Rare Metal Materials and Engineering
Volume 46, Issue 8, August 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(8): 2070-2075.

ARTICLE

Effect of Rare Earth Metals on Mechanical and Corrosion Properties of Al-Zn-Mg-Cu-Zr Alloy

Gao Yan, Chen Wenlin, Guo Zhen, Wang Liang

Hefei University of Technology, Hefei 230009, China

Abstract: The effect of rare earth metals on mechanical and corrosion properties of 7085 aluminum alloy (Al-7.5Zn-1.5Mg-1.4Cu-0.15Zr) was investigated by means of optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Intergranular, exfoliation corrosion, hardness, tensile test and electrical conductivity test were performed Al alloys on both with and without rare earth additives. Results show the Al alloys with rare earth metals present better mechanical properties such as higher strength and hardness as a result of finer microstructure in comparison with those without the additives. The corrosion resistance is greatly improved by adding rare earth metals. Intergranular corrosion resistance is enhanced from Level IV to Level II, the denudation level for 48 h is improved from E_B to P_A and I_{SSRT} reflecting stress corrosion resistance was enhanced from 65% to 96%.

Key words: 7085 aluminum alloy; rare earth metals; inter granular corrosion; exfoliation corrosion; stress corrosion cracking

7085 alloy (Al-7.5Zn-1.5Mg- 1.4Cu-0.15Zr) is developed as the new generation aluminum alloy, and applied to the areas of large aircraft[1]. However, one of the main drawbacks for its wider application is the corrosion resistance.

One of the most important properties for Al alloys in aircraft is corrosion resistance, since they often suffer various conditions such as temperature, loading stress, creep, and fatigue[2]. Although corrosion resistance can be enhanced by solid-solution treatment, the strength is thus reduced as a result of it.

In order to improve comprehensive property of alloys, some researchers studied 7085 aluminum alloy from different respects. Xiao et al.[3] reported that partial resolution heat treatment improved corrosion resistance but decreased the strength. Luo et al.[4] demonstrated that enhanced-solid-solution raised the denudation level from E_B to P_B. Rare earth metals can refine recrystallized grains, leading to the length of boundaries per unit volume increase and precipitates more sparsely distributed along grain boundaries to present coarse catenary formation, which benefits the corrosion resistance[5]. The purpose of this work is to investigate the effect of rare earth metals on mechanical and corrosion properties of 7085 aluminum alloys, so as to improve corrosion resistance without sacrificing the strength.

1 Experiment

1.1 Materials preparation

Experiments were carried out on 7085 aluminum alloy with main chemical composition (wt%) of 7.5 Zn, 1.5 Mg, 1.4 Cu, 0.15 Zr and Al balance. Cuboid samples were cast in the water-cooled copper mold. The ingots were subjected to homogenization in the air resistance furnace, then through rolling deformation, the final thickness was 1 mm. Specimens were solution treated at 470 ℃ for 2 h and artificially aged at 120 ℃ for 24 h.

1.2 Experimental methods

The micro-hardness testing was performed on a MH-3L hardmeter with a load of 100 g for 15 s. The microstructures were examined using optical microscopy and transmission electron microscopy. Samples for OM observation were chemically etched in Keller's reagent. Thin foils for TEM were prepared by mechanical polishing to 100 μm and

Received date: August 13, 2016
Foundation item: National Natural Science Foundation of China (51171209)
Corresponding author: Chen Wenlin, Ph. D., Professor, School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, P. R. China, Tel: 0086-551-62904578, E-mail: wlchen8761@126.com

final twin-jet electro polishing in the solution of 25% HNO_3 +75% CH_3OH at –25 ℃.

Inter granular corrosion test was carried out as GB7998-2005. Samples were suspended in the corrosion fluid (made up of 57 g NaCl and 10 mL HCl, and 1 L distilled water) for 6 h. The temperature was controlled at (35±2) ℃, and surface to volume ratio A/V was 20 mm^2/mL.

Exfoliation corrosion test was carried out according to ASTM G34-2001. The concentrations of NaCl, KNO_3 and HNO_3 were 4.0, 0.5 and 0.1 mol/L, respectively. The temperature was controlled at (25±2) ℃, and V/A was 20 mL/cm^2. The EXCO surface morphology was record for a certain time by a digital camera.

The SCC susceptibility was evaluated by the slow strain rate test (SSRT) at a strain rate of 10^{-6} s^{-1} in air and in 3wt% NaCl +0.5vol% H_2O_2 solution. Rectangular tensile specimens with a gauge length of 30 mm and a width of 10 mm were used. The susceptibility to SCC was calculated by the ratio of elongation. It was defined as follows: $I_{SSRT} = I_{Corr}/I_{Air}$, where I_{Air} is the elongation in air, and I_{Corr} is the elongation in corrosion solution. The higher I_{SSRT} is, the better the corrosion resistance is.

The polarization curve test was conducted at CHI660D, and saturated calomel electrode and platinum electrode were used as reference electrode and auxiliary electrode, respectively. The solution system was 4.0 mol/L NaCl+0.5 mol/L KNO_3+0.1 mol/L HNO_3. The experimental temperature was controlled at (25±2) ℃.

2 Results and Discussion

2.1 Microstructure

Fig.1 shows the cast microstructure of 7085 aluminum alloys with and without rare earth additives. Grains of alloy without rare earth are coarse and heterogeneous. The average grain size is about 80 μm (Fig.1a). The grains of 7085-Y aluminum alloy are refined, and grains are homogeneous. The average grain size is about 41 μm (Fig.1b). 7085-Er alloy is equivalent to that of 7085-Y alloy with a decreased grain size of 34 μm (Fig.1c). However, with rare earth Sc addition, the grains of alloy are significantly refined, and the average grain size is only 25 μm (Fig.1d).

In order to further explore the grain refinement mechanisms of rare earth metals on the alloys, this work studied 7085 and 7085-0.15Sc alloys. It's found from Fig.2, there were a large amount of small primary phase, and they diffusely distributed in the matrix. In order to further probe into the composition of these primary phases, two trial districts were randomly selected to be applied to EDS analysis (Figs.2a, 2c and 2b, 2d). We found that the primary phase of 7085 alloy included Zn, Mg, Cu, Zr elements, while 7085-Sc alloy precipitated a lot of particles with Sc. Therefore, we can conclude the grain refinement mechanisms of rare earth metals on 7085 aluminum alloy as follows: rare earth promptes alloys to generate small $MgZn_2$, Al_2Cu and Al_3Sc precipitates. They are diffusely distributed in the matrix and play an important role as a kind of alterant. When the alloy is solidifying, precipitates become heterogeneous nucleation cores and decrease the strain energy of nucleation, which obviously refine the grains[6,7].

2.2 Mechanical properties

Table 1 shows the mechanical properties of four samples. Both tensile strength and elongation of samples with rare earth additives are higher than those without rare earth, indicating the rare earth improves the mechanical property. Specifically, after adding Sc, the tensile strength is as high as 608.3 MPa, the elongation is 12.48%, the hardness HV is 1889 MPa. Compared with the alloys without rare earth, they are increased by 14.4%, 23.7% and 10.9%, respectively.

The fracture morphologies of four samples are shown in Fig.3. The fracture morphologies of samples after aging treatment are obviously different. The fracture surfaces of 7085 alloy are characterized by river pattern, and the fracture mode is transgranular and cleavage fracture (Fig.3a). The fracture mode of 7085-Y alloy is also transgranular and cleavage fracture, and cleavage crack extending along low index surfaces leads to cleavage fracture (Fig.3b). The fracture surfaces of 7085-Er and 7085-Sc alloy are characterized by heterogeneous dimples, and the fracture mode is transgranular and quasi-cleavage fracture, as a result of cleavage crack extending along high index surfaces (Figs.3c and 3d). The dimples of 7085-Er alloy are larger and denser, so its plasticity is better and the elongation is higher.

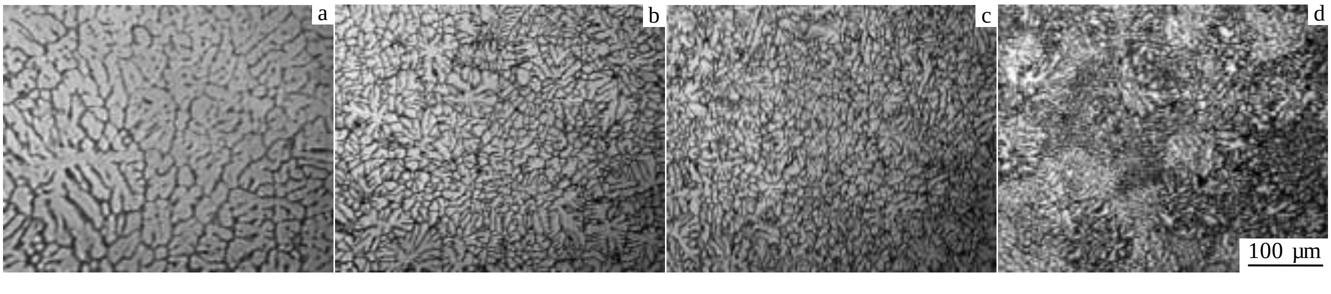

Fig.1 Microstructures of 7085 (a), 7085-Y (b), 7085-Er (c), and 7085-Sc (d) alloys

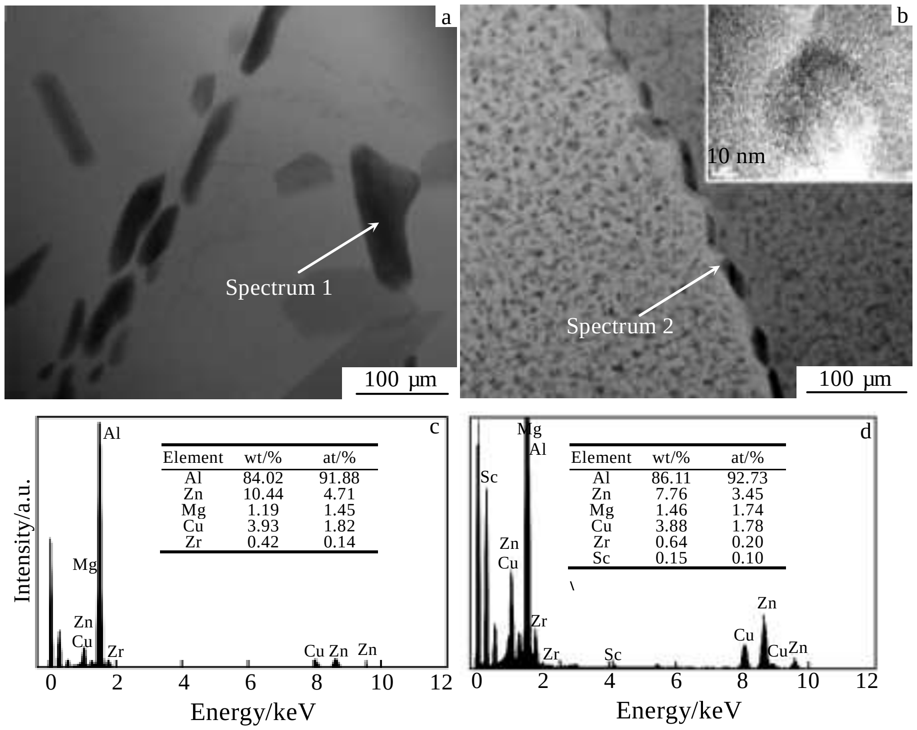

Fig.2 SEM images of precipitates (a, b) and its EDS spectra (c, d): (a, c) 7085 and (b, d) 7085-S

2.3 Intergranular corrosion

Four samples were soaked in corrosion solution for a certain time. At the beginning, and there were some bubbles, then surfaces began to present tan and were covered by white materials. 6 h later, each sample was corroded to different degrees. Fig.4 shows the microstructure of four alloys after intergranular corrosion. The maximum depth of inter granular corrosion of 7085 alloy is 220 μm, belonging to Level IV (Fig.4a). However, the maximum depths of alloys containing rare earth metals are 110, 40, 23 μm, which achieve Level III, Level II, Level II, respectively (Figs.4b, 4c and 4d). Intergranular corrosion is mainly ascribed to an anodic dissolution of grain boundary precipitates (GBPs) and precipitate free zone (PFZ). Precipitates' potential is different from that of matrix and depleted region close to boundaries. Generally, the grains are the cathode, while the boundaries are the anode. Boundaries are rich in defects, impurities and alloying elements; thus their potential is lower than that of intra crystalline, and this tends to form micro corrosion cells presenting intergranular corrosion [8]. When alloys are dipped into corrosion solution, phases with lower potential are the anode and the most corroded places. Therefore, if GBPs continuously distribute along the boundaries, the intergranular corrosion susceptibility will be increased. Adding rare earth metals can refine grains, which increase the length of boundaries per unit volume and precipitates distribute more sparsely along grain boundaries so as not to form coarse catenary, and this improves the corrosion resistance.

The polarization curves of the specimens in corrosion solution are shown in Fig.5. The electrochemical parameters are listed in Table 2, where the higher the corrosion potential, the more difficult the electrochemical corrosion, while the corrosion current density reflects the rate of corrosion. It's found that there is no significant difference on the corrosion potential. Meanwhile, the corrosion current density of 7085 is the highest, 7085-Y and 7085-Er are equivalent, and the corrosion current density of 7085-Sc is the lowest, indicating that the corrosion resistance is improved after adding rare earth.

2.4 Exfoliation corrosion

Fig. 6 shows the surface rating of four samples after soaked in EXCO solution for different time. It indicates that the surface condition of 7085 alloy was the gravest, only 14 h later, the surface started to present exfoliation corrosion. 7085-Y alloy was the second, and it took 24 h for the surface to present exfoliation corrosion. While the exfoliation corrosion resistance of 7085-Sc alloy is the best, it does not present exfoliation corrosion until 48 h. Moreover, the sur-

Table 1 Mechanical properties of four samples

Alloy	σ_b/MPa	δ/%	HV/MPa
7085	531.9	10.09	1704
7085-Y	567.7	11.14	1752
7085-Er	596.6	13.40	1820
7085-Sc	608.3	12.48	1889

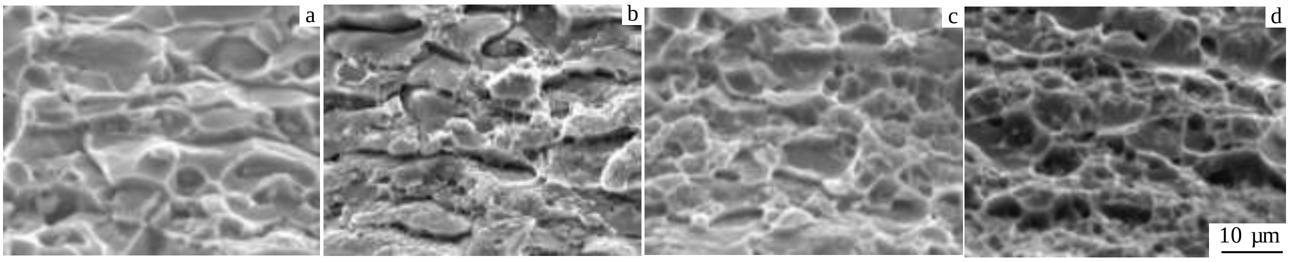

Fig.3 SEM fracture surface of 7085 (a), 7085-Y (b), 7085-Er (c), and 7085-Sc (d) alloys

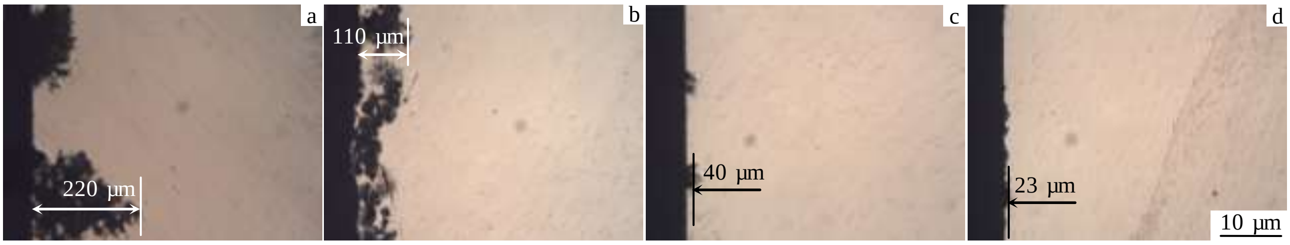

Fig.4 Microstructures of four specimens after inter granular corrosion: (a) 7085, (b) 7085-Y, (c) 7085-Er, and (d) 7085-Sc

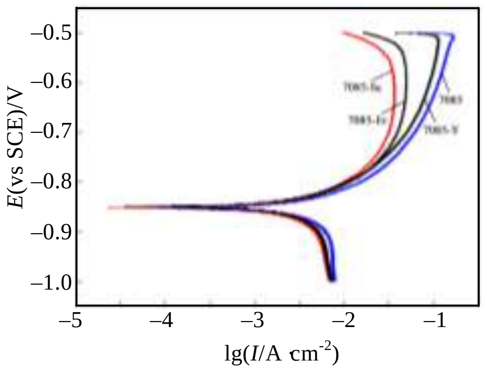

Fig.5 Polarization curves of four specimens

Table 2 Electrochemical parameters of the specimens

Alloy	E_{corr}/V	I_{corr}/$\times10^{-3}$A·cm^{-2}	R_p/Ω·cm^2
7085	–0.857	3.41	2.08
7085-Y	–0.854	2.37	4.65
7085-Er	–0.855	2.81	6.22
7085-Sc	–0.860	1.83	4.47

face was not serious after soaked for 96 h, and the surface rating was only E_B.

Exfoliation corrosion is associated with intergranular corrosion susceptibility. When intergranular corrosion occurs in structures with high directivity, the volume of corrosion products is larger than that of metals consumed, "wedging effect" emerging, and this would jack up the top metal and cause delamination peeling[8]. The grains of alloys with rare earth additives are more homogeneous, so this could decrease exfoliation corrosion susceptibility. In terms of exfoliation corrosion, grain boundaries play an important role. The more serious the inter granular corrosion, the more serious the exfoliation corrosion, so the results of exfoliation corrosion are consistent with those of intergranular corrosion.

2.5 Stress corrosion cracking

Fig.7 shows the results of slow strain rate testing in atmosphere and in 3wt% NaCl + 0.5vol% H_2O_2. It is found that both tensile strength and elongation of the samples in the 3wt% NaCl + 0.5vol% H_2O_2 solution are lower than those in atmosphere, indicating the alloys have the SCC susceptibility.

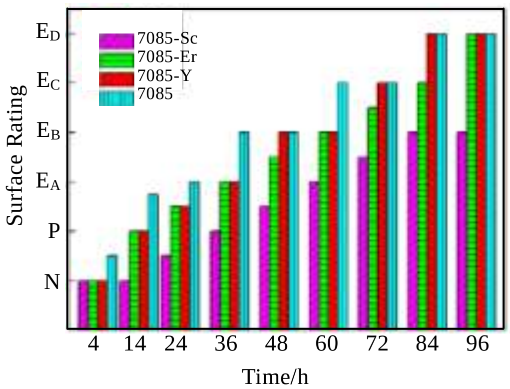

Fig.6 Surface rating after soaked for different time

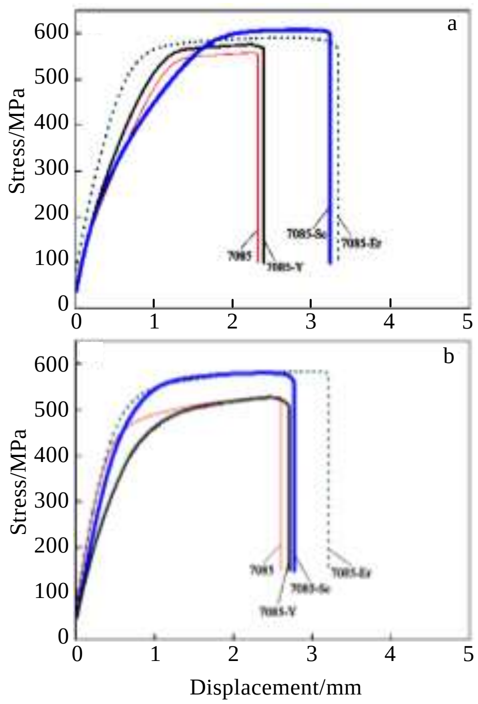

Fig.7 SSRT curves of 7085 alloys containing different rare earth: (a) in air and (b) in 3wt% NaCl + 0.5vol% H_2O_2

In order to understand the relationship between rare earth and SCC better, I_{SSRT} is an efficient method to evaluate the SCC resistance. The higher the I_{SSRT} is, the better the SCC resistance is. Fig.8 shows the ISSRT of different samples. 7085-Sc shows the highest SCC resistance. The SCC resistance of 7085-Er alloy is higher than that of 7085-Y alloy, while the SCC resistance of 7085 aluminum alloy is the lowest.

Due to 7085 aluminum alloys containing rare earth metals and the micro alloying of Re and Zr, $Al_3(Zr_x,Re_{1-x})$ particles develop intense pinning effect. Therefore, this blocks dislocations' movement and improves strength and hardness. At the same time, rare earth metals could refine grains and increase boundaries, which lengthened the corrosion channel and improved the corrosion resistance. On the other hand, there are a large amount of low angle grain boundaries, while precipitates tend to gather on high angle grain boundaries rather than low angle grain boundaries, while wouldn't form anodic corrosion channel and not improve the corrosion resistance [9].

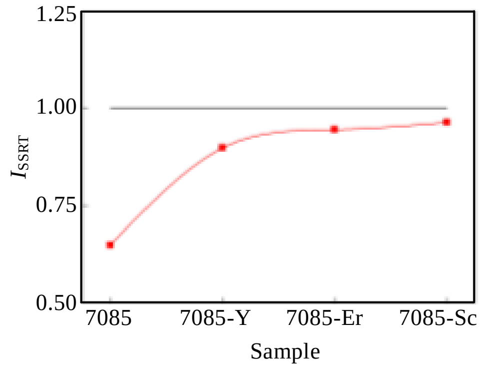

Fig.8 Stress corrosion factor of four specimens

The major microstructural evolution during aging heat treatment of Al-Zn-Mg-Cu alloy is associated with the size, distribution and the content of matrix precipitates and GBPs. Fig.9 shows the TEM images of four alloys under T6 aging treatment. In 7085 alloy, high density precipitates distribute homogeneously in matrix, and GBPs are strip and continuously distributed, and there is not PFZ (Fig.9a). Compared to 7085 alloy, GBPs are coarser and more sparsely distributed in the 7085-Re alloys, and the width of PFZ increases remarkably (Figs.9b, 9c and 9d), which increases the corrosion resistance. While added rare earth metals, GBPs are coarser and more sparsely distributed, and PFZ is broadened, leading to the tendency of anodic dissolution and hydrogen embrittlement decreasing, and stress corrosion resistance is improved.

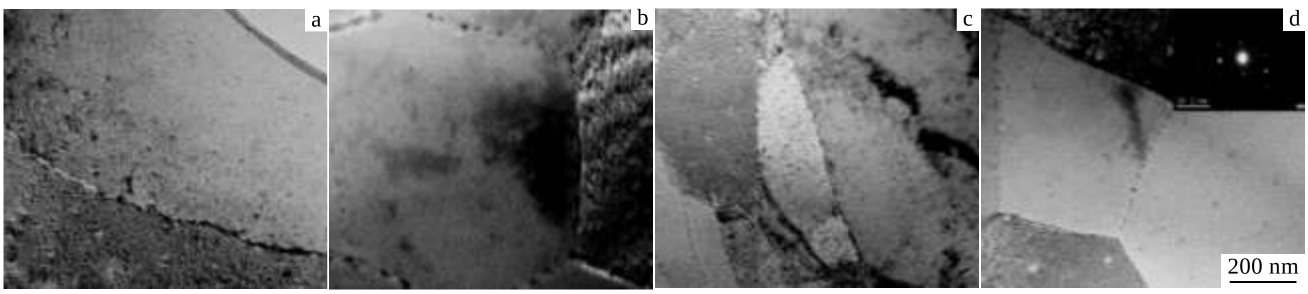

Fig.9 TEM images of four specimens after aging treatment: (a) 7085, (b) 7085-Y, (c) 7085-Er, and (d) 7085-Sc

3 Conclusions

1) In 7085 aluminum alloys, minor of rare earth metals can refine grains, and the average grain size of as-cast alloy decreases from 80 μm to 25 μm.

2) With rare earth metals addition, the strength, hardness and elongation of alloy are improved, especially the strength of 7085-Sc is up to 608.3 MPa, and the elongation of 7085-Er is 13.4%.

3) Rare earth metals improve the corrosion resistance of the alloy, especially for the alloy containing minor of Sc.

4) The degree of improvement of rare earth metals on mechanical and corrosion properties of 7085 aluminum alloy is: 7085-Sc>7085-Er>7085-Y.

References

1 Manabu N, Takehiko E. *Materials Science and Engineering A*[J], 2000, 285(1): 62

2 Heinz A, Haszler A, Keidel C *et al*. *Materials Science and Engineering A*[J], 2000, 280(1): 102

3 Xiao Daihong, Chen Kanghua, Luo Weihong. *Rare Metal Materials and Engineering*[J], 2010, 39(3): 494 (in Chinese)

4 Luo Yong, Xu Xiaojing, Wu Guichao *et al*. *Rare Metal Materials and Engineering*[J], 2012, 41(S2): 262 (in Chinese)

5 Dixit M, Mishra R, Sankaran K. *Materials Science and Engineering A*[J], 2007, 478(1-2): 163

6 Shuey R, Barlat F, Karabin M *et al*. *Metallurgical Transactions A*[J], 2009, 40(2): 365

7 Cai B, Adams B L, Nelson T W. *Acta Materialia*[J], 2006, 55(5): 1543

8 Chen Songyi, Chen Kanghua, Dong Pengxuan *et al*. *Transactions of Nonferrous Metals Society of China*[J], 2014, 24(37): 2320

9 Goswami R, Lynch S, Holroyd N J *et al*. *Metallurgical and Materials Transactions A*[J], 2013, 44(3): 1268

微量稀土对 **Al-Zn-Mg-Cu-Zr** 合金力学性能与腐蚀性能的影响

高 妍，陈文琳，郭 震，王 梁

(合肥工业大学，安徽 合肥 230009)

摘 要：采用慢应变速率拉伸试验、显微硬度和电导率测试、晶间腐蚀和剥落腐蚀试验、光学显微镜、扫描电镜、透射电镜等分析方法，研究微量稀土对7085铝合金（Al-7.5Zn-1.5Mg-1.4Cu-0.15Zr）力学性能和腐蚀性能的影响。结果表明，与未添加稀土的合金相比，添加微量稀土使合金组织细化，时效后强度硬度提高。同时，合金的耐腐蚀性明显提高，其中抗晶间腐蚀性能由4 级提高为2 级、48 h下的剥落腐蚀性能由E_B 提高为P_A、反映应力腐蚀性能的 I_{SSRT} 值由65%提高到96%。

关键词：Al-Zn-Mg-Cu-Zr 合金；微量稀土；晶间腐蚀； 剥落腐蚀；应力腐蚀

作者简介：高 妍，女，1990 年生，硕士，合肥工业大学材料科学与工程学院，安徽 合肥 230009， E-mail: gaoyan9065@163.com