Microstructure evolution and bonding mechanism of Ti_2SnC - Ti6Al4V joint by using Cu pure foil interlayer

Abstract

Ti_2SnC , as one of functional ceramics with self-healing ability, was studied in welding with Ti6Al4V (TC4) through Cu interlayer under an applied mechanical pressure 10MPa in Ar atmosphere. Electron probe microanalyses indicated that the outward diffusion of Sn from Ti_2SnC played a critical role in the chemical composition of the joining interface. After 60 min, the reaction layers consisted of five zones: an interleaved zone (V) of $\beta\text{-Cu(Sn)}$ and $\alpha\text{-Cu(Sn)}$, an enriched zone (IV) of Sn and intermetallic $\text{CuTi}_{0.5}\text{Sn}_{0.5}$ phase, the intermetallic zones (III) and (II) composed of TiCu_4 and Ti_3Cu_4 , a zone (I) consisting of $\beta\text{-Ti (Cu)}$ phase. After shear tests, the corresponding fractographs indicated that the cracks mainly propagated in the Ti_2SnC matrix with an intergranular fracture mode.

Keywords: Dissimilar welding; Interfacial diffusion; Shear strength

1. Introduction

TC4-based alloys are attractive candidates for many industries due to their high resistance to corrosion, high strength-to-density ratio and biocompatibility[1]. However, due to biotoxicity of vanadium element, TC4 has limited biomedical applications. To overcome this question, Gao and Miyamoto conducted diffusion welding experiments between Ti_3SiC_2 MAX phase and TC4 in the temperature range of 1200 °C to 1400 °C. The bending strength of the joints was $100\text{MPa} \pm 20\text{MPa}$ when processed at 1350 °C for 1 h. The fracture occurred in the single layer of $\text{Ti}_5\text{Si}_3\text{C}_x$ formed at the interface. [2]

MAX phases, where M stands for early transition metal, A for A-group element, and X for either carbon or nitrogen, have aroused extensive attention on this unique nanolaminate ternary. Due to the combination of metal-like and ceramic-like properties, MAX phases materials are machinable, not susceptible to thermal shock, plastic at high temperature and exceptionally damage tolerant.[3-5]. Recently, it has also been demonstrated that MAX phases are able to restore mechanical damages by crack healing similarly to a biological healing process.[6] For example, Ti_3AlC_2 and Ti_2AlC could heal millimeter-sized cracks through the formation of intermediate solid phases resulting from the oxidation of the diffused A-element (Al).[4, 7-9] . Moreover, Li et al. showed that strong joints of Ti_3AlC_2 can be achieved at 1400 °C through the formation of Al_2O_3 layer at the whole joining interface.[10] In addition, dissimilar welding results, such as $\text{Ti}_3\text{AlC}_2/\text{TiAl}$ [11] and $\text{TiAl}/\text{Ti}_3\text{SiC}_2$ [12] systems, showed obvious microcracks originating from the thermal expansion mismatch between bonded substrates during the cooling process. Due to this drawback, the metal interlayer has been added to reduce the influence of thermal expansion mismatch in different systems, such as $\text{TiAl}/\text{Ni}/\text{Ti}_3\text{SiC}_2$ [12], $\text{Ti}_3\text{AlC}_2/\text{Zr}$ or Ni/TiAl [13] and

Ti₂AlC/Ag-Cu/Cu [14]. Furthermore, it was found that the addition of metal interlayer could significantly decrease the joining temperature [12, 13].

Compared to the other MAX phases, due to the weak bond of Sn-Ti in Ti₂SnC lattice, metallic Sn appeared in the subsurface layer of the oxide scale after the oxidation of Ti₂SnC at 500–700 °C.[15] During crack healing experiments, it has been observed that Ti₂SnC can even repair millimeter-sized cracks and heal cracks at relatively low temperature of 800 °C within only 1 hour. The flexural strength and the electrical conductivity were almost fully recovered after healing. [16] On the other hand, copper has a good compatibility with TC4 and the Cu-Sn alloy becomes liquid above 730°C when the ratio Cu:Sn is under 3:1 according to Cu-Sn phase diagram.[17] Herein, welding experiments between TC4 and Ti₂SnC through Cu interlayer should be considerable. Therefore, this experiment was conducted at 750°C with different soaking times. Meanwhile, the diffusion mechanism of different elements was investigated before the mechanical evaluation of the joints by shear test.

2. Experimental procedure

2.1 Material preparation

The chemical composition of TC4 was: Ti: Base, Al: 6.5wt%, V: 3.7wt%, Fe: 0.18wt%. Bulk Ti₂SnC was prepared by hot pressing a mixture of Ti, Sn, C powders with a molar ratio of 2:1:1 at 1250 °C under an applied pressure of 30 MPa during 60 min in vacuum. Specimens were cut from the bulk materials by electrical discharge machine with cylindrical dimensions of $\phi 12\text{ mm} \times 4\text{ mm}$ and $\phi 8\text{ mm} \times 5\text{ mm}$ for TC4 and Ti₂SnC respectively. As discussed in introduction, the addition of metal interlayer could significantly decrease the joining temperature [12, 13]. Moreover, due to the mismatch of the coefficient of thermal expansion (CTE), cracks always occurred when direct diffusion bonding TiAl intermetallic ($\text{CTE} = 7.8 \times 10^{-6}\text{K}^{-1}$) to Ti₂SnC

ceramic ($CTE = 9.0 \times 10^{-6} K^{-1}$). Herein, the interlayer pure Cu foil (99.9%, 50 μm thick) was adopted. Finally, the pelletized sandwiches of TC4/Cu/Ti₂SnC were heated in high-frequency induction device under constant parameters of 6.0 A and 225 kHz. During this stage, the heating rate was 20°C/min, the applied mechanical pressure was 5MPa under Ar atmosphere and the soaking temperature of 750°C (Fig.1(b)).

2.2 Sample characterization

Scanning electron microscopy (Zeiss Merlin Germany) and electron probe micro-analyzer (EPMA, JSM-7001f) were adopted to investigate the microstructure of the joining interface and to analyze the chemical composition of different phases. The polished interface was also analyzed by X-ray diffraction (Cu K α , Rigaku D/max-2004, Japan). Focused ion beam (FIB, Carl Zeiss Auriga Cross Beam FIB-SEM Workstation, Germany) was used to prepare specimen perpendicular to the joining interface with a Ga ion source operated at 30 kV. The cross-sectional laminae were then observed by Transmission electron microscopy (TEM) at 200 kV for detailed analysis of the microstructure through selected-area electron diffraction (SAED).

2.3 Shear test

A specific experimental setup was designed to determine the bond shear strength[18], as shown in Fig.2. The shear strength test was performed with a ZWICK-Z020 material test system at constant speed of 1mm/min. The average shear strength value of bonded joints was obtained by measuring 4 samples. Finally, the fracture surface was also observed by scanning electron microscopy.

3. Results and discussion

3.1 Interfacial microstructure of TC4/Ti₂SnC bonded joints

Fig.3 presents the interfacial microstructure of the TC4/Ti₂SnC joint using Cu interlayer bonded at 750°C during 60 minutes under 10MPa. For the convenience,

Only Ti, Cu and Sn elements were measured. In reference to Cu-Sn diagram [19] and EPMA point analysis, the uniformly interleaved bright area (81.6%Cu and 18.4%Sn in atoms) and grey area (91.6%Cu and 8.4%Sn in atoms) in layer (V) should be β -Cu(Sn) and α -Cu(Sn), respectively, as observed in the joint. Concerning about the TC4 side, the formation of layer I is resulted from the atomic migration of Cu into β -Ti titanium due to the more opened crystallography of β -Ti [20]. Layer II is composed of 54.6% Cu, 45.4% Ti in atomic fraction, supposed to be Ti_3Cu_4 . Layer III was characterized by 82.1% Cu, 17.9% Ti, supposed to be TiCu_4 . Layer IV contained 63.5% Cu, 5.4% Ti, 31.1% Sn, supposed to be $\text{CuTi}_{0.5}\text{Sn}_{0.5}$ and Sn. Closed to Ti_2SnC side, Fig.3(c) shows a distinct migration of Sn atoms (bright color) along the grain boundary. According to previous studies, destabilization of the MAX phases crystal lattice tend to release A atoms and leave vacancies at A positions, as shown in Fig.7(a) [3, 21]. Even more, the destabilization temperature of Ti_2SnC is much lower (700°C) due to the high mobility of Sn in Ti_2SnC and its low migration energy (0.66eV), as well as the presence of fluid flow above the low melting point of Sn (232°C) [9, 16].

Fig.4 (a) and (b) present the corresponding surface morphologies obtained after soaking times of 20 and 35 min, respectively. The curve corresponding to Sn declined aparted from the Ti_2SnC side towards to TC4, which clearly indicates Sn atoms diffused out of Ti_2SnC and moved towards to TC4 side. When the soaking time is increased, the EPMA line scan shows that Sn atoms accumulated at the adjacent side to TC4, as shown in the dotted circles in Fig.4 (b). In detail, the chemical composition of the different layers labeled in the insets is summarized in Table 1. Regardless of the processing time, the chemical composition of layers I, II and III did not change. As diffusion of Ti into Cu is effective to decrease the activity of Sn [22], Sn began to accumulate adjacent to Cu(Ti) layer with the increasing processing time. Finally, Sn

and Cu(Ti) layer combined into one single layer, which is enriched in Sn and in intermetallic Ti-Cu-Sn phase.

In order to analyze the elemental composition at the interface between Ti_2SnC and the Cu-Sn joint, the specimen was prepared using FIB according to the procedure illustrated in Fig.5. During ion milling, pores are formed due to sample fragility (Fig. 5(c)). After milling, in-situ back scattered electron (BSE) images show two contrasts (Fig. 5(d)). Moreover, the grain marked as 1 in Fig.5 (d) is surrounded by white dots. Fig. 6 (a) shows the corresponding TEM image of Fig.5 (d). No decomposition of Ti_2SnC is found in grain 1, but the ratio between Ti and Sn decreased from 2:1.01 to 2:0.73. Theoretical works have demonstrated that Ti_2AlC MAX phase has an Al-vacancy concentration down to the sub-stoichiometry of $\text{Ti}_2\text{Al}_{0.5}\text{C}$ and still keeps a stable structural integrity [23]. For Ti_2SnC , it is expected that Sn vacancies form a substoichiometric phase $\text{Ti}_2\text{Sn}_x\text{C}$ ($x \leq 0.5$) with a partial loss of Sn[24]. The low melting temperature (232 °C) and low migration energy of Sn (0.66 eV[9]) could trigger the deintercalation of Sn from Ti_2SnC at low temperatures. In addition, the presence of Sn around grain 1 is confirmed by selected area electron diffraction (SAED) pattern (inset in Fig. 6c). In Fig. 6 (d), Cu signal was detected along Ti_2SnC grain boundaries, which indicates that Cu atoms could infiltrate the grain boundaries of Ti_2SnC . The EDS point analysis shows that the atomic ratio between Cu and Sn is 9:1, which suggests a solid solution of Cu(Sn) is formed along Ti_2SnC grain boundaries. This result is different from the chemical interaction of Ti_3SiC_2 substrate with silver–copper (Ag–Cu) melt at 800 °C. In this report, Cu atoms could insert into the crystallographic structure of Ti_3SiC_2 MAX phase. [25]

Based on the above analysis, the reaction in $\text{TiC}_4/\text{Cu}/\text{Ti}_2\text{SnC}$ bonded joints can be described using the following reaction route (Eq.1-5).

Upon heating at 750°C, Sn atoms diffused out from the Ti₂SnC crystal lattice, leaving Sn vacancies in the Ti₂Sn_{1-x}C, as can be seen in Fig.7 (a) and (b)

Furthermore, to confirm the reaction detail between TC4 and Cu, the sandwiched TC4/Cu foil/TC4 was conducted. Fig.7(c) and (d) reveal that four layers formed in the interface between Ti and Cu, which can be summarized as:

When one side of TC4 is replaced by Ti₂SnC, Sn atoms began to diffuse out from the Ti₂SnC to Cu(Ti) (layer IV) layer at 750°C. With the accumulation of Sn in Cu(Ti) layer, the layer IV is composed of Sn and the formed intermetallic phase CuTi_{0.5}Sn_{0.5}.

3.2 Mechanical properties of the Ti₂SnC/Cu/ TC4 after diffusion bonding

The joining properties of bonded joints performed at 750°C after 60 min were evaluated via shear strength test. The shear strength of the joint was 85.7 ±10MPa. This value is higher than the previous reported one of 52.3MPa in Ti₃SiC₂/Ni/TiAl.[12] Fig.8 (a) reveals that the brittle intergranular fracture mode is dominant. Only few grains with delamination of the nano-laminar structure can be observed after shear test. This fracture behavior is different from diffusion bonding of Ti₃SiC₂/Ni/TiAl obtained at 1000 °C for 60 min, in which delamination, kink bands, and crack deflection are prevalent.[12] As reported in the literature, MAX phases with fine grain size have a much higher hardness and young's modulus than those with coarse grain size.[26, 27] In addition, the Sn traces (bright color) was found along the

grain boundaries in Fig.8 (b). This confirms that Sn has diffused out of the Ti_2SnC matrix.

4 Conclusions

Dissimilar welding of Ti_2SnC and TC4 has been successfully performed in Ar atmosphere at relative low temperature (750°C) using Cu foil as interlayer under 10MPa. The results demonstrated that Sn can diffuse out from Ti_2SnC grains and into Cu foil. Simultaneously, Cu atoms could migrate along Ti_2SnC grain boundaries. With the increasing processing time, Sn atoms have been accumulated at the side adjacent to TC4, while Ti diffused into Cu-Sn to decrease the activity of Sn. After 60 min, the reaction layers consisted of five zones: an interleaved $\beta\text{-Cu(Sn)}$ and $\alpha\text{-Cu(Sn)}$ zone (V), an enriched zone of Sn and intermetallic phase $\text{CuTi}_{0.5}\text{Sn}_{0.5}$ (IV), the intermetallic zones (III) and (II) composed of TiCu_4 and Ti_3Cu_4 , a zone of $\beta\text{-Ti (Cu)}$ phase(I). Shear test results showed that the maximum shear strength reached $85.7\pm 10\text{MPa}$. Corresponding fractographs indicated that the crack mainly propagated along the Ti_2SnC substrate adjacent to the bonding zone, accompanied with a brittle intergranular fracture mode.

Acknowledgements

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References

1. Veiga, C., J.P. Davim, and A.J.R. Loureiro, *Properties and applications of titanium alloys: A brief review*. Reviews on Advanced Materials Science, 2012. **32**(2): p. 133-148.
2. Gao, N. and Y. Miyamoto, *Joining of Ti_3SiC_2 with Ti-6Al-4V Alloy*. Journal of materials research, 2002. **17**(01): p. 52-59.
3. Barsoum, M.W. and T. El-Raghy, *The MAX phases: unique new carbide and nitride materials*. American Scientist, 2001. **89**(4): p. 336-345.
4. Yu, W., et al., *Solid solution effects in the $\text{Ti}_2\text{Al(CxNy)}$ MAX phases: Synthesis, microstructure, electronic structure and transport properties*. Acta Materialia, 2014. **80**: p. 421-434.
5. Hettinger, J., et al., *Electrical transport, thermal transport, and elastic properties of M_2AlC ($\text{M} = \text{Ti, Cr, Nb, and V}$)*. Phys Rev B, 2005. **72**(11): p. 115120.

6. Van der Zwaag, S., et al., *Self-healing behaviour in man-made engineering materials: bioinspired but taking into account their intrinsic character*. Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 2009. **367**(1894): p. 1689-1704.
7. Song, G.M., et al., *Oxidation-induced crack healing in Ti_3AlC_2 ceramics*. Scripta Materialia, 2008. **58**(1): p. 13-16.
8. Li, S., et al., *Multiple crack healing of a Ti_2AlC ceramic*. Journal of the European Ceramic Society, 2012. **32**(8): p. 1813-1820.
9. Liu, B., et al., *Theoretical investigation of A-element atom diffusion in Ti_2AC (A= Sn, Ga, Cd, In, and Pb)*. 2009.
10. Li, A., et al., *Joining of Ti–Al–C ceramics by oxidation at low oxygen partial pressure*. Journal of the European Ceramic Society, 2009. **29**(12): p. 2619-2625.
11. Cao, J., et al., *Diffusion bonding of TiAl intermetallic and Ti_3AlC_2 ceramic: Interfacial microstructure and joining properties*. Materials & Design, 2014. **56**: p. 115-121.
12. Liu, J., et al., *Evaluation on diffusion bonded joints of TiAl alloy to Ti_3SiC_2 ceramic with and without Ni interlayer: Interfacial microstructure and mechanical properties*. Materials & Design, 2014. **57**: p. 592-597.
13. Liu, J., et al., *Interfacial microstructure and joining properties of TiAl/ Ti_3AlC_2 diffusion bonded joints using Zr and Ni foils as interlayer*. Vacuum, 2014. **102**: p. 16-25.
14. Zhang, J., et al., *Effect of joining temperature and holding time on microstructure and shear strength of Ti_2AlC/Cu joints brazed using Ag-Cu filler alloy*. Materials Science and Engineering: A, 2013. **567**: p. 58-64.
15. Zhou, Y., H. Dong, and X. Wang, *High-temperature oxidation behavior of a polycrystalline Ti_2SnC ceramic*. Oxidation of metals, 2004. **61**(5-6): p. 365-377.
16. Li, S., et al., *Crack healing induced electrical and mechanical properties recovery in a Ti_2SnC ceramic*. Journal of the European Ceramic Society, 2016. **36**(1): p. 25-32.
17. Osório, W.R., et al., *The role of Cu-based intermetallics on the pitting corrosion behavior of Sn–Cu, Ti–Cu and Al–Cu alloys*. Electrochimica Acta, 2012. **77**: p. 189-197.
18. Torun, O., et al., *Diffusion bonding of AZ91 using a silver interlayer*. Materials & Design, 2008. **29**(10): p. 2043-2046.
19. Li, D., et al., *The Cu–Sn phase diagram part II: New thermodynamic assessment*. Intermetallics, 2013. **34**: p. 148-158.
20. Ghosh, M. and S. Chatterjee, *Diffusion bonded transition joints of titanium to stainless steel with improved properties*. Materials Science and Engineering: A, 2003. **358**(1): p. 152-158.
21. Cui, B., D.D. Jayaseelan, and W.E. Lee, *Microstructural evolution during high-temperature oxidation of Ti_2AlC ceramics*. Acta Materialia, 2011. **59**(10): p. 4116-4125.
22. Zhao, H., J. Cao, and J.-c. Feng, *Microstructure and mechanical properties of $Ti_6Al_4V/Cu-10Sn$ bronze diffusion-bonded joint*. Transactions of Nonferrous Metals Society of China, 2009. **19**: p. s414-s417.
23. Wang, J., et al., *A first-principles investigation of the phase stability of Ti_2AlC with Al vacancies*. Scripta Materialia, 2008. **58**(3): p. 227-230.
24. Zhang, J., et al., *Low-temperature instability of Ti_2SnC : a combined transmission electron microscopy, differential scanning calorimetry, and X-Ray diffraction investigations*. Journal of Materials Research, 2009. **24**(01): p. 39-49.
25. Dezellus, O., et al., *Experimental evidence of copper insertion in a crystallographic structure of Ti_3SiC_2 MAX phase*. Scripta Materialia, 2015. **104**: p. 17-20.
26. Li, S.B., et al., *Mechanical properties of low temperature synthesized dense and fine-grained Cr_2AlC ceramics*. Journal of the European Ceramic Society, 2011. **31**(1–2): p. 217-224.

27. Benitez, R., et al., *Room temperature stress-strain hysteresis in Ti_2AlC revisited*. Acta Materialia, 2016. **105**: p. 294-305.

Fig.1: (a) microstructure and X-ray diffraction results of the bulk Ti_2SnC , (b) schematic illustration of the experimental assembly.

Fig.2: Schematic of shear test.

Fig.3: (a) BSE image of the polished surface with EPMA line scans for the profiles of different elements obtained after 60min; (b) and (c) The insets show the magnification image of the reaction zones adjacent to TC4 and Ti_2SnC , respectively. (d) X-ray diffraction pattern of the joint.

Fig.4: SEM image of the polished surface with EPMA line scans for the profiles of different elements with different processing times, (a) 20min and (b) 35 min. The insets are magnification images of the reaction zones adjacent to TC4 side.

Fig.5: (a), (b) and (c) schematic illustration of the preparation of TEM specimen using FIB, (d) image in back scattered electron (BSE) mode.

Fig.6: (a) In situ observation of the milled zones made by FIB. (b) (c) and (d) selected area electron diffraction patterns of the zones marked as 1, 2 and 3 in Fig.6a. Insets are EDS point analysis of points 1 and 3.

Fig.7: (a) and (b) Sn diffusion from Ti_2SnC in the crystal lattice. V_{Sn} denotes Sn vacancy. (c) SEM image of the polished surface of TC4/Cu/TC4 obtained after 60mins, (d) the magnification image implies the reaction zone between Cu foil and TC4.

Fig.8. (a) Secondary electron image of fractured zone inside the $Ti_2SnC/Cu/TC4$ bonded joint at 750°C after 60 min under 10MPa. (b) The inset is the backscattered electron image of the enlarged area marked in (a).

Table 1. Summary of the chemical compositions of different layers as labeled in the insets with different processing times.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

Fig.8

Table 1

Labe I	Elements		Sn atoms%	Cu atoms%	Ti atoms%	Possible phases
	Time (mins)					
I			0	4.6	95.4	β -Ti(Cu)
II			0	54.6	45.4	Ti_3Cu_4
III			0	82.1	17.9	$TiCu_4$
IV	20		0	96.8	3.2	Cu(Ti)
	35		6.8	88.0	5.2	Poor Sn and Cu(Ti)
	60		31.1	63.5	5.4	Rich Sn $CuTi_{0.5}Sn_{0.5}$