

## Mechanical properties of reticulated aluminum foams with electrodeposited Ni–W coatings

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The struts of reticulated aluminum foams were coated with nanocrystalline Ni–W by electrodeposition. The thickness and composition of these high-strength coatings are controlled by varying the bath chemistry, applied current conditions and deposition time. Despite an increase in density as compared to the uncoated foams, the coated foams exhibit improvements in both absolute and specific strength, as well as in absolute energy absorption.

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Reticulated aluminum foams with open-cell structures have attracted much attention for their promise as ultra-light structures with good specific strength, stiffness and surface area, combined with simple casting processing [1–3]. However, because aluminum and its alloys have relatively low strength, a low melting point and, in some cases, poor resistance to corrosion, the use of aluminum foams in many cases is limited to ambient-temperature applications that require only modest strength in mild environmental conditions. For example, while open-cell aluminum foams exhibit high thermal conductivity desirable for heat exchanger applications, their low creep resistance and low melting point limit their applicability above ambient temperature [4].

One widely used approach to tailor and improve the properties of a given material is to coat it with another material that exhibits superior properties. Electrodeposition, also known as electroplating, provides a route to uniform metallic coatings on conductive surfaces at low processing temperatures. While electrodeposition has been used for coating of monolithic materials for decades, it has been applied to metallic foams only recently, and advancements in this area are mostly concentrated on nickel foam manufacturing. For example, hollow-strut, open-cell nickel foams can be prepared by nickel coating the surface of a polymer foam template, which is subsequently burned out [5,6]. Electrode-

position has also been performed on nickel foams to improve catalyst efficiency [7] or oxidation resistance [8], and to increase internal surface area [9].

Electrodeposition has also been extensively investigated as a versatile means of developing materials with nanocrystalline grain sizes, providing high strength, corrosion resistance, wear resistance and enhanced fatigue endurance [10–12]. Thus, these developments in nanocrystalline metal plating can be applied to the existing electrodeposition technologies used for foams, to produce coated foams with improved properties. For example, electrodeposited nanocrystalline Ni–Fe [13] has recently been applied as a coating on pyramidal truss core aluminum, increasing load-bearing capacity by up to a factor of 12 [14]. In the present work, we demonstrate the use of electrodeposition to coat open-cell reticulated aluminum foams with nanocrystalline Ni–W alloys, with the aim of enhancing the foams' mechanical properties. Nanostructured Ni–W alloy electrodeposits are particularly interesting because their grain size and thus strength can be precisely tailored over a broad range through modification of processing parameters [15,16]. These deposits can achieve very high hardness (2–7 GPa, depending on grain size), which in turn can offer an effective route to improve the mechanical and surface properties of aluminum foams. Coated reticulated foams are expected to be mechanically more efficient, since struts are typically deforming by bending with the maximum stress localized in the high-strength coating.

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The aluminum foam specimens employed in this study were fabricated from Al–0.7Mg–0.1Si alloy using the reticulation casting method [3]. They exhibited a relative density of 8% and pores with average size of 1.7 mm (15 pores per inch). Ni–W electrodeposition was performed on  $25 \times 13 \times 4 \text{ mm}^3$  foam samples using pure platinum mesh as the anode, with aqueous bath chemistry:  $18\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $53\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ,  $168\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $31\text{NH}_4\text{Cl}$ ,  $18\text{NaBr}$  (all  $\text{g l}^{-1}$ ). The temperature was kept constant at  $73^\circ\text{C}$  and two applied current schemes were used: (i) a direct current (DC) condition at  $0.1 \text{ A cm}^{-2}$ , and (ii) periodic reverse pulsing (RP), with forward pulses of  $0.1 \text{ A cm}^{-2}$  for 20 ms, and reverse pulses of  $0.1 \text{ A cm}^{-2}$  for 3 ms, following a general procedure discussed in Ref. [15]. Deposition was conducted for durations ranging from 0.5 to 3.7 h. To improve the bonding between aluminum and the Ni–W coating, some foams were initially pre-treated using the zincate technique, which involves sequential dipping of the specimens in 1.2 M NaOH, 69.5%  $\text{HNO}_3$  and commercial zincate solution (from Caswell Inc., Lyon, NY). Furthermore, the use of a standard Watts bath ( $300 \text{ g l}^{-1} \text{ NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $45 \text{ g l}^{-1} \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $45 \text{ g l}^{-1} \text{ H}_3\text{BO}_3$  [17]), which is W-free and thus allows deposition of pure Ni coatings, was also performed in DC mode at  $0.1 \text{ A cm}^{-2}$  and at  $65^\circ\text{C}$ .

Energy-dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and optical microscopy were employed to characterize the composition and morphology of the coated specimens. To assess the influence of the coating on mechanical response of the foams, i.e. compressive strength and energy absorption, the foam specimens were subjected to uniaxial compressive testing at ambient temperature, performed at an initial strain rate of  $4 \times 10^{-4} \text{ s}^{-1}$ , with strain measured by cross-head displacement after machine compliance correction.

Figure 1 presents the weight fraction of the coating deposits, with respect to the uncoated aluminum foams, as a function of deposition duration. Compared to the RP conditions, the use of DC conditions resulted in a more rapid deposition rate and higher W content within the coatings, as determined by EDS. The W contents in the DC and RP electrodeposited Ni–W coatings, measured as 20 at.% (44 wt.%) and 13 at.% (33 wt.%), respectively, correspond to average grain sizes of  $\sim 10$

and  $\sim 30 \text{ nm}$ , respectively, as determined from a prior study [15]. The stabilization of such ultra-fine grain sizes was shown to be related to grain boundary segregation of W in these alloys [18] and leads to very high hardnesses (7 and 5 GPa, respectively). However, the Ni–W coatings exact a large mass penalty on the foams, since the density of the Ni–13W and Ni–20W (at.%) alloys are  $10.8$  and  $11.7 \text{ g cm}^{-3}$ , respectively, as compared to  $2.7 \text{ g cm}^{-3}$  for pure Al. The foam densities are listed in Figure 1 and vary between  $0.22 \text{ g cm}^{-3}$  for the uncoated aluminum foam and  $1.2 \text{ g cm}^{-3}$  for the coated foam with the densest and thickest Ni–W coating. As compared to the Ni–W coatings, the Ni coatings produced by a Watts bath are thus both lower in density ( $8.9 \text{ g cm}^{-3}$ ) and faster in deposition rates, but their strength is known to be relatively low ( $\sim 1 \text{ GPa}$  hardness) [15].

The foams were found to be coated on all struts, but the near-surface volumes of the samples exhibited thicker coatings (by about a factor 2) than their cores. The morphology of the Ni–W coatings was smooth at the  $10\text{--}100 \mu\text{m}$  scale, as observed by SEM. Figure 2a–d shows optical micrographs of strut cross-sections for foams coated under various conditions. Intimate contact between the Ni–W coatings and the strut original surface is observed and the adhesion of the coating, which was subjected to stresses during metallographic preparation, appears reasonable. This is likely due, at least partly, to the intricate architecture and intrinsic surface roughness of the original aluminum strut surfaces, which promote mechanical interlocking. The coating thicknesses visible on cross-sections are upper-bound values, given the random orientation of the struts with respect to the cross-sections. The cross-sections show that the Ni–W coatings are uniform at the strut level. Similarly to the Ni–W coatings, the Ni coatings are uniform and show fair adhesion with the aluminum struts. The zincate treatment resulted in an apparent improvement in adhesion (as determined qualitatively from a decrease number of delaminations in the metallographic specimens) and gave an increase in the deposition rate (Fig. 1).

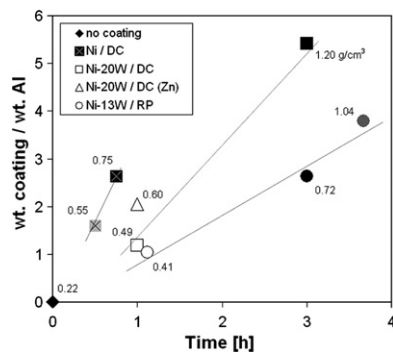


Figure 1. Mass of the coatings normalized by mass of original Al foam, as a function of deposition time, bath chemistry and current conditions. The foam densities (in  $\text{g cm}^{-3}$ ) are indicated next to the data points.

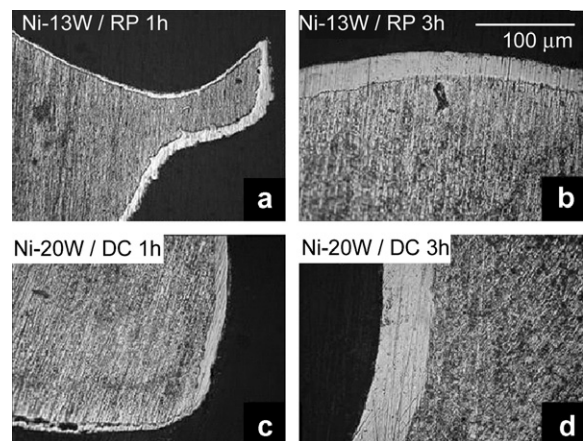


Figure 2. (a–d) Representative cross-sections of Al foams coated with nanocrystalline Ni–W, as processed using different current conditions (RP or DC) and deposition times (1 or 3 h), as marked at upper left of micrographs.

Figure 3 shows representative compressive stress–strain curves of Ni–W-coated foams (fabricated in the RP mode) compared to the uncoated aluminum foam. While the latter foam (with density of  $0.22 \text{ g cm}^{-3}$ ) exhibits a stress–strain curve with a near constant ( $\sim 2 \text{ MPa}$ ) plateau stress characteristic of ductile reticulated foams, the coated foams show much higher peak stresses, increasing with coating thickness from  $\sim 5 \text{ MPa}$  for the foam coated for 1 h ( $0.41 \text{ g cm}^{-3}$ ) to  $\sim 7 \text{ MPa}$  for the foam coated for 3 h ( $0.72 \text{ g cm}^{-3}$ ). The peak stress is followed by a broad stress drop with multiple serrations, indicative of a series of coating delamination events. At a compressive strain of  $\sim 0.2$ , the stress reached approximately the same level as the plateau stress of the uncoated aluminum foam, indicating complete loss of load-bearing capacity of the coating, as expected if delamination is extensive. A summary of all strength results is shown in Figure 4 which reveals that the nanocrystalline Ni–W coating considerably strengthens aluminum foams with compressive stresses increased by a factor up to six (Fig. 4a). For comparison, a strength increment factor of about ten was reported for Ni–Fe-coated periodic cellular aluminum with much thicker coatings ( $\sim 300\text{--}400 \mu\text{m}$ ) [14]. Delamination of the coatings from the aluminum surfaces appears to limit foam strength, and it is thus likely that higher strength could be achieved with improved coating adhesion, as illustrated when comparing the zincated and non-zincated foams. As shown in Figure 4, the increased strength of the coated foams is accompanied by an increase by a factor up to two in relative density, as calculated by the rule of mixtures, and by a factor of up to five in absolute density. Also plotted in Figure 4a is the compressive strength  $\sigma$  of hypothetical, uncoated aluminum foams as a function of their relative density  $\rho$  (calculated with respect to the density of the solid aluminum alloy) as given by the relationship [19]

$$\sigma = C\sigma_s(\rho/\rho_s)^{3/2}, \quad (1)$$

where the subscript ‘s’ refers to the solid material, and  $C$  is a scaling pre-factor. The term  $C \cdot \sigma_s$  was determined experimentally from the uncoated aluminum foam.

From Figure 4a, it is apparent that all but one of the nanocrystalline Ni–W coatings increase the foam

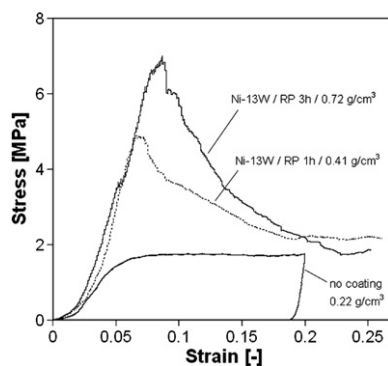


Figure 3. Compressive stress–strain curves of aluminum foams with and without Ni–13W coatings produced in the reverse pulsing (RP) mode for 1 and 3 h.

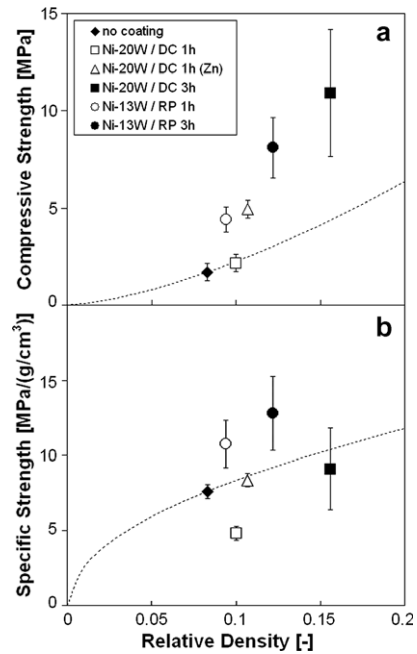
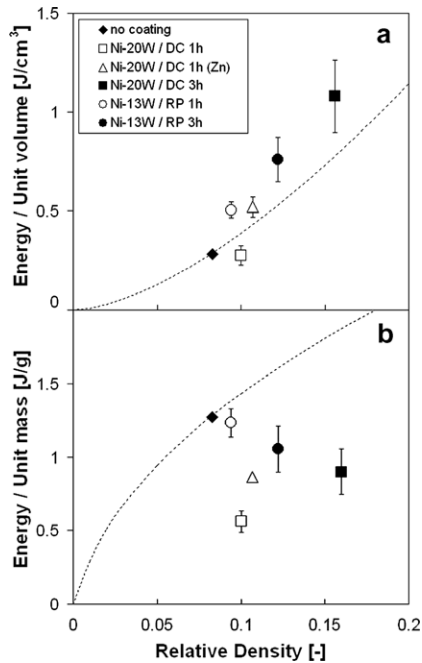


Figure 4. (a) Compressive strength and (b) specific compressive strength of Al foams coated with nanocrystalline Ni–W alloys (uncoated foam given for comparison). The error bars are standard deviation determined from duplicate tests. The lines represent the anticipated mechanical response of a hypothetical non-coated Al foam (Eq. (1) for (a) and Eq. (2) for (b)).

strength by a factor 2–3 as compared to a hypothetical aluminum foam of the same relative density. The DC deposition mode provides higher strength improvement than the RP mode for a given deposition time, because it leads to thicker coatings as well as higher intrinsic strength due to the finer grain structure [11]. However, this strength enhancement is also accompanied by a sizeable increase in foam density, given that the DC mode produces coatings that are both thicker and richer in W. This point is illustrated in Figure 4b, which presents the specific strength of the foams (i.e. compressive strength in Figure 4a normalized by foam density) as well as that of hypothetical uncoated aluminum foams calculated from Eq. (1) as

$$\sigma/\rho = C\sigma_s\rho^{1/2}/\rho_s^{3/2}. \quad (2)$$

It is apparent from Figure 4b that all but one coated foam showed higher specific strength than the uncoated foam. However, as compared to hypothetical uncoated aluminum foams of the same relative density with specific strength calculated from Eq. (2), only the foams coated using the RP mode are superior. The foams coated using the conventional DC deposition method are penalized by their larger increases in absolute density, resulting from the higher W concentration in the coating. This results in a specific strength comparable to that of uncoated aluminum foams or even inferior to it (for the non-zincated foams DC-coated for 1 h, cf. Fig. 4b). In comparison to another type of reinforced foam, i.e. closed-cell Al foams containing 20% SiC fabricated by the melt-foaming agent method, at approximately the same absolute density of  $0.7 \text{ g cm}^{-3}$ ,



**Figure 5.** Energy absorbed (a) per unit volume and (b) per unit mass for deformation to a strain of 0.2 for Al foams coated with nanocrystalline Ni–W alloys (uncoated foam given for comparison). The error bars are standard deviations determined from duplicate tests. The lines represent the anticipated mechanical response of a hypothetical non-coated Al foam at various relative densities (Eq. (3) for (a) and Eq. (3) normalized by density  $\rho$  for (b)).

the present open-cell Al foams with Ni–W electrodeposited coatings exhibit both strength and specific strength that are lower by about a factor of two [20].

The energy absorption of the foams, as calculated by integrating the stress–strain curves up to a strain  $\varepsilon_{\max} = 0.2$ , is shown in Figure 5a as a function of the foam relative density. As expected from the large boost in strength, the coatings increase significantly (by a factor 2–4) the energy absorption of the foams. Figure 5a also shows a curve for the energy absorption  $U$  for hypothetical uncoated aluminum foams, calculated as

$$U \approx \sigma_y (\varepsilon_{\max} - 0.5\varepsilon_y), \quad (3)$$

assuming a constant plateau stress  $\sigma_y$  (from Eq. (1)) beyond the yield strain  $\varepsilon_y = \sigma_y/E$ , with the foam Young's modulus calculated as  $\bar{E} = E_s(\rho/\rho_s)^2$  [19]. As for strength, all but one of the coated foams perform better than these hypothetical uncoated foams. However, when normalizing the energy density by the foam density (resulting in energy absorbed per unit mass), this improvement disappears, as shown in Figure 5b, when compared to either the original uncoated aluminum foam or the hypothetical aluminum foams of the same relative density calculated as  $U/\rho$  from Eq. (3). This is due to the sharp decrease in strength past the peak stress. Thus, better coating adhesion resulting in a plateau stress that is constant rather than decreasing with strain would significantly improve the specific energy absorption of the foams.

In summary, the struts of a reticulated, low-density aluminum foam were electroplated with high-strength, nanocrystalline Ni–W coatings of varying thickness and composition by tailoring deposition time, bath chemistry and applied current conditions. The coatings increase significantly both the foam strength and energy absorption in compression, but at the expense of increased foam density. When these mechanical properties are scaled with the foam density, coated foams produced under pulse-reverse conditions remain advantageous in term of strength. Based on known properties of these nanocrystalline coatings, further benefits are expected for the coated foams, including better corrosion and wear resistance, higher hardness and increased maximum operating temperatures. Finally, the Ni-based coatings may also confer ferromagnetic and catalytic properties to the foams.

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- [1] J. Banhart, Prog. Mater. Sci. 46 (2001) 559.
- [2] Y. Conde, J.F. Despois, R. Goodall, A. Marmottant, L. Salvo, C.S. Marchi, A. Mortensen, Adv. Eng. Mater. 8 (2006) 795.
- [3] A.H. Brothers, D.C. Dunand, Adv. Eng. Mater. 8 (2006) 805.
- [4] W. Azzi, W.L. Roberts, A. Rabiei, Mater. Design 28 (2007) 569.
- [5] K. Lee, J.J. Lewandowski, Mater. Sci. Tech. 21 (2005) 1355.
- [6] C.S. Dai, D.L. Wang, Z.G. Hu, F. Ding, J. Appl. Electrochem. 35 (2005).
- [7] W. Yang, S. Yang, W. Sun, G. Sun, Q. Xin, Electrochim. Acta 52 (2006) 9.
- [8] L. Yang, X. Wu, D. Weng, Scripta Mater. 55 (2006) 107.
- [9] R. Campbell, M.G. Bakker, J. Porous Mater. 11 (2004) 63.
- [10] L. Lu, M.L. Sui, K. Lu, Science 287 (2000) 1463.
- [11] C.A. Schuh, T.G. Nieh, H. Iwasaki, Acta Mater. 51 (2003) 431.
- [12] H. Li, F. Ebrahimi, Acta Mater. 54 (2006) 2977.
- [13] C. Cheung, F. Djuanda, U. Erb, G. Palumbo, Nanostruct. Mater. 5 (1995) 513.
- [14] M. Suralvo, B. Bouwhuis, J.L. McCrea, G. Palumbo, G.D. Hibbard, Scripta Mater. 58 (2008) 247.
- [15] A.J. Detor, C.A. Schuh, Acta Mater. 55 (2007) 371.
- [16] T. Yamasaki, R. Tomohira, Y. Ogino, P. Schlossmacher, K. Ehrlich, Plat. Surf. Finish. 87 (2000) 148.
- [17] A. Saraby-Reintjes, M. Fleischmann, Electrochim. Acta 29 (1984) 557.
- [18] A.J. Detor, M.K. Miller, C.A. Schuh, Philos. Mag. 86 (2006) 4459.
- [19] L.J. Gibson, M.F. Ashby, Cellular Solids, Cambridge University Press, Cambridge, UK, 1997.
- [20] M.C. Gui, D.B. Wang, J.J. Wu, G.J. Yuan, C.G. Li, Mater. Sci. Eng. A 286 (2000) 282.