Deterioration of Open-cell Aluminum Foam in Strong Sulfuric Acid

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Abstract. Open-cell aluminium foam was fabricated by pressure infiltration and salt leaching method. The processing conditions to obtain uniform interconnected pore structure aluminium foam were melting at 650°C for 1.5 h with the applied pressure of 1.5 bar. Aluminum foams were sectioned into thin pieces to investigate for deterioration behaviour in strong sulfuric acid for 30 days. Significant weight reduction of about 50% was observed when the specimen piece was submerged in 1.0 M H₂SO₄ in the first three days after which the weight reduction slightly increased to 60%. Al and Cu were the two main elements that had been leached out from the surface of aluminum foam in contact with the acid resulting in the formation of sulfates.

1. Introduction

Aluminum alloys are lightweight and have good mechanical properties as well as good environmental resistance from oxidation corrosion. They can withstand mild acid/base environments therefore are very useful in various industries such as packaging, automotive and heat exchangers. Aluminum foam possesses attractive characteristics when compared to the bulk solid. In the past, when the cast products contained pores, they were considered as defects but in recent years porous metals or metal foams have shown some excellent engineering applications and have been widely investigated. They can be applied as lightweight structures, sound absorbing materials, heat exchanger materials. They also possess high energy dissipation ability. Many fabrication techniques have been developed to produce porous structures and they can be fabricated as open-cell or closed-cell structures [1-4]. Open-cell metal foam has interconnected solid strut network. This structure allows easy fluid or gas flow within it and can be applied in heat exchanger and filter applications [5]. Li et.al. [6] investigated heat exchanging behavior in hot fluid in a complex network of metal foams and they found uneven fluid turbulence. The higher open porosity and hence the higher surface area of the thin solid struts resulted in better heat transfer. Hooman and Malayeri [7] mentioned that metal foam can be applied as filter in non-fully combusted engines. However, there must be concerns over the pressure drop, the blockage and also the corrosion from hot gases. Sergej et al. [8] investigated corrosion in hybrid composite sandwiched with aluminum foam. They said that it was important to consider for galvanic corrosion and electrolytic environment. In their experiment, the variables consisted of pore size and pore type of aluminum foam and also the tested environment in sprayed salt for 240 h.

The replication method is simple and cheap for fabricating aluminum foams with uniform open-cell structures. Replication method consists of infiltrating a leachable preform which is subsequently removed by dissolution in water or solvent. The effective material to be used as a replication preform is sodium chloride salt since it has a melting point at 800°C which is above the melting point of aluminum. It is non-toxic, chemically inert during melting and infiltration and also can be easily dissolved in water. Pore shape and pore size of open-cell aluminum foams can be controlled by the shape and size of the
salt grains. In this current study, the effect of infiltration pressure was investigated in order to find suitable condition for fabricating uniform column aluminum foam. A commercial ADC12 aluminum alloy was investigated in this study since it had lower melting point and better fluidity than pure aluminum. If the aluminum foam was to be applied as a heat exchanger in severe acidic condition it would be interesting to study for the effect on strong acid corrosion. Therefore, deterioration study in sulfuric acid was investigated to see if there were any changes on the physical and chemical characteristics of an aluminum foam.

2. Experimental
This study followed the method developed by Goodall et al. [1] and the detailed procedures can be found from the work of Lara-Rodriguez et al. [3] and Corde et al. [4]. The difference from the related literatures was that in this study vacuum was not used during the melting process. It was evident that our technique was able to produce good and uniform column aluminum foams provided that the melting conditions were carefully controlled. Argon gas was used for the infiltration process of molten liquid aluminum in a tightly closed stainless steel mold. The aluminum alloy utilized in this work was commercial ADC12 in which the composition was near to eutectic Al-Si system with low melting point and low viscosity melt. The alloy was supplied by Smooth International Co. Ltd (Thailand) with a chemical composition: 85.84 Al, 10.03 Si, 1.81 Cu, 0.86 Fe, 0.90 Zn, 0.17 Mg, 0.20 Mn and others.

Australian salt was used to make a preform in this process. It had the size range of 10-17.5 mm with angular morphology and the average size was 10 mm. The dimensions of the stainless steel cylindrical mold were 5 cm inner diameter and 15 cm height. Melting temperature at 650°C and melting time of 2 h were sufficient to give good infiltration of the melt through the salt gaps. The only controlling factors in this study were the applied pressure which was varied between 0.5-2.0 bar and the infiltration time between 10-30 seconds. After obtaining suitable conditions for producing uniform aluminum foam sample. The samples were cut into thin pieces with 2 cm thickness and 5 cm diameter for the subsequent deterioration test in strong sulfuric acid of concentrations 0.1, 0.5 and 1.0 M. The specimens were immersed in closed-lid containers, each with 150 ml sulfuric acid in it. One specimen piece was randomly selected for each acid concentration for the test. The weight change was measured every 3 days for total period of 30 days using a 4-digit balance. The physical appearances were observed by a digital camera and microscopic as well as chemical compositions of the important phases were investigated by FE-SEM Tescan Mira3 equipped with an EDX spectroscopy.

3. Results and discussion
The ADC12 alloy was a low melting point grade and hence melting at 650°C for 2 h resulted in low viscosity melt. The applied pressure of 2 bar was too high to penetrate the melt at the extent to cause large pores or holes on the top part of the specimen after the salt grains had been leached away (figure 1, in the red circled area). A uniform aluminum foam with reproducibility should have be prepared at pressure lower than 2 bar. This study found that good specimens had to be prepared using pressure of 1.0-1.5 bar. Bulk density and % open porosity of aluminum foams prepared by 1.5 bar pressure were averaged from 10 pieces. The values were 0.82 g.cm⁻³ and 69.6%, respectively.

The pressure lower than 0.5 bar was not have enough to infiltrate the salt preform. Figure 2a showed ADC12 bar and its aluminum foam product with a shiny surface. Figure 2c showed an SEM micrograph on the 1 µm polished and etched surface. Phase morphologies consisted mainly of α-Al and eutectic Si. These were labelled as “A” and “B” respectively. Other minor phases or solid solution may have also existed in the microstructure.
For deterioration test in sulfuric acid, it can be seen in figure 3 that the % weight reduction was almost not observed when the specimen pieces were immersed in 0.1 M H$_2$SO$_4$. When the concentration was raised to 0.5 M, the weight reduction of around 10% was seen in the first 3 days. After that, the weight remained quite constant with submerging time. The inset micrograph showed rather rough surface and some surface cracks within the thin solid struts of aluminum alloy. This was different from the starting specimen piece where the surface was smooth. There could be corrosion product/s leached out from the specimen at this concentration. At 1.0 M concentration, it was evident that significant weight reduction occurred. There was fast rate of weight reduction to about 50% at the first 3 days then the weight steadily change in less extent up to about 60% at 30 days. The low corrosion from day 3 to 30 may be related to the formation of oxidized passive film competing with the reaction with strong sulfuric acid.
The visual inspection of the specimens in different HSO₄ concentrations was shown in figure 4. The specimens became dull and darker in color at higher acid concentration. The loss of shiny surface could be mainly related to aluminum element leached out. The formation of oxidized layers could have also changed the reflectivity of the surface. Higher magnification images in figure 5, revealed that the specimen in 1.0 M HSO₄ had rougher structure and more solid parts were leached out from the thin solid struts. Chemical analysis by small area scan using EDX had focused on Si and Cu rich phases in which the two elements were the two most appeared elements in the alloy. Figure 6 showed the difference in the relative X-ray counts in specimens from 0.1 M and 1.0 M HSO₄, all obtained from 30-day specimens. It was evident that Si content increased at higher acid concentration. This roughly
confirmed that aluminum element and oxide or hydroxide of aluminum were leached out from the specimen. It could be dissolved as ions in the liquid media or precipitated out to form aluminum sulphate, Al(SO₄)₃. The suggested chemical reaction that had occurred over time period would be:

$$2\text{Al} (s) + 3\text{H}_2\text{SO}_4 (aq) \rightarrow \text{Al}_2(\text{SO}_4)_3(s) + 3\text{H}_2(g)$$

In the Cu-rich area, it was evident that higher acid concentration reacted with Cu significantly leaving less Cu appeared on the specimen surface. This had been confirmed with different analysed areas, although the data in figure 6 were not from the same area. In the case of copper, the corrosion product formed could be solid Cu(SO)₄, CuO or copper ions in acid solution. As far as the bright spots (or white particles) in figure 5c was concerned, it could be related to the copper-rich phase which had been leached out from the alloy and still adhered within the surface of solid struts.

Figure 5 Micrographs of the specimens in different H₂SO₄ concentrations (a) 0.1 M (b) 0.5 M (c) 1.0 M at 30 days

Figure 6 EDX analysis of area with high Si content (a) 0.1 M H₂SO₄, (b) 1.0 M H₂SO₄and area with high Cu content (c) (a) 0.1 M H₂SO₄, (b) 1.0 M H₂SO₄, all from 30-day specimens

After 30 days in 1.0 M H₂SO₄, the solvent in the beaker was dried to see if there was any solid precipitated at the bottom. The dried solid was crushed into a fine powder and the morphology under
microscope was shown in figure 7. It shows angular morphology which is a characteristic of solid salts which could be related to aluminum sulphate and copper sulphate although the actual phases was not confirmed due to low crystallinity. The associated phase analysis by XRD using Shimadzu D-6100 found unclear diffraction peaks.

Figure 7 Corrosion products after drying and the XRD for phase analysis

4. Conclusion

Open-cell aluminum foams were fabricated in-house design system. The process involved pressure infiltration and salt leaching without the use of vacuum as suggested by other literatures. The uniform interconnected pore structure aluminum foams can be prepared at pressures 1.0-1.5 bar. Deterioration behavior in strong sulfuric acid showed significant weight reduction of about 50% when immersed in 1.0 M concentration. EDX analysis revealed that Al and Cu were the main elements leached out from aluminum foam that formed sulfate salts as the corrosion products.

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