Journal of Materials Processing Technology 221 (2015) 285–290

Contents lists available at ScienceDirect

Journal of Materials Processing Technology

journal homepage: www.elsevier.com/locate/jmatprotec

Interface reaction in ultrasonic vibration-assisted brazing of aluminum to graphite using Sn–Ag–Ti solder foil

Wei-yuan Yu, Sen-hui Liu*, Xin-ya Liu, Min-pen Liu, Wei-gang Shi

State Key Laboratory of Advanced Processing and Recycling of Non-ferrous Metals, Lanzhou University of Technology, Lanzhou 730050, China

ARTICLE INFO

Article history:
Received 18 November 2014
Received in revised form 30 January 2015
Accepted 19 February 2015
Available online 27 February 2015

Keywords:
Graphite
Aluminum
Interaction
Active solder
Brazing
Ultrasonic vibration

ABSTRACT

The microstructures and formation mechanism of the interface between pure aluminum and graphite were studied when performed the active brazing in atmospheric conditions using assistive ultrasonic vibration. At the C/solder interface, the active component (Ti) in the Sn5Ag5Ti active solder can reduce the surface tension on the surface of graphite through the interface reaction between Ti and C atoms, which is the dominant driving force during wetting process on the surface of graphite; at the Al/solder interface, Ag and Al atoms can form a type of substitutional solid solution due to occupy the positions of diffused Al atoms and affect the diffusion path between Al and Ti atoms under the brazing temperature, which can reduce the surface tension, lowering the energy of whole system and improving the wetting behavior of the liquid solder on the aluminum surface. The application of ultrasonic vibration can remove the surface oxidation films of the base metals and molten solders; hence, ultrasonic vibration can enhance the wettability of liquid solder on the surface of the base metals and accelerate the element diffusion rates of interfacial reactions.

1. Introduction

The main challenges in brazing carbon materials to metal lie in their metallurgical incompatibility and the mismatch of their physical properties. Graphite has a covalently bonded structure with extreme physical and chemical stability. This makes it very difficult for metallic solders, which contain metallic bonds, to wet graphite surfaces. Because of the large difference in the thermal expansion coefficients and the melting point of metallic materials compared to graphite, the fusion-welding method can rarely provide a high-quality welding joint. Instead, a large stress gradient and thermal residual stress will be produced in the heat-affected area of the welding joint. Active brazing is one of the most effective ways for brazing graphite with metallic solder because the active components in the filler metal can react with the graphite, forming a stable gradient layer to connect the two materials by Hao et al. (1995) and Zhong et al. (2009). However, the active components can be oxidized quickly and will, therefore, lose activity in atmospheric conditions. The oxide films of solder formed in air will block the spreading and wetting process of the liquid filler metal on the solid surface of base metals. Therefore, most active brazing operations are performed under vacuum or in an atmosphere of protective gases at a high temperature (at least 1000K or higher).

However, it is necessary to find an efficient way to address the problems of oxidization and wetting of the filler metal on the base metal where performed the active brazing in atmospheric conditions. One promising option for solving this problem is ultrasonic assisted brazing technology, which has been shown to be superior to traditional brazing technology, investigated by Saxty (1999) and Ishikawa et al. (1980). Besides, Xu et al. (2005) and Zhang et al. (2010) also believed that the ultrasonic brazing technology could effectively improve the wettability of liquid solder; therefore, it is very suitable and reliable for brazing materials with poor wettability, such as graphite, especially when the materials are dissimilar and have large differences in the melting points and expansion coefficients

In this study, ultrasonic waves were used with tin-based active brazing technology to braze graphite to aluminum in atmospheric conditions at 773 K. This low-temperature wetting activity of solders and the interface formation mechanism between solders to base metals under ultrasonic waves were studied, and the function of the ultrasonic waves in the brazing process was also analyzed.

Abbreviations: EDS, energy dispersive X-ray spectroscopy; EN, electronegativity; SEM, scanning electron microscopy; TEM, transmission electron microscopy; XRD, X-ray diffraction; IMC, intermetallic compound.

* Corresponding author at: Department of Materials Science and Engineering, Lanzhou University of Technology, State Key Laboratory of Advanced Processing and Recycling of Non-ferrous Metals in Gansu Province, Lanzhou City, Gansu Province 730050, China. Tel.: +86 0931 2976833; fax: +86 0931 2976702.
E-mail address: lshwanbb@163.com (S.-h. Liu).

http://dx.doi.org/10.1016/j.jmatprotec.2015.02.028
0924-0136/

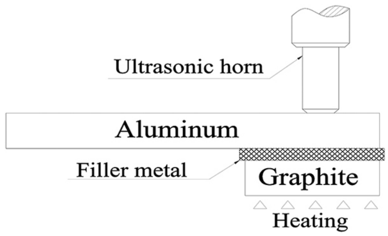

Fig. 1. Schematic diagram of the brazing process with ultrasonic waves.

The scientific basis of this brazing process will be provided to enhance the wide range of applications of brazing technology for metal/carbon materials and to provide theoretical guidance for this process.

2. Experiment materials and methods

Pure aluminum Plate 1060 and graphite were used as the base metals to be joined, the sizes of the graphite and aluminum alloy specimens were 20 mm × 20 mm × 5 mm and 100 mm × 20 mm × 2 mm, respectively. The filler metal was Sn5Ag5Ti active solder. The active filler metal was smelted in a vacuum high-frequency induction furnace using a tin bar, silver grains, and titanium foil, each with purity of 99.99%. The brazing procedure is shown in Fig. 1 in atmospheric conditions. The frequency and amplitude of the applied ultrasonic waves were 20 kHz and 0–50 μm, respectively. The brazing temperature was 773 K. Prior to brazing, the surfaces of the two base metals and the filler metal foil were polished mechanically and then cleaned thoroughly with acetone. The active solder was rolled into the shape of a foil to fill the space between the graphite and pure aluminum. First, the graphite must be heated to 773 K by resistance-heated furnace in air, and then the ultrasonic vibration is activated for 5 s. After that, the whole brazed joint will remain in the furnace as it cools to room temperature. The ultrasonic horn must be imposed on the aluminum surface of the lap joint to acquire a stable and reliable brazed joint as the porosity of graphite can absorb most of the ultrasonic energy. The interfacial microstructures of the brazed joints were imaged using scanning electron microscopy (SEM, QUANA-FEG450) and transmission electron microscopy (TEM, FEI-TECNAI G2-TF20), and the phases of the interfacial reaction products were analyzed using X-ray diffraction (XRD). Energy dispersive X-ray spectroscopy (EDS) was also used to detect the element diffusion and distribution in the transverse sections.

3. Results and discussion

3.1. Microstructures of brazing joint

The XRD results and the microscopic structure of filler metal are shown in Figs. 2 and 3, respectively. The filler metal primarily consisted of alloys in the Sn–Ag eutectic phase, including Sn_3Ti_2, Sn_3Ti_5, and Sn_5Ti_6, and the intermetallic compounds of Sn–Ti presented needle-shaped or spotty distribution on the bases of the β-Sn and Ag_3Sn eutectic structure materials. When the active solder was melted in air at the brazing temperature (773 K) in the absence of ultrasonic waves, the liquid solder was rapidly encapsulated by its own oxidation films. These oxide films will prevent the liquid solder from properly wetting the surface of the base metals. By applying ultrasonic waves, it was possible to break through the oxidation film barrier and allow the active solder to properly wet the surface of the base metals. The elemental line scan of the brazing joint is shown in Fig. 4. Mutual diffusions of the elements between the two base metals and the Sn–5Ag–5Ti active solder are evident

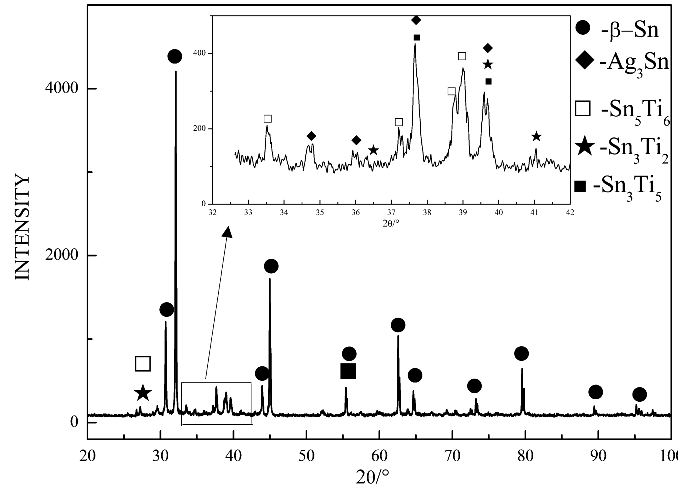

Fig. 2. The XRD pattern of the Sn–Ag–Ti ternary alloy.

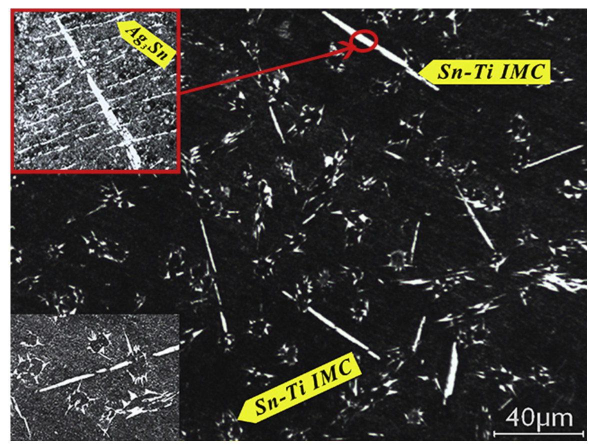

Fig. 3. Microstructure of the filler metal.

where the Ag and Al atoms are enriched at the boundary of aluminum, and where Ti and C are concentrated at the boundary of graphite. Additionally, certain carbon contents could be detected inside the aluminum and filler metals.

The elemental mapping of the graphite/solder interface is shown in Fig. 5, and the chemical compositions of the four feature points indicated in Fig. 5 are listed in Table 1. According to the EDS data, the content of the Ti element at the interface (point 1) is considerably larger than the initial content in the Sn–5Ag–5Ti alloy. This increase is due to the positive absorption of the active element (Ti) at the boundary of graphite, and the epiphase concentration of Ti is much higher than its bulk-phase concentration, which occurs because Ti has a tendency to accumulate at the graphite side. Thus, the active component that has selective positive segregation (in this case, Ti) plays a crucial role in the solid–liquid interface to form a reaction layer, which affects the wettability of the liquid solder on the graphite in this brazing process.

Table 1
EDS point analysis results of the interface at the four points indicated in Fig.5.

Elements	wt%			
	1	2	3	4
Sn	21.3	8.2	53.3	94.7
Ag	48.1	0.9	0.7	1.4
Ti	18.2	34.8	43.6	0.0
C	12.5	30.2	2.4	3.9

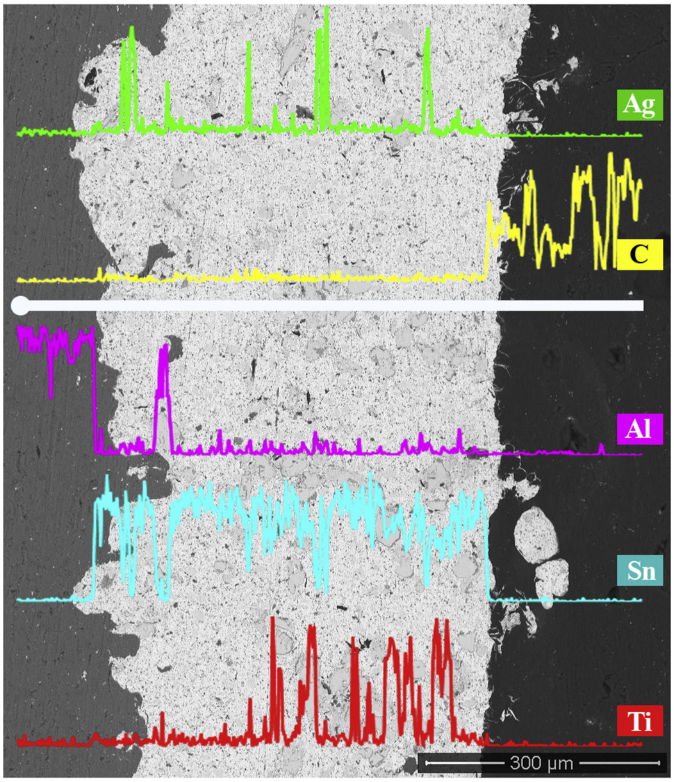

Fig. 4. The SEM micrograph of the soldered joint with overlaid elemental line scans for Ag, C, Al, Sn, and Ti.

Table 2
The EDS point analysis results of the interface at the three points indicated in Fig.6.

Elements	wt%		
	A	B	C
Sn	66.0	4.2	0.2
Ag	4.8	55.2	0.0
Ti	0.0	0.1	0.0
C	25.3	11.9	13.8
Al	3.8	28.5	86.0

The elemental mapping of the aluminum/solder interface is shown in Fig. 6, and the chemical compositions of the three feature points indicated in Fig. 6 are listed in Table 2. Along this interface, a substitutional solid solution with intensive segregation of Ag and Al atoms had been formed. Additionally, C atoms have homogeneously diffused into the aluminum body. From the XRD patterns of the brazed joint transverse section (Fig. 7), some new Al–Ti compounds are evident inside the brazed joint, and insufficient initial Sn–Ti intermetallic phases of the solder are present in the joint. The TEM bright field images in Fig. 8 show that Sn–Ag–Ti active solders with a fine grain size reacted with the graphite to generate common grains, and that C atoms were also detected in the aluminum body.

When a given component can reduce the surface tension of the system, that component will be adsorbed onto the interface in Fang and Feng (2005)'s book. The active element in the solder can impact the wetting behavior of liquid solder to the surface of base metals, which is the dominant driving force in the wetting process, according to the studies of Naidich et al. (2008) and Xian (1991). Moreover, the selective segregation of the active element (Ti) is related to the surface states of the base metals, which means that adsorption phenomenon will occur under a stable planar solid–liquid interface (such as the interface of graphite to liquid solder) and that the

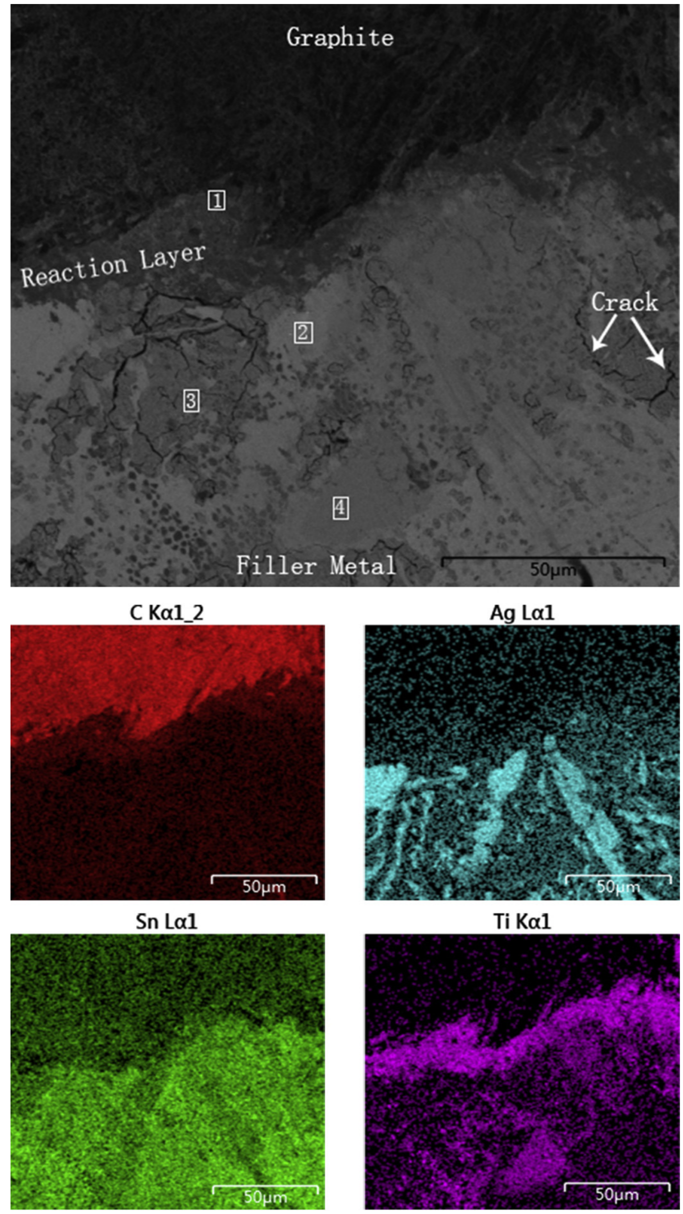

Fig. 5. The SEM image of the graphite/solder interface and corresponding C, Ag, Sn, and Ti EDS maps.

surface of solid base metal will not be significantly dissolved by the liquid solder under the brazing temperature.

However, in this work, the inactive element (Ag) occupied the positions of aluminum atoms that had been consumed by diffusions and reactions, which mean that the Ag atoms were absorbed along the aluminum interface, reducing the surface tension and lowering the energy of the system. Besides, when two different elements have a large difference in electronegativity (EN), they will have a strong chemical affinity for one another. Thus, Ag atoms can slow down the diffusion rate of Al to Ti, as the chemical affinities between Ag (EN: 1.93) and Al (EN: 1.61) and between Ag and Ti (EN: 1.54) are both strong, which evaluated in Roy Morrison (1977)'s book. Based on the similar atomic radii, Ag (0.144 nm) and Al (0.143 nm) can form a kind of substitutional solid solution, which leads to appreciable solid solution strengthening by lattice distortion. Moreover, the solid solubility of C element in Al at the brazing temperature is extremely lower, the dark dots in the brazed joint shown in Fig. 8 are formed by the diffusion of C atoms from the base metal, which

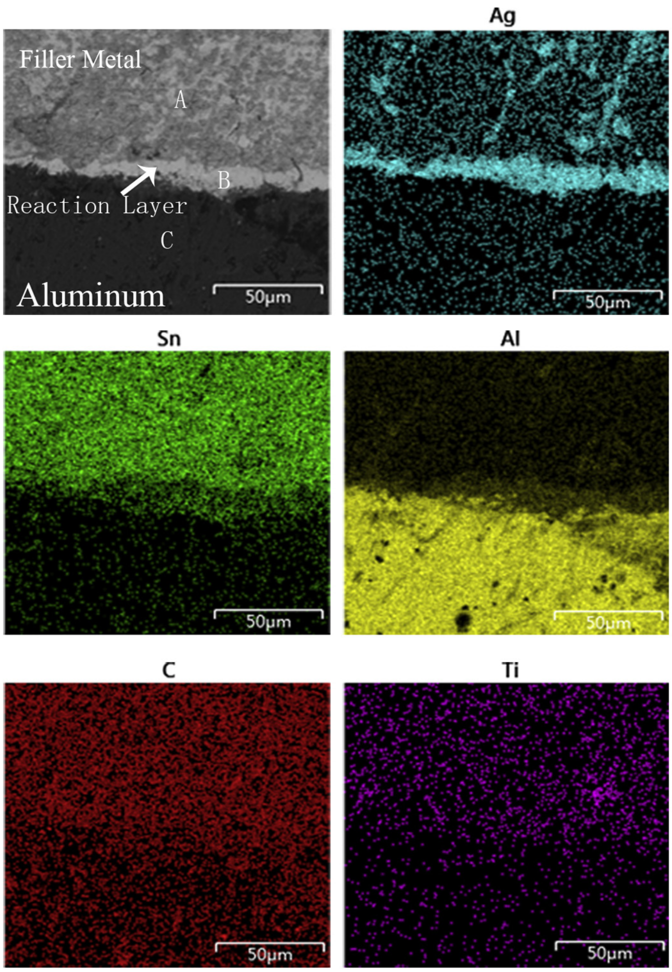

Fig. 6. The SEM image of the aluminum/solder interface and corresponding Ag, Sn, Al, C, and Ti EDS maps.

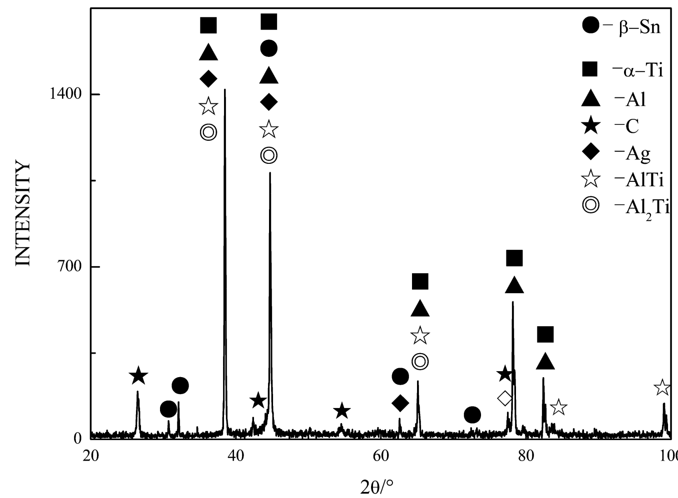

Fig. 7. The XRD patterns of the brazed joint transverse section.

precipitated with graphitic morphology once the brazed joint cooled to room temperature as described in Лякишев (2008)'s book.

During the brazing process, the Sn–Ag eutectic phases were melted as a liquid channel to accelerate the diffusion and reaction rates of other elements. The solubility of Sn in the two base metals is very low, and Sn can decrease the melting point of the Sn–Ag–Ti ternary alloy. Therefore, the activity coefficient of Ti in the solution can be increased by incremental variation of the Ag content. Moreover, a certain solubility of Ti in Sn at the brazing temperature can provide a large number of active Ti atoms to react with base metals during the brazing process that obtained in Tang and Li (2012)'s paper.

As the free energy of formation of TiC is higher than that of Sn–Ti intermetallic compounds, C atoms can bond with Ti atoms from Sn–Ti intermetallic compounds in interfacial reactions to generate TiC phases. The liquid solder acting as the solvent of the protective body contains Ti elements as the solute to ensure the low-temperature activity of Ti elements in this process. As shown in Figure 9, the dominant driving force of the uphill diffusion of Ag and Ti atoms is the transformation of the chemical potential in the alloy solution, and the differences in the chemical potential concentration drive the downhill diffusion process from the two base metals to the solder.

The addition of ultrasonic vibration energy to the brazing process can promote interfacial reactions because the alloy solutions absorb propagating ultrasonic waves and convert them to heat. Additionally, both capillary action and the fillability of the liquid solder are intensified under ultrasonic vibration, especially at the surface of graphite, which can lead to further infiltration of the solder into the base metal. In this brazing method, the active element plays a crucial role in affecting the surface tension and wettability of the liquid solder on the base metals through its significant positive absorption in the solid–liquid interface. As a result, the brazed joint produced in this study is composed of AlTi, Al_2Ti, and TiC phases, which are produced by interfacial reactions at the brazing temperature, along with other original solder structural compounds. The average shear strength of this brazed joint is 13 MPa, which is high than the graphite (Fig. 10).

3.2. Formation mechanism of brazed joint

After the brazing process, Sn_3Ti_2, Sn_3Ti_5, and Sn_5Ti_6 in the original solder disappeared from the brazed joint in whole or in part.

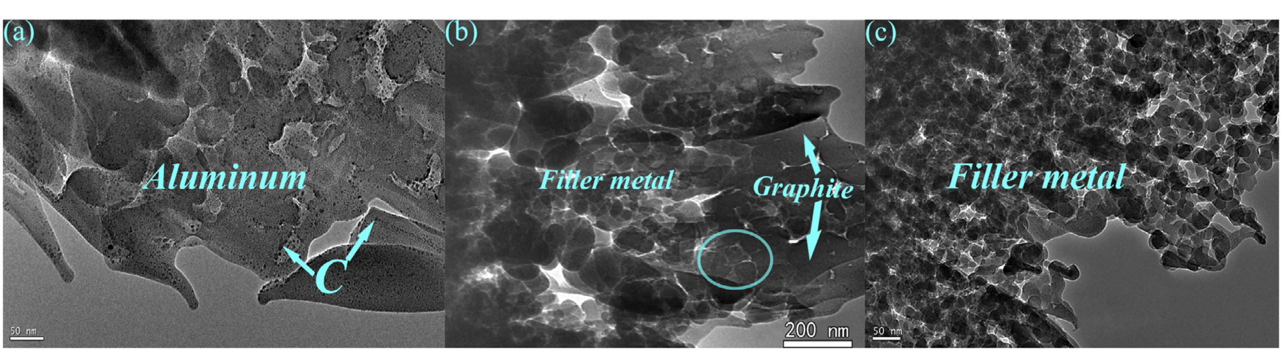

Fig. 8. The TEM bright field images of the interfacial microstructures of the soldered joint.

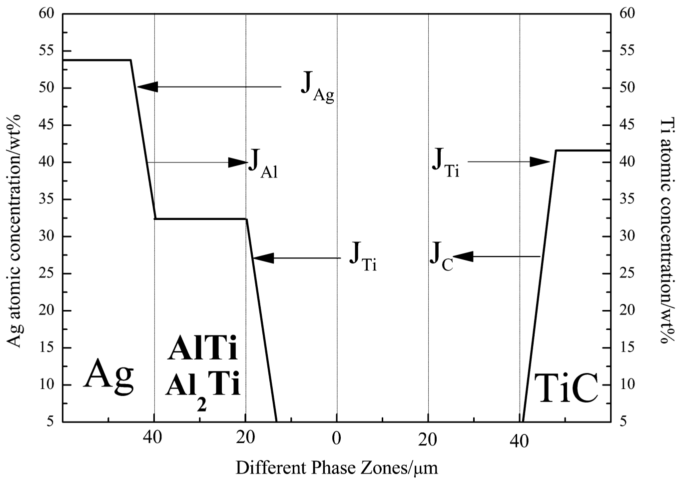

Fig. 9. Schematic diagram of the concentration and diffusion direction of atoms in the brazed joint system.

Table 3
Temperature dependence of free energy of formation of the C/Ti interface reaction.

Reaction equations	Free energy of formation, ΔG_f (J/mol)
(1)	$-183{,}142.62 + 10.0873T$
(2)	$-94{,}056.58 - 407.60691T$
(3)	$-485{,}459.34 - 510.50988T$
(4)	$-473{,}755.85 - 78058095T$

Moreover, AlTi and Al_2Ti were produced at the boundary of aluminum, while TiC was produced at the boundary of graphite. The EDS data show that C and Ti are enriched at the boundary of graphite, and Al and Ag are enriched at the boundary of aluminum. From this, we believe that the following replacement reactions, which are based on calculations using data from Dalun and Jianhua (2002), Barin and Knacke (1997) and Liu et al. (2005), may have occurred at the boundary of graphite (Table 3):

$$[\alpha\text{-Ti}] + C(s) = TiC(s) + \Delta H \quad (1)$$

$$[Sn_3Ti_2] + 2C(s) \rightarrow 2TiC(s) + 3Sn(l) \quad (2)$$

$$[Sn_3Ti_5] + 5C(s) \rightarrow 5TiC(s) + 3Sn(l) \quad (3)$$

$$[Sn_5Ti_6] + 6C(s) \rightarrow 6TiC(s) + 5Sn(l) \quad (4)$$

Similarly, based on calculations using data in Dalun and Jianhua (2002), Peng et al. (2005), Yang and Weatherly (1996) and Sujata et al. (1997), the following reactions may have occurred at the boundary of aluminum.

$$2[\alpha\text{-Ti}] + Al_3Ti = 3AlTi(l) + \Delta H \quad (5)$$

$$AlTi(s) + [Al] = Al_2Ti(l) + \Delta H \quad (6)$$

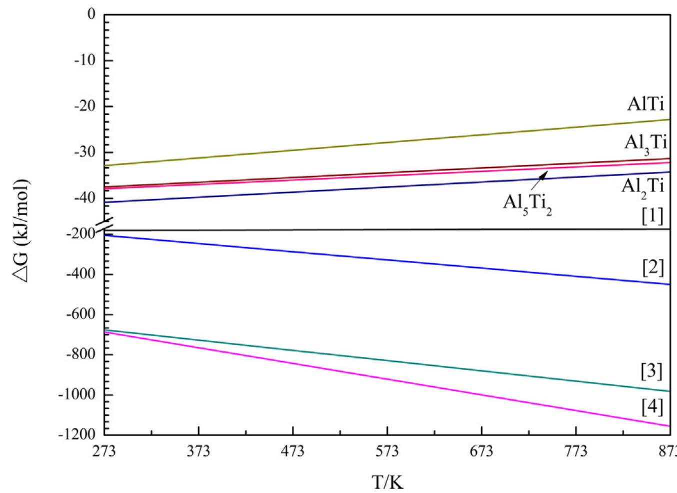

Fig. 11. Free energy of formation of Eqs. (1)–(4) and different Al–Ti compounds as a function of temperature.

Table 4
Temperature dependence of the free energy of formation of different Al–Ti compounds.

Compounds	Free energy of formation, ΔG_f (J/mol)
AlTi	$-37{,}445.1 + 16.79376T$
Al_2Ti	$-43{,}858.4 + 11.02077T$
Al_3Ti	$-40{,}349.6 + 10.36525T$
Al_5Ti_2	$-40{,}495.4 + 9.52964T$

In theory, Al_2Ti phases are initially formed at the Ti/Al interface. During this time, the Al atoms can continually diffuse through the Al/Al_2Ti zones to react with Ti atoms, which have been verified by Sun et al. (2013) and Mirjalili et al. (2013), hence the Al_2Ti and AlTi phases can nucleate along the Ti/Al interface in succession. At the same time, a large number of Ag atoms, which decomposed from the Ag_3Sn phase, diffused and occupied the positions of reacted Al atoms, decelerating the diffusion rate between Al and Ti atoms and reducing the whole system to its lowest energy during the cooling process. Though the Al_3Ti and Al_5Ti_2were not observed in the brazed joint, it is considered to be too few to be detected (Table 4 and Fig. 11).

As the temperature gradually decreases during the brazing process, the solubility of Ti in Sn also decreases, which means that some free Ti cannot form new compounds (like TiC, AlTi or Al_2Ti), but exists as solid elemental Ti in the brazed joint. The Sn–Ti alloys are hard and brittle intermetallic compounds, which can increase the melting point of the active solder and decrease its usability. In this brazing technology, the brazed joint was generated after the liquid solder had wetted the base metals, throughing mutual

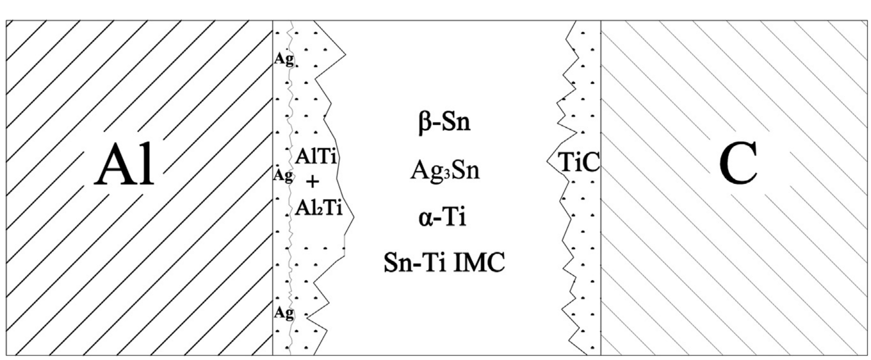

Fig. 10. Schematic diagram of the structural components of the brazed joint.

diffusion between the base metals and the active solder, producing TiC and Al–Ti intermetallic compounds as reaction products.

4. Conclusions

Applying ultrasonic waves during the brazing of aluminum to graphite using Sn–Ag–Ti active solder in air can produce a stable and reliable brazed joint. The selective positive segregation of Ti and Ag atoms to the C and Al base metals, respectively, is the dominant driving force in reducing the surface tension during the wetting process. A stable and reliable brazed joint is formed when the active element and the base metals interact favorably. Ultrasonic vibration can remove surface oxidation films on both the base metals and on the solder itself, thereby improving the wetting and spreading behavior of the liquid solder and reducing the energy required to initiate interfacial reactions.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 51465032). The authors are grateful to Jing-yuan Ma and Rong-yan Xin from Department of Materials Science and Engineering in Lanzhou University of Technology for their help with the SEM analysis and the solder manufacture.

References

Barin, I., Knacke, O., 1997. Themochemical Properties of Inorganic Substances. Springer, Supplement, Berlin.

Ye, D., Hu, J., 2002. The Manual of Practical Inorganic Thermodynamics. Metallurgical Industry Press, Beijing (in Chinese).

Fang, H., Feng, J., 2005. Interfacial Behavior of Material Brazing. Harbin Institute of Technology Press, Harbin (in Chinese).

Hao, H., Yonglan, W., Zhihao, J., Xiaotian, W., 1995. Interfacial reaction of alumina with Ag–Cu–Ti alloy. J. Mater. Sci. 30, 1233–1239.

Ishikawa, K., Kawase, H., 1980. Mechanism of cavitation erosion in ultrasonic soldering of aluminum. J. Light Met. Weld. Constr. 18 (10), 447–475.

Liu, C., Klotz, U.E., Uggowitzer, P.J., Löffler, J.F., 2005. Thermodynamic assessment of the Sn–Ti system. Monatshefte Chem. Chem. Mon. 136, 1921–1930, http://dx.doi.org/10.1007/s00706-005-0392-x.

Mirjalili, M., Soltanieh, M., Matsuura, K., Ohno, M., 2013. On the kinetics of $TiAl_3$ intermetallic layer formation in the titanium and aluminum diffusion couple. Intermetallics 32, 297–302, http://dx.doi.org/10.1016/j.intermet.2012.08.017.

Naidich, Y.V., Zhuravlev, V.S., Gab, I.I., et al., 2008. Liquid metal wettability and advanced ceramic brazing. J. Eur. Ceram. Soc. 28 (4), 717–728, http://dx.doi.org/10.1016/j.jeurceramsoc.2007.07.021.

Peng, L.M., Wang, J.H., Li, H., Zhao, J.H., He, L.H., 2005. Synthesis and microstructural characterization of Ti–Al_3Ti metal–intermetallic laminate (MIL) composites. Scr. Mater. 52, 243–248, http://dx.doi.org/10.1016/j.scriptamat. 2004.09.010.

Roy Morrison, S., 1977. The Chemical Physics of Surface. Plenum Press, New York/London.

Saxty, P., 1999. Ultrasonic soldering a farewell to flux. Weld. Met. Fabr. 67 (3), 15–174.

Sujata, M., Bhargava, S., Sangal, S., 1997. On the formation of $TiAl_3$ during reaction between solid Ti and liquid Al. J. Mater. Sci. Lett. 16, 1175–1178.

Sun, Y., Liu, M., Ge, S., Ma, F., Ma, C., 2013. Preparation of multilayered Ti–Al alloys by solid reaction. Mater. Sci. Forum 747–748, 1–8, http://dx.doi.org/10.4028/www.scientific.net/MSF.747-748.1.

Tang, Y., Li, G., 2012. Thermodynamic study of Sn–Ag–Ti active filler metals. Phys. Procedia 25, 30–35.

Xian, A., (Ph.D. dissertation) 1991. Wetting and Bending of Metal–Ceramic. Institute of Metal Research, Academia China (in Chinese).

Xu, Z.W., Yan, J.C., Wu, G.H., et al., 2005. Interface structure and strength of ultrasonic vibration liquid phase bonded joints of A1203/6061 composites. Scr. Mater. 53 (7), 835–839.

Yang, W.Y., Weatherly, G.C., 1996. A study of combustion synthesis of Ti–Al intermetallic compounds. J. Mater. Sci. 31, 3707–3713.

Zhang, Y., Yan, J.-C., Chen, X.-G., et al., 2010. Ultrasonic dissolution of brazing of 55% SiCp/A356 composites. Trans. Nonferr. Met. Soc. China 20, 746–750.

Zhong, Z., Zhou, Z., Ge, C., 2009. Brazing of doped graphite to Cu using stress relief interlayers. J. Mater. Process. Technol. 209 (5), 2662–2670, http://dx.doi.org/10.1016/j.jmatprotec.2008.06.021.

Лякишев, Н.П., 2008. The Manual of Metal Binary Phase Diagram. Chemical Industry Press, Beijing (in Chinese).