

# Density-Graded Aluminum Foams by the Corrosion Method

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**Abstract.** Optimum corrosive density-grading of T6- and solution-treated alloys was studied using NaOH solutions. Rough corroded strut surfaces in aluminum foams were found to transform to smooth metallic surfaces with an increase in pH from 10 to 13. For instance, during immersion in pH13 solutions, pits with large curvatures appeared on strut surfaces, and corrosive mass losses increased. Strut diameters also decreased, and open cell windows became wider, without an increase in visible damage. Processing parameters such as pH, corrosion rate, and the surface state of the struts were examined to optimize final structure. An experimental method for grading of relative density continuously between 10% and 5% is described.

# Introduction

Metallic foams having cellular structures are super-light materials and exhibit unique multifunctional properties. These properties give them strong potential for applications such as sandwich panels and other lightweight structural components, energy absorption systems for impact protection, heat sinks for electronic devices, and acoustic insulation [1-3]. In some cases, for instance momentum transfer devices, fluid filters, or thermal insulations, controlled density gradients would allow optimization of foam properties to best meet specific application requirements.

Recently, Koerner et al. [4] demonstrated an integral foam molding method for light metals. Molded parts had characteristic cellular structures, density profiles, and pore size distributions. Two molding techniques for integral metallic foam, involving low- and high-pressure processing, were proposed. Brothers and Dunand [5] introduced a different processing method based on investment casting. Their method for obtaining continuous density gradients involved replication of polymer precursors that were density-graded via nonuniform deformation. In this method, graded open-celled metallic foams could be obtained easily, and such density-controlled structures are expected to simplify design, reduce production cost and weight, and optimize stiffness and overall strength.

A novel processing method to obtain desirable density gradients in 6101 aluminum alloy foams is described in this report. First, the influence of immersion condition (i.e., pH of a corrosive solution) on uniform corrosion of the foams was examined. By controlling the dripping rate of a corrosive bath from a container in which foams were suspended from a hanger, a method of changing relative density from 10% to 5% continuously was developed. Next, the condition of strut surfaces after corrosion of foams given solutionizing or T6 treatments was examined, and the magnitude of damage and change in diameters were compared. From the results, a

closely-controlled method of density-grading by immersion using an alkali solution was proposed for optimization of foam characteristics.

## **Experimental Procedures**

**Uniform Corrosion Analysis.** Duocel® open-cell aluminum foams were fabricated from 6101 aluminum alloy by ERG Aerospace (Oakland, CA) using a casting method described by Ashby et al. [2]. The nominal pore density of the foam is 20 pores per inch (PPI), corresponding to 0.8pores/mm, and the designed relative density is 10%. After fabrication, the foams were given a T6 heat treatment for strengthening. This treatment involves solutionizing at 527°C for 8h, prior to water quenching and aging at 177°C for 8h, and was performed by the manufacturer. In order to consider the influence of Mg<sub>2</sub>Si precipitates on corrosion characteristics, both in foam and plate samples, additional solution treatment (ST) at 530°C for 30min (for foams) or 1h (for plates) was given to certain samples.

Using a diamond saw, quadrilateral foam samples  $(10 \times 10 \times 5 \text{mm}^3)$  were cut from a foam sheet provided by the manufacturer. Bulk coupons  $(6 \times 25 \times 1.5 \text{mm}^3)$  were cut from rolled plates, polished with 1200 grit SiC paper, and cleaned before immersion. To analyze uniform corrosion characteristics, immersion tests were performed in 1000mL baths of various aqueous NaOH solutions. Relative density changes and corrosion rates for the specimens were calculated at four different pH values, 10, 11, 12 and 13, by varying the concentration of NaOH. After immersion, the samples were washed in deionized water and ethanol, and then dried. Corrosion rates were then estimated from mass losses, and true mass losses were calculated using data that the manufacturer (ERG Aerospace) provided for estimating the total foam surface areas [6]. In addition, to compare the strut surfaces after corrosion of the foams, scanning electron microscopy (SEM) using a Hitachi S3500-N was used to obtain secondary-electron images, and both the magnitude of damage and the corroded strut diameters were evaluated for uniformly-corroded samples.

**Density Grading.** In order to continuously grade the density of 6101 aluminum foams, corrosion in pH-controlled NaOH solution was used. The dripping rate of this solution from a bell-jar-type reagent bottle with an exhaust port was controlled in order to produce a constant decrease in the fluid level inside the bottle, where a foam sample had been fixed. First, a T6-treated sample of size  $19 \times 5 \times 50$  mm<sup>3</sup> was graded. The measured rate of change of the relative density of this sample during uniform corrosion in pH13 NaOH at room temperature was 1.1%/h. Therefore, a rate of change of fluid level (determined by a particular dripping rate from the vessel) of 6mm/h was chosen to grade a foam sample down to half its initial relative density. The resulting graded foam sample was mounted in an epoxy resin and polished to a  $0.1\mu$ m finish using an aqueous  $Al_2O_3$  suspension. The change in area fraction of the foam struts was calculated by image analysis, and thereby the change in relative density was evaluated.

#### **Results and Discussion**

**Relative Density, Mass Loss and CPR.** Fig. 1 shows relative density changes of open-cell 6101 foams, as calculated from mass losses, for NaOH alkali solution environments from pH10 to pH13. As-received foam samples (having T6 treatments), and those with an additional solutionizing treatment (30min at 530°C, designed to redissolve precipitated Mg<sub>2</sub>Si), are represented by open and closed circles, respectively. After immersion in a weak pH10 alkaline solution, no change in relative density was observed, even after 220h immersion. Consequently, reduction in strut size via corrosion was not expected, either. With increasing pH value from 10 to 13, however, changes to relative density increased remarkably. For instance, using pH13 alkali solutions, even with short immersions of 8h, relative density was found to decrease from 12.3% to 5.1%. These density



Fig. 1 Relative density changes of 6101 foams estimated from the mass loss measurements in the pH range of 10 to 13 using aqueous NaOH solutions.

changes showed similar trends, irrespective of heat treatment (i.e., T6 vs. ST). Accordingly, it was determined that corrosion in strong NaOH alkali solutions is effective for decreasing strut diameter and/or shrinking of foam nodes. Also, evidence of structural damage, such as strut fracture by preferential attack at grain boundaries or  $Mg_2Si$  precipitates, was not observed. Therefore this condition will be recommended as suitable density grading for a comparatively short time.

Fig. 2 shows corrosion penetration rate (CPR) calculated from mass loss results in various NaOH solution baths. For alkali concentrations between  $10^{-4}$  and  $10^{-2}$ M, comparatively low corrosion rates of 15mm/y or less were measured during immersion in stirred solution. However, in  $10^{-1}$ M solution, accelerated corrosion rates of 70mm/y or more were measured for 6101 foams. It was reported [7] that general-use 1100-H14 aluminum alloy shows an average penetration rate of 2mm/y or more in NaOH solutions exceeding pH11 ( $10^{-3}$ M), and this penetration rate increases rapidly with a further rise of pH. Although the corrosion data of high strength electric conduction



Fig. 2 Rate of attack of 6101 foams and bulk coupons in NaOH solution baths at ambient temperature (23°C).



Fig. 3 SEM images of T6 treated 6101 aluminum foams (20PPI) after immersion in pH13 NaOH solution at room temperature. (a) Strut and node surfaces of the foam (relative density: 7.5%). (b) and (c) Individual strut of a foam (relative densities: 7.5% and 5%, respectively).

material 6101 in NaOH solution is not understood yet, the T6 and ST foams have a rapid penetration rate of 4-5mm/y, even in the solution of pH11. In addition, a diameter dependency in corrosion rate was not found, because similar corrosion rates were measured in foams, consisting mainly of thin struts, and in bulk material. Recently, Sakashita et al. [8] reported such a diameter dependency in corrosion rates for high carbon steel wire in aqueous NaCl solution, and proposed that increase of the corrosion rate by decrease in wire diameter originated in reduction of dissolved oxygen or promotion of a cathodic reaction involving hydrogen ions. However, corrosion mechanisms for 6101 aluminum foams immersed in NaOH solution have not been reported previously, so it is unclear whether such a mechanism should apply in this case. Despite the lack of a significant change between foam and bulk corrosion rates, it is notable that corrosion rates between T6- and ST-treated samples showed a slight difference. Possibly, damage through preferential attack near the grain boundaries and precipitates in T6 samples causes a slight acceleration in corrosion rate in those samples.

**Strut Surface.** Although many papers describing mechanical properties of foams are available, these reports focus on cell structure [9-11], cavity quality [11-13], and internal defects [14], with little discussion of surface states. However, it is likely that the surface quality of the struts and nodes in corroded aluminum foam will affect its mechanical properties (e.g., compressive properties, bending ductility, shear strength, etc.). In order to get maximum performance from partially-corroded aluminum foams, it is necessary to identify the least damaging processing methods.

Fig. 3a-c show SEM images of struts and nodes in T6-treated 6101 aluminum foams corroded in a NaOH solution (pH13) at room temperature. Shallow, hemispherical corrosion pits with large curvatures were uniformly distributed on the surfaces of struts and nodes. Although the relative



Fig. 4 SEM images of the solution-treated (ST) 6101 aluminum foams (20PPI) after immersion in pH13 NaOH solution at room temperature. (a) and (b) Individual strut of a foam (relative densities: 7.5% and 5%, respectively).

density of the foam shown in Fig. 3b had been decreased from 10% to 7.5%, struts with slightly sharp edges remained. Strut thickness and width were confirmed to have decreased to about three quarters simultaneously. In addition, grain boundaries on strut surfaces could be observed clearly. As shown in Fig. 3c, sharp edges have largely disappeared from the struts of the foam having relative density 5%, while the hemispherical pits on grain boundaries became larger. Some struts appeared to preferentially thin near the middle of their lengths, and seemed prone to fracture at these points.

Solution-treated 6101 aluminum foams (Fig. 4a-b) were investigated in the same way. Interestingly, the density of the hemispherical corrosion pits decreased, and strut and node surfaces with minimal damage and shallow pit depth were obtained. Even in foams reduced to relative densities of 5%, sharp strut edges remained and grain boundaries were not exposed. Thus, when solution treatment was performed to redissolve  $Mg_2Si$  precipitates, 6101 aluminum foams were corroded more uniformly, and it was found decreases in strut and node sizes were possible without significant visible damage. Additional T6 treatment after density grading of solutionized foams is expected, therefore, to largely recover the initial mechanical properties of the as-received 6101-T6 aluminum alloy foam.

Density grading by corrosion was conducted in pH13 NaOH solutions. Grading. Relative density was reduced in this way to about 5% in highly-exposed regions of the foam. Since the relative density of a T6-treated foam with initial density of 10% was found to decrease at a rate of 1.1%/h, the first grading was attempted using a foam sample of length 50mm immersed in a bath whose drip rate led to a change in bath level of 6mm/h. The relationship between strut area fraction and the distance from the upper foam edge, estimated by image analysis, is shown in Fig. 5. The cross-sectional image used for the analysis is also shown as an inset to Fig. 5. The left side of this image is the upper part of the sample, and right side is the lower part, experiencing the longest The measured area fraction changed from 10% to 5% near-linearly with the distance immersion. from the upper edge. The rapid density change near a position of 30mm was due to strut fracture by severe corrosion, as well as handling damage. Thus, if the dripping rate of solution were optimized in this method, density-graded foams could be obtained with ease.



Fig. 5 Relationship between strut area fraction and the distance from the foam edge

#### Summary

A process for corrosive density-grading of 6101 aluminum foams with open-cell structures was investigated. It was found that pH13 NaOH solutions permitted rapid corrosion rates, and could significantly reduce foam strut and node sizes without causing excessive surface damage. When this idea was implemented, relative density was found to decrease from 10% to 5% continuously, suggesting that the proposed corrosion method can allow controllable and continuous density gradients to be introduced with ease.

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### References

- [1] G. J. Davies and S. Zhen: J. Mater. Sci. Vol. 18 (1983), p. 1899
- [2] M. F. Ashby, A. Evans, N. A. Fleck, L. J. Gibson, J. W. Hutchinson and H. N. G. Wadley: *Metal foams: a design guide* (Butterworth Heinemann, Boston, MA 2000).
- [3] B. -K. Park, G. Yandong and B. -Y. Hur: Fabrication and Mechanical Properties of Open-cell Al-Si Foam, Program and Abstracts of the 4<sup>th</sup> International Conference on Porous Metals and Metal Foaming Technology (METFOAM 2005), Kyoto, September 2005, JIMIC-4, p. 37-C44.
- [4] C. Koerner, M. Hirschmann and R. F. Singer: Integral Foam Molding of Light Metals. ibid. p. 5-B7
- [5] A. H. Brothers and D. C. Dunand: Density-graded Aluminum Foams. ibid. p. 17-B47
- [6] ERG Materials and Aerospace Corp.: Duocel Aluminum Foam, *Duocel Foam Literature and Reports* (ERG Aerospace, Oakland, CA).
- [7] E. H. Hollingworth and H. Y. Hunsicker: Corrosion of aluminium and aluminium alloys, ASM Metals Handbook, Vol. 2: Properties and Selection, Nonferrous Alloys and Pure Materials (ASM International, Materials Park, OH 1990).
- [8] S. Sakashita, T. Nakayama, N. Ibaraki and K Ochiai: Kobe Steel Engineering Reports Vol. 50 (2000), p. 61 (in Japanese)
- [9] A. -M. Harte, N. A. Fleck and M. F. Ashby: Acta Mater. Vol. 47 (1999), p. 2511
- [10] H. Bart-Smith, A. –F. Bastawros, D. R. Mumm, A. G. Evans, D. J. Sypeck and H. N. G. Wadley: Acta Mater. Vol. 46 (1998), p. 3583
- [11] K. A. Dannemann and J. Lankford Jr.: Mater. Sci. Eng. A Vol. A293 (2000), p. 157
- [12] T. G. Nieh, K. Higashi and J. Wadsworth: Mater. Sci. Eng. A Vol. A283 (2000), p. 105
- [13] J. Zhou, P. Shrotriya and W. O. Soboyejo: Mech. Mat. Vol. 36 (2004), p. 781
- [14] C. S. Marchi, J. -F. Despois and A. Mortensen: Acta Mater. Vol. 52 (2004), p. 2895