International Journal of Minerals, Metallurgy and Materials
Volume 20, Number 4, April 2013, Page 365
DOI: 10.1007/s12613-013-0736-1

Brazing 6061 aluminum alloy with Al-Si-Zn filler metals containing Sr

Wei Dai[1)], *Song-bai Xue*[1)], *Feng Ji*[1)], *Jiang Lou*[2)], *Bo Sun*[2)], *and Shui-qing Wang*[2)]

1) School of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China.

2) Zhejiang Xinrui Welding Material Co., Ltd, Shaoxing 312000, China

(Received: 24 June 2012; revised: 19 July 2012; accepted: 9 August 2012)

Abstract: Al-6.5Si-42Zn and Al-6.5Si-42Zn-0.09Sr filler metals were used for brazing 6061 aluminum alloy. Air cooling and water cooling were applied after brazing. Si phase morphologies in the brazing alloy and the brazed joints were investigated. It was found that zinc in the Al-Si filler metals could reduce the formation of eutectic Al-Si phase and lower the brazing temperature at about 520°C. Adding 0.09wt% Sr element into the Al-6.5Si-42Zn alloy caused α-Al phase refinement and transformed acicular Si phase into the finely fiber-like. After water cooling, Zn element dissolved into the Al-Si eutectic area, and η-Zn phase disappeared in the brazed joints. Tensile strength testing results showed that the Sr-modified filler metal could enhance the strength of the brazed joints by 13% than Al-12Si, while water-cooling further improved the strength at 144 MPa.

Keywords: aluminum alloys; brazing; joints; filler metals; cooling; strontium

1. Introduction

Due to cost and safety reasons, brazing is widely used to join 6061 Al alloy in the automotive industry. However, the brazing of 6061 aluminum is still a great challenge because of the relatively low melting temperature of the base alloy as compared to the commonly used Al-12Si brazing metals. To obtain a high-quality 6061 aluminum brazing joint, several efforts have been done by researchers, and an important way is to lower the brazing temperature. Some authors have tried to add a third element, such as Cu, Zn, Sn, and Ag, into the Al-Si binary system, and a series of Al-Si-Cu filler metals were developed [1-6]. The Al-Si-Cu filler metal plays an important role in the brazing of aluminum alloys, but copper element in the filler metal would form Al-Cu intermetallic compounds, which greatly deteriorate the ductility of the brazing alloy as well as the brazed joints [7]. Meanwhile, Ge was also introduced to lower the melting point of fillers [8-9]. Chang *et al.* [10] used the Ge-containing filler metal for 6061 Al and Ti-6Al-4V brazing in a vacuum furnace at 530°C, but the application was confined because of expensive Ge price.

Meanwhile, phase morphologies greatly affect the properties of the welding joints. It is reported that adding a small amount of rare earth elements could refine the second crystalline phases, such as Mg_2Si and $CuAl_2$, and reduce the brittleness of the 6061 Al brazing joint [11]. In this study, a novel Al-Si-Zn-Sr alloy was introduced for 6061 Al brazing, and the conventional Al-Si alloy was also used for comparison. Two different cooling conditions (air cooling and water cooling) were used to obtain different cooling rates; the microstructures and properties of the brazed joints were investigated as well as the fractography of the joints.

2. Experimental

The composition of the filler metals and different cooling methods used in this study are list in Table 1. The preparation of the Al-Si-Zn filler metal was conducted in a crucible electrical resistance furnace at (750 ± 10)°C, Sr was added by a Al-10Sr master alloy, and then, the melting filler metals were poured into a steel mould. The base metal was wrought aluminum alloy 6061-T6 plates with dimensions of 60 mm × 25 mm × 3 mm in Fig. 1; the chemical composition was Al-0.6Si-1.1Mg-0.25Cu (wt%). Differential thermal analysis was used to determine the melting temperature of the filler metals, which were heated from room temperature to 600°C under argon atmosphere at a heating rate of 10°/min. Prior to brazing, the spec-

Corresponding author: Song-bai Xue E-mail: xuesb@nuaa.edu.cn

imens and the filler metal were degreased in acetone and ground by SiC paper. Magnesium in 6061Al will diffuse out, forming magnesium oxide, which is very stable and difficult to be removed during brazing. Therefore, a modified aluminum flux that includes some cesium element was applied for the purpose of oxide removal [12]. The melting temperature of this flux is in the range of 460-550°C. Stable heating equipment with four torches was used in this experiment, the gas was controlled with a flow meter, and the heating time was controlled with an automatic welding dolly.

The strengths of brazed joints were tested on a SANS electromechanical universal testing system, and the average value of tested results were calculated and used. To ensure the accuracy of the results, five specimens were brazed at the same conditions with the same brazing alloy. The microstructures of the filler and joints were characterized by optical microscopy and field-emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX).

Table 1. Chemical composition of the alloys

Joint No.	Filler metal / wt%				Cooling method
	Si	Al	Zn	Sr	
1	11.8	Bal.	—	—	Air cooling
2	6.5	Bal.	42	—	Air cooling
3	6.5	Bal.	42	0.09	Air cooling
4	6.5	Bal.	42	0.09	Water cooling

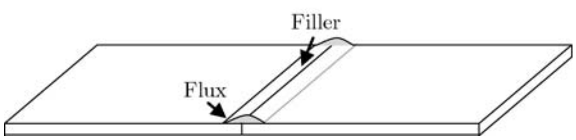

Fig. 1. Schematic illustration of the brazed joint.

3. Results and discussion

The X-ray diffraction patterns of Al-6.5Si-42Zn and Al-6.5Si-42Zn-0.09Sr filler metals are given in Fig. 2, and the results determine that both alloys contain α-Al solid solution, η-Zn, and Si phase. The XRD analysis suggests that the amount of Sr in the alloy is too small in volume as compared to the bulk phases to be detected.

Fig. 3 shows the microstructures of as-cast Al-6.5Si-42Zn and Al-6.5Si-42Zn-0.09Sr alloys. In the figure, α-Al, Al-Si eutectic, and primary Si phase could be found. η-Zn phase in the filler metal was in the form of eutectoid Al-Zn phase from the Al-Zn equilibrium diagram [13]. The addition of small amount Sr into the Al-6Si-42Zn alloy significantly changed the microstructure of the filler metal, and the Si phase transformed from acicular phases to finely fiber-like shapes after Sr doping. Sr is considered as an important element in the modification of Si phase in Al-Si cast alloys [14-17]. It was also found to be a potential effective grain refiner for magnesium alloys [18-19]. In this study, the same result was also found in the Al-Si-Zn system.

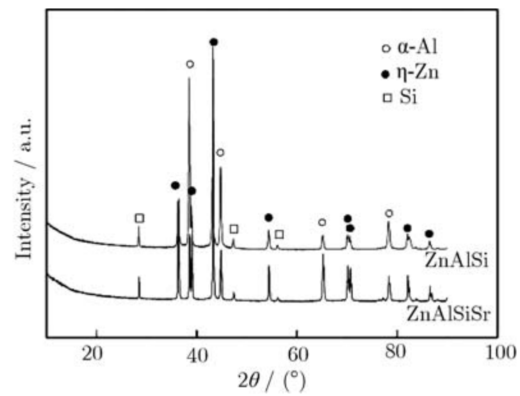

Fig. 2. XRD patterns for the filler metals.

The average hardness values of the filler metals are 131.3 HV and 142.6 HV. From microstructure observations, Sr addition refined the microstructure of the α-Al solid solution and modified the Si phase. Due to the strengthening effect of grain refinement, the hardness of the Sr modified brazing alloy is higher than that of the Al-6.5Si-42Zn alloy.

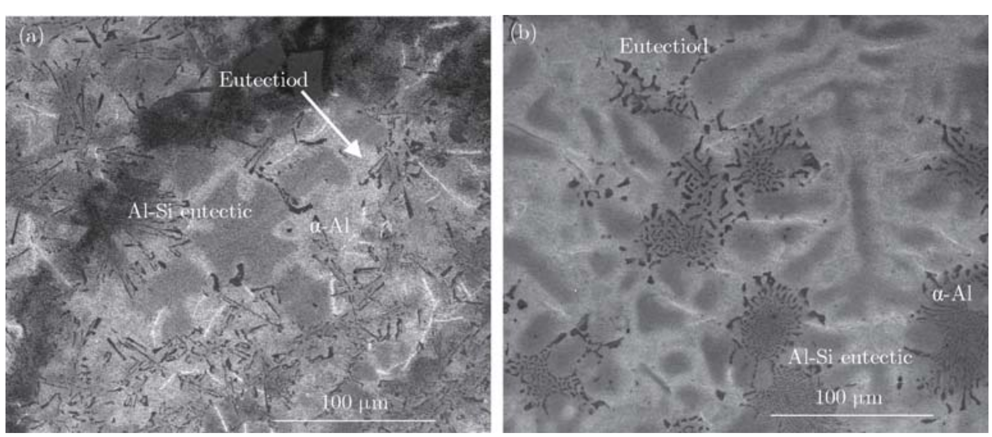

Fig. 3. Microstructures of filler metals: (a) Al-6.5Si-42Zn; (b) Al-6.5Si-42Zn-0.09Sr.

The solidus and liquidus temperatures of the filler metals, as determined by differential thermal analysis (DTA), are summarized in Table 2. The addition of 42wt% zinc in the filler metal results in about 83 and 61°C decreases in the solidus and liquidus temperatures, respectively. Meanwhile, the addition of 0.09wt% Sr does not change the melting point of the filler metals remarkably. The melting temperature of Al-Si-Zn and Al-Si-Zn-Sr filler metals is much lower than that of the Al-12Si brazing alloy and similar to the melting point of the Al-Si-20Cu alloy [3].

The microstructure of the 6061 Al brazing joints is shown in Fig. 4. The bulk eutectic Si phase, dark phase, and white phase were found in the brazing seam when using the Al-6.5Si-42Zn filler metal (Fig. 4(a)). SEM-EDX analyses determine that the dark phase consists of 65.03wt% Al, 34.12wt% Zn, and 0.85wt% Si, while the white phase consists of 26.28wt% Al and 73.72wt% Zn. From the Al-Zn binary equilibrium phase diagram, the dark phase is assumed as α-Al phase with Si element solution in it, while the white phase is Zn-Al eutectic phase. With a small amount of Sr addition, the microstructure of the brazing seam shows the same evolution as that in the filler metals, as shown in Fig. 4(b). The acicular eutectic silicon phase disappeared, and the small fiber-like and rod-like Si phases formed in the brazing seam. Meanwhile, the white phase could also be found in the brazing seam, with the composition of 19.34wt% Al and 80.66wt% Zn, and accordingly assumed to be Zn-Al eutectic phase. The dark phase in the brazing consists of 75.44wt% Al, 23.82wt% Zn, and 0.75wt% Si, which should be α-Al phase. After water-cooling, the Si phases and the α-Al dendrites in the brazed joint are much smaller due to high cooling rate. The white area (Zn-Al eutectic), which could be found in Figs. 4(a) and 4(b), disappeared after water cooling, and the eutectic Si area in the water cooled joints was much different (Fig. 4(c)). SEM-EDX analyses indicate that dark α-Al phase in the water cooled joint consists of 75.37wt% Al, 23.70wt% Zn, and 0.93wt% Si, and the composition of the eutectic Si area consists of 41.20wt% Al, 52.23wt% Zn, and 6.57wt% Si. It could be clearly seen that the composition of dark α-Al phase in all the three joints was almost the same, and the solid solubility of Si in α-Al was increased by water-cooling.

Table 2. Solidus and liquidus temperatures of Al-12Si, Al-Si-Zn and Al-Si-Zn-Sr filler metals.

Alloy	Solidus temperature / °C	Liquidus temperature / °C
Al-Si	577.0	583.0
Al-Si-Zn	494.0	521.7
Al-Si-Zn-Sr	495.4	523.5

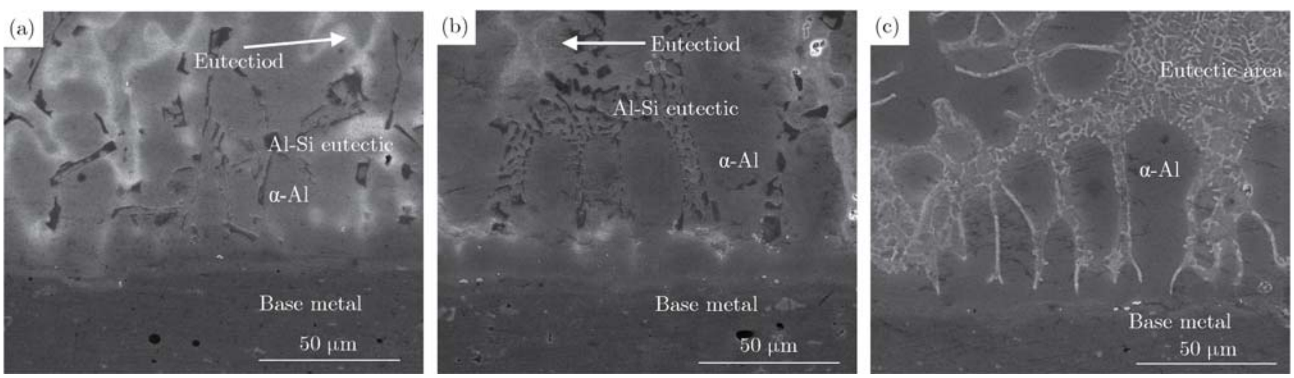

Fig. 4. Micrographs of the 6061 aluminum alloy brazing joints with (a) Al-Si-Zn filler metal, (b) Al-Si-Zn-Sr filler metal, and (c) Al-Si-Zn-Sr filler metal using water cooling.

Si reacted with Al to form Al-Si eutectic, but Si could hardly resolve in Zn according to the Zn-Si equilibrium diagram. Meanwhile, Zn-Al-Si could not form a ternary compound. Because of the large solid solubility of zinc in aluminum, the α-Al solid solutions contain zinc. At the beginning of solidification, α-Al formed first in the joint, and then, Al-Si eutectic phase and the Al-Zn eutectoid phase formed at the end of solidification. However, in the water cooled joints, due to the increased undercooling degree, the eutectic reaction and eutectoid reaction almost occurred at the same time, so the eutectoid structure and the eutectic phase formed together and could not separate in the joint. Therefore, the eutectic Si areas contain a high content of Zn. From the element line scanning results of the Al-Si-Zn-Sr water-cooled joint interface (Fig. 5), a diffusion zone can be found. The Al content decreases, while Zn element increases near the interface, therefore, Zn element dissolves into the base metal when brazing.

The XRD patterns of the brazed joints are presented in Fig. 6, showing that the brazing seam consists of α-Al, η-Zn, and Si phase, and this is similar to the results of the filler metals. The addition of Sr did not change the consistency of the brazed joint. However, after water-cooling, the peak of η-Zn phase decreased, maybe because of the higher Zn content in the α-Al phase.

Fig. 7 shows the comparison results of tensile strength

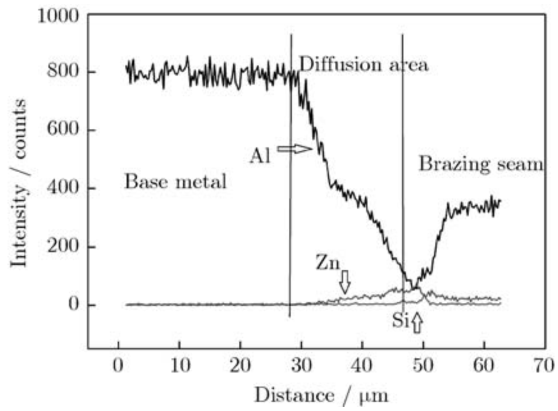

Fig. 5. Element line scanning results of the Al-Si-Zn-Sr water-cooled joint interface.

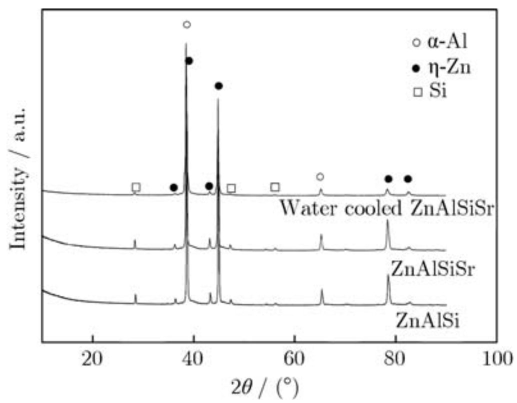

Fig. 6. XRD patterns of the brazed joints.

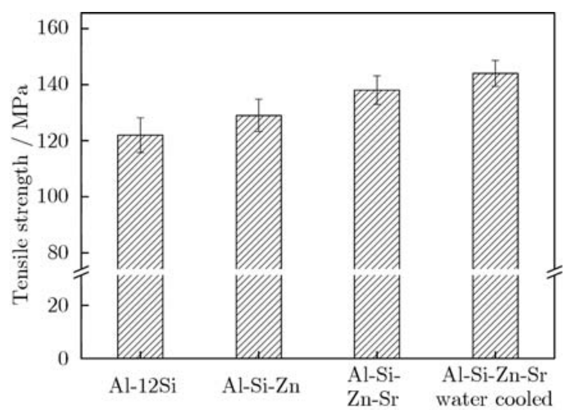

Fig. 7. Tensile strengths of 6061 aluminum alloy brazing joints.

for the brazed joints using various filler metals. The 6061 aluminum alloy brazing joints possess the average tensile strengths of about 122 MPa, 129 MPa, and 138 MPa using Al-12Si, Al-6.5Si-42Zn and Sr modified Al-6.5Si-42Zn-0.09Sr filler metals, respectively. The mechanical properties of the brazed joints were improved by the addition of Zn due to the decrease in the volume fraction of acicular eutectic Al-Si phase. The results also indicate that the refinement of Si phase by Sr is beneficial to increase the tensile strength of the 6061 Al joint. Furthermore, the element distribution of Al, Zn, and Si in the brazing seam was improved by water-cooling, which gave a minor increase of tensile strength than the air-cooled joints.

The microhardness of the joints is shown in Fig. 8. It can be clearly observed that the microhardness of the brazing seam is higher than that of the 6061 substrate (about 50 HV). The average hardness of the Al-12Si brazing seam is about 80 HV due to the diffusion of Si element in the eutectic reaction. The hardness of the Al-Si-Zn and Al-Si-Zn-Sr brazing seams is similar, but the average value is above 140 HV, meanwhile, the transition area (diffusion area) near the interface between base metal and brazing seam can be found in the microhardness distribution. After water-cooled, the microhardness of the base metal increases to 80 HV, and the hardness of the brazing seam is also improved.

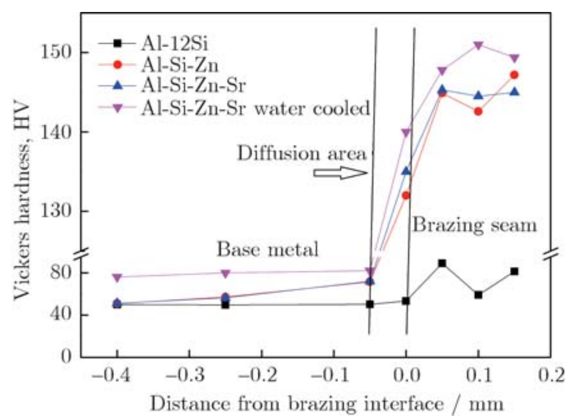

Fig. 8. Microhardness distributions of the 6061 aluminum alloy joints.

Typical fracture morphologies of the 6061 Al brazed joints are shown in Fig. 9. It is clear that the fracture morphologies significantly change with different brazing materials and different cooling rates. The fracture of Al-12Si joint belongs to brittle fracture, and the typical eutectic laminar structure can be observed, as shown in Fig. 9(a). Some ductile dimples are found in Fig. 9(b), and the Zn addition changes the fracture status of the joints. However, due to thermal expansion coefficient differences between Si and the base (α-Al, η-Zn), cracks were found in the fracture. Fine ductile dimples could be found from the fracture of the Al-Si-Zn-Sr brazing joint, and cracks disappeared. The ductile dimples were much deeper and smaller in the water-cooled brazed joint fracture. Si phases in the brazed joints were modified by Sr addition and high cooling rate; therefore, the brazed joints changed from brittle fracture to ductile fracture. It is concluded that the formation of acicular Si phases would be the crack source of the brazed joints and microstructure refinement by Sr addition and water-cooling could improve the properties of the brazed joints.

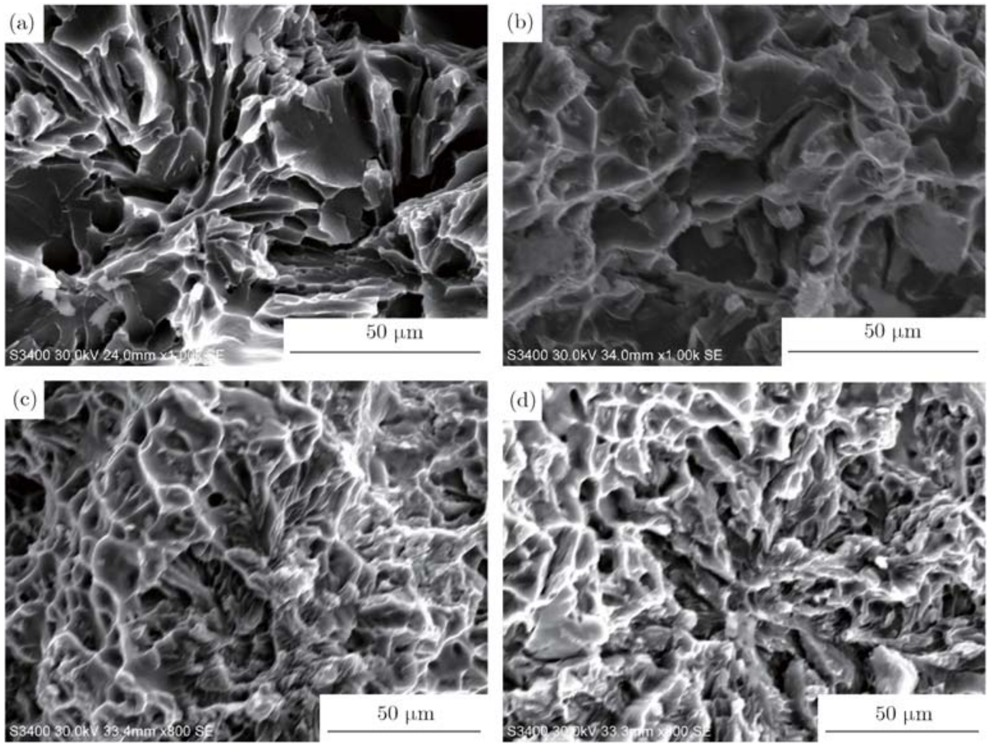

Fig. 9. Fractographs of 6061 aluminum alloy joints brazed with (a) Al-12Si filler metal, (b) Al-Si-Zn filler metal, (c) Al-Si-Zn-Sr filler metal, and (d) Al-Si-Zn-Sr filler metal under water cooling.

4. Conclusions

The brazing of 6061 aluminum alloy was achieved using the developed Al-6.5Si-42Zn low-melting-point filler metals. The addition of zinc resulted in a decrease of the melting point to about 520°C. By further adding 0.09wt% Sr element, the Si morphologies changed from acicular to fiber-like phase, but trace amount of Sr element had little effect on the melting temperature. By doping the refinement element Sr, the Si morphologies in the brazed joints could be modified. Meanwhile, the microstructures could also be improved by water-cooling. The tensile strengths of the Al-12Si joints and the Al-6Si-42Zn joints are 122 MPa and 129 MPa, respectively, while about 138 MPa for the Sr modified brazed joint. By water-cooling, η-Zn phase disappeared in the brazing seam, and the strength could be achieved at about 144 MPa. Typical fracture morphology indicated that fine Si particles in the brazing seam significantly improved the mechanical properties of the joints.

Acknowledgements

The project is financially supported by the Foundation of Scientist and Technician Serving the Enterprise, the Ministry of Science and Technology of China (No. 2009GJC20040). The authors specially thank to Takeshi Okamura from Daishin Industrial Co., Ltd for the assistance in providing experimental facilities.

References

[1] D.M. Jacobson, G. Humpston, and S.P.S. Sangha, A new low-melting-point aluminum braze, *Weld. J.*, 75(1996), p. 243.

[2] Y.W. Shi, Y. Yu, Y.P. Li, Z.D. Xia, Y.P. Lei, X.Y. Li, and F. Guo, Study on the Microstructure and wettability of an Al-Cu-Si braze containing small amounts of rare earth erbium, *J. Mater. Eng. Perform.*, 18(2008), No. 3, p. 278.

[3] S.Y. Chang, L.C. Tsao, T.Y. Li, and T.H. Chuang, Joining 6061 aluminum alloy with Al-Si-Cu filler metals, *J. Alloys Compd.*, 488(2009), No. 1, p. 174.

[4] L.C. Tsao, M.J. Chiang, W.H. Lin, M.D. Cheng, and T.H. Chuang, Effects of zinc additions on the microstructure and melting temperatures of Al-Si-Cu filler metals, *Mater. Charact.*, 48(2002), No. 4, p. 341.

[5] C.Y. Li, X.T. Wang, and W.X. Yuan, Properties of Ag-Au-Ge medium temperature solder. *J. Univ. Sci. Technol. Beijing*, 30(2008), No. 12, p. 1402.

[6] Z. Wang, Y. Lu, P. Lin, and S. Jian, Effects of Cu, Si, Ni and rare earth elements on melting temperature and properties of Al-Si filler metals, *China Weld.*, 18(2009), No. 4, p. 43.

[7] C.J. Hanga, C.Q. Wang, M. Mayer, Y.H. Tian, Y. Zhou, and H.H. Wang, Growth behavior of Cu/Al intermetallic compounds and cracks in copper ball bonds during isothermal aging, *Microelectron. Reliab.*, 48(2008), No. 3, p. 416.

[8] T. Kayamoto, J.H. Kim, S. Saito, and T. Onzawa, Brazing of Al-Mg alloy and Al-Mg-Si alloy with Al-Ge filler metal, *Q. J. Jpn. Weld. Soc.,* 12(1994), No. 4, p. 495.

[9] W.C. Moshier, J.S. Ahearn, and D.C. Cooke, Interaction of Al-Si, Al-Ge, and Zn-Al eutectic alloys with SiC/Al discontinuously reinforced metal matrix composites, *J. Mater. Sci.*, 22(1987), No. 1, p. 115.

[10] S.Y. Chang, L.C. Tsao, Y.H. Lei, S.M. Mao, and C.H. Huang, Brazing of 6061 aluminum alloy/Ti-6Al-4V using Al-Si-Cu-Ge filler metals, *J. Mater. Process. Technol.,* 212(2012), No. 1, p. 8.

[11] S.H. Wang, H.P. Zhou, and Y.P. Kang, The influence of rare earth elements on microstructure and properties of 6061 aluminum alloy vacuum brazed joints, *J. Alloys Compd.,* 352(2003), No. 1-2, p.79.

[12] S.B. Xue, L. Zhang, Z.J. Han, and X. Huang, Reaction mechanism between oxide film on surface of Al-Li alloy and CsF-AlF_3 flux, *Trans. Nonferrous Met. Soc. China*, 18(2008), No. 1, p. 121.

[13] W. Dai, S.B. Xue, J.Y. Lou, Y.B. Lou, and S.Q. Wang, Torch brazing 3003 aluminum alloy with Zn-Al filler metal. *Trans. Nonferrous Met. Soc. China*, 22(2012), No. 1, p. 30.

[14] H.C. Liao and G.X. Sun, Mutual poisoning effect between Sr and B in Al-Si casting alloys, *Scripta Mater.*, 48(2003), No. 8, p.1035.

[15] H. Sathyapal and K.N. Prabhu, Modification of eutectic silicon in Al-Si alloys, *J. Mater. Sci.*, 43(2008), No. 9, p. 3009.

[16] W. Dai, S.B. Xue, J.Y. Lou, and S.Q. Wang, Development of Al-Si-Zn-Sr filler metals for brazing 6061 aluminum alloy, *Mater. Des.*, 42(2012), p. 395.

[17] H.R. Lashgari, M. Emamy, A. Razaghian, and A.A. Najimi, The effect of strontium on the microstructure, porosity and tensile properties of A356-10%B_4C cast composite, *Mater. Sci. Eng. A*, 517(2009), No. 1-2, p. 170.

[18] X.Q. Zeng, Y.X. Wang, W.J. Ding, A.A. Luo, and A.K. Sachdev, Effect of strontium on the microstructure, mechanical properties, and fracture behavior of AZ31 magnesium alloy, *Metall. Mater. Trans. A*, 37(2006), No. 4, p. 1333.

[19] S.F. Liu, L.Y. Liu, and L.G. Kang, Refinement role of electromagnetic stirring and strontium in AZ91 magnesium alloy, *J. Alloys Compd.*, 450(2008), No. 1-2, p.546.