

Effect of Aging Treatment on Corrosion Resistance of Al-Li Alloy Joint Welded by Electron Beam Welding

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Abstract: The post-weld heat treatment (PWHT) was carried out to Al-Li alloy joints welded by electron beam welding (EBW), and the behaviour of intergranular corrosion (IGC), exfoliation corrosion (EXCO) and electrochemical corrosion of different zones of welded joint before and after PWHT were investigated. Results show that the quantity of phase T_1 (Al_2CuLi) in grain boundary of weldment increases after solution and aging treatment, and the obvious precipitate free zone (PFZ) forms in grain boundary. The IGC does not occur in the joint in as-welded (AW) condition, while the pitting corrosion occurs in both heat-affected zone (HAZ) and base metal of welded joint. The susceptibility to IGC of joint increases after aging treatment, both the pitting corrosion and IGC occurred in HAZ, and the severe IGC appears in base metal. It has excellent EXCO resistance for both weld metal and HAZ in AW condition, while the susceptibility to EXCO is higher for base metal. The EXCO resistance can be improved in base metal after aging treatment; however the susceptibility to EXCO will increase in HAZ. Results of electrochemical corrosion measurement show that compared to the weldment after aging treatment, the self-corrosion potential of weldment is a little higher in AW condition, and its density of self-corrosion current is lower; consequently, it has the relatively better corrosion resistance.

Key words: Al-Li alloy; electron beam welding; post-weld heat treatment; microstructure; corrosion resistance

Al-Li alloys have excellent comprehensive properties, such as low density, high specific strength and specific modulus. They are widely used in many high technology fields such as aerospace and nuclear industry. As a type of aging strengthening alloy, a lot of strengthening phases such as T_1 (Al_2CuLi), δ' (Al_3Li) and θ' (Al_2Cu), will precipitate in Al-Li alloy after heat treatment. However, the potential between precipitate and base metal is different, local corrosion such as intergranular corrosion (IGC), exfoliation corrosion (EXCO), easily occur in Al-Li alloys under the condition of moisture and salt spray, and it greatly influences the security service of Al-Li alloy components^[1,2]. The corrosion resistance of Al-Li alloy mainly depends on the size, distribution and quantity, etc of precipitate in its microstructure^[3,4].

At present, many researchers have investigated the corrosion behaviour of Al-Li alloys. J. A. Moreto^[5] et al investigated the corrosion resistance of alloy AA2198-T851

by scanning vibrating electrode technique (SVET), scanning kelvin probe (SKP) and electrochemical impedance spectroscopy (EIS). H. Y. Li^[6] et al researched the EXCO behaviour of new Al-Li alloys by EIS technique, and results show that the EXCO susceptibility to Al-Li alloy by T6 heat treatment is higher than that of by T8. M. Guérin^[7] et al studied the corrosion behavior of alloy 2050 under varying conditions of exposure, and the results show that the existence of T_1 phase in alloy after aging does not aggravate the IGC susceptibility to alloy. The result of local corrosion behaviour of alloy 2195 shows that the occurrence of IGC is due to alternate anodic dissolution between phase T_1 and precipitate free zone (PFZ) along grain boundary^[8]. With the increase of aging temperature, both the IGC and EXCO susceptibility of alloy 2195 increase, while the stress corrosion cracking (SCC) susceptibility is hardly influenced^[9]. J. Goebel^[10] et al studied the relationship between microstructure and SCC behavior of alloy 2099, and they

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concluded that the phase $\delta'(Al_3Li)$ can cause pitting in alloy and play a predominant role in the initiation and propagation of SCC. Generally, the corrosion behaviour of alloy is mainly affected by the precipitation of strengthening phase in alloy, but X. Zhang^[11] et al found that the subgrain boundaries within unrecrystallized grains of alloy 2A97-T3 are preferentially attacked during immersion test. They proposed that the energy stored in grain plays a decisive role in the corrosion process. The subgrain boundaries within unrecrystallized grains have higher stored energy and high density of dislocations, which make it more susceptible to corrosion.

Recently, the new generation high strength Al-Cu-Li alloys such as 2198 and 2060, are often used as welded structure in industrial application. Compared to other fusion welding processes, electron beam welding (EBW) has many advantages such as heat concentration, large ratio of weld depth to width, narrow heat-affected zone (HAZ), small weld deformation and good protective atmosphere. It is very appropriate to weld Al-Li alloys. However, in as-welded (AW) condition, due to the dissolution of precipitation phase in weld metal, the strengthening effect decreases and the softening phenomenon occurs in welded joint. The mechanical properties of joint is not so high in AW condition; consequently, the post-weld heat treatment (PWHT), namely solution and aging treatment is necessary to welded joint after welding. The PWHT has great effect on corrosion resistance of weld zone of Al-Li alloy joints. V. Proton^[12] et al have investigated the corrosion behaviour of Al-Cu-Li alloy 2050-T3 joint by friction stirring welding (FSW) in 1 mol/L NaCl solution, and the effect of PWHT on the susceptibility to joint was analyzed. However, there is little investigation on corrosion resistance of Al-Li joint by EBW. Based on them, in the present work, the PWHT is conducted to welded joint of Al-Li alloy, and the corrosion resistance is investigated on different zones of welded joint before and after aging treatment, so the theoretical basis can be provided for Al-Li alloy joint in practical application.

1 Experiment

The base metal was Al-Cu-Li alloy plate with the thickness of 4 mm, and its chemical composition is as follows (wt%): Al-3.2Cu-1.0Li-0.5Mg-0.4Ag-0.35Zn-0.11Zr-0.5Mn. The base metal was machined into welding sample with the dimension of 200 mm×100 mm×4 mm. The LARA52 type vacuum electron beam welding machine was used, and the Al-Cu-Li alloy plate was welded along longitudinal direction with butt joint. The welded joints with good appearance were obtained. The PWHT was carried out to welded joint. The heat treatment procedure is as follows: solution treatment with heating temperature 510 °C and duration time 1 h, water quenching, subsequently, aging treatment with heating temperature 155 °C and aging time 16 h. MM6 type optical

microscope and FEI Tecnai G2 type transmission electron microscope (TEM) were used to observe the microstructure of welded joint before and after heat treatment respectively. The IGC, EXCO and electrochemical corrosion experiments were carried out to Al-Li alloy joints in AW condition, as well as PWHT, and the corrosion behaviour of joint in different zones before and after PWHT were evaluated.

The IGC was conducted according to the standard GB/T 7998-2005. The solution system was 57 g NaCl+1 L H₂O+10 mL H₂O₂, the ratio of solution volume to sample area was 15 mL/cm², experimental temperature was kept at (35±1) °C, exposure time was 6 h. The corroded sample was immersed in HNO₃ solution, and it was cleaned with distilled water, and dried. Taking its transverse section to prepare metallographic specimen, the morphology of corroded sample was observed by optical microscope.

The EXCO was carried out according to the standard GB/T 22639-2008. The solution system was 4.0 mol·L⁻¹ NaCl + 0.5 mol·L⁻¹ KNO₃ + 0.1 mol·L⁻¹ HNO₃, the ratio of solution volume to sample area was 20 mL/cm², experimental temperature was (25 ± 3) °C. Interval observation was conducted after different immersion time, and the macrograph of sample was obtained after cleaning up the corrosion production. In terms of standard GB/T 22639-2008, corrosion degree of sample was evaluated. The symbol of corrosion degree is as follows: N stands for no obvious corrosion, P stands for pitting corrosion, EA→EB→EC→ED stands for EXCO gradually becoming heavy.

Electrochemical corrosion measurement was carried out by CHI660D type workstation. Pt electrode was used as an auxiliary electrode, saturated calomel electrode (SCE) was used as a reference electrode, the exposure area of sample was 0.4 cm², and non-exposure surface of sample was enveloped by epoxy resin. The scanning rate was 10 mV/s during the measurement of polarization curve. The scanning frequency range was 0.01~20 kHz for EIS tests, the perturbation signal was sinusoid with the amplitude of 10 mV, solution system was 3.5%NaCl solution, and experimental temperature was room temperature.

2 Results and Discussion

2.1 Microstructure of joint before and after heat treatment

The property of Al-Cu-Li alloy is closely related to its microstructure. Phase T₁ is the main strengthening phase in Al-Cu-Li alloy joint, and it is prone to precipitate at crystal defects such as grain boundary, subgrain boundary and dislocations. Because phase T₁ has higher electrochemical activity, it is easy to cause IGC^[6,8]. Obviously, the microstructure of Al-Cu-Li alloy joint has great effect on its corrosion resistance; thus it is necessary to analyze the microstructure of base metal and weld zone of Al-Cu-Li alloy before and after heat treatment.

The microstructure of base metal (BM) and weld metal (WM) of Al-Cu-Li alloy joint are shown in Fig.1. The microstructure of base metal is rolled morphology, and grain presents distribution of long strip shape, as shown in Fig.1a. In AW condition, weld metal is as cast microstructure due to rapid solidification, while weld center is the mixture microstructure of equiaxed grains and dendrite, as shown in Fig.1b. The microstructure of weld metal presents equiaxed grains distributed homogeneously after aging treatment, as shown in Fig.1c.

The sub-microstructure of weld metal is further analyzed by TEM. The TEM images of weldment of Al-Cu-Li alloy joints before and after aging treatment are shown in Fig.2. It can be seen that the main strengthening phase in grain boundary of weldment before and after aging is phase T_1 . In AW condition, the phase T_1 in weldment is sparse and coarsened, as shown in Fig.2b. After aging, the quantity of phase T_1 in grain boundary of weldment obviously increases, the phase β' (Al_3Zr) particles appear, and the PFZ forms at ambient grain boundary, as shown in Fig.2c. During aging, the phase Al_3Zr particles with small size and dispersive distribution precipitate in weld metal of Al-Cu-Li alloy joint. It has the strong pinning effect to grain boundary; therefore the nucleation and growth of recrystallization grains is suppressed, which is advantageous to improve the mechanical properties of welded joint. Moreover,

the subgrain boundary has higher ability to corrosion resistance^[13].

2.2 Intergranular corrosion

Investigation on corrosion mechanism of Al-Li alloy 2195 indicates that the quantity of phase T_1 in grain boundary is much more, and the drive force provided from corrosion couple between phase T_1 and θ' or grain boundary PFZ increases^[13]. The anodic dissolution of phase T_1 will increase susceptibility to IGC. The beginning of IGC in Al-Li alloy is usually from pitting corrosion, and it primarily expands along straight direction of grain boundary^[4]. The microstructure of weld zone of Al-Cu-Li alloy will be varied during EBW and PWHT; consequently, the corrosion resistance of different zones in welded joint will be different.

The corrosion morphologies of each zone of welded joints before and after aging are shown in Fig.3. It can be seen that, no IGC phenomenon is found in weld metal before and after aging. In AW condition, the severe pitting corrosion occurs in HAZ, and the quantity of corrosion pit is much more. There exists bigger corrosion pit in base metal, and it penetrates deeply to Al-Cu-Li alloy, while the obvious feature of IGC is not found, the maximum depth of corrosion is 68.7 μm . After aging, there is pitting corrosion in HAZ, and the IGC occurs in the margin of corrosion pit. The evident morphology of

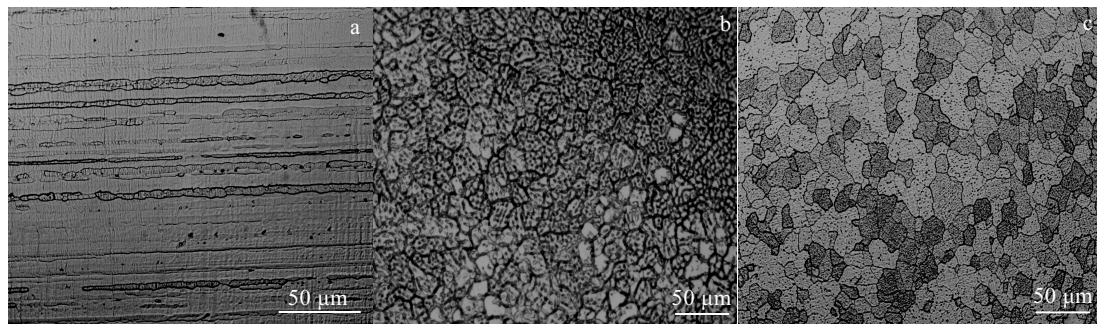


Fig.1 Microstructures of base metal and weld metal of Al-Cu-Li alloy joint: (a) base metal, (b) weld metal in AW condition, and (c) weld metal after aging treatment

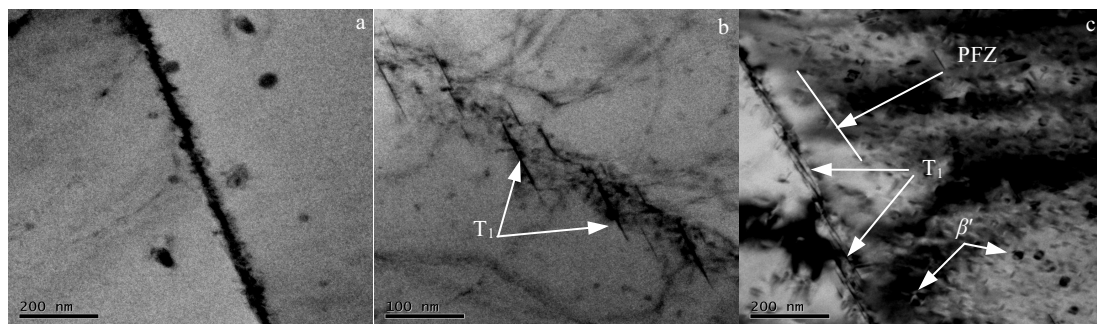


Fig.2 Microstructures of grain boundary of Al-Cu-Li alloy weldment before and after aging treatment: (a) weld metal in AW condition, (b) phase T_1 of weld metal in AW condition, and (c) weld metal after aging treatment

IGC appears and the depth of corrosion is about 50.0 μm . Moreover, the severe IGC occurs in base metal, the IGC morphology obviously presents reticulation shape, and the maximum depth of corrosion is about 111.6 μm .

During EBW, the formation of weld metal is through fusion of base metal by high temperature and solidification by rapid cooling. The strengthening phases in molten pool are completely melted during welding, the original continuous path of IGC no longer exists; consequently, the susceptibility to IGC greatly decreases, and the IGC does not occur in weld metal. However, with the dissolution of strengthening phase, alloying elements are prone to aggregate in grain boundary. The energy of grain boundary is higher than that of within grain, and it can constitute corrosion couple with ambient base metal in corrosion solution, which causes the light pitting corrosion, as shown in Fig.3a. It is also found that the effect of aging treatment on IGC in weld metal is not obvious, as shown in Fig.3b.

After aging, the trend of IGC increases both in HAZ and base metal. The IGC of Al-Cu-Li alloy is caused by anodic dissolution of precipitate or PFZ in grain boundary^[14], so the susceptibility to IGC is closely related to microstructure of grain boundary. The main precipitate is phase T_1 in Al-Cu-Li alloy joint. During aging, phase T_1 has the priority to nucleate and grow in grain boundary. During EBW, the joint HAZ undergoes high temperature due to weld thermal cycle, some precipitate phases dissolve in grain boundary, and the distribution of microstructure becomes non-uniform. Some precipitate phases without fusion still can form continuous corrosion path to IGC, which causes reticulation morphology of IGC. When the precipitate phase which locally forms continuous path to IGC is

dissolved, the continuity of corrosion path is damaged, and thus the susceptibility to IGC decreases. In AW condition, the joint HAZ is under the action of weld thermal cycle, and the overaging phenomenon occurs. Consequently, the quantity of strengthening phase T_1 is low, and the severe pitting corrosion appears, as shown in Fig.3c. After aging, the quantity of strengthening phase T_1 increases in joint HAZ, which causes obvious IGC, as shown in Fig.3d.

Potential difference exists between base metal and phase T_1 in Al-Li alloy, the potential of phase T_1 is negative compared to that of base metal, and the corrosion couple can be constituted each other. Phase T_1 is corroded with priority, and it gradually develops to corrosion pit; thus the severe corrosion pit is observed in base metal of welded joint, as shown in Fig.3e. After aging, in welded joint, when phase T_1 is continuously distributed in grain boundary, it and adjacent precipitate will be exposed in corrosion solution. At this time, the continuous path to corrosion is formed, and it presents reticulation crack along grain boundaries, so the macro IGC is generated, as shown in Fig.3f.

J. F. Li^[8] et al put forward a mode with simultaneous dissolution of phase T_1 and PFZ, namely, when phase T_1 precipitates in grain boundary of Al-Cu-Li alloy, the active element Li is dissolved firstly, subsequently, the potential of precipitate phase elevates to convert to cathode, PFZ acts as anode to constitute micro-couple, such cycle, new phase T_1 continuously exposes, and thus the continuous IGC occurs. In the present work, the precipitate phase in grain boundary of Al-Cu-Li alloy joint is mainly phase T_1 , as shown in Fig.2. In AW condition, the quantity of phase T_1 precipitated in grain boundary is low, the number of micro-cells constituted

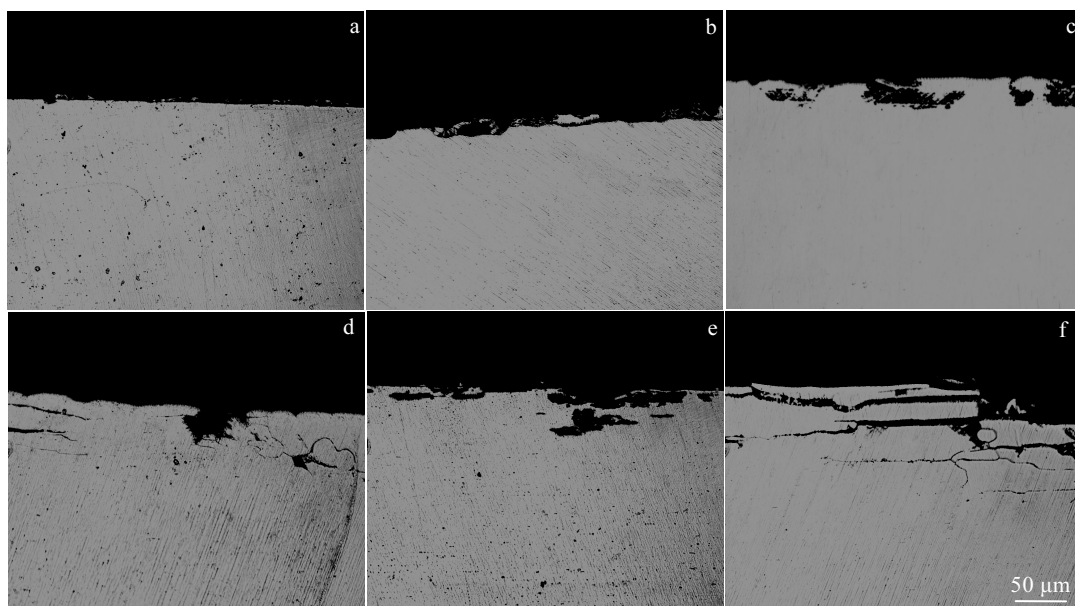


Fig.3 IGC morphologies of different zones in Al-Cu-Li alloy joint before and after aging treatment: (a) WM in AW condition, (b) WM in aging treatment, (c) HAZ in AW condition, (d) HAZ in aging treatment, (e) BM in AW condition, and (f) BM in aging treatment

is low; thus the resistance to IGC is better. The quantity of phase T_1 precipitated in grain boundary increases after PWHT, and it can absorb large quantity of elements Cu and Li to form PFZ; consequently, the susceptibility to IGC increases.

2.3 Exfoliation corrosion

The EXCO is closely related to IGC; it usually develops from pitting corrosion to IGC, and rapidly expands along grain boundary. When the grain boundary is corroded to form corrosion path, the wedge tension will be produced to ambient grains, and it causes tearing of non-corroded parts; the exfoliation occurs in a large area, and even makes alloy break up^[4]. The morphologies of Al-Cu-Li alloy joint immersed in EXCO solution before and after PWHT are shown in Fig.4. The course of EXCO development of Al-Cu-Li alloy joint is given in Table 1.

From Fig.4 and Table 1, it can be seen that the susceptibility to EXCO in different weld zones is different before and after PWHT. The obvious EXCO morphology is formed in base metal of welded joint after immersion for 6 h in AW condition. After immersion for 60 h, the severe EXCO occurs in base metal, the corrosion product drops and the fresh metal surface is exposed. However, the HAZ and weld metal of joint still keep surface bright and are not corroded. There are a lot of corrosion pits in both HAZ and base metal after immersion for 6 h in joint by aging treatment. With the increase of immersion time, the pitting corrosion becomes more and more severe, and the bubbling occurs in both HAZ and base metal after immersion for 48 h, and the EXCO morphology appears after immersion for 60 h.

Form Fig.4a and 4b, it can be seen that, in AW condition, the weldment has high resistance to EXCO, while the susceptibility to EXCO of base metal is higher. It is because

that the base metal has the prerequisite to EXCO, namely, the microstructure of base metal is strip rolled grain, as shown in Fig.1a. However, the weld metal consists of equiaxed grain, as shown in Fig.1b and 1c; thus the susceptibility to EXCO decreases. After immersion for 60 h in EXCO solution, the corrosion degree of HAZ and weld metal is basically the same, no EXCO phenomenon is found in both of them, as shown in Fig.4b. It is probable that the HAZ undergoes weld thermal cycle during welding, some precipitate phases in grains are dissolved, and the original corrosion path is damaged. As a result, both of IGC and EXCO are not easy to generate. While the weld metal undergoes fusion by high temperature and recrystallization, the grain presents the equiaxed shape rather than the strip shape, and it is no longer parallel to the alloy surface; thus the susceptibility to EXCO is greatly lower than that of base metal. The trend of IGC in joint increases after aging treatment; however, the trend of EXCO decreases, as shown in Fig.4c and 4d. It is probable that the quantity of precipitate phase within grain is lower in AW condition, a little phase T_1 is precipitated in grain boundary, while there are a lot of fine and dispersive particle phases precipitated within grains after aging treatment, as shown in Fig.2c. Because there is large quantity of Cl^- ion in EXCO solution which induces pitting corrosion, the pitting corrosion is mainly produced at the first stage of immersion in joint after aging treatment.

2.4 Electrochemical corrosion

2.4.1 Polarization curve

When electrochemical corrosion occurs in metal material, corrosion rate depends on the value of self-corrosion current (or self-corrosion current density). Usually, the higher its self-corrosion current is, the higher the corrosion rate is, and the corrosion dimension is deeper in a unit time; thus the

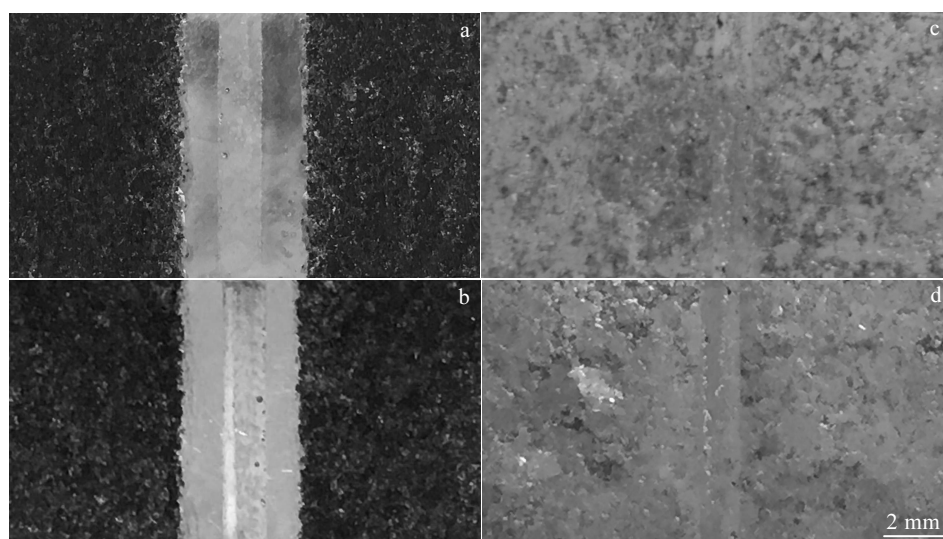


Fig.4 Morphologies of Al-Cu-Li alloy joint immersed in EXCO solution for 6 h (a) and 60 h (b) in AW condition; 48 h (c) and 84 h (d) in aging treatment

Table 1 Course of EXCO development of Al-Cu-Li alloy joint

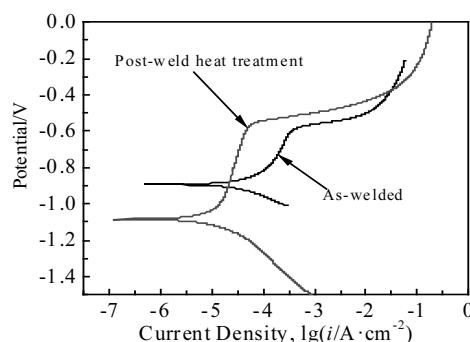
Immersion time/h	Joint in AW condition			Joint in aging treatment		
	WM	HAZ	BM	WM	HAZ	BM
6	N	N	ED	N	P	P
48	N	N	ED	N	P	P
60	N	N	ED	N	EA	EA
84	N	N	ED	N	EB	EB
96	N	N	ED	P	EC	EC

corrosion in the material is more severe, and it means a low corrosion resistance. The polarization curves of Al-Cu-Li alloy weldment before and after aging treatment in 3.5%NaCl solution are shown in Fig.5. The electrochemical corrosion parameters obtained by analyses of polarization curves are given in Table 2. From Fig.5 and Table 2, it can be seen that the self-corrosion potential decreases lightly after PWHT, which demonstrates that the possibility to corrosion increases. Compared to the self-corrosion current of weldment in AW condition, the self-corrosion current of weldment increases after PWHT, which leads to the increase of corrosion rate of weldment.

Usually, in the aggressive medium containing Cl^- ion, the corrosion of A-Cu series alloys occurs with priority nearby strengthening phase or interface between strengthening phase and base metal, and the inhomogeneous distribution of element Cu is the main reason to cause the decrease of corrosion resistance of A-Cu alloys. In the present work, the microstructure of weldment is as cast in AW condition, the precipitation of strengthening phase is insufficient, and the distribution of element Cu is homogeneous, which make the weldment have better corrosion resistance in AW condition. The self-corrosion potential of weldment decreases lightly after PWHT, and the self-corrosion potential is related to phase T_1 in weld metal^[15]. There are more T_1 phases precipitated in grain boundary of weldment after aging treatment, which causes the decrease of content of element Cu dissolved in weld metal^[16]; therefore the self-corrosion potential decreases lightly after aging treatment, as shown in Table 2. Compared to that in AW condition, there exists a difference in quantity and distribution of precipitated phase in grain boundary of weldment after aging treatment, and it influences the susceptibility to electrochemical corrosion to a certain extent.

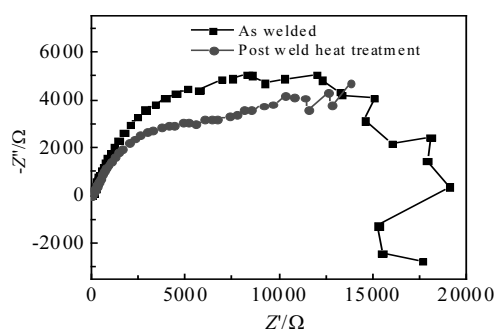
2.4.2 Electrochemical impedance spectroscopy

The EIS of Al-Cu-Li alloy weldment before and after aging treatment in 3.5%NaCl solution are shown in Fig.6. It can be seen that the weldments have the same characteristic of EIS before and after aging treatment, namely, both of them consist of one capacitance arc. The electrochemical impedance radius of weldment in AW condition is slightly bigger than that of in aging treatment, which indicates that the resistance of electrochemical reaction in AW condition is

**Fig. 5** Polarization curves of Al-Cu-Li alloy weldment in 3.5%NaCl solution**Table 2** Electrochemical corrosion parameters of Al-Cu-Li alloy weldment in 3.5%NaCl solution

Sample	E_{corr}/V	$I_{\text{corr}}/\mu\text{A}$	E_{pit}/V	$(E_{\text{pit}}-E_{\text{corr}})/\text{V}$
AW	-0.894	4.753	-0.574	0.320
Aging	-1.084	10.614	-0.552	0.532

Note: self-corrosion potential, E_{corr} ; self-corrosion current, I_{corr} ; pitting corrosion potential, E_{pit} ; passivation interval, $(E_{\text{pit}}-E_{\text{corr}})$

**Fig. 6** EIS of Al-Cu-Li alloy weldment before and after aging treatment in 3.5%NaCl solution

higher, and the corrosion rate is slower, which is consistent with the density of self-corrosion current measured by polarization curves.

3 Conclusions

1) IGC does not occur in joint in AW condition, while the pitting corrosion occurs in both HAZ and base metal. The trend of IGC in joint increases after PWHT. Both pitting corrosion and IGC occur in joint HAZ after aging treatment, and the severe IGC occurs in base metal.

2) Both weld metal and HAZ have high resistance to EXCO in AW condition, while the base metal has higher susceptibility to EXCO. The resistance to EXCO of base metal increases after PWHT, but the susceptibility to EXCO

of HAZ increases at the same time.

3) Compared to the weldment after PWHT, the self-corrosion potential of weldment is higher in AW condition, the density of self-corrosion current is low, and the impedance value is higher. Thus it has the better corrosion resistance.

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时效处理对铝锂合金电子束焊接头耐蚀性能的影响

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摘要: 对铝锂合金电子束焊接头进行焊后热处理, 研究了时效处理前后接头各区域的晶间腐蚀、剥蚀和电化学腐蚀行为。结果表明, 接头经过时效处理后, 焊缝晶界析出的 $T_1(Al_2CuLi)$ 相数量增加, 并且形成了明显的晶界无沉淀带(Precipitate Free Zone, PFZ)。焊态下接头未出现晶间腐蚀, 热影响区和母材区均出现了孔蚀; 焊后时效处理增大了接头的晶间腐蚀倾向, 热影响区同时发生了孔蚀和晶间腐蚀, 母材区出现了严重的晶间腐蚀。焊态下焊缝和热影响区均具有优异的抗剥蚀能力, 母材区对剥蚀的敏感性较高; 焊后时效处理可提高接头母材区的抗剥蚀能力, 但会增大热影响区的剥蚀敏感性。电化学腐蚀测试表明, 与时效后的接头焊缝相比, 焊态下焊缝的自腐蚀电位较高, 腐蚀电流密度小, 具有相对较好的耐蚀性。

关键词: 铝锂合金; 电子束焊; 焊后热处理; 微观组织; 耐蚀性

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