

Mechanical Properties and Corrosion Behavior of Cellular Al-Sc-Zr Foams

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Abstract—By using Ca particles as thickening agent and titanium hydride as blowing agent Cellular Al-0.16Sc-0.08Zr foams with a porosity of $72.5\pm 0.5\%$ were successfully fabricated by the melt-foaming method Isochronal aging treatments are beneficial to improve the mechanical properties and corrosion resistance significantly. Observation on the cell wall microstructure at $400\text{ }^\circ\text{C}$ confirms the precipitation of nano-size $\text{Al}_3(\text{Sc,Zr})$ particles that are coherent with Al matrix with an average radius of 4.1 nm. This suggests that these $\text{Al}_3(\text{Sc,Zr})$ particles can inhibit the grain boundary sliding and dislocation movement, thus, strengthening the cell walls and increasing the compressive strength of the foams. In addition, the Sc_2O_3 protective film over the detective surface improves the corrosion resistance of the aged Al-0.16Sc-0.08Zr foam.

Keywords—Al-Sc-Zr foams; isochronal aging treatment; compressive strength; immersion corrosion; polarization

I. INTRODUCTION

Al foams are a light weight cellular material with excellent impact resistance and energy absorption capacity. So far, Al foams have been widely used in the fields of automobile, aerospace, shipment, civil construction and so on [1, 2]. During the last two decades, extensive researches have been carried out on mechanical reinforcement, for instance, alloying of the matrix [3], composited enhanced framework [4] and making opportune heat treatment [5], but corrosion resistance has been ignored. In order to meet more complex environment, the researches on improving the corrosion resistance become essential.

Zhang et al. [6] have discussed the corrosion resistance of Al foams, Al-Mg-RE foams, and Al-Cu foams fabricated via melt forming method in neutral sodium chloride solution. The Al-Mg-RE foams have shown the best corrosion resistance properties due to the excellent corrosion resistance of Al-Mg-RE alloy. Our research [7] also demonstrates that the mass loss of cellular Al-0.41Sc foams is greater than the cellular Al foam caused by the primary Al_3Sc phase which has a negative influence on the corrosion resistance of cellular Al-based foams. However, up to now, a study on the corrosion behavior of Al-based foams is still very limited.

It is well-known minor Sc and Zr addition in Al alloy can radically improve the mechanical property and weld ability by forming fine Al_3Sc and $\text{Al}_3(\text{Sc,Zr})$ phase during suitable heat

treatment [8, 9]. Similarly, our earlier studies show minor Sc addition can also significantly improve the mechanical property of the cellular Al foams after the T6-treatment [10]. Considering the price and the enhancement to corrosion resistance of Al-based foams, the content of Sc should be decreased and partially replaced by Zr to avoid the formation of primary coarsen Al_3Sc or $\text{Al}_3(\text{Sc,Zr})$ particles.

In this paper, cellular Al, Al-0.16Sc-0.08Zr and Al-5Cu (all compositions are in wt.%) foams with homogenous pore structure were fabricated successfully by the melt-foaming method. The effects of Sc and Zr on the mechanical and corrosion properties of the cellular Al foam were investigated by studying the compressive strength, immersion test and polarization behavior of the foams.

II. EXPERIMENTAL

A. Fabrication of Al and Al Alloy Foam

Cellular Al, Al-0.16Sc-0.08Zr and Al-5Cu foams (Al-0.16Sc-0.08Zr master alloys were prepared by melting pure Al, Al-2.0Sc, and Al-1.6Zr alloy) were prepared by the melt-foaming method using the titanium hydride (purity >99.8%, $40\mu\text{m}$ in diameter) and Ca particles (purity >99.9%) as the blowing agent and the thickening agent, respectively. The foams with a porosity of $72\pm 0.5\%$ and average pore size of 1.0 mm were obtained by controlling the process parameters. The cellular Al-0.16Sc-0.08Zr foams were isochronally in $100\text{ }^\circ\text{C}$ steps lasting 5h each, beginning at $200\text{ }^\circ\text{C}$ and terminating at $600\text{ }^\circ\text{C}$. For Al-5Cu foams, the Al-Cu-Ca phase [11] formed during the aging treatment has little effect on the mechanical property. The fabrication process of the cellular Al-based foams has been demonstrated particularly in [3].

B. Pore Structures Characterization

Porosity and pore size are two important parameters to characterize the pore structures of metal foams. Porosity of a foam, Pr , can be calculated by the following equation:

$$Pr (\%) = [V - (M/\rho_s)]/V \times 100\% \quad (1)$$

where, ρ_s is the density of the matrix (For Al and Al-Sc-Zr foams, the ρ_s are equal to 2.78 g/cm^3 ; for Al-5Cu foam, the ρ_s is equal to 2.82 g/cm^3), M and V are the mass and volume of the specimen, respectively.

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The number of pores and corresponding pore size (D) of a foam sample can be approximately estimated by observations on the sections of the sample using a digital stereo microscope.

C. Mass-loss Study

Immersion corrosion test is adopted in this work. The corrosion samples were machined into the dimension of $\Phi 30 \times 40$ mm from the Al alloy foams by an electro-discharging machine.

All the foams with similar porosity, assumed to have the same surface areas, were firstly stripped with deionised water and then ultrasonic cleaned in acetone to remove grease, finally dried. After, these samples were immersed in the artificial seawater ($3.5\% \text{NaCl} + 1.0\% \text{H}_2\text{O}_2$) for 96h by adding $0.25\% \text{H}_2\text{O}_2$ every 24h during this process, then washed by $5\% \text{HNO}_3 + 1\% \text{K}_2\text{Cr}_2\text{O}_7$ solutions and deionized water, finally dried and weighted. The weight loss was obtained by;

$$L_r = [(m_0 - m_1) / m_0] \times 100\% \quad (2)$$

where, L_r is the mass loss rate after the corrosion, m_0 is the initial mass of the sample, m_1 is the mass of the sample after the immersion.

Macro-morphology of the samples was observed by an image scanner. Surface morphology of the samples was investigated by scanning electron microscope (SEM, ZEISS SUPRA 55).

D. Electrochemical Measurements

Polarization measurements on the cellular Al-based foams were implemented on Electrochemical Workstation with a traditional three electrodes system, using the saturated calomel electrode as the reference electrode and a Pt electrode as the counter electrode. The samples were cut into the size of $10\text{mm} \times 10\text{mm} \times 10\text{mm}$ by using an electro-discharging machine, then sealed in epoxy resin with a bare area of 1.0cm^2 and polished like a mirror. Next, these sample was immersed in the solution for 20 minutes to achieve stable state, and then the potentiodynamic polarization tests were carried out to measure the corrosion potential and current with the scan rate of 30mv per min . Electrochemical impedance spectroscopy (EIS) tests were carried out at the open circuit potential in the frequency ranging from 1Hz to 100kHz , using a 5mV AC signal.

E. Compression Tests

The quasi-static compression tests of the foam samples with the dimension of $\Phi 30 \times 40$ mm were conducted on the CMT 4305 universal testing machine with a constant strain rate of $3 \times 10^{-3} \text{s}^{-1}$ at room temperature. For the metallic foams, the peak stress or the interception of the initial stress and the stress plateau slope is defined as the yielding strength σ_s^* , and the details of yielding strength determination have been elaborated in [10]. Microstructures of the cell wall of the cellular Al-Sc-Zr foam after aging treatment was characterized by a JEM 2100 transmission electronic microscope (TEM).

III. RESULTS

A. Compressive Behavior Study

Fig. 1(a) displays the precipitation behavior of the cellular Al-0.16Sc-0.08Zr foams during isochronal aging, as monitored by the yielding strength. It is confirmed that the age-hardening effect can be detected in the Al-0.16Sc-0.08Zr foams, according to Fig. 1(a). The Al_3Sc particles begin to precipitate at 200°C as demonstrated by the increasing yielding strength. The strength increases rapidly and achieves the peak value at 400°C , then decrease and reach that of the as-cast condition. The curves in Fig. 1(b) depict the stress-strain curves of the Al, peak-aged Al-0.16Sc-0.08Zr and Al-5Cu foams. The values of the yielding strength are 24.72MPa , 23.58MPa , and 16.56MPa , respectively, corresponding to the Al-Sc-Zr, Al-Cu and Al foams. It is cleaned that the peak-aged Al-Sc-Zr foam shows the best yielding strength among them and also still higher than 1MPa compared to the Al-5Cu foam with a similar porosity. Relative to the Al foam, the yielding strength of the Al-0.16Sc-0.08Zr foam processing with suitable aging treatment increases by 50% .

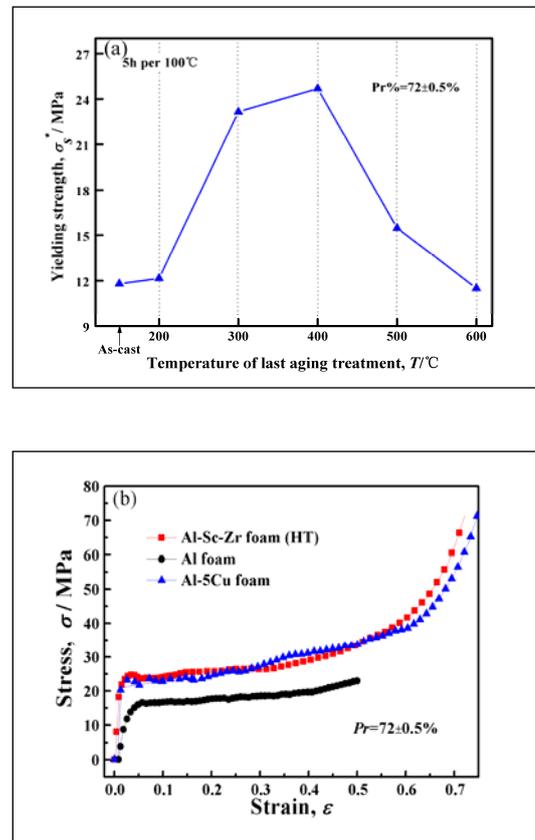


Fig. 1. Compressive strength of the Al-based foams: (a) variation of the yielding strength during the isochronal aging-treatment for the Al-0.16Sc-0.17Zr foam; (b) σ - ϵ curves of foams after aging process.

B. Mass-loss Study

The mass-loss of peak-aged Al-0.16Sc-0.08Zr, Al and Al-5Cu foams after immersing in the artificial sea water for 96h are listed in Table I. It is confirmed that the peak-aged Al-

0.16Sc-0.08Zr foam shows the best corrosion resistance among them with the lowest mass-loss. The mass-loss of Al foams are a little higher than the peak aged Al-Sc-Zr foams, but less than Al-5Cu foams obviously. The Al-5Cu foam has largest mass-loss and shows the worst corrosion resistance. Therefore, Sc+Zr (0.24%) addition and suitable age-treatment can significantly improve the corrosion resistance property of the Al foams. The dimensional and morphological changes of the cross-sectional area before and after the corrosion further demonstrate the good performance of age-treatment to corrosion resistance (as shown in Fig. 2). In order to observe more intuitively, the samples were placed on a blank sheet with a hole in a diameter of approximate 30 mm.

TABLE I. MASS-LOSS OF THE AL, AL-SC-ZR AND AL-CU FOAMS IN THE IMMERSION CORROSION TEST

Sample	Porosity (%)	Status	m_0 (g)	m_t (g)	L_r (%)
Al foam	71.8	T	22.1539	21.9102	1.10
Al-Sc-Zr foam	72.0	F	21.9968	21.8736	0.56
Al-Cu foam	72.3	F	22.0750	17.5938	20.3

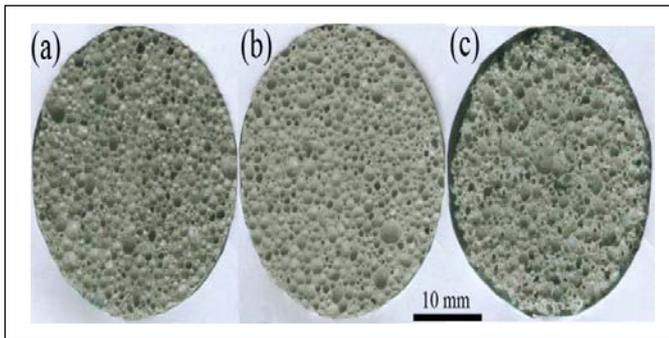


Fig. 2. Cross-section images of the cellular Al-based foams after immersion corrosion: (a) Al foam; (b) peak-aged Al-0.16Sc-0.08Zr foam; (c) Al-5Cu foam.

C. Microstructure of the Al-Based Foams

Fig. 3(a) and Fig. 3(b) display the microstructure of the Al foam and aged Al-0.16Sc-0.08Zr foam before immersion test observed by SEM. It is seen that Al_4Ca phases almost distribute on grain boundaries and the $Al_{20}CaTi_2$ phase are observed in the matrix. Moreover, no primary Al_3Sc or Al_3Zr phase is found in Al-0.16Sc-0.08Zr foam caused by the relative few Sc and Zr. Fig. 3(d) and Fig. 3(e) show the microstructure of the Al and aged Al-Sc-Zr foams after immersion test. Obviously, for the Al and Al-Sc-Zr foams, the corrosion behavior begins at the grain boundaries and most of the Al_4Ca phases have been eroded. It is concluded that the Al_4Ca phase possesses the lower self corrosion potential compared with the α -Al and $Al_{20}CaTi_2$ phase. However, for the

aged Al-Sc-Zr foams, there is still some Al_4Ca phase in the grain boundaries and the Al_4Ca phase in the Al foam has been etching off after the same immersion condition, demonstrating the better corrosion resistance of the aged Al-Sc-Zr foams than the Al foam. Our recent research [11] indicates that the Cu element will be consumed by Ca element, forming fishbone-like eutectic Al-Cu-Ca phase which can be seen in Fig. 3(c). As seen in Fig. 3(f), the matrix of the Al-Cu foams has developed serious corrosion. The α -Al around the Al-Cu-Ca and Al phases has almost been etched, similar with the corrosion behavior of the dense Al-Cu alloys. It is illustrated that the Al-Cu-Ca and $Al_{20}CaTi_2$ phases are nobler than α -Al. Generally, based on the microstructure of the Al-based foams after immersion test, the aged Al-Sc-Zr foam exhibits best corrosion resistance.

D. Electrochemical Corrosion Analyses

The corrosion resistance of the foams is further illustrated by Tafel polarization curves and Nyquist plots, as shown in Fig. 4(a) and Fig. 4(b). The corrosion potential (E_{corr}), corrosion current density (I_{corr}) and charge-transfer resistance (R_t) derived from the polarization curves and Nyquist plots are evaluated, as shown in Table II. The E_{corr} of the peak aged Al-Sc-Zr foam is very close to the Al foam (a little negative), demonstrating that the Sc and Zr additions almost have no influences on the E_{corr} of the Al foams, which is corresponding with the result in the literature [12]. However, the I_{corr} of the peak-aged Al-Sc-Zr foams is about one order of magnitude lower than the Al foams (the smaller I_{corr} , the lower corrosion rate of the sample). Moreover, the peak-aged Al-Sc-Zr foam with greatest R_t among them indicates the lowest passive film dissolution rate.

TABLE II. ELECTROCHEMICAL CHARACTERISTICS OF AL ALLOYS POLARIZED IN 3.5WT.% NaCl SOLUTION

Sample	E_{corr} (mv)	I_{corr} (A/cm ²)	R_t (Ω /cm ²)
Al foam	-0.6664	1.1032×10^{-3}	1332
Al-Sc-Zr foam	-0.6956	3.9566×10^{-4}	1692
Al-Cu foam	-0.5934	3.7161×10^{-3}	597.3

The corrosion performance of the Al foam is significantly better than that of the Al-5Cu foam, although E_{corr} of the former is still more active. The I_{corr} of the Al foam is about a quarter of that of the Al-5Cu foam, and the R_t of the former is also greater than the Al-5Cu foam. The results of polarization measurement agree well mass-loss experiments mentioned above.

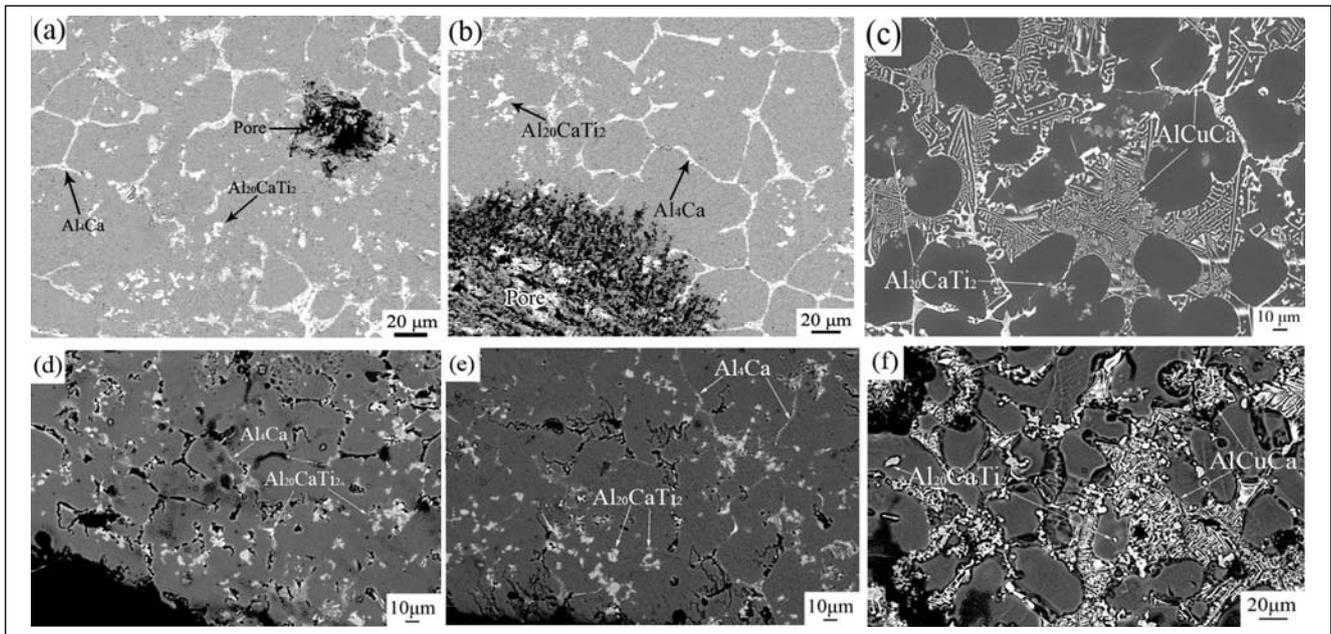


Fig. 3. The SEM morphologies of the Al-based foams before and after immersion test: (a) and (d) are Al foams, (b) and (e) are peak aged Al-Sc-Zr foams, (c) and (f) are Al-Cu foams.

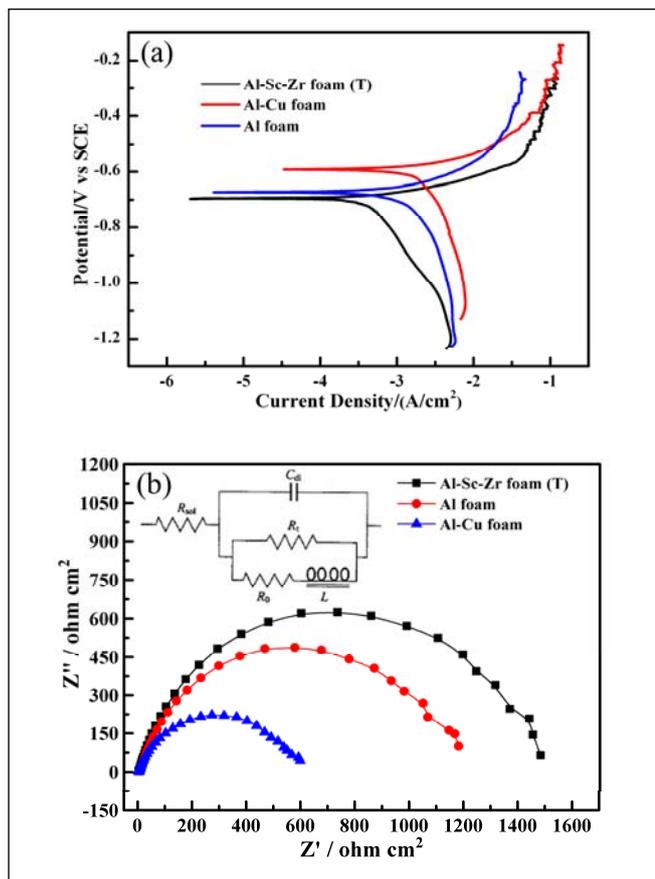


Fig. 4. Experimental and fitted impedance spectra of the Al-based foams (a) Potentiodynamic polarization, (b) Nyquist plots and the equivalent circuits used to fit the behaviour of the Al-based foams is shown in the upper left corner of Fig.4 (b).

IV. DISCUSSION

According to above result, a small amount addition of Sc and Zr can increase the corrosion resistance against seawater and the yielding strength of the Al foams. Thus, the appropriate Sc and Zr addition can effectively improve the corrosion behavior and mechanical property.

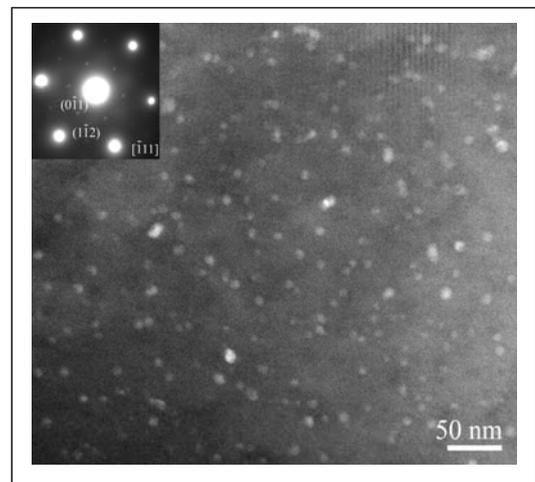


Fig. 5. TEM image of cell wall after isochronal aging at 400 °C for 5 h.

After the aging treatment, coherent nano-sized $\text{Al}_3(\text{Sc,Zr})$ particles have been precipitated in Al-Sc-Zr foams, as shown in Fig. 5. As stated earlier, numerous nano-sized $\text{Al}_3(\text{Sc,Zr})$ phase could pin the grain boundary sliding and dislocation movement, thus strengthening the cell walls and finally increasing the macroscopic strength of the aged Sc, Zr-containing Al-based foams. Calculated by Image Pro. 6.0

software, the average radius of the nano-sized $\text{Al}_3(\text{Sc,Zr})$ particles is about 4.1 nm, and the Orowan strengthening are dominated in the strengthening effect [13].

It has been suggested earlier that the passive film on the surface of conventional Sc-containing Al alloys are consist of two components [14]. Sc is partially oxidized by the oxygen of water to scandium oxide (Sc_2O_3) fine particles, which accumulates and deposit on the surface and prevent the pits occurred. In addition, aluminum oxy-hydroxides is formed in the defective surface layer (bayerite or boehmite), and Sc_2O_3 having relatively lower density, which accumulates onto the upper part of this layer. Consequently, the corrosion rate of the Al-Sc-Zr foam decreases and the RT increases. Moreover, the Zr addition can also contribute to the corrosion resistance of the Al foams. The Zr has a tendency to be enriched in the passive film, because of its lower electro-negativity and higher oxygen affinity compared to Al [15]. The Al_3Sc precipitates allow a minimum cathodic current to be sustained compared to Al and Al_3Zr precipitates. It is concluded that the $\text{Al}_3(\text{Sc,Zr})$ is virtually a killer of oxygen reduction reaction kinetics [16].

Our earlier work illustrates that the Al-0.41Sc foam exhibits a worse corrosion resistance than Al foams caused by the primary $\text{Al}_3(\text{Sc,Ti})$ which leading to the possible initiation sites in the process of pitting corrosion [7]. Therefore, it can be suggested that together with suitable heat treatment, the small amount of Sc and Zr additions in Al foams without formation of primary $\text{Al}_3(\text{Sc,Zr})$ particles can significantly improve the corrosion resistance of the Al-based foams. For the application in the seawater environment, the contents of the addition Sc and Zr of the Al-based foams should be controlled precisely, to avoid the formation of the primary $\text{Al}_3(\text{Sc,Zr})$ in the matrix and cost effective.

V. CONCLUSIONS

The effect of multiple Sc and Zr on the mechanical and corrosion resistance properties of the cellular Al-Sc-Zr foams via the melt-foaming method was investigated. Primary $\text{Al}_3(\text{Sc,Zr})$ particle is not found in the as-cast Al-0.16Sc-0.08Zr foam due to the relatively low content of Sc and Zr. Isochronal aging treatment can improve the mechanical and corrosion performance of the cellular Al-0.16Sc-0.08Zr foams due to the uniform precipitation of Sc with a number of coherent nano-sized $\text{Al}_3(\text{Sc,Zr})$ particles. The peak-aged cellular Al-0.16Sc-0.08Zr foams (isochronal aged to 400°C) express excellent corrosion resistance and noble than Al foams and Al-5Cu foams with the best compressive strength. Generally, the cellular Al-0.16Sc-0.08Zr foams followed by suitable isochronal aging treatment can acquire the comprehensive

excellent corrosion resistance and mechanical properties with relatively low cost.

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