Processing of NaCl powders of controlled size and shape for the microstructural tailoring of aluminium foams

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Abstract

NaCl powders are prepared by anti-solvent crystallisation, varying in controlled fashion the morphology and size of resulting powders. These powders are then used to produce open-cell pure aluminium foams by infiltration, using the replication process. The microstructure and the compressive mechanical behaviour of these foams are compared with those of similar foams made using commercial NaCl powders of less regular shape and size. It is found that, while the foam pore shape does not influence strongly the initial power-law behaviour of the foam, it causes variations in the strain at which the foam deviates from power-law behaviour.

Keywords: Sodium chloride; Crystallisation; Infiltration; Replication process; Aluminium foam; Compressive behaviour

1. Introduction

There exists at present a relatively wide palette of methods for the production of metal foams; these are comprehensively reviewed in several recent publications [1,2]. Amongst current foam-production methods, the replication technique is well suited for the production of uniform and fine open-cell foams of lower melting-point metals such as aluminium [3]. Replication processing consists in infiltrating a leachable porous preform of sintered powder that is subsequently removed by dissolution. Given its low cost, its chemical inertness in contact with aluminium, its relatively high melting point and its ease of dissolution in water, sodium chloride (NaCl) is often used as the preform filler material for aluminium foams [4–6].

In replicated foams, the pore shape is predominantly controlled by the initial shape of the leachable powder that was used to produce the infiltrated preform: save for powder geometry changes induced while bonding the preform, pores of the resulting foam “replicate” the initial shape of these powder particles. Changing the shape of the powder used to produce the preform therefore provides a pathway for the exploration of microstructure/property relations in open-pore metal foams.

As with many water-soluble inorganic salts, industrial production of NaCl crystals is generally conducted by evaporative crystallisation. When NaCl crystallisation is conducted from brine under slow evaporation conditions, large cube-like transparent crystals are obtained. With an aim to reduce energy costs in NaCl production, a new route has recently been developed, named anti-solvent crystallisation. This consists in inducing precipitation of NaCl crystals from brine by adding a second “anti-solvent” liquid, in the presence of which the solubility of NaCl drops significantly. Classical organic anti-solvents include 2-isoproxyethanol [7], N-dimethylisopropylamine [8] or N-diisopropylamine [9]. The resulting NaCl particles possess relatively large sizes and feature a bimodal distribution; however, it has been shown that NaCl particles of narrowly distributed size in the range 2–3 μm can be produced using acetone as the anti-solvent [10].

An interesting feature of anti-solvent precipitation is that it affords some level of control over particle size and shape. The main factors influencing crystal growth and morphology with this technique can be classified in two main categories:
2. Experimental procedure

2.1. Materials

Citric acid (C(OH)(COOH)(CH$_2$COOH)$_2$; 99.5 mass%), poly(acrylic acid) (MW 2000), sodium hydroxide and ethanol were all purchased from Aldrich (Buchs, Switzerland). Fine NaCl used in the virgin state for preform preparation and infiltration (called hereafter “commercial salt”) was purchased from Salines de Bex SA (Bex, Switzerland). The NaCl powder (99% purity) used to prepare these powders and assess their mechanical behaviour by means of compression testing of miniature specimens, with a goal to explore the influence of pore morphology on the deformation behaviour of open-celled metal foams.

2.2. Preparation of precipitated sodium chloride particles

Different NaCl powders were prepared by precipitation using aqueous and organic liquids. Saturated brine was prepared by dissolving 450 g Fluka NaCl powder in one litre of distilled water. The organic liquid was produced either by dissolving solid organic additive (polyacrylic acid or citric acid) directly in ethanol, or alternatively by mixing 1 mol/l sodium hydroxide solution with ethanol. Precipitation was then carried out in a glass vessel by rapid addition of a controlled volume of brine into the organic solution under ambient conditions. The mixture was homogenised by magnetic stirring at 370 rpm. Depending on the powder lot produced, stirring was maintained (Powders I, IV, VI and VII) or stopped after 30 s (Powders II, III and V). The total precipitation time was varied in one instance, with a goal to observe the influence of powder particle coarsening. The resulting precipitates were then filtered, washed twice with ethanol, and dried under vacuum for about 5 h. Experimental parameters defining the seven powder lots produced in this work are given in Table 1.

2.3. Preparation of aluminium foams by the replication process

Aluminium foams were prepared using Powders IV, V and VI; these are respectively called Foams IV, V and VI. NaCl preforms were first prepared by cold isostatic pressing (CIPing) the NaCl powder in a silicone rubber mould (of internal diameter 20 mm and internal height 20 mm) for 1 min under 12.7 MPa.

These NaCl preforms were infiltrated with molten pure (99.99%) aluminium heated to 710°C under 10 MPa argon gas and then solidified directionally. The Al/NaCl composites so produced were machined to produce metallographic samples and cylindrical compression test specimens. The salt pattern was then finally dissolved by immersion in distilled water.

2.4. Microstructural characterisation

NaCl crystal X-ray diffractograms were obtained under Cu K radiation using a Siemens Model D500 diffraction apparatus (Munich, Germany). Powder compositions were determined using IR transmittance spectra in the range from 400 to 2000 cm$^{-1}$ recorded with 256 scans on a Nicolet 510

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Table 1

<table>
<thead>
<tr>
<th>Powder number</th>
<th>Organic solution</th>
<th>Aqueous solution</th>
<th>Precipitation parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ethanol volume (ml)</td>
<td>Additive Concentration (mol/l)</td>
<td>Volume (ml)</td>
</tr>
<tr>
<td>I</td>
<td>10 Polyacrylic acid</td>
<td>0.06</td>
<td>5</td>
</tr>
<tr>
<td>II</td>
<td>20 Sodium hydroxide*</td>
<td>0.20</td>
<td>5</td>
</tr>
<tr>
<td>III</td>
<td>20 Citric acid</td>
<td>1.02</td>
<td>10</td>
</tr>
<tr>
<td>IV</td>
<td>10 Citric acid</td>
<td>0.06</td>
<td>10</td>
</tr>
<tr>
<td>V</td>
<td>300 Citric acid</td>
<td>1.02</td>
<td>150</td>
</tr>
<tr>
<td>VI</td>
<td>20 Citric acid</td>
<td>1.02</td>
<td>10</td>
</tr>
<tr>
<td>VII</td>
<td>20 None</td>
<td>–</td>
<td>10</td>
</tr>
</tbody>
</table>

* In this case the total volume of the organic solution is equal to 25 ml which corresponds to 5 ml of 1 mol/l sodium hydroxide solution and 20 ml of ethanol.
FT-IR spectrometer (Madison, USA). The size and morphology of NaCl particles or pores in aluminium foams were examined by low voltage scanning electron microscopy of powders directly deposited on an aluminium stub without gold sputtering, using a Philips SFEG high-resolution scanning electron microscope (Eindhoven, The Netherlands).

As particles have a cubic aspect, characteristic dimensions of each particle are quantified using their Féret diameter (largest axis between two parallel tangents on opposite sides of the particle) and by their aspect ratio (ratio between the largest axis to the minor one) [13,14]. For all experiments, the mean Féret number and the mean aspect ratio were calculated by counting approximately 50–80 particles on several scanning electron micrographs.

Foams were characterised and examined using standard techniques of metallographic preparation and observation, using the optical and the scanning electron microscope.

2.5. Mechanical testing of the aluminium foams

Compression tests were performed on a screw-driven 10 kN universal testing machine. Spherically aligned platens were used, after coating their surfaces with Teflon spray so as to reduce friction with the specimen end surface. All tests

<table>
<thead>
<tr>
<th>Experiment n°</th>
<th>Morphology</th>
<th>Mean Féret number (standard deviation)</th>
<th>Mean aspect ratio (standard deviation)</th>
<th>S.E.M. micrographs</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (additive: 0.06 M polyacrylic acid)</td>
<td>Polydisperse rectangular particles.</td>
<td>12.1 μm (5.7 μm)</td>
<td>1.8 (0.5)</td>
<td>(1.I) 20 μm</td>
</tr>
<tr>
<td>II (additive: 0.2 M sodium hydroxide)</td>
<td>Four-leaf clover-like particles.</td>
<td>58.2 μm (5.9 μm)</td>
<td>1.1 (0.1)</td>
<td>(1.II) 50 μm</td>
</tr>
<tr>
<td>III (additive: 1 M citric acid)</td>
<td>Pierced cube-like particles.</td>
<td>46.6 μm (6.7 μm)</td>
<td>1.1 (0.2)</td>
<td>(1.III) 20 μm</td>
</tr>
<tr>
<td>IV (additive: 0.06 M citric acid)</td>
<td>Small cubic particles.</td>
<td>3.3 μm (1.1 μm)</td>
<td>1.2 (0.2)</td>
<td>(1.IV) 10 μm</td>
</tr>
</tbody>
</table>

Fig. 1. Influence of chemical parameters on the NaCl crystal morphology. SEM micrographs of NaCl powders precipitated in presence of (1(I)) polyacrylic acid; (1(II)) sodium hydroxide; (1(III)) high citric acid concentration and (1(IV)) lower citric acid concentration.
were run in crosshead displacement control at a speed of 2 μm/s. The deformation of the foam was monitored using three LVDTs with a resolution of 1 μm located symmetrically around the specimen so as to verify that the platens remain parallel during the test.

Due to the small amounts of powder produced by precipitation, it was only possible to produce and test sub-sized compression specimens; these had a diameter of approximately 15 mm and a height between 2 and 5 mm depending on powder lot size. Cylinders with a diameter of 20 mm and a height of 20 mm were machined from the foam produced with commercial NaCl powder.

3. Results

3.1. NaCl powder precipitation

NaCl powders can be precipitated by pouring an aqueous NaCl solution in ethanol, as this reduces sharply the solubility of NaCl [15]. Powder VII, produced in this manner without additives, comprised polydisperse aggregated cubic particles. Additives were therefore studied, with a goal to improve the NaCl powder shape and size distribution.

Powders I–III were produced in order to test the influence of the additive nature on the NaCl powder morphology. Three different additives were explored: a polymeric additive (polyacrylic acid, Powder I), a basic additive (sodium hydroxide, Powder II) and tricarboxylic acid (citric acid, Powder III). Results are given in Fig. 1.

When a polymeric additive is used (Powder I), parallelepipedic powders are obtained, somewhat elongated along one axis with perpendicular flat faces (Fig. 1(I)). This is reflected in an average aspect ratio equal to 1.8 ± 0.5 for this powder.

The two other additives result in equiaxied particles, of aspect ratio around 1.1–1.2 (Fig. 1). Using sodium hydroxide as the additive (Powder II), the NaCl crystal morphology changes to what can be described as four-leafed clover-like cuboidal particles (Fig. 1(II)). A third morphology is obtained when citric acid in ethanol is employed as the organic phase,
Powder III: cubical particles featuring a stepped pyramidal hollow on each facet (Fig. 1(III)).

The influence of variations in the concentration of citric acid was explored with Powder IV, produced using 0.06 mol/l citric acid (instead of 1 mol/l for Powder III), with stirring maintained throughout precipitation. Far smaller and neatly cubical unagglomerated particles are obtained (Fig. 1(IV)). This powder features the most homogeneous grain size distribution of all, with the lowest size dispersion.

The influence of precipitation physical conditions was tested with Powders V and VI. Fig. 2 presents the corresponding micrographs. These are to be compared with Powder III. Powder V was held for 60 instead of 30 min, allowing more time for particle coarsening. Filled cubical particles of roughly the same size are obtained (Fig. 2(V)). Powder VI was stirred, as opposed to Powders III and V, which were not. The major changes induced by stirring are the production of particle fragments and a mixture of two main morphologies: hollow pyramid-faced cubical particles with more closed surfaces than Powder III, and hollow single-pyramid particles. The Féret number distribution is also more scattered.

Powder infrared spectra were gathered to investigate the presence or absence of the additive on the surface of the particles. The reference spectrum of pure citric acid (Fig. 3(a)), shows the characteristic stretching vibration bands of carboxyl groups at about 1730 cm$^{-1}$, together with other group vibrations causing two characteristic band series in the ranges 1100–1200 and 1300–1400 cm$^{-1}$. The other spectra of Fig. 3 correspond to the powders synthesized with low (0.06 mol/l, Powder IV) or high (1 mol/l, Powders III, V and VI) citric acid concentration. It appears that citric acid is only adsorbed onto the powders prepared with the 1 mol/l solution (Fig. 3(c)–(e)). The infrared spectrum of Powder II was also measured, to find that there is no evidence for the adsorption of ethanolate anions since no methyl group vibrations were observed.

X-ray diffraction patterns were also gathered on the powders. When comparing these X-ray patterns to those of commercial purity NaCl, no detectable difference in peak position can be found. It thus appears that citric acid does not penetrate into the crystals.

#### 3.2. The metallic foams

Fig. 4 contains micrographs of the aluminium foams obtained successively with Powders IV (Foam IV Fig. 4(a) and (b)), Powder V (Foam V Fig. 4(c) and (d)), and Powder VI (Foam VI Fig. 4(e) and (f)). In Foams V and VI, the metal pores clearly replicate in negative the shape of the NaCl particles. With Foam IV, on the other hand, the pores seem somewhat more rounded than the initial powder (compare Fig. 1(IV) and 4(b)). For comparison, the structure of the foam produced from 63 to 90 µm commercial NaCl powders is given in Fig. 4(g) and (h).

The NaCl preform made of Powder IV contained around 30% porosity. Measuring the volume and the mass of Foam IV yields the expected porosity of 70%. The corresponding values for Powder V and Foam V are respectively, 33 and 68%. Aluminium Foam VI on the other hand shows a porosity of 53%, while the porosity of the Powder VI NaCl preform was 57% and hence differed from the expected value of 47% (100 – 53).

The internal structure of each foam after compression to the final strain of the test is shown in Fig. 5 by observation of the compression sample surface in the scanning electron microscope after testing (hence the occasional presence of dust particles trapped in the foam). These micrographs are to be compared with those in Fig. 4.

#### 3.3. Mechanical properties of the metallic foams

Restrictions placed on sample dimensions by the limited batch sizes of “in-house” NaCl powders implied that test specimens were limited to a few millimetres in height. The consequence was that even slight imperfections in the alignment of parallel faces of the specimens caused significant experimental error in the measured stress–strain curves. This was apparent in that, at low strain, these curves featured an initially low and increasing slope gradually leading to an inflexion point, something that is contrary to the power-law elastoplastic behaviour exhibited at low strain by this class of foam. We provide in Appendix A a simple slice-model analysis of the consequences of non-parallel specimen faces on compression of a power-law material, to show that (i) it explains the observed low-strain stress–strain curve features, and more importantly that (ii) past the point of full contact of the platen with the sample end surfaces, the influence exerted by non-parallel specimen faces on the stress–strain curve...
becomes negligible. As a consequence, the only correction that is required to compensate for this effect is to shift the strain origin to a proper value. This value is easily deduced graphically, knowing that the present pure aluminium foam stress–strain curves obey the standard power law of deformation with a stress exponent near 0.25 [5]. Lower-strain data are then erased from the curve. The analysis and data reduction procedure are detailed in Appendix A.

All foam compression curves reported here are thus plotted after correction for non-parallel specimen face artefacts. Results for Foams IV–VI are given in Fig. 6(a)–(c), respectively, together with a plot for a foam of similar density.
Fig. 5. Aluminium foams after compression (a) and (b) compression of the foam made with NaCl Powder IV; (c) and (d) compression of the foam made with NaCl Powder V; (e) and (f) compression of the foam made with NaCl Powder VI and (g) and (h) compression of a foam made with a commercial 63–90 µm NaCl powder.
Fig. 6. Engineering stress $s$ - engineering strain $e$ compression curves (a) for Foam IV (----) and a foam made from commercial NaCl particles 10 μm in size of relative density 32% (-----); (b) Foam V (-----) and a foam made from commercial NaCl particles 63–90 μm in size of relative density 32% (-----) and (c) Foam VI (-----) and a foam made from commercial NaCl particles 63–90 μm in size of relative density 45% (-----). All curves are plotted after data processing as described in Appendix A for correction of non-parallel specimen faces effects.

and relatively close pore size produced using commercial NaCl powders. Specifically, the commercial salt was sieved into two size ranges: near 10 μm (comparable to Foam IV (Fig. 6(a))) and 63–90 μm (comparable to Foams V and VI (Fig. 6(b) and (c)), respectively densified to densities near those of Foams IV and V (32 vol.%) and VI (45 vol.%).

4. Discussion

4.1. Factors controlling the NaCl crystallisation

Additives, even in small quantities, clearly influence the precipitation of NaCl from brine with ethanol as the “anti-solvent”. Additives can be selectively adsorbed on crystal facets, such that the growth of individual nuclei is deactivated and the interfacial energy between the crystal and the solution is altered; these changes in turn influence the particle size distribution and the particle morphology [16].

Organic polymers are known to influence the crystallisation of solid particles from a solution, by adsorption at the solid–liquid interface. The particle size or morphology of the precipitating powder can then depend on the molecular weight, concentration, global charge or conformation of polymers [17–19]. This can be explained by steric constraints or structure-directing interactions of the polymers on the nucleation and crystal growth of the inorganic powders [20–23]. Given the low polymer concentration and the large size of polymeric molecules, it is reasonable to expect that the polymer distribution on each facet is not homogeneous: this may be why non-equiaxed particles are obtained.

With sodium hydroxide, two anionic species can be created in solution: hydroxyl anions, and ethanolate anions formed by reaction of hydroxyl anions with the ethanol solvent. These anions may be directly adsorbed onto the growing particle surface and act as growth modifiers, resulting in the observed strong crystal morphology modification. Since the infrared spectrum of Powder II shows no evidence for the adsorption of ethanolate anions, it is most reasonable to conclude that hydroxyl adsorption is responsible for the growth-induced particle shape modification (hydroxyl adsorption cannot be distinguished from water adsorption in the range 3000–3600 cm$^{-1}$).

With citric acid, Powder III, the stairs descending towards the cube centre from their edges can be explained as resulting from a disturbance in the growth of facets from the edge inwards [24]. The presence of citric acid was identified on the IR spectrum of particles of Powder III Fig. 3(c)). This implies effective adsorption of carboxylic acid onto the particles: adsorption of this species must be responsible for the observed strong crystal morphology modification. Since the infrared spectrum of Powder II shows no evidence for the adsorption of ethanolate anions, it is most reasonable to conclude that hydroxyl adsorption is responsible for the growth-induced particle shape modification (hydroxyl adsorption cannot be distinguished from water adsorption in the range 3000–3600 cm$^{-1}$).

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To explain the differences induced by agitation (Powder VI), one can suppose that (i) particle growth is destabilised...
by stirring and (ii) growing particles are broken. Attentive examination of recorded micrographs shows indeed that hollow pyramids can be directly formed by fragmentation of the pierced cube-like particles: the observed hollow pyramids correspond to an interior face of the observed hollow-faced cube-like particles of Powder III.

To summarise, one can rationalise some of the differences in the powder morphology by assuming citric acid adsorption on growing NaCl particles with 1 mol/l citric acid, resulting in complicated particle shapes. On the other hand, little adsorption seems to occur at an acid concentration of 0.06 mol/l: the organic acid seemingly then only acts as a size stabiliser and agglomeration reducer.

### 4.2. The metallic foam structure

Comparing Powder IV with Powder V reveals that the use of similar cube-shaped NaCl particles of different sizes leads to different foam morphologies: the smaller cubic particles of Powder IV produce an aluminium foam with smooth and rounded struts (Fig. 4(a) and (b)) while the larger particles of Powder V, also of cubical shape, lead to a foam with far more angular and neatly cubical voids (Fig. 4(c) and (d)). Although the finer Powder IV cubes are indeed a bit more rounded than the larger Powder V cubes, the difference between the two metal foams exceeds that a priori expected given the initial particle shape alone. This difference between the two foams must therefore be attributed to a difference in sintering behaviour during the time spent by the preform in the infiltration furnace (1 h at 710°C). This makes sense: transport processes responsible for powder sintering and pore rounding are known to be far more rapid and potentially different with finer powders, i.e. for Powder IV than for Powder V [26]. We note in passing that Foam IV is perhaps the finest low-density aluminium foam produced to date.

The comparatively higher density of Foam VI is explained by the lower initial salt preform density obtained with Powder VI. This is not unexpected, given the more intricate and hollow particle shapes obtained. The difference between the observed porosity of Foam VI, of 53%, and the expected porosity based on the density of the Powder VI NaCl preform, of 43% (100 − 57), is a sign of incomplete infiltration of the preform by the metal. This is in all likelihood due to closed voids in individual NaCl particles forming Powder VI. Given the presence of hollows in the particles, this would indeed be realistic.

### 4.3. Mechanical behaviour

Many aluminium foams tested in compression [27–31] exhibit a stress–strain behaviour similar to the idealised schematic curve proposed by Gibson and Ashby [32] for foams made of an elastic-perfectly plastic material, namely (i) stress rising linearly with strain at low stresses (elastic deformation), followed by (ii) a nearly flat portion of the curve called the “collapse plateau” and finally, (iii) a densification regime where the cell walls come in contact one with another, causing an abrupt rise in the flow stress. Unlike the Gibson–Ashby model (where the plateau is a result of the assumed perfectly plastic behaviour), the plateau observed on the compression curves of today’s commercial closed-cell aluminium foams results from localisation of their plastic deformation: cells collapse in successive discrete bands at a relatively constant stress [33–37].

The aluminium foams produced here by the replication process behave differently. Setting aside the very early stages of foam deformation, which as shown are influenced by slight imperfections in test specimen face alignment (see Appendix A), two regimes can be distinguished in the present compressive stress–strain curves, consistent with what was found in an earlier investigation of similar replicated pure aluminium foams [5]:

(i) a region of power-law deformation with a strain exponent near 0.25 where the engineering stress $s$ is related to the engineering strain $\varepsilon$ by:

$$s = K \varepsilon^{0.25},$$

(ii) a region at higher strains where both the stress and the rate of work hardening rise above values corresponding to the power-law behaviour of Region (i).

No stress plateau is thus observed, furthermore, the foam deforms homogeneously throughout the test, with no visible collapse bands. Values for $K$ in Region (i) of foam deformation for the present foams are reported in Table 2. According to San Marchi and Mortensen [5], two work hardening mechanisms operate in the present foams: (i) the intrinsic work hardening inherent to deformation of the metal making the foam and (ii) another mechanism, which increases in importance as the foam is compressed to become noticeable above a compressive strain on the order of 10%. The power-law behaviour is expected to result from the first work hardening mechanism alone, based on elementary mechanical analysis [5]. The second work hardening mechanism is at present not fully identified, however, as argued in ref. [5] available evidence suggests that it involves strut impingement, i.e. the formation of new solid material contacts across the open pores of the foam, to an extent that increases gradually with foam compression.

To evaluate the strain at which the second mechanism becomes noticeable and to compare the mechanical behaviour of the various specimens we define the “transition strain” $\varepsilon_1$ as that where the stress–strain curve deviates from power-law behaviour of Region (i), Eq. (1). This strain was measured at the point where curves of $e^s = f(e)$ deviate from a straight line (Fig. 7) resulting values for $\varepsilon_1$ are given in Table 2.

Comparing the finest foams, i.e. Foam IV and the commercial 10 µm salt foam, it is difficult to reach a conclusion concerning the influence of pore shape on flow stress parameter $K$. Indeed, this parameter is significantly higher for the
Foam mechanical behaviour parameters

<table>
<thead>
<tr>
<th>Precursor salt</th>
<th>IV (Commercial)</th>
<th>V (Commercial)</th>
<th>VI (Commercial)</th>
<th>VI (Commercial)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (μm)</td>
<td>5 10 50</td>
<td>63–90 50</td>
<td>63–90</td>
<td></td>
</tr>
<tr>
<td>( V_{fA} ) (%)</td>
<td>31 32</td>
<td>32 32</td>
<td>47 45</td>
<td></td>
</tr>
<tr>
<td>( e_t ) (%)</td>
<td>6.4 8.9</td>
<td>7.3 10.1</td>
<td>3.1 4.7</td>
<td></td>
</tr>
<tr>
<td>( K ) (MPa)</td>
<td>4.8 3.8</td>
<td>3.9 4.0</td>
<td>6.4 7.6</td>
<td></td>
</tr>
</tbody>
</table>

\( V_{fA} \) is the volume fraction of metal in the foam, \( e_t \) the transition strain defined as the strain where the curve \( e^2 = f(e) \) deviates from a straight line and \( K \) a proportionality constant in the power-law relation \( (s = Ke^{0.25}) \) describing the beginning of the stress–strain behaviour of replicated Al foams in compression.

more regularly structured Foam IV; however, there is also a scale (i.e. pore-size) effect in replicated aluminium foams akin to what is seen in composites: the flow stress of the foam rises with decreasing pore size [38]. For this reason, it cannot be said to what extent the difference in \( K \) is a pore scale or pore shape effect. Examination of the data (Fig. 7) suggests that the scaling effect is dominant. Indeed, the curves are nearly parallel, which suggests a uniform hardening of the metal, also, there is no such effect with Foam V.

Foams V and VI can be compared with commercial salt foams of similar pore size and density (Table 2). Foam VI has a somewhat lower flow stress constant \( K \) than its equal-density commercial-salt counterpart. This is not surprising given the morphology of Powder VI, with its numerous pyramids. These constitute “dead metal” regions that contribute essentially nothing to load bearing in the foam, raising its density with no benefit in terms of foam mechanical performance at low strain. In other words, at a given volume fraction of metal, the amount of material constituting the struts is lower in Foam VI, lowering in turn the flow stress compared with the foam made with commercial salt.

Comparing Foam V and the commercial 63–90 μm salt foam of the same density one finds that \( K \) varies on the other hand relatively little, despite the rather different internal architecture of the two pairs of foam (compare respectively Fig. 4(c) and (d) with Fig. 4(g) and (h)). The implication must then be that initial deformation of the foams is primarily concentrated in regions that have a relatively similar shape and orientation regardless of the overall pore shape. Most likely, these are narrower metal struts inclined perpendicularly to the stress axis. There is, indeed, in both foam types significant bending of narrower struts after deformation (Fig. 5).

Taken together, the present data indicate that the influence of pore shape on the flow stress constant at lower strain is relatively minor for the range explored here. The main reason for a decrease in flow stress seems to be the presence of highly convex pore surfaces, which raise the foam density by addition of “dead metal” that does not contribute to load bearing in the foam.

The transition strain, \( e_t \), on the other hand, varies significantly with the foam internal structure (Table 2) (compare also the curves in Fig. 6). For all three more regularly shaped and sized “anti-solvent precipitation” salt foams the transition strain is about 25% lower than its value for corresponding foams made with commercial salt. In the higher strain regime the former thus have a higher flow stress than the latter.

For Foam VI this is expected if indeed deviations upwards from the power-law are due to strut impingement: NaCl particle facet hollows result in a foam structure containing...
convex pyramids. These are bound to touch at lower strains than concave pores of the foam produced with commercial salt, as seen indeed in Fig. 5(e) and (f).

Foams IV and V also show earlier dominance of the second hardening mechanism attributed to strut impingement than corresponding foams produced from commercial powders. Here, the reason is less obvious, as there are no convex geometrical features in these foams such as the pyramids of Foam VI; however, one can still argue that the cubical pores of this foam are less convex than the nearly spherical pores of the commercial NaCl foams. If we assume for simplicity that strut impingement becomes significant when nearest opposing pore faces begin to meet in regions of high local foam deformation, it follows that the rounder the pores, the later strut contact should set in. This is illustrated in simple terms in Fig. 8: strut contact should appear in a foam with cubical pores (Foams IV and V) at a strain roughly equal to 80% of the strut contact strain for a foam of equal density containing spherical pores (commercial powder foams).

This is roughly the difference in transition strain between the two foam types. This explanation thus accounts for the difference observed; however, it is of course very tentative and incomplete. Indeed, local strains for pore face contact are far higher than the observed foam transition strains e_t, the transition strain for Foam VI should then be even lower, and perhaps strut contact is not the reason for the increased rate of work hardening. This interpretation would indicate that, the less convex the pore shape is, the earlier the stress–strain behaviour of a replicated foam should deviate upwards from the power-law behaviour of the metal of which it is composed.

At still higher strains as shown in Fig. 5 that in Foam V flat aluminium facets formed between salt cubes have collapsed, resulting in a structure that resembles a loose piling of aluminium platelets: clearly, local crushing of individual pores has occurred.

5. Conclusion

Five different NaCl particles morphologies have been produced by “anti-solvent” precipitation of NaCl from brine using ethanol in the presence of one of the following additives: poly(acrylic acid), sodium hydroxide or citric acid. With citric acid the additive concentration plays a role in determining the NaCl crystal morphology, as do physical precipitation parameters such as agitation or coarsening time.

The present anti-solvent precipitated NaCl particles can be divided in two categories according to the particle size range. Low concentrations of citric acid or polyacrylic acid lead to fine NaCl particles (smaller than 15 μm). Particles with complex morphologies and of average size above 15 μm are obtained with higher concentrations of sodium hydroxide or citric acid additives. With citric acid, additive adsorption is shown to play a role in precipitation.

Replication processing can be used to produce aluminium foams from these particles, with pores down to 5 μm in average diameter. Compressive stress–strain curves display a power-law hardening region, followed by a region of increasing apparent work hardening rate, consistent with an earlier study of replicated aluminium foam. It is found that the particle shape exerts relatively little influence on the low-strain power-law constant. On the other hand, the powdery properties of the foam stress–strain curve deviates from power-law behaviour. This deviation is observed with foams produced from regularly shaped and sized cube-derived NaCl particles at a compressive nominal strain around three-quarters its value for less regular and more rounded commercial salt. Assuming that this deviation is caused by mutual strut impingement during deformation, this study indicates that, the less convex the pore shape is, the earlier the deviation in flow stress upwards from power-law behaviour is in replicated aluminium foams.

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Appendix A. Cylindrical metal foam sample compression testing: influence of sample face misalignment

Consider a cylindrical sample of metal foam, of diameter 2r and height L_0, that has its top and bottom surfaces slightly non-parallel. It is tested in compression between two parallel platens. If a is the angle between the two non-parallel sample faces, we define the misalignment parameter a as a = d tan(a) (Fig. 9). Unless the top and bottom sample faces are grossly misaligned, a ≪ L_0.
We assume that, as found in an earlier study [5], the metal foam material exhibits common power-law (exponent \( n \)) hardening behaviour in engineering stress–strain coordinates, \( s = K e^n \) where \( s \) is nominal (engineering) stress, \( e = \Delta L/L_0 \) with \( \Delta L = L_0 - L \) is the nominal (engineering) strain and \( K \) is a constant. During the compression test, the force \( f(x) \) exerted on a sample slice of thickness \( dx \) and constant height located at distance \( x \) from the axis of the cylinder is:

\[
 f(x) = 2k \left( \frac{(a/2r)(r - x) - (a - \Delta L)}{L_0} \right)^n \sqrt{r^2 - x^2} \, dx
\]

when the compression platens have moved closer to one another by distance \( \Delta L \) measured from the moment of first contact with the highest point of the cylinder (Fig. 9).

Assuming that the responses of the different slices are independent from one another (i.e. using a simple slice model), the global force \( F = pr^2s \) on the specimen is:

\[
 F = \int_{-r}^{C} \left[ 2k \left( \frac{(a/2r)(r - x) - (a - \Delta L)}{L_0} \right)^n \sqrt{r^2 - x^2} \right] \, dx
\]

for \( L = a \) (A-2a)

with \( -r \leq x \leq C = r(2\Delta L/a - 1) \), and

\[
 F = \int_{-r}^{C} \left[ 2k \left( \frac{(a/2r)(r - x) - (a - \Delta L)}{L_0} \right)^n \sqrt{r^2 - x^2} \right] \, dx
\]

for \( L = a \) (A-2b)

Fig. 10 shows, after numerical integration of these equations, the influence of varying misalignment \( a \) on the resulting engineering stress–engineering strain curve from the compression test, all other parameters remaining constant.

![Fig. 9. Profile drawing of compressed cylindrical sample with non-parallel faces, defining parameters in the calculation.](image)

These curves display the general shape of experimental curves found in the present experiments, indicating that the initial portion of the curves in this work is indeed influenced by face misalignment (the effects of which become noticeable because of the small sample height \( L_0 \)).

If we consider a foam of strain hardening exponent \( n \approx 0.25 \) (as found for replicated pure Al foams produced analogously to the present material [3]), a plot of \( s^4 \) versus \( e \) will yield a straight line in the absence of misalignment (\( a = 0 \)).

With \( a > 0 \), the \( s^4 \) versus \( e \) curve does not follow a straight line at small strain; however, as shown in Fig. 11, calculations show that once the apparent engineering strain \( \Delta L/L_0 \) exceeds \( e_{mis} = a/L_0 \), the curve very rapidly becomes linear and parallel to the \( s^4 \) versus \( e \) curve obtained with \( a = 0 \).

Past this point, thus, the engineering stress–strain curve is essentially unaffected by misalignment. In short, misalignment perturbs the stress–strain curves mainly by causing an artificial shift in the strain origin. This creates an inflexion

![Fig. 11. Same as Fig. 10 in coordinates of \( s^{1/n} \) vs. apparent strain \( e = \Delta L/L_0 \), showing that the plots are essentially identical past the point where \( \Delta L = a \), save for an artificial shift in the strain origin caused by the misalignment.](image)
point in the curve, before which the data have no real significance.

Compressive engineering stress–strain curves measured in this work were thus plotted with a strain origin defined at the intercept with the horizontal axis of the extrapolated linear curve through $s^2$ plotted versus $(\Delta L/L_0)$. Such a linear portion was present for all samples tested here, confirming that $\gamma \approx 0.25$ for these pure aluminium foams. The early portions of the data are plotted as a dotted line, to indicate that these portions of the stress–strain curves are to be discarded.

We note in closing that, were the misalignment caused by lack of parallelism of the platens and not the sample faces, the derivation and the consequences are essentially the same.

References