Cu or Ti at high temperature, and then Al separates out from Cu or Ti and reacts with Ti forming Ti_3Al with the decreasing of temperature. Meanwhile, with the increasing of Al content in joint, TiB whiskers become much more uniform and fine as shown in Fig. 2(g)–(k). It can be conclude that Al can refine TiB whiskers during brazing. Moreover, Layer IV is the TiB whiskers basically distributing area as shown in Fig. 2, which is consistent with the distribution of Ti atoms as shown in Fig. 4(b). The forming of a large number of TiB whiskers consumes vast Ti content in Layer IV.

3.2. Effect of holding time on the microstructure of brazed joints

Fig. 5 shows the interface of Al_2O_3/Ti–6Al–4V alloy joints brazed with brazing temperature is 930 °C, holding time is 0 min, 5 min, 10 min, 20 min and 30 min, respectively. The microstructure of joints has no obvious changes with different

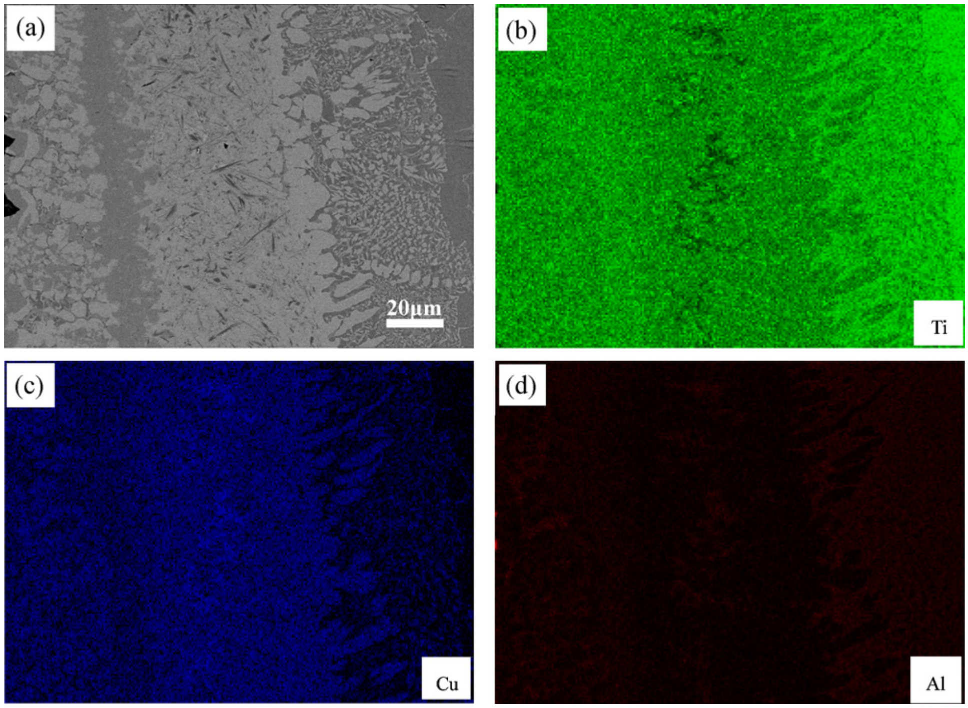

Fig. 4. Brazed joint of Al_2O_3/Ti–6Al–4V alloy: (a) microstructure of joint, distribution of element (b) Ti, (c) Cu and (d) Al on the joint.

holding time. Layer III consisted of Ti_2(Cu,Al) becomes compact in the center of joint, with the holding time increasing, because long holding time can make Ti and Al atoms diffuse toward Layer III adequately. However, the thickening and compacting of Layer III may be lead to cracks occur in joints owing to the brittleness of Ti_2(Cu,Al). Extending the holding time to 30 min, cracks clearly appear nearby Al_2O_3, and within Layer III as well (Fig. 5(e)). For different holding time, TiB whiskers morphologies are presented with high magnification figures as shown in Fig. 5(f)–(j). TiB whiskers become much

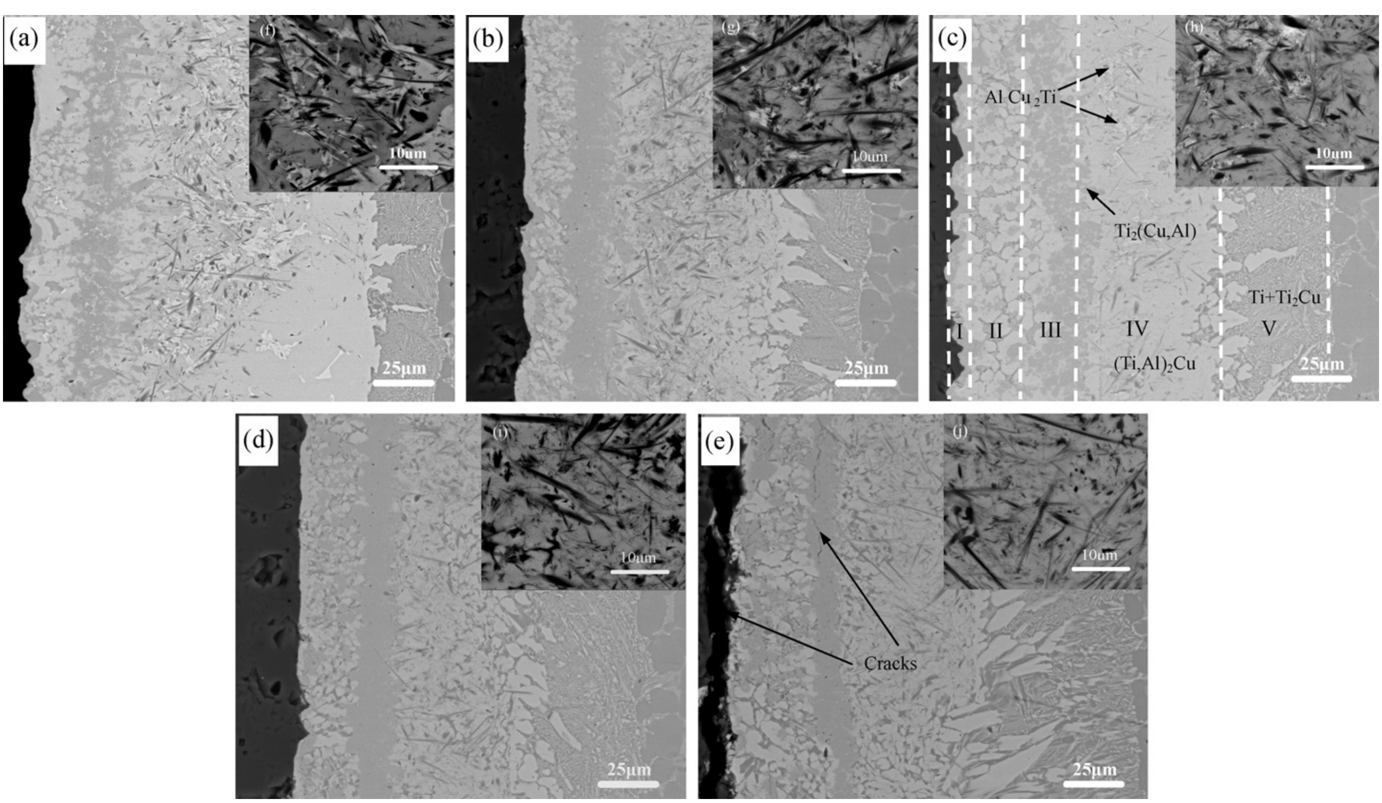

Fig. 5. The microstructure of the joints brazed at 930 °C for different holding time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min.

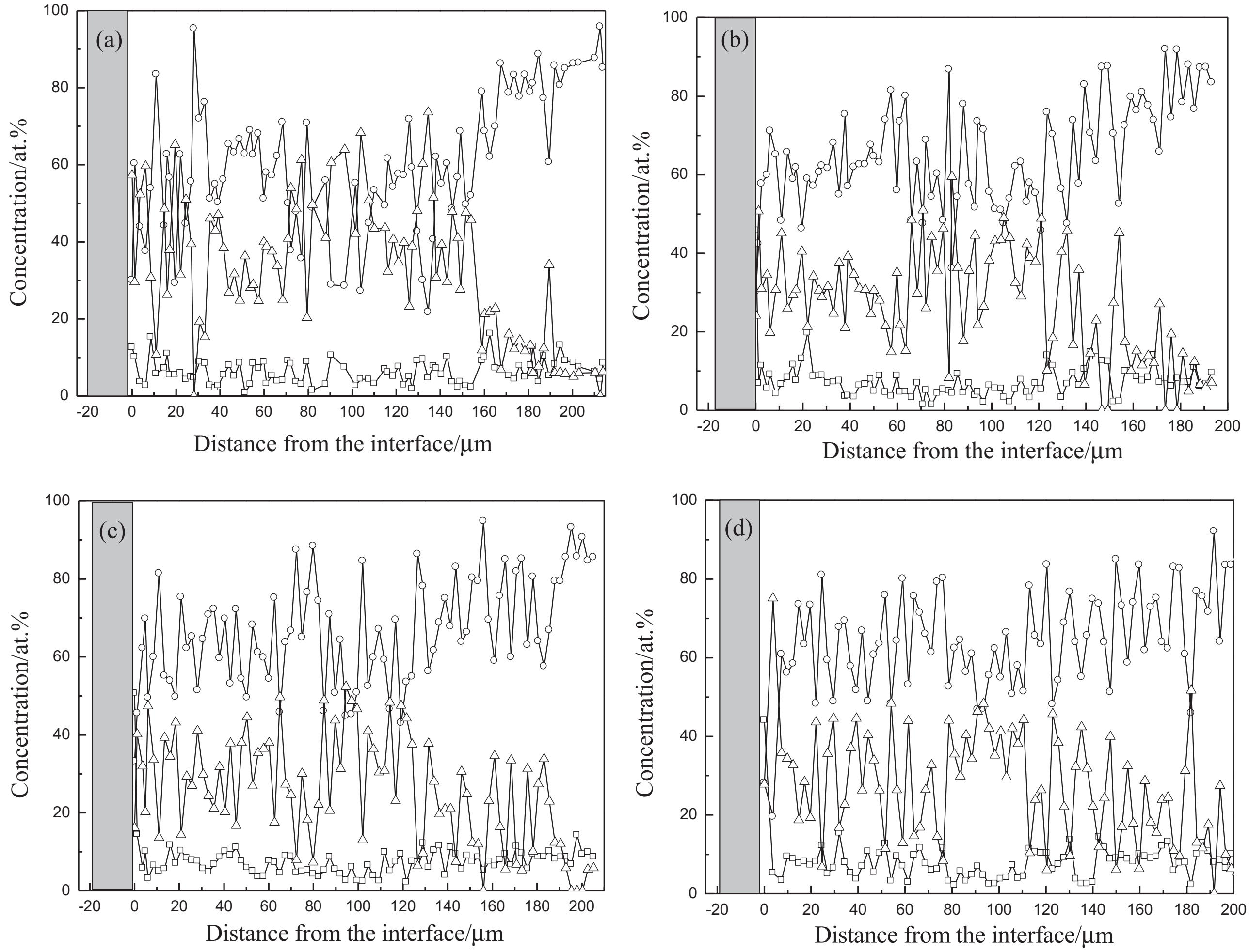

Fig. 6. Quantitative EDS elemental profiles across joint interfacial region corresponding to Fig. 3, joints were bonded at 930 °C for different holding time (a) 0 min, (b) 5 min, (c) 20 min, (d) 30 min (○, Ti; △, Cu; □, Al).

more uniform and fine with holding time increasing. It is consistent with the effect of brazing temperature on TiB whiskers morphologies, that Al can refine TiB whiskers in brazed joints. However the variation is not dramatic, compared with the effect of brazing temperature. It is believed that holding time mainly affects the diffusion of Ti elements, yet dissolution of Ti elements from Ti–6Al–4V is affected by brazing temperature. Simultaneously, Layer V thickens and Ti_2Cu content increases with the holding time extending, due to the decreasing eutectoid transformation temperature of Ti + Ti_2Cu, led by the diffusion and dissolution of Cu toward the Ti–6Al–4V alloy increasing [16].

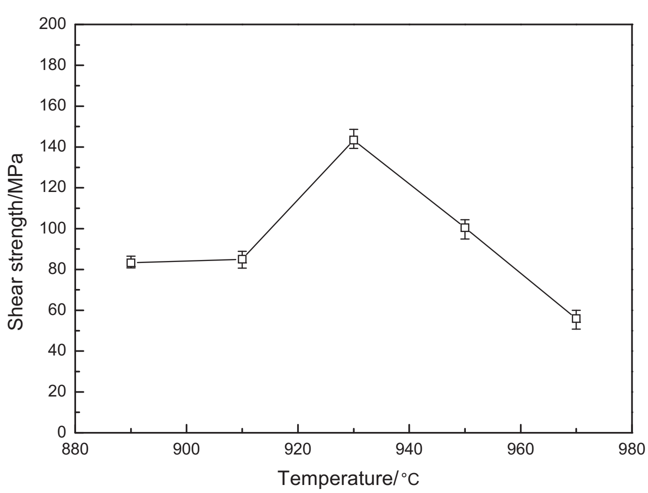

Fig. 7. Variation of shear strength of the Al_2O_3/Ti–6Al–4V alloy joints at different brazing temperature for 10 min.

In Fig. 6, the line-scanning of the Ti, Cu, and Al elements across the interfaces corresponding Fig. 5 verifies the above conclusions in the end. The content of Ti increases and the atoms distribute uniformly in joints with the holding time extending, because Ti atoms dissolve and diffuse into brazing alloy with adequate time.

3.3. Mechanical properties of Al_2O_3/Ti–6Al–4V alloy joints

Figs. 7 and 8 indicate the shear strength of joints brazed at different brazing temperature and holding time, respectively. Fig. 7 shows that joint shear strength increases when brazing temperature ranges from 890 °C to 930 °C and remarkably drops ranging from 950 °C to 970 °C, as the holding time is 10 min. Fig. 8 indicates that joint shear strength rises when holding time varies from 0 to 10 min and decreases varying

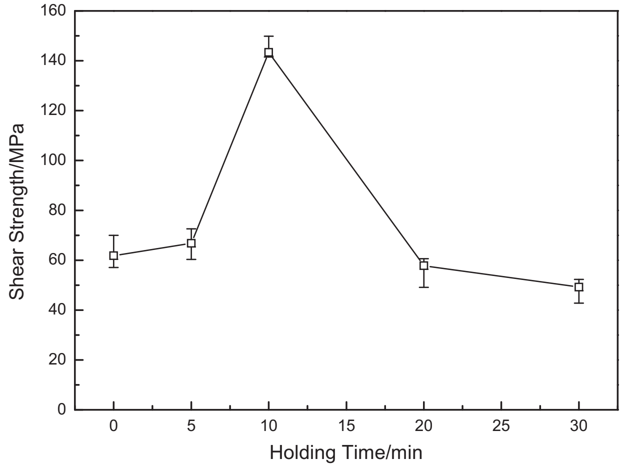

Fig. 8. Variation of shear strength of the Al_2O_3/Ti–6Al–4V alloy joints at 930 °C for different holding time.

from 15 to 30 min, as the brazing temperature is 930 °C. Finally, the maximum shear strength of joint is 143.3 MPa acquired at 930 °C for 10 min.

The joint shear strength is well dependent on the joint microstructure. Thickness of the reaction layer between Al_2O_3 and brazing alloy is an essential factor in determining the joints shear strength [17,18]. When brazing parameter is low, formation of $Ti_4(Cu,Al)_2O$ layer is insufficient to bear large shear force, and the shear strength is low. However, $Ti_4(Cu,Al)_2O$ layer is too thick, that increases joints residual stress, and fractures in Al_2O_3, as excessive brazing parameters are utilized.

Moreover, thickness and components of each layer alter joints residual stress with different brazing parameter. Among others, with the increasing of brazing temperature, joints shear strength drops by the increasing of Ti_3Al content. Similar to the effect of Ti_3Al, Layer III is compact with the increasing of $Ti_2(Cu,Al)$ when holding time extends, that eventually makes Layer III too thick to relieve the residual stress. Then residual stress will cause fracture in Al_2O_3 under a much lower stress value compared with the strength of Al_2O_3.

Generally, TiB whiskers distributed in Layer IV can alleviate the residual stress, because TiB whiskers possess the least CTE (8.6×10^{-6}/°C) among all of reaction phases in joint [19]. The most desirable CTE gradation of each layer in joint is not the simple linear decrease from one base material to the other; rather presence of alternate ductile–rigid–ductile multiple layer, which will reduce the strain energy most effectively [20–

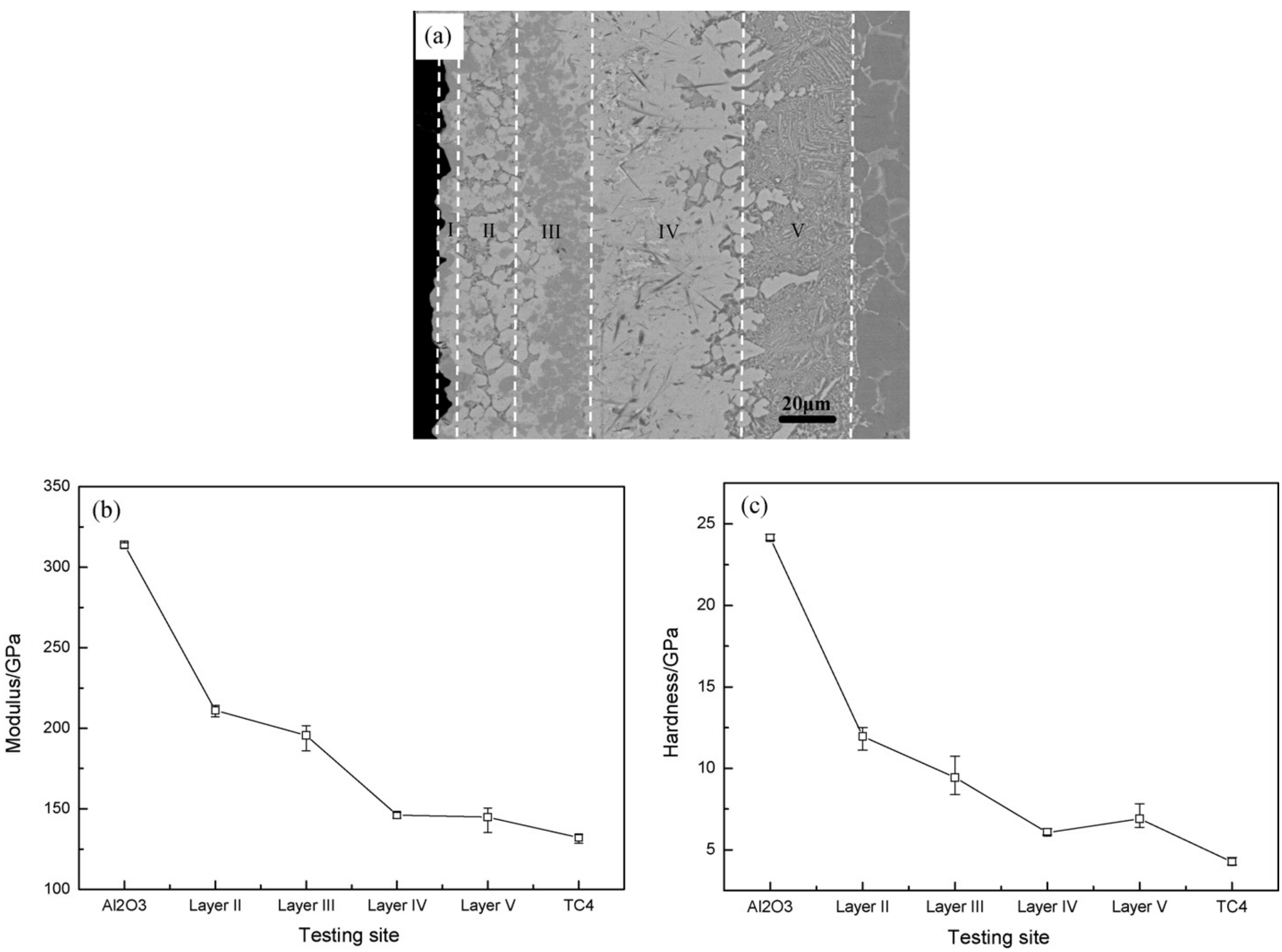

Fig. 9. (b) Elastic modulus and (c) hardness of each layer on the (a) Al_2O_3/Ti–6Al–4V alloy joint brazed at 930 °C for 10 min.

22]. With the joint brazed at 930 °C for 10 min to be example (Fig. 9), there is gradual change of hardness and elastic modulus measured by nano-indentation testing from Al_2O_3 to Ti–6Al–4V alloy, except that Layer I is too thin to accurately measure its hardness and modulus. The measurement of Layer IV only is elastic modulus Ti_2(Cu,Al) or $AlCu_2Ti$. In situ synthesized TiB whiskers distribute in Ti_2(Cu,Al) and $AlCu_2Ti$ making Layer IV become metal matrix composite liked structure. Thus, the accurate elastic modulus of Layer IV is given by following equation [23].

$$E_c = (1 - f)E_m + fE_m + fE_f \frac{4f^2sE_m + 2E_m}{E_f + 4f^2sE_m + E_m}$$

E_c, E_m and E_f is the elastic modulus of composite material, matrix and fiber, respectively. f is the volume fraction of fibers. s is the ratio of length and diameter of fiber.

Combining with the measurements and calculations of elastic modulus, Layer III (195 GPa)–Layer IV (370 GPa)–Layer V (146 GPa) satisfies the multi-layer structure (ductile–rigid–ductile). It is an important reason that residual stress is reduced and the shear strength of the joints is improved.

4. Conclusions

Al_2O_3 and Ti–6Al–4V alloy have been successfully brazed with 65.9Cu–24.4Ti–9.7TiB_2 (wt.%) composite filler. 30 vol.% TiB whiskers are in situ synthesized in joints. Brazing temperature and holding time have significant influence on the joints microstructure and joints shear strength. The maximum shear strength is 143.4 MPa when the brazing temperature is 930 °C and the holding time is 10 min. The appropriate thickness of $Ti_4(Cu,Al)_2O$ layer, as well as the proper content of Ti_3Al and Ti_2(Cu,Al) are effective to reduce the joints residual stress. TiB whiskers not only adjust the mismatch of CTE between Al_2O_3 and brazing alloy, but also make Layer IV act as metal matrix composite liked structure. The alternate ductile–rigid–ductile (Layer III–Layer IV–Layer V) multiple layer appears in joints, which can reduce the strain energy most effectively and help to alleviate the joint residual stress.

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References

[1] H. Zhao, T. Liang, B. Liu, Synthesis and properties of copper conductive adhesives modified by SiO_2 nanoparticles, Int. J. Adhes. Adhes. 27 (2007) 429–433.

[2] A.R. Boccaccini, C. Kaya, Alumina ceramics based on seeded boehmite and electrophoretic deposition, Ceram. Int. 28 (2002) 893–897.

[3] J.A. Fernie, R.A.L. Drew, K.M. Knowles, Joining of engineering ceramics, Int. Mater. Rev. 54 (2009) 283–331.

[4] H.H.K. Xu, J.B. Quinn, D.T. Smith, A.A. Giuseppetti, F.C. Eichmiller, Effects of different whiskers on the reinforcement of dental resin composites, Dent. Mater. 19 (2003) 359–367.

[5] J. Xiong, J. Huang, Z. Wang, G. Lin, H. Zhang, X. Zhao, Joining of Cf/SiC composite to Ti alloy using composite filler materials, Mater. Sci. Technol. 25 (2009) 1046–1050.

[6] G. Blugan, J. Kuebler, V. Bissig, J. Janczak-Rusch, Brazing of silicon nitride ceramic composite to steel using SiC-particle-reinforced active brazing alloy, Ceram. Int. 33 (2007) 1033–1039.

[7] M. Galli, J. Cugnoni, J. Botsis, J. Janczak-Rusch, Identification of the matrix elastoplastic properties in reinforced active brazing alloys, Composites Part A 39 (2008) 972–978.

[8] J.G. Yang, H.Y. Fang, X. Wan, Al_2O_3/Al_2O_3 joint brazed with Al_2O_3-particulate-contained composite Ag–Cu–Ti filler material, J. Mater. Sci. Technol. 21 (2005) 782–784.

[9] G.B. Lin, J.H. Huang, H. Zhang, X.K. Zhao, Joints of Cf/SiC composite to Ti-alloy with in-situ synthesized TiC_x improved brazing layers, Mater. Trans. 47 (2006) 1261–1263.

[10] G.B. Lin, J.H. Huang, Brazed joints of C_f-SiC composite to Ti alloy using Ag–Cu–Ti–(Ti + C) mixed powder as interlayer, Powder Metall. 49 (2006) 345–348.

[11] G.B. Lin, J.H. Huang, H. Zhang, H.Y. Liu, Microstructure and mechanical performance of brazed joints of Cf/SiC composite and Ti alloy using Ag–Cu–Ti–W, Sci. Technol. Weld. Joining 11 (2006) 379–383.

[12] B.S.S. Daniel, V.S.R. Murthy, G.S. Murty, Metal–ceramic composites via in-situ methods, J. Mater. Process. Technol. 68 (1997) 132–155.

[13] C.X. Cui, Y.T. Shen, F.B. Meng, S.B. Kang, Review on fabrication methods of in situ metal matrix composites, J. Mater. Sci. Technol. 16 (2000) 619–626.

[14] B. Reddy, K. Das, S. Das, A review on the synthesis of in situ aluminum based composites by thermal, mechanical and mechanical–thermal activation of chemical reactions, J. Mater. Sci. 42 (2007) 9366–9378.

[15] G.M. Liu, G.S. Zou, A.P. Wu, D.K. Zhang, Improvements of the Si_3N_4 brazed joints with intermetallics, Mater. Sci. Eng. A 415 (2006) 213–218.

[16] A. Elrefaey, W. Tillmann, Effect of brazing parameters on microstructure and mechanical properties of titanium joints, J. Mater. Process. Technol. 209 (2009) 4842–4849.

[17] Z. Chen, M.S. Cao, Q.Z. Zhao, J.S. Zou, Interfacial microstructure and strength of partial transient liquid-phase bonding of silicon nitride with Ti/Ni multi-interlayer, Mater. Sci. Eng. A 380 (2004) 394–401.

[18] J.C. Feng, D. Liu, L.X. Zhang, X.C. Lin, P. He, Effects of processing parameters on microstructure and mechanical behavior of SiO_2/Ti–6Al–4V joint brazed with AgCu/Ni interlayer, Mater. Sci. Eng. A 527 (2010) 1522–1528.

[19] M.X. Yang, T.S. Lin, P. He, Y.D. Huang, In situ synthesis of TiB reinforcements in the joints of Al_2O_3/TC4 during brazing, Mater. Sci. Eng. A 528 (2011) 3520–3525.

[20] G. Chaumat, B. Drevet, L. Vernier, Reactive brazing study of a silicon nitride to metal joining, J. Eur. Ceram. Soc. 17 (1997) 1925–1927.

[21] X.H. Wang, D. Li, L.D. Lu, X. Wang, Synthesis of substituted M- and W-type barium ferrite nanostructured powders by stearic acid gel method, J. Alloys Compd. 237 (1996) 45–48.

[22] X.L. Wang, C.R. Hubbard, S. Spooner, S.A. David, B.H. Rabin, R.L. Williamson, Mapping of the residual stress distribution in a brazed zirconia–iron joint, Mater. Sci. Eng. A 211 (1996) 45–53.

[23] Z.H. Jiang, J.S. Lian, D.Z. Yang, S.L. Dong, An analytical study of the influence of thermal residual stress on the elastic and yied behavious of short fiber-reinforced metal matrix composites, Mater. Sci. Eng. A 248 (1998) 256–275.