Light, strong, and stable nanoporous aluminum with native oxide shell

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Aluminum (Al) metal is highly reactive but has excellent corrosion resistance because of the formation of a self-healing passive oxide layer on the surface. Here, we report that this native aluminum oxide shell can also stabilize and strengthen porous Al when the ligament (strut) size is decreased to the submicron or nanometer scale. The nanoporous Al with native oxide shell, which is a nanoporous Al-Al\(_2\)O\(_3\) core-shell composite self-organized in a galvanic replacement reaction, is nonflammable under ambient conditions and stable against coarsening near melting temperatures. This material is stronger than conventional foams of similar density consisting of pure Al or Al-based composites, and also lighter and stronger than most nanoporous metals reported previously. Its light weight, high strength, and excellent stability warrant the explorations of functional and structural applications of this material, if more efficient and scalable synthesis processes are developed in the future.

INTRODUCTION

Nanoporous metals prepared by dealloying have received widespread attention for a variety of functional applications including catalysis (1, 2), supercapacitors (3), energy storage (4), actuation (5–7), and other stimuli-responsive functionalities (8–11). During dealloying (12, 13), the reactive elements are selectively dissolved, and the remaining, less reactive elements organize themselves into a uniform nanoporous structure. The mechanical responses of dealloyed nanoporous metals are particularly important, because (i) excellent mechanical stability is essential for most functional applications such as actuation (5–7) and (ii) the dealloyed nanoporous structure represents a new type of self-organized strong and light material (14–17). It has been widely reported that shrinking the size of a solid to the submicron or nanometer scale can enhance its strength even to theorectical values (18, 19). This “smaller is stronger” effect has been explored for the development of stiff and strong lattice materials by assembling submicron or nanoscale objects into a spatially periodic network, for example, by three-dimensional (3D) printing (20, 21). Although dealloyed nanoporous structures are rather random and mechanically less effective than 3D-printed lattice materials, dealloying is simple and can easily generate nanometer-scale structures with a strong “size effect” in macroscopic materials. An optimized nanoporous metal could even be several times stronger than a fully dense precursor alloy before dealloying (16).

Several nanoporous metals [Pt (17, 22), Au (12), Ag (23, 24), Ni (25), Cu (26), Al (27, 28), and Mg (29)] have been successfully fabricated by dealloying. However, most previous mechanical studies were performed on noble metals such as nanoporous Au (9, 14, 15, 30–32) and Pt (17), partly because their synthesis has been optimized to obtain high-quality samples (without cracks). It has long been expected that mechanical studies on nanoporous aluminum (Al) will be undertaken, not only for the low cost, light weight, and potential applications of Al [as demonstrated in porous Al (33)] but also for all the benefits arising from a passive aluminum oxide (alumina) layer that naturally occurs on the Al surface.

Nanoporous metals often exhibit high strength but poor thermal stability. Because of a large excess surface energy, nanoporous metals (such as Au) are prone to coarsening even at an ambient temperature (34). Biener et al. (35) solved this problem by covering ligaments with a layer of Al\(_2\)O\(_3\) or alumina using atomic layer deposition (ALD), which stabilized nanoporous Au against coarsening up to the melting temperature. Moreover, it was demonstrated that nanoporous Au (35) and Au nanowires (36) could be further hardened by the ALD layer of alumina. Recent studies also revealed that, in addition to a smaller-is-stronger effect (37–41), a native layer of alumina (approximately 5-nm thick) lent additional strengthening to submicron Al pillars (42, 43). It is thus anticipated that, if the structure size of a macroscopic porous Al is reduced to the submicron or nanometer scale, because of the presence of a passive layer of alumina, the material might simultaneously gain excellent thermal stability and high strength without the aid of ALD. However, this result has not been experimentally realized in previous studies.

Aluminum is so reactive that the synthesis of nanoporous Al often involves nonaqueous solutions such as ionic liquids (27), in which dealloying is slow. Suitable precursor alloys for the synthesis of nanoporous Al are also limited. At present, nanoporous Al can only be dealloyed from Mg-Al alloys because Mg is one of the few elements that is more reactive than Al and can be alloyed with Al to form a precursor alloy. Directly dealloying Mg-Al alloys can generate very fine-structured nanoporous Al (with a ligament size of 10 to 20 nm), which is, however, flammable in the atmosphere owing to the rapid oxidation of Al ligaments (28). Recently, we successfully fabricated nonflammable, crack-free nanoporous Al with a relatively coarse (~200 nm) structure by using the galvanic replacement reaction (GRR) (27). This development provides an opportunity to explore the mechanical properties of nanoporous Al, although the sample size is limited by a slow reaction rate (~50 μm/day).

In this study, we report that the nanoporous Al self-organized in GRR is a nanoporous core-shell Al-Al\(_2\)O\(_3\) composite. Mini-compression and tension tests revealed that this material is considerably stronger than conventional foams of pure Al or Al-Al\(_2\)O\(_3\) composites. The specific strength of nanoporous Al-Al\(_2\)O\(_3\) composite is also substantially higher than that of nanoporous metals previously prepared by

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dealing. The native alumina shell on ligaments, which occupies a large fraction of the sample volume, is key to this thermal stability and mechanical performance and might enable applications of nanoporous Al-based materials in the future.

RESULTS AND DISCUSSION

Microstructure and thermal stability of nanoporous Al with native oxide shell

Nanoporous Al was prepared by GRR of Al$_2$Mg$_3$ in an [EMIM]$^+$ AlCl$_4^-$ ionic liquid. Mg atoms in Al$_2$Mg$_3$ were oxidized and dissolved, and Al$^{3+}$ ions in the ionic liquid were reduced and deposited. In the first process, the selective dissolution of Mg from Al$_2$Mg$_3$ generated a dealloyed network skeleton of Al with an initial relative density, $\phi$, of 0.32. In the second, a conformal deposition of Al on the Al skeleton thickened Al ligaments and enhanced $\phi$ to approximately 0.65 (forming 10-nm-thick oxide on ligament surface further increases $\phi$ to ~0.70). The obtained nanoporous structure was uniform and free of cracks throughout these samples. Residual Mg was undetectable and the Cl content was below 1 atomic % (at %) in nanoporous Al (fig. S1), according to energy-dispersive x-ray spectroscopy (EDS).

The scanning electron microscopy (SEM) image (Fig. 1A) shows an open and uniform porous structure of as-prepared nanoporous Al, with an average ligament diameter of approximately 200 nm. We annealed the sample at 600°C for 0.5 hours in Ar, examined the same region using SEM, and found that the structure remained unchanged after annealing (Fig. 1B). After further annealing at 650°C (10°C lower than the melting temperature of Al) for 0.5 hours, some fragment-like structural damages emerged at the surface of this sample (Fig. 1C).

Transmission electron microscopy (TEM) images show that the grain size was equivalent to the ligament size in nanoporous Al (Fig. 1D) and after annealing (Fig. 1E and F). TEM examination (Fig. 1F) also shows that the nanoporous structure remained intact after annealing up to 650°C. The fragments and damages shown in Fig. 1C were not observed in the TEM samples, which were cut from the sample interior. This finding indicates that the surface damage shown in Fig. 1C may result from overheating at the sample surface during annealing. As shown in fig. S2 (B to E), the structures of all annealed nanoporous Al samples were well interconnected, including a sample that was annealed at 650°C for 24 hours.

The histograms for ligament size and grain size of nanoporous Al are shown in Fig. 1 (G and H), respectively. Both ligament and grain sizes were retained after annealing for 0.5 hours at 600°C and coarsened to 270 to 280 nm at 650°C. After the annealing time was extended to 24 hours, the ligament size and grain size of the nanoporous Al increased to approximately 300 nm at 600°C and 580 nm at 650°C (fig. S2).

Nanoporous Al is also stable against sintering or densification, which usually proceeds via grain boundary diffusion, as in the sintering of compacted polycrystalline powders. Although nanoporous Al contains a high density of grain boundaries, the change in sample length (and thickness) was very small (2.5 to 3.0%) after it was annealed at 600°C for 24 hours (Fig. 1I).

The excellent thermal stability of nanoporous Al originates from the presence of an alumina layer on the ligament surfaces. Some nanoporous Al samples were heated at 700°C (for 0.5 hours), which was 40°C above the melting point of Al. Despite slight sample curling, the material remained intact and the sample dimensions were retained after annealing (see Fig. 1I). These results indicate that the network of the alumina shell was rather rigid and did not fully collapse under capillary pressure. For a ligament size of 200 nm, the capillary pressure induced by the surface tension of liquid Al was approximately −2.0 MPa, according to the Young-Laplace equation. At this temperature, alumina was not wetted by liquid Al (44); thus, the capillary pressure was negative and the alumina shell was repelled to liquid Al. These findings are consistent with the observations in fig. S3 that some Al “droplets” were expelled out of the sample surface after being annealed at 700°C.

Because the oxide shell occupies a substantial fraction of material volume, and the native oxide layer plays important roles in their thermal stability and mechanical response (see below), nanoporous Al samples prepared by GRR are the nanoporous Al-Al$_2$O$_3$ core-shell composites. For convenience and accuracy, nanoporous Al is called nanoporous Al-Al$_2$O$_3$ composite in the following sections.

Mechanical properties of nanoporous Al-Al$_2$O$_3$ composite

GRR-generated nanoporous Al-Al$_2$O$_3$ composites were free of native cracks and were therefore suitable for mini-compression and mini-tension tests. Figure 2A shows that these samples were plastic under compression. The yield strength, defined by the stress at a plastic strain of 0.5%, was approximately 73 MPa for the as-prepared nanoporous Al-Al$_2$O$_3$ composite. The yield strength of the annealed samples did not decrease but rather increased with increasing annealing.
Yield strength, $Y$, increased with increasing $T_a$ but decreased at $T_a = 650°C$ when the annealing temperature was very close to the melting temperature of Al. The high-accuracy strain measurements (47) by digital image correlation in tensile tests (Fig. 2B) was allowed for the determination of the Young’s modulus (Y) of nanoporous sample. We found that Y increased monotonically with annealing temperature $T_a$, from 16 GPa for the as-prepared samples to 25 GPa for the samples at $T_a = 650°C$, as shown in Fig. 2D.

As summarized in Fig. 3, the strength of previous nanoporous metals decreased more rapidly with decreasing density and was not really high compared with those of conventional foam metals. The high strength of nano-ligaments in these nanoporous metals has been offset by poor load-bearing efficiency of the dealloyed structure (32, 48, 49). As shown in Fig. 3, the density of nanoporous Al-Al$_2$O$_3$ composite prepared by GRR is lower than that of most previous nanoporous metals; in contrast, nanoporous Al-Al$_2$O$_3$ is as among the strongest nanoporous materials prepared by dealloying, both under tension and compression, although its structure size is coarser than that of most nanoporous metals. The strength of nanoporous Al-Al$_2$O$_3$ is also considerably higher than that of conventional foams of similar density consisting of pure Al and Al-based composites (50–53). Consequently, nanoporous Al-Al$_2$O$_3$ lies in the top left of this strength-density chart. In other words, the specific strength (strength-to-density ratio) of nanoporous Al-Al$_2$O$_3$ is higher than that of previous porous metals, porous Al-oxide composites, and nanoporous metals.
Native oxide layer on ligament surfaces

As shown in Fig. 4 (A to C), the high-angle annular dark-field (HAADF) scanning TEM (STEM) and EDS images of the as-prepared nanoporous sample show a large quantity of oxygen on the ligament surfaces (Fig. 4C). High-resolution TEM (HRTEM) images (Fig. 4D) show a sharp boundary between Al and the alumina layer. The fast Fourier transform pattern shown in this figure reveals the amorphous structure of the surface alumina layer, which agrees with previous reports (42). The amorphous structure of the alumina layer was maintained in all the annealed samples in this study. X-ray photoelectron spectroscopy confirmed that the surface amorphous oxide layer was Al2O3. As shown in Fig. 4E and fig. S4, the thickness of the alumina layer varied between 3 and 18 nm, with an average value of approximately 10 nm for the as-prepared nanoporous Al-Al2O3 composite. The thickness of the alumina layer did not increase; rather, it decreased by 24%, on average, after annealing (Fig. 4, E and F, and fig. S5). Apparently, further oxidation was prevented and the alumina layer experienced densification (35) during annealing (in Ar).

Alumina may be formed on the Al ligament surface during GRR because the ionic liquid inevitably contained water [the water content was approximately 1400 parts per million (ppm) for the ionic liquid solution used in this study]. Because of the high electrical insulation of the alumina layer, metallic Al may not be deposited on ligaments with a passive layer of alumina during GRR. This explains why the deposition of Al halted on the surface of ligaments behind the reaction front or on the outside surface of the sample, where the ligament surface was covered by alumina after long-time exposure to ionic liquid (water). Most likely, GRR took place at the reaction front before the alumina layer was formed. This phenomenon is highly similar to the self-limited growth of atomic-thick films on complex surfaces in each ALD reaction cycle (54). The initial passive layer that prevented Al deposition during GRR in this study could have been thinner than 10 nm and may have thickened to ~10 nm or higher during the longer GRR in ionic liquid or when the sample was exposed to air.

The surface alumina layer observed on Al ligaments was thicker than that on flat Al surfaces [typically 4- to 5-nm thick (42)], probably because nanosized Al ligaments are more reactive than bulk Al. The presence of this thin, self-healing alumina layer was responsible for the high thermal stability of nanoporous Al-Al2O3 composite and maintained the shape of the sample at 700°C when the Al cores melted. Notably, this material is also nonflammable and stable in the atmosphere at high temperatures. When annealed in air, the thickness of the alumina layer hardly changed at 400°C and increased from 10 nm to approximately 36 nm after annealing at 600°C for 10 hours (see fig. S6).

Plastic deformation of nanoporous Al-Al2O3 composite: The roles of grain boundaries and oxide layer

The plastic deformation in nanoporous Al-Al2O3 composite was uniform after compression to a strain of 0.30. As shown in the TEM image in Fig. 5A, most pore channels remained open after compression. Localized slip bands, which were often observed in compression of submicron-scale single-crystal Al (38, 40, 55), were rarely observed in deformed Al ligaments (see Fig. 5A and SEM images in fig. S7). Previous studies (38, 40, 41) have shown that deformation of bicrystal Al micropillars was more uniform than single-crystal Al pillars under compression, because grain boundary can suppress localized slip by impeding dislocation motion or promoting dislocation nucleation at grain boundaries. Some studies (42, 56) have also shown that surface oxide could [but not always (57)] induce strain hardening and lead to uniform plasticity under tension, suggesting that surface oxide may suppress localized slip under certain stress states. Accordingly, uniform deformation of Al ligaments observed in this study might have resulted from the combined effects of grain boundaries, alumina passive layer, and complex stress state of Al ligaments.

Further HAADF-STEM examinations revealed dislocations in some grains after compression (see Fig. 5, B and C). The dislocation density was relatively low, and very little dislocation tangle was...

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Fig. 4. Native oxide layer on ligament surface of nanoporous Al. (A) High-angle annular dark-field STEM image and (B and C) EDS elemental maps showing the spatial distribution of Al and O, respectively. (D) HRTEM image showing naturally formed alumina on the surface of Al ligaments. Inset fast Fourier transform patterns confirm crystalline Al core (bottom left) and amorphous-structured surface alumina shell (top right). (E and F) Quasi in situ TEM images of alumina layer (E) before and (F) after annealing at 600°C for 0.5 hours. Dashed lines indicate alumina/Al boundaries. Dotted lines are grain boundaries (G.B.).

Fig. 5. TEM/HAADF-STEM images of a deformed nanoporous Al-Al2O3 composite with compression strain of 0.30. (A) A typical bright-field TEM image of deformed nanoporous Al-Al2O3 composite. (B and C) HAADF-STEM images showing lattice dislocations bounded by (B) surface and (C) grain boundaries in deformed ligaments.
observed in the nanoporous sample after compression. The dislocation density in nanoporous sample can be roughly estimated from HAADF-STEM images by counting the number of dislocations in each grain (58). This method may, however, underestimate the dislocation density because some dislocations are invisible under certain zone axes. The obtained data are thus only a rough order-of-magnitude estimate of the dislocation density. It was found that the dislocation density increased from approximately $10^{11}$ m$^{-2}$ for the as-prepared nanoporous sample to the order of $10^{13}$ m$^{-2}$ for the sample with a compression strain of 0.30.

The dislocation density in deformed nanoporous Al-Al$_2$O$_3$ is one order of magnitude lower than that reported in deformed bulk Al (dislocation density: $~10^{14}$ m$^{-2}$) (59) or bicrystal Al micron-scale pillars (dislocation density: $~10^{14}$ m$^{-2}$) (41) under similar plastic strain. This indicates that, in our case, the grain boundaries were not so effective in blocking dislocation motion; instead, grain boundaries may provide preferential sites for dislocation nucleation (40) or annihilation (38) as reported previously in the deformation of submicron-scale Al pillars. This scenario is consistent with previous reports that introducing grain boundary can slightly, but not substantially, increase the strength of (bicrystal) submicron-scale Al pillars (38, 40). The strength is predominantly controlled by the pillar size, although grain boundaries may affect the strain hardening rate (38, 40, 41). This phenomenon may also apply to nanoporous Al-Al$_2$O$_3$ composite, in which the size of Al grains is not remarkably smaller than the ligament size.

Compared with grain boundaries, the alumina layer might have contributed more evidently to the strength of this nanoporous material. On one hand, the alumina layer is far stronger than the Al ligaments. Previous studies (40, 60, 61) showed that the yield strength of Al pillars with diameters of 200 to 300 nm, which is comparable to the ligament diameter in this study, varied between 500 and 700 MPa. The strength of the natural (amorphous) alumina layer on Al is approximately 3.85 GPa, according to Li et al. (42). For a 200-nm-thick Al cylindrical ligament with a 10-nm-thick alumina shell, the volume fraction of alumina was approximately 20%. Using the rule of mixture, the strength of 200-nm-thick Al ligaments with a 10-nm-thick alumina shell is estimated to be $\sigma_\text{f} = 1136$ to 1300 MPa. This analysis indicates that the alumina layer may have contributed nearly half the strength of this nanoporous material. On the other hand, the alumina shell can strengthen the metallic core of the Al ligaments by hindering the nucleation and escape of dislocations at the alumina/aluminum interface. This “interface effect” is more pronounced when the ligament diameter is below the submicron scale. Jin and Weissmüller (9) revealed that even a monolayer oxide on the ligament surface can substantially enhance the strength of nanoporous gold. For nanoporous gold with a ligament size of 200 nm, the strength increased by approximately 20% after monolayer oxidation. Similarly, surface modification–induced strengthening has been observed in other nano-objects (62, 63). Since the alumina layer in this study is substantially thicker (and harder to break through by dislocations) than monolayer oxide as shown in previous studies (9, 62–64), the additional strengthening effect from surface oxide could be even more pronounced, particularly for the densified alumina layer, as will be discussed below.

**Densification of native oxide layer during annealing**

As shown in Fig. 1 (A and B), the geometrical structure [and ligament (Fig. 1G) and grain sizes (Fig. 1H)] of nanoporous Al-Al$_2$O$_3$ composite remained unchanged after annealing at 600°C for 0.5 hours. It was thus unlikely that the stiffening and strengthening during annealing (below 600°C) was induced by the evolution of the network structure or the strengthening of the core material (pure Al). It was also not induced by the growth of the alumina layer; as shown in Fig. 4F, the alumina layer became thinner after annealing (in Ar).

The only possibility is that the structure and mechanical properties of the alumina shell changed during annealing. Further characterization revealed that the amorphous Al$_2$O$_3$ shell did not crystallize during annealing, which is reasonable because the crystallization temperature for amorphous Al$_2$O$_3$ (>800°C) (65, 66) is well beyond the annealing temperatures used in this study. The reduction of alumina thickness suggests that the amorphous alumina layer might have experienced densification during annealing, as also proposed by Biener et al. (35) when interpreting the stiffening and hardening of annealed nanoporous Au with an ALD layer of Al$_2$O$_3$. It is unlikely that the thinning of alumina layer was induced by the diffusion of oxygen into Al gains, because of the very limited solubility of oxygen in Al. Secondary-ion mass spectroscopy (SIMS) also revealed a reduction in the hydrogen content during annealing (see fig. S8), which is consistent with a previous report (65) that the densification of amorphous Al$_2$O$_3$ was accompanied by hydrogen desorption.

In addition to the desorption of weakly bound species, the densification of amorphous Al$_2$O$_3$ also involves a reorganization of the amorphous network [a transformation from a corner-sharing polyhedral to an edge-sharing octahedral (67)], thus enhancing the strength and elastic modulus of the alumina layer. Tane et al. (68) reported that, for an amorphous Al$_2$O$_3$ film formed by electron beam deposition, the elastic modulus increased by 28%, while the density of this film increased by 4% (or a film thickness reduction of approximately 4%) after annealing at 700°C for 12 hours. The thickness of an ALD layer of amorphous alumina deposited at 300°C was reduced to 15% after densification at 700°C (65). Our observation of a 24% reduction in alumina thickness on Al ligaments is reasonable, because the native alumina shells were formed at the ambient temperature and could be less dense. Such a large densification can greatly increase the elastic modulus and strength of the alumina layer and also account for the stiffening and strengthening of annealed sample in this study.

**Load-bearing efficiency**

As shown in Fig. 3, nanoporous Al-Al$_2$O$_3$ composite stood out with the highest specific strength partly because its relative density and thus load-bearing efficiency are higher than those of previous nanoporous metals [including nanoporous Au with ALD coating of alumina (35)]. The following analysis indicates that the load-bearing efficiency of nanoporous Al-Al$_2$O$_3$ composite is still below the theoretical value and there is room for further improvement.

The Young’s modulus ($Y_f$) of isotropic open-cell foams can be related to that of solid struts ($Y_s$) and relative density ($\varphi$), via the Gibson-Asby scaling equation (33)

$$Y_f = Y_s \cdot \varphi^2$$

where the subscripts f and s denote foam and solid struts or ligaments, respectively. Although the Gibson-Asby scaling equation for strength applies only to foams with $\varphi < 0.30$ (33), the equation for Young’s modulus (Eq. 1) is valid over the full range $0 < \varphi < 1$.
Previous studies have shown that the Young’s modulus of an Al beam is size-independent when its thickness is larger than 10 nm (70). The Al ligaments in this study are one order-of-magnitude thicker than this threshold size. Thus, the Young’s modulus of the ligaments is equal to that of bulk Al ($Y_\text{f} = 70$ GPa). Using this data, according to Eq. 1, we obtain a predicted value of $Y_1 = 29.6$ GPa for nanoporous Al with $\varphi = 0.65$. As summarized in Fig. 2D, the Young’s modulus of nanoporous Al (15 to 25 GPa) measured in this study is substantially lower than the theoretically predicted value.

The aforementioned analysis ignored the alumina shell, which is stronger and stiffer than Al. The Young’s modulus of amorphous alumina is approximately 211 GPa (42). Using the rule of mixture, we obtained $Y_\text{f} = 97$ GPa for the Al ligaments. Accordingly, for nanoporous Al-Al$_2$O$_3$ composite with $\varphi = 0.65$, Eq. 1 predicted a Young’s modulus of 41 GPa, which is remarkably larger than our experimental data.

The analysis suggests that, despite the high relative density of nanoporous Al-Al$_2$O$_3$ composite, its structure is still less efficient in load-bearing than that proposed by the Gibson-Ashby model. On one hand, this makes it difficult to quantitatively interpret the mechanical properties of nanoporous Al-Al$_2$O$_3$ composite, particularly the contributions of the alumina layer. On the other hand, it presents the possibility for further stiffening and hardening of this material in the future by optimizing their geometrical structures and further refining the structure sizes.

### Coarsening and network structural evolution

The Young’s modulus of nanoporous Al-Al$_2$O$_3$ composite increased but its strength decreased when $T_\text{a}$ increased from 600° to 650°C. This reduction cannot be attributed to the densification of the oxide layer, as discussed above, which simultaneously increases the elastic modulus and strength. We emphasize that the presence of the alumina shell suppressed, but did not prevent, coarsening. The coarsening of nanoporous Al-Al$_2$O$_3$ composite is negligible at or below 600°C for an annealing time of 0.5 hours but is evident at a higher annealing temperature or for a longer annealing time. As shown in Fig. 1 (G and H), both ligament size and grain size increased unexpectedly to 270 nm after annealing at 650°C. The mechanism of this coarsening is still unclear. Most likely, this coarsening is controlled by the diffusion of the core material (Al) but not that of the alumina because the nanoporous Au with alumina coating is stable at 650°C (35).

Structural coarsening might account for the decreased strength and increased elastic modulus of nanoporous Al-Al$_2$O$_3$ when $T_\text{a}$ increased from 600° to 650°C. Coarsening (of the ligament and grain sizes) might decrease the strength of ligaments and thus lower the strength of this material. However, the coarsening may “heal” the network structure, improve its load-bearing efficiency, and give rise to an increase in the macroscopic elastic modulus (it is size-independent at this scale). It has been reported in nanoporous Au (in the absence of a surface alumina layer) that the geometrical structure evolves in annealing: For low-density nanoporous Au with $\varphi < 0.30$ (32, 48, 49, 71), ligaments tend to pinch off; thus, material becomes less efficient in load bearing, leading to one order-of-magnitude drop in the Young’s modulus. This also explains why the strength of nanoporous metals decreases more rapidly with decreasing density compared with that of conventional foam metals (see Fig. 3). For high-density nanoporous Au with $\varphi > 0.30$, the network structure can be “healed” by straightening the ligaments, as evidenced by the enhanced Young’s modulus after annealing (32, 72). This phenomenon might have occurred in nanoporous Al-Al$_2$O$_3$ composite, whose relative density is well beyond this threshold value. The annealing-induced structural “healing” increases the elastic modulus but not the strength, because the latter is more sensitive to size. The softening of Al ligament induced by coarsening might have prevailed over the strengthening induced by topological structure evolution and alumina densification.

### Nanoporous Al(Zn) by GRR of Mg(Zn) alloy

The abovementioned nanoporous Al-Al$_2$O$_3$ composite was prepared by GRR of Mg-Al line compound, whose composition varies in a very narrow range. Consequently, the relative density of the obtained nanoporous sample is fixed at around 0.65 (without oxidation). Here, we show that Mg solid solutions can also be subjected to GRR for the synthesis of nanoporous Al alloys with different (lower) relative densities.

As reported in Yang et al. (27), GRR can transform a piece of pure Mg into a pure Al with a poorly interconnected nanobundle-like structure, as shown in Fig. 6A. In this case, the precursor sample (Mg) is completely dissolved during GRR, and the entire resultant material is composed of deposited Al. The connectivity of the GRR product can be improved by adding a small amount of Zn (~5 at %) to the Mg precursor. Zn was less reactive than Al and remained unetched at the GRR front. As shown in Fig. 6 (B and C), GRR of Mg$_{95}$Zn$_5$ led to a uniform, fine, and well-interconnected nanoporous structure, with a relative density of 0.49. Furthermore, minor alloying of Zn (~7 at % Zn in nanoporous Al) has refined ligament diameter from 175 ± 81 nm (Fig. 6A) to 44 ± 17 nm (Fig. 6C).

During GRR of the Mg(Zn) precursor, Mg is selectively dissolved from Mg(Zn), and undissolved Zn atoms might segregate at the interface at the reaction front. The Zn cluster may evolve into a network-like structure that acts as a template for Al deposition, eventually leading to an isotropic nanoporous Al(Zn), which was curtailed passivated with alumina. From this point of view, minor alloying of pure Mg with Zn has enabled dealloying in the corrosion process of GRR, similar to that observed in GRR of Al$_2$Mg$_3$.

Nanoporous Al(Zn) was not fully oxidized (see fig. S9), and its structure was stable against coarsening, despite its small structure size. As shown in Fig. 6D, the ligament size increased very slightly from 44 ± 17 nm to 50 ± 17 nm after annealing at 500°C for 0.5 hours, whereas the melting point (solidus temperature) of Al$_{93}$Zn$_7$ is approximately 590°C. The mechanical characterization of nanoporous Al(Zn) with passive oxide layer is hindered by the presence of high-density cracks. Several successful strategies (17, 30, 73–75), which have been developed for mitigating cracks in dealloyed materials, might also apply to GRR-made nanoporous Al(Zn) and other Al alloys.

Nanoporous Al-Al$_2$O$_3$ composite (or nanoporous Al with native oxide shell) prepared by GRR is stronger than conventional porous metals and porous Al-oxide composites with a similar density. Nanoporous Al-Al$_2$O$_3$ composite is also lighter, stronger, and more stable than most nanoporous metals prepared by dealloying. The native oxide layer on the surface of Al nano-ligaments is the major reason for the excellent thermal stability of nanoporous Al-Al$_2$O$_3$ composite. The combined effects of oxide layer, ligament size, and topological structure are responsible for the high strength (and high specific strength) of this material. We anticipate that the light, strong, and stable nanoporous Al-Al$_2$O$_3$ composite would be explored for...
As-prepared

Annealed

Fig. 6. Nanoporous Al(Zn)-Al₂O₃ composite formed by GRR of a Mg(Zn) alloy. SEM images of (A) a nanobundle-structured Al formed by GRR of pure Mg, (B and C) an nanoporous Al(Zn) formed by GRR of Mg₉₅Zn₅ in [EMIM]⁺Al₂Cl₇⁻ ionic liquid, and (D) an nanoporous Al(Zn) annealed at 500°C for 0.5 hours. The relative density is approximately 49% for nanoporous Al and Al(Zn).

functional applications such as high-temperature plasmonics (76, 77), micro heat exchangers (78), and electrodes for batteries and other electrochemical devices (79, 80). The current study also suggests that refining the structure size to the submicron or nanometer scale might greatly improve the performance of porous Al or Al foams (33) for structural applications, because structure refinement not only introduces the size effect but also amplifies the passive-oxide effect on strength. Currently, the thickness of nanoporous Al-based samples is limited by the slow rate of GRR in ionic liquids. Further studies are required to develop simpler, more efficient, and cost-effective routes to fabricate large-scale, high-quality, and more-ductile nanoporous Al-based materials, which are essential for practical applications.

MATERIALS AND METHODS

Sample preparation

Precursor alloy ingots with nominal compositions of Al₂Mg₃ and Mg₉₅Zn₅ were prepared by melting high-purity Al (>99.9 at %), Zn (>99.9 at %), and Mg (>99.9 at %) (Beijing Jiaming Platinum Nonferrous Metals Co. Ltd.) in a resistance furnace in an Ar atmosphere. These ingots were sealed in a quartz tube in an Ar atmosphere, homogenized by annealing at 420°C for 24 hours, then quenched in water. Before the GRR, the samples cut from the alloy ingots were polished with a SiC abrasive paper up to 3000 grit size and then cleaned using ethanol. The GRR was conducted by immersing precursor samples (Al₂Mg₃, pure Mg, and Mg₉₅Zn₅) in an [EMIM]⁺Al₂Cl₇⁻ ionic liquid. This ionic liquid was prepared by slowly adding AlCl₃ (anhydrous powder, 99.99%: Alfa Aesar) to 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl; 97%; Acros Organics B.V.B.A.) with a molar ratio of 2:1 under magnetic stirring to prevent overheating and thermal decomposition of the electrolyte. The ionic liquid was stirred for 12 hours to ensure uniformity and then refined with pure Al wires for 12 hours. The water content of the ionic liquid was ~1400 ppm, as characterized by a Karl Fischer Coulometer (AKF-3, HOGON). All experiments involving ionic liquids were performed in an argon atmosphere glove box at around 28°C, where the oxygen content and moisture were maintained below 0.1 ppm. The obtained nanoporous samples were carefully rinsed in acetone (AR, Sinopharm Chemical Reagent Co. Ltd.) and then dried before they were removed from the glove box for other measurements. The sample dimensions and volume essentially remained unchanged during GRR. Thus, the density of nanoporous Al and Al alloys prepared by GRR can be obtained as \( \rho_{np} = \left( \frac{m_{np}}{m_{pre}} \right) \rho_{pre} \), where \( \rho_{pre} \) and \( \rho_{np} \) are the densities of the precursor and nanoporous sample, and \( m_{pre} \) and \( m_{np} \) are the sample masses before and after GRR, respectively. The relative density of nanoporous samples was determined from the stoichiometry (composition change) of the GRR, assuming that sample volume did not change during GRR. Surface oxidation has been considered in the estimation of relative density. The measured density value (1.74 ± 0.03 g/cm³) agrees fairly well with that (1.98 g/cm³) estimated from relative density, considering that both methods involved indirect estimations. The latter (the larger one) is used in Fig. 3. Annealing of the as-prepared nanoporous Al and Al(Zn) samples was performed by sealing these materials in a quartz tube with an argon atmosphere and then annealing them in a tube furnace at different temperatures and various times.

Structural characterization

Microstructural morphology was characterized using SEM (FEI Verios SEM 460) operated at 10 kV. Quasi in situ SEM examination of nanoporous Al-Al₂O₃ composite before and after annealing was performed on a surface milled using an ion-beam milling system (Leica EM RES101). The cross section of nanoporous Al-Al₂O₃ composite was revealed by manually breaking the sample using tweezers. TEM and HRTEM observations were performed on an FEI Tecnai F20 operated at 200 kV. TEM and HRTEM, along with HAADF STEM and EDS observations, were performed on an FEI Talos F200X, operated at 200 kV. The samples used for TEM were mechanically polished to approximately 30 μm and then ion-milled on a Gatan 695. The sample annealed at 600°C for 10 hours in air used for TEM characterization was cut by dual beam focused ion beam (focused ion beam/SEM FEI Nanolab Helios 650). The distribution of the ligament diameter was determined from the SEM images of finely polished surfaces using AQUAMI (81). The distribution of the grain size was determined by measuring the size of 350 to 600 grains for each sample from the dark-field TEM images.

The surface oxide layer was characterized by x-ray photoelectron spectroscopy (ESCALAB250) using an Al Ku x-ray source. The compositions of the surface oxide layer before and after annealing were characterized by time-of-flight SIMS (ION TOF-SIMS V) using a Cs ion source. The dislocation density was measured by counting the number of dislocations in each grain in the HAADF-STEM images (58). The dislocation density was estimated as \( \rho = n / (N \cdot d^2) \), where \( n \) is the number of dislocations in a STEM map, \( N \) is the number of grains in this map, and \( d \) is the mean grain size. For each sample, the dislocation density was obtained by analyzing ~20 STEM images, with 30 to 40 grains in each image.
Mechanical tests
The microhardness (Vickers hardness) of nanoporous Al-Al$_2$O$_3$ composites was measured using an automatic microhardness tester (Qness Q10 A+) with a load of 10 g and a holding time of 10 s, on a surface milled using an ion-beam milling system (Leica EM RES101). Uniaxial compression tests were performed on a SHIMADZU AG-X testing system at a constant strain rate of 2.5 × 10$^{-4}$ s$^{-1}$. The tensile tests were performed using a custom-made microtensile testing system at a constant strain rate of 4 × 10$^{-4}$ s$^{-1}$. The details of the system and testing procedure can be found in You et al. (82). The tensile sample was “dog-bone”-like with a gauge section of approximately 100 μm × 80 μm and a gauge length of approximately 250 μm. The strain was measured by digital image correlation with a high accuracy (82). The tensile strain was measured by digital image correlation with a high accuracy (100).

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Acknowledgments: We thank X. G. Zheng for assistance in the sample preparation. We also thank Dr. L. and G. J. Hu for measuring the water content of ionic liquid. Funding: This work was supported by grants from the National Key R&D Program of China (2017YFA0204401) and the National Natural Science Foundation of China (51971218). Author contributions:
H.-J. conceived, designed, and oversaw the project. W.Y. prepared the samples. Z.-P.L., H.X., and W.Y. performed the SEM and TEM characterizations. W.-K.B., Z.-S.Y., and W.Y. conducted the mechanical tests. All authors contributed to the data analysis. W.Y. and H.-J.J. wrote the manuscript. 

**Competing interests:** The authors declare that they have no competing interests.

**Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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**Submitted 31 March 2020**

**Accepted 26 May 2021**

**Published 9 July 2021**

**Citation:** W. Yang, Z.-P. Luo, W.-K. Bao, H. Xie, Z.-S. You, H.-J. Jin, Light, strong, and stable nanoporous aluminum with native oxide shell. *Sci. Adv.*, 7, eabb9471 (2021).