

# Synthesis of nickel–aluminide foams by pack-aluminization of nickel foams

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## Abstract

Nickel–aluminide foams were synthesized from unalloyed nickel foams by using a two-step, high-activity pack-aluminizing process at 1273 K. After processing, the nickel–aluminide foams exhibited the original structure of the original nickel foams (open-cells with hollow struts and low density). Single-phase NiAl foams, with average composition within 1 wt.% of stoichiometry and with 92% open porosity, were produced by first selecting the appropriate aluminizing time, and then annealing to homogenize the structure. Foams of average Ni<sub>3</sub>Al composition were produced by the same method, but multiple intermetallic phases remained due to large variations in strut thickness and thus local composition. Nickel wires and tubes were also aluminized at 1273 K and homogenized for different times to further investigate the aluminizing kinetics and the creation of Kirkendall pores. For aluminization depths up to about 100 μm, Kirkendall pores can be avoided, leading to pore-free struts in the foam. © 2001 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Metallic foams exhibit low density and high specific strength, stiffness and surface area, which make them attractive for acoustic and thermal insulation use and for structural applications such as sandwich panels [1]. Developing an intermetallic foam with high melting temperature, high creep strength and good corrosion- and oxidation resistance would allow many novel applications at elevated temperatures [2], e.g. as foam-filled cores of insulating sandwich panels for aerospace skins or engine casings, or as a core within hollow gas turbine blades. A nickel–aluminide foam would be particularly interesting, as NiAl and Ni<sub>3</sub>Al in bulk form have been the subject of extensive research over the last decades and have sparked interest for many high-temperature applications [3,4]. Traditional liquid-phase methods for processing metal foams, when applied to nickel aluminides, present severe challenges due to the high melting temperatures and high reactivity of the melt. Alternatively,

solid-state techniques can be used, as shown by Chung et al. [5] who pack-aluminized a partially-sintered nickel anode into porous NiAl. Self-propagating high-temperature synthesis of nickel aluminides from elemental powders can also result in porous NiAl and Ni<sub>3</sub>Al [6]. However, for both of the above methods, the shape, size, spacing and connectivity of the pores is difficult to control and the porosity achieved is much lower than typically associated with foams. To our knowledge, no highly-ordered, cellular intermetallic foams have been produced by any method to date.

Starting with a cellular nickel foam (which can be produced, e.g. by nickel deposition in the liquid or gas phase upon a sacrificial polymer foam), we investigate in the present paper the fabrication of a nickel–aluminide foam by pack aluminization. This method has been extensively used in the past to provide protective coatings on nickel and nickel-base superalloys, as it creates a corrosion-, oxidation- and temperature-resistant intermetallic layer of NiAl or Ni<sub>3</sub>Al. The kinetics and thermodynamics of layer aluminization have been discussed elsewhere [7–10]. Previous research on pack aluminization focused on aluminide surface layers used as coatings, which were much thinner than the substrate. In contrast,

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we investigate in the present paper the complete conversion of nickel to nickel–aluminide specimens by pack-aluminization. Furthermore, we focus specifically on the complex geometry of open-cell foams.

## 2. Experimental procedures

### 2.1. Initial nickel foams

Two unalloyed nickel foams (>99.0% purity) were used: a coarse foam with 20 ppi (pores per linear inch) from Astro Met (Cincinnati, OH), fabricated by reduction of nickel oxide [11], and a finer foam with 80 ppi from Goodfellow (Cambridge, UK) made by Chemical Vapor Deposition (CVD) [12]. The foams span a range of relative densities (ratio of foam density and solid density) and geometric parameters (cell size, strut width, strut wall thickness), as presented in Table 1. Scanning electron microscope (SEM) micrographs were used to measure the cell geometric parameters. Foam density was determined from mass and volume measurements.

### 2.2. Aluminization process

To produce NiAl foams, a high-activity, two-step pack-aluminizing process was chosen, as described for the formation of aluminide layers on bulk nickel [7–10,13]. The aluminum source in the pack determines the activity of the pack [13] where an aluminum content  $\geq 60$  at.% Al is generally considered a high-activity pack. The pack consisted of 3 wt.%  $\text{NH}_4\text{Cl}$  activator from Fisher Scientific (Pittsburgh, PA), 15 wt.% Al (99.8% pure,  $-40+325$  mesh) from Alfa Aesar (Ward Hill, MA), and 82 wt.%  $\text{Al}_2\text{O}_3$  powder filler from C-E Minerals (Baton Rouge, LA). A total pack mass of 25 g was contained in a nickel crucible with 75 ml capacity, covered with a high-chromium stainless-steel sheet. The nickel foam (mass ranging from 0.21 to 0.26 g for the 80 ppi foam and 0.33 to 0.44 g for the 20 ppi foam) was embedded within a layer of pure  $\text{Al}_2\text{O}_3$  powder which extended 2 mm above and below the foam and was located midway within the pack. This arrangement prevented direct contact between the nickel foam and the aluminum powders in the pack, which was found to

result in a highly exothermic reaction leading to localized melting of the nickel struts.

Aluminization was conducted under an argon atmosphere with the crucible initially placed in the water-cooled end of a vertical tube furnace (700 mm in length) and subsequently rapidly raised into the hot zone of the furnace. The aluminization process was carried out at 1273–5 K for times ranging from 10 min to 4 h, after which the crucible was rapidly lowered back to the water-cooled end and allowed to cool to room temperature under argon. Because it was found that the pack was exhausted after about 5 h at 1273 K, longer aluminization times were not investigated.

To determine the kinetics of aluminization for more simple geometries, aluminization experiments were also conducted on nickel tubes and wires. The nickel wires (99.99% purity, from Alfa Aesar) had a diameter of 1000 and 500  $\mu\text{m}$ , and a length ranging from 32 to 39 mm. Two pairs of wires were aluminized simultaneously under the same conditions as the nickel foams for times ranging from 10 min to 4 h. The nickel tubes (99.5% purity, from Alfa Aesar) exhibited an outer diameter of 350  $\mu\text{m}$  an inner diameter of 300  $\mu\text{m}$ , and a length ranging from 29 to 36 mm. Aluminization of five tubes per pack was carried out for 2 or 4 h, following the procedures described above, except that the total mass of the pack was reduced to 2 g. Both ends of all tubes were polished to ensure that they were open, thus allowing the ingress of the aluminum halide gases.

### 2.3. Homogenization treatment

After weighing to record the aluminum mass gain following aluminization, samples were encapsulated in evacuated quartz tubes and annealed at 1273 K for times ranging from 8 to 24 h. Small pieces of  $\text{Ni}_2\text{Al}_3$  were added to the capsules to prevent aluminum losses during heat-treatment. The phases and compositions of all aluminized and homogenized samples were checked by two or more of the following methods: microbalance weight measurements ( $\pm 0.3$  mg), optical microscopy, Vickers microhardness measurements (100 g load for 15 s), energy dispersive spectroscopy (EDS) in a SEM ( $\pm 1.2$  wt.%), and wet chemical analysis. The EDS profile and Vickers test were calibrated using NiAl,  $\text{Ni}_3\text{Al}$ ,  $\text{Ni}_2\text{Al}_3$ , Ni and Al

Table 1  
Geometric parameters of nickel foams

Pores per linear inch (ppi) <sup>a</sup>	Foam thickness (mm)	Cell diameter (mm) <sup>b</sup>	Strut width ( $\mu\text{m}$ )	Strut wall thickness ( $\mu\text{m}$ )	Relative density (%)	Supplier
80	1.6	0.32	54.9 $\pm$ 5.0	6.0 $\pm$ 1.1	3.5	Goodfellow
20	8.7	1.27	224 $\pm$ 34	83.5 $\pm$ 21.3	2.2	Astro Met

<sup>a</sup> Data from supplier.

<sup>b</sup> Calculated from ppi value.

standards for which composition was known within 0.01 wt.%.

### 3. Results

#### 3.1. Nickel tubes and wires

Fig. 1a–c shows optical micrographs of 500  $\mu\text{m}$  diameter nickel wires aluminized for 4 h and subsequently homogenized for 0, 8 or 24 h. Fig. 1a shows the aluminized wire without further heat-treatment, for which only two phases can be clearly identified: a  $\text{Ni}_2\text{Al}_3$  shell with average thickness of 100  $\mu\text{m}$  and an inner Ni core with average diameter 387  $\mu\text{m}$ ; the intermediate NiAl and  $\text{Ni}_3\text{Al}$  layers are too thin to be seen on the micrographs (high magnification observation revealed an irregular NiAl/ $\text{Ni}_3\text{Al}$  layer with thickness of less than 5  $\mu\text{m}$ ). The average nickel composition of the wire is about 82 wt.% Ni; thus, after complete homogenization, a two-phase NiAl/ $\text{Ni}_3\text{Al}$  is expected (i.e. an inner core of  $\text{Ni}_3\text{Al}$  and an outer shell of nickel-rich NiAl). Fig. 1b presents the same sample after 8 h of homogenization, where the NiAl/ $\text{Ni}_3\text{Al}$  layer has grown at the expense of the nickel core. Also, there was a significant decrease in the  $\text{Ni}_2\text{Al}_3$  layer microhardness (from about 700 to about 500 HV), indicating a shift in composition towards NiAl (with hardness 250 HV at stoichiometry), as also observed in Ref. [17]. Fig. 1c shows a sample homogenized for 24 h. Rather than the expected NiAl/ $\text{Ni}_3\text{Al}$  structure described above; the wire consists of a thin irregular outer shell of  $\text{Ni}_2\text{Al}_3$  in contact with a large inner shell of Al-rich NiAl. These shells are separated by an almost continuous ring of voids from an inner core of nickel.

Fig. 2a shows a nickel tube aluminized for 2 h, with an average nickel composition of 80 wt.%. The structure consists of four concentric shells, with the following compositions (starting from the outside diameter):  $\text{Ni}_2\text{Al}_3$ , NiAl,  $\text{Ni}_3\text{Al}$  and Ni. Most of the porosity is located within the nickel layer and there is no separation of layers by porosity, unlike the situation shown in Fig. 1c. Fig. 2b illustrates a tube homogenized for 10 h after aluminization under the same conditions as Fig. 2a (and with the same composition). Two phases are visible, which, according to the average composition, are expected to be NiAl and  $\text{Ni}_3\text{Al}$ . Most of the porosity within the nickel shell (Fig. 2a) appears to have migrated towards the inner surface of the tube.

#### 3.2. Nickel foams

Fig. 3 gives an overall view of both 80 and 20 ppi foams before and after aluminization. Fig. 3a and b illustrates the cellular structure and the different cell size of the 20 and 80 ppi nickel foams, while Fig. 3c and d depicts the shape, width and wall thickness of the nickel

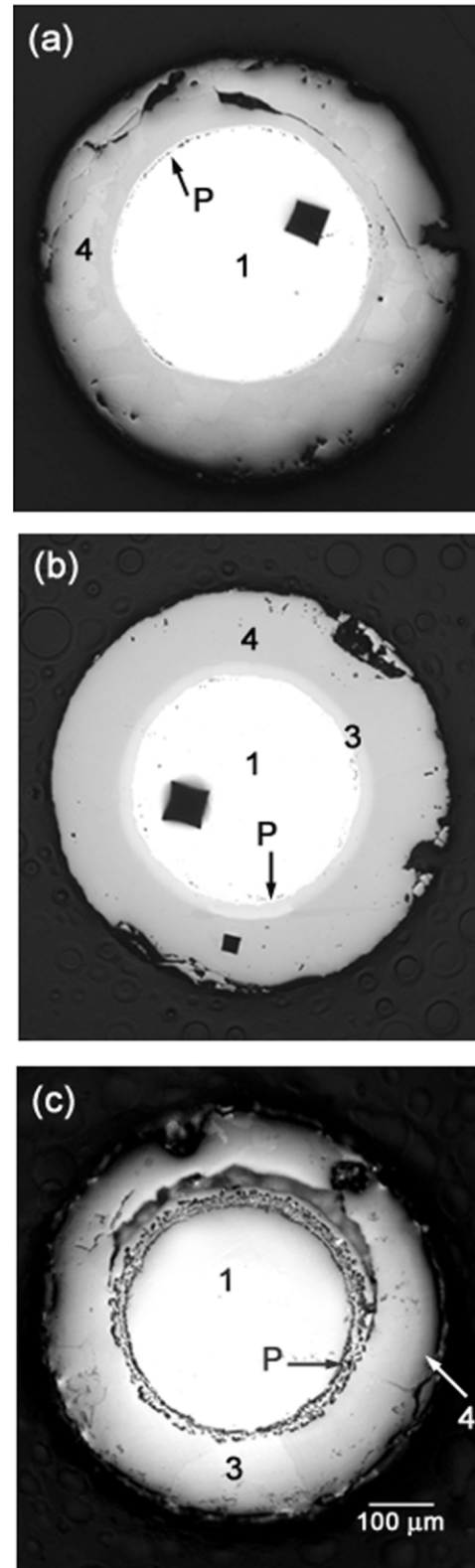


Fig. 1. Optical micrographs of nickel wires (500  $\mu\text{m}$  diameter) aluminized for 4 h (82 wt.% Ni) and homogenized at 1273 K for: (a) 0 h, (b) 8 h and (c) 24 h. Cracks and indentations are due to metallographic preparation and micro-Vickers testing. Phases are labeled as follows—1: Ni, 2:  $\text{Ni}_3\text{Al}$ , 3: NiAl, 4:  $\text{Ni}_2\text{Al}_3$ , P: pores.

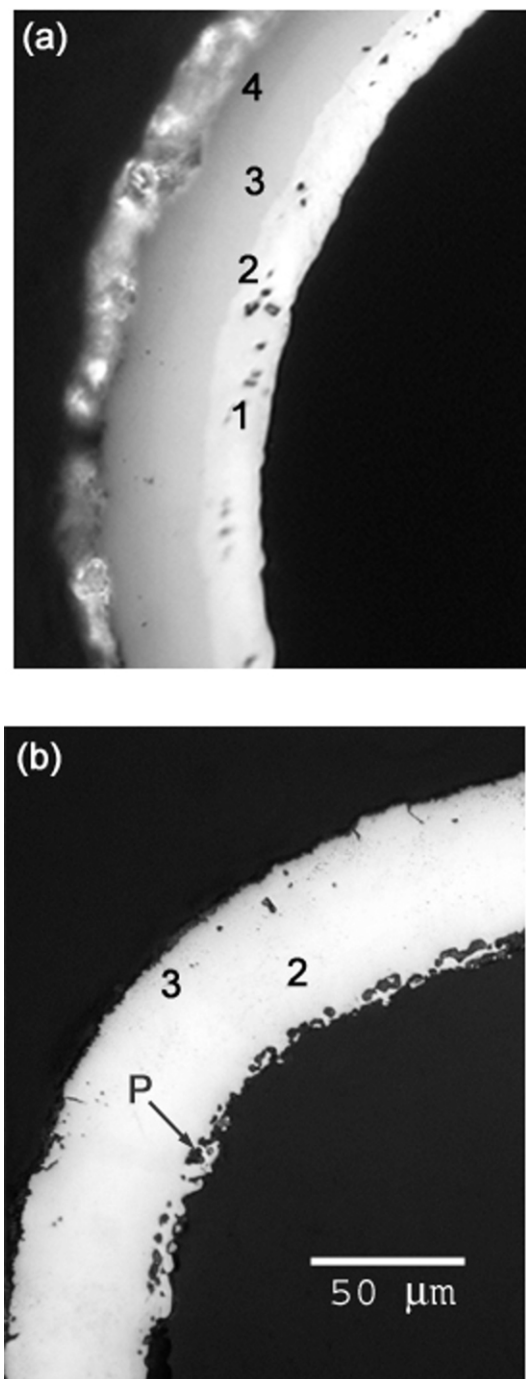


Fig. 2. Optical micrographs of nickel tubes (350  $\mu\text{m}$  outside diameter and 25  $\mu\text{m}$  wall thickness) aluminized for 2 h (80 wt.% Ni) and homogenized for: (a) 0 h and (b) 10 h. Phases are labeled as follows—1: Ni, 2:  $\text{Ni}_3\text{Al}$ , 3:  $\text{NiAl}$ , 4:  $\text{Ni}_2\text{Al}_3$ , P: pores.

struts (values listed in Table 1), which were fractured to show their hollow structure. Fig. 3e and f, showing both foams after aluminization, demonstrate that the overall foam architecture and the hollow strut morphology are maintained after aluminization; however, a rougher surface topography is observed. All foams conserved their original macroscopic shape and size, as expected if

volume increase occurs solely in the radial direction of the struts.

Aluminizing of 80 ppi nickel foams produced a multi-phase nickel aluminide structure. Fig. 4a shows an 80 ppi foam aluminized for 0.5 h and with average composition of 78 wt.% Ni (in the  $\text{NiAl}/\text{Ni}_3\text{Al}$  two-phase field). The foam wall thickness is 6–14  $\mu\text{m}$  but the plane of polishing is not perpendicular to the strut axis, leading to larger apparent dimensions. The enclosed black areas represent the internal cavities of the hollow struts (visible in Fig. 3c for the nickel foam). In Fig. 4a, the outer surface layer is  $\text{Ni}_2\text{Al}_3$ , which is in contact with a thin layer of  $\text{NiAl}/\text{Ni}_3\text{Al}$  next to a Ni core. The same layer sequence is visible from the inner wall surface, indicating that aluminization also occurred from the inner surface of the struts. Fig. 4b shows a foam aluminized for 1.5 h and with an average composition of 68.2 wt.% Ni, close to stoichiometric  $\text{NiAl}$ . As in Fig. 4a, the outer layer is  $\text{Ni}_2\text{Al}_3$ , followed by a larger  $\text{NiAl}$  layer and a thin  $\text{Ni}_3\text{Al}$  layer, with some isolated inner Ni regions. Fig. 4c shows the same specimen as in Fig. 4b after 8 h of homogenization. A single  $\text{NiAl}$  phase is present, with grades of color due to compositional variations within that phase. The average strut wall thickness increased from an initial value of about 6  $\mu\text{m}$  in the initial 80 ppi nickel foam to about 14  $\mu\text{m}$  after 1.5 h of aluminizing. Average grain area, as measured on metallographic sections by optical microscopy, increased from an initial value of 21.2 to 1364  $\mu\text{m}^2$  after aluminization and subsequent homogenization (corresponding to approximate grain sizes of 5 and 37  $\mu\text{m}$ , respectively). The relative density after homogenization was measured as 7.7%.

Fig. 5a shows the as-received 20 ppi nickel foam, which exhibits significant porosity due to the oxide reduction process used to make the foam. Fig. 5b depicts an aluminized 20 ppi foam with an average composition of 86.3 wt.% Ni (very near stoichiometric  $\text{Ni}_3\text{Al}$ ) after 1.5 h of aluminization and homogenized for 10 h, for which two phases can be seen ( $\text{NiAl}/\text{Ni}_3\text{Al}$  or  $\text{Ni}/\text{Ni}_3\text{Al}$ ).

A summary of results from the aluminizing study of foams is presented in Table 2. All but one of the 80 ppi foams have average composition within the broad  $\text{NiAl}$  phase field (64–76.5 wt.% Ni [15]) and one of the three 80 ppi foams had average composition within the narrow  $\text{Ni}_3\text{Al}$  phase field (85–87 wt.% Ni [15]).

### 3.3. Aluminization kinetics

Fig. 6 shows the aluminum weight gain (expressed as average aluminum concentration) as a function of aluminization time both wires (500 and 1000  $\mu\text{m}$  diameter) and both foams (20 and 80 ppi). Variations in aluminization kinetics reflect the different surface-to-volume ratios or, equivalently, the different diffusion depths for full aluminization. While the 1000  $\mu\text{m}$  thick wires did

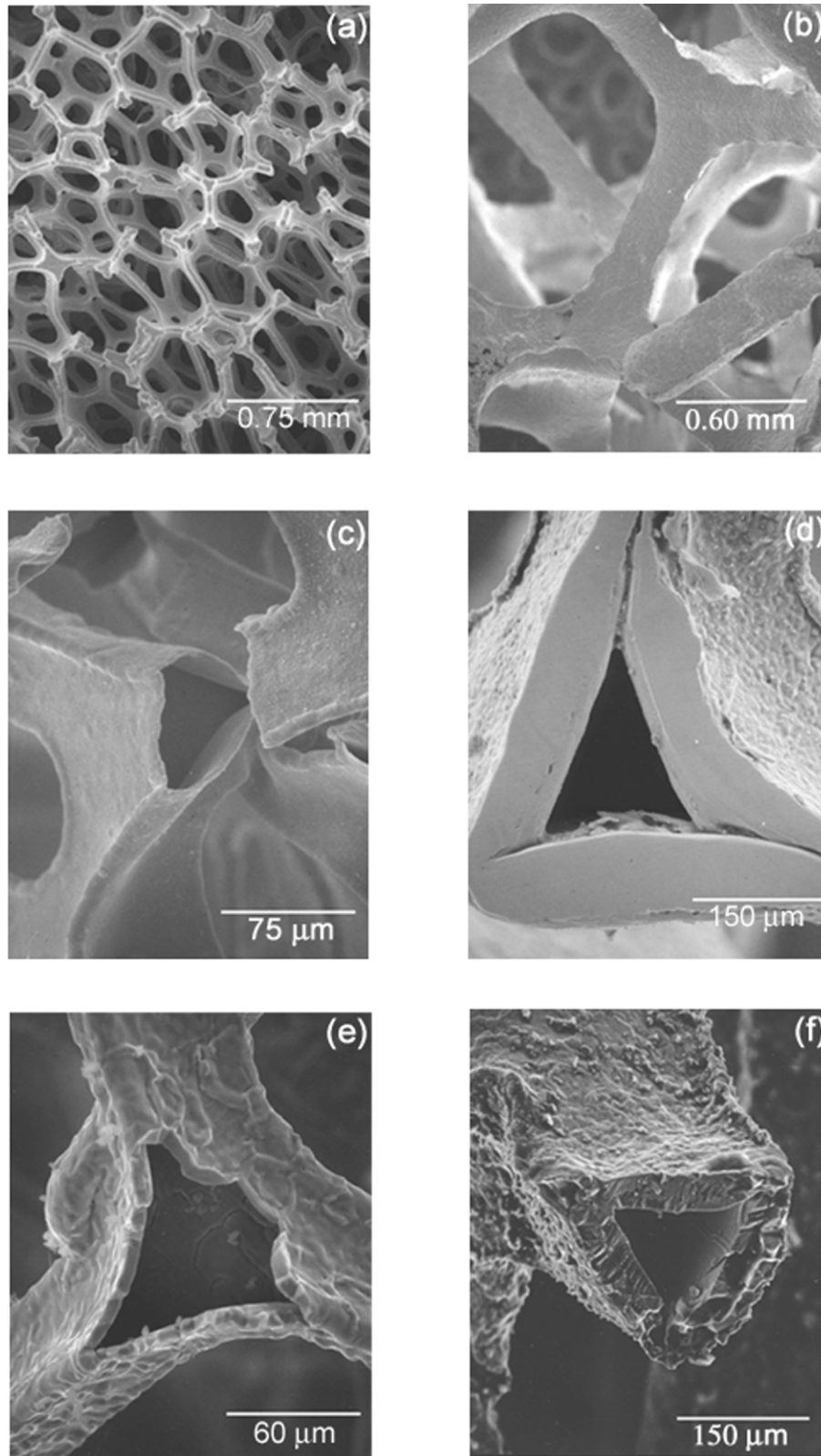


Fig. 3. SEM micrographs of 80 ppi foams (left column) and 20 ppi foams (right column): (a) and (c) as-received 80 ppi foam, (b) and (d) as-received 20 ppi foam and (e) aluminized 80 ppi foam (aluminized 4 h), (f) aluminized 20 ppi foam (aluminized 2 h).

not gain enough aluminum to be homogenized to a single phase, the 500  $\mu\text{m}$  wires gained enough aluminum to display average composition within the  $\text{Ni}_3\text{Al}$  composition

after 2 h and within the  $\text{NiAl}$ – $\text{Ni}_3\text{Al}$  two-phase field after 4 h of aluminization. The 20 ppi foam with 84  $\mu\text{m}$  wall thickness reached the average  $\text{Ni}_3\text{Al}$  composition

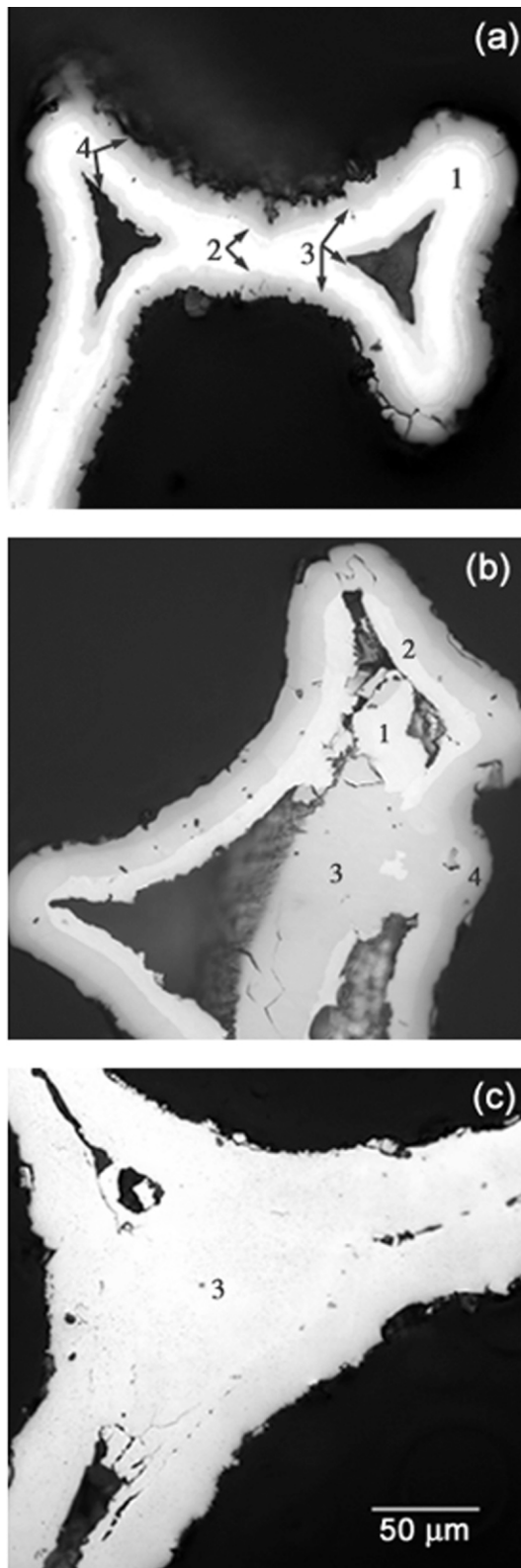


Fig. 4. Optical micrographs of 80 ppi foams: (a) aluminized for 0.5 h (78.0 wt.% Ni), (b) aluminized for 1.5 h (68.2 wt.% Ni), (c) aluminized for 1.5 h (68.2 wt.% Ni) and homogenized for 8 h. Phases are labeled as follows—1: Ni, 2:  $\text{Ni}_3\text{Al}$ , 3:  $\text{NiAl}$ , 4:  $\text{Ni}_2\text{Al}_3$ .

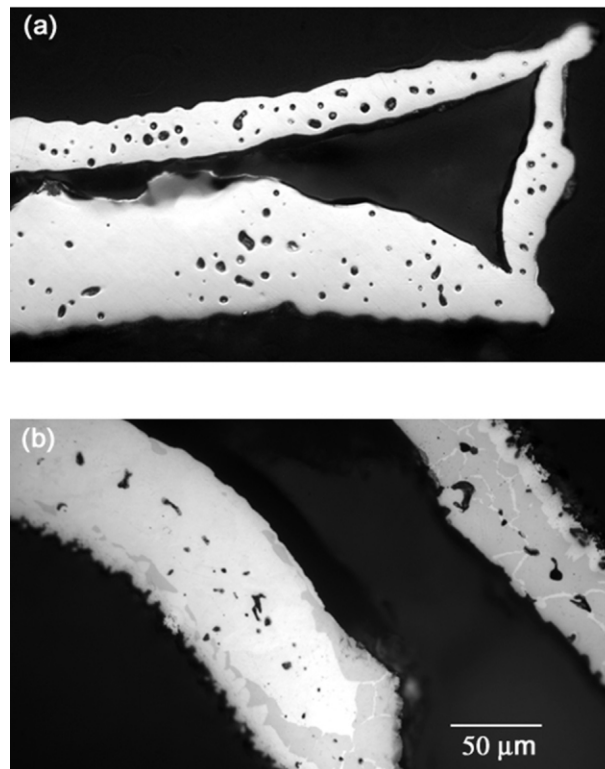


Fig. 5. Optical micrographs of 20 ppi foam: (a) as-received state, showing porosity within struts and (b) after aluminizing for 1.5 h and subsequent homogenization for 10 h (86.3 wt.% Ni), with porosity and two phases.

Table 2

Summary of aluminization and homogenization experiments at 1273 K

Pores per linear inch (ppi)	Aluminizing time (h)	Homogenizing time (h)	Composition (from mass gain) (wt.% Ni)
80	0.5	0	78.4
	1	8	71.9
	1.5	8	66.8 (68.0) <sup>a</sup>
	1.5	8	68.2
	2	0	64.35
20	1.5	10	85.9 (86.3) <sup>a</sup>
	2	8	84.3
	4	0	78.8

<sup>a</sup> From wet chemical analysis.

after 1.5 h of aluminization and could reach stoichiometric  $\text{NiAl}$  composition after about 19 h (by extrapolation of the best-fit power-law curve). The 80 ppi foam with 6  $\mu\text{m}$  wall thickness showed the fastest Al weight gain, reaching the  $\text{Ni}_3\text{Al}$  composition after about 0.25 h and staying within the  $\text{NiAl}$  field after 1–2 h of aluminization (stoichiometric  $\text{NiAl}$  was reached after about 1.5 h).

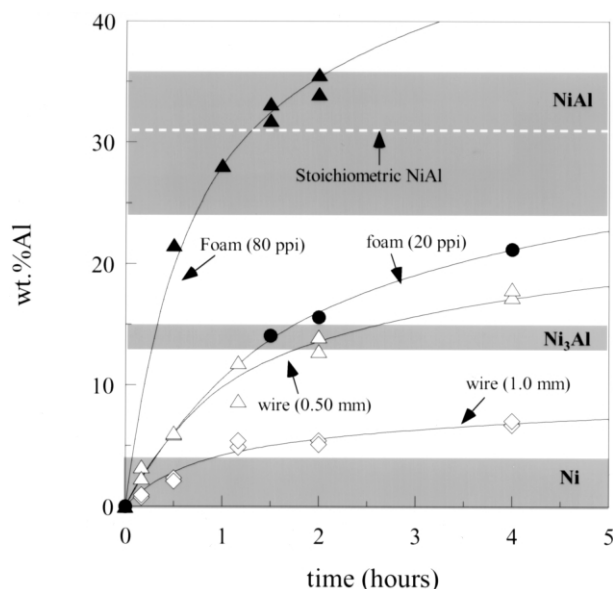


Fig. 6. Time dependence of average composition upon aluminization at 1273 K for 500 and 1000  $\mu\text{m}$  diameter wires and for 20 and 80 ppi foams. Composition ranges of Ni,  $\text{Ni}_3\text{Al}$  and NiAl are shown. Power-law curves are fitted through the data.

## 4. Discussion

### 4.1. Phases

Optical micrographs of aluminized nickel rods, tubes and foams (Figs. 1, 2 and 4) revealed a clear contrast between the Ni, NiAl– $\text{Ni}_3\text{Al}$  and  $\text{Ni}_2\text{Al}_3$  layers. As reported by other researchers [14,16], the NiAl/ $\text{Ni}_3\text{Al}$  layer was very thin before homogenization, preventing the identification of its individual phases. After heat-treatment, complete homogenization to NiAl was observed for the 80 ppi foam. However, the 20 ppi foam with average  $\text{Ni}_3\text{Al}$  composition did not become a single-phase foam upon homogenization. This is probably due to the large variations in strut thickness ( $83.5 \pm 21.3 \mu\text{m}$ ) in the nickel foam: given a constant aluminum-surface concentration and diffusion time, nickel struts thicker than average will be Al-poor (leading to a Ni– $\text{Ni}_3\text{Al}$  mixture) and struts thinner than average will be Al-rich (leading to a NiAl– $\text{Ni}_3\text{Al}$  mixture).

Unlike the tubes, the foams show aluminum deposition taking place from both the inner and outer surfaces of the struts. The lack of aluminum deposition from within the tube despite the open ends, suggest that the halide gases did not penetrate deeply into the long hollow core of the tube (with a length to inner diameter ratio of about 100). The fact that aluminization occurs from within the hollow struts of the foams indicates that there are many openings in the walls of the struts, which were probably created during the removal of the polymer foam after nickel deposition. Ingress of halide gas is thus much easier than for the tubes.

As expected for a diffusion-controlled mechanism, the aluminization kinetics in Fig. 6 shows a power-law time-dependence with exponent less than unity. A simple parabolic behavior is not expected, as the diffusion problem is complicated by the many phases present which lead to large variations in diffusion constants and the presence of moving phase boundaries. Modeling of these results will be addressed in a separate publication [18].

### 4.2. Volume change

The aluminization of nickel samples leads to a volume increase because of the additional volume taken by the deposited aluminum. For a given sample, the ratio  $R$  of the final volume of the intermetallic to the initial volume of the nickel can be expressed as:

$$R = \frac{1}{w_{\text{Ni}}} \cdot \frac{\rho_{\text{Ni}}}{\rho_{\text{Ni}_x\text{Al}}} \quad (1)$$

where  $w_{\text{Ni}}$  is the weight fraction of nickel in the intermetallic, and  $\rho_{\text{Ni}}$  and  $\rho_{\text{Ni}_x\text{Al}}$  are the density of nickel and the intermetallic phase, respectively. For the formation of stoichiometric NiAl ( $\rho_{\text{NiAl}} = 5.65 \text{ g/cm}^3$ ) and  $\text{Ni}_3\text{Al}$  ( $\rho_{\text{Ni}_3\text{Al}} = 7.50 \text{ g/cm}^3$ ), the ratio  $R$  is 2.30 and 1.37, respectively.

For long wires and tubes, the flux of aluminum and nickel is almost entirely radial, so the volume increase is accommodated by a diameter increase without length change (as observed experimentally in this work). Then the ratio  $R$  is:

$$R = \frac{d_o^2 - d_i^2}{d_o'^2 - d_i'^2} \quad (2)$$

where  $d_o$  and  $d_i$  are the outer and inner diameters of the nickel tube ( $d_i = 0$  for a wire), and the prime is used to denote the aluminized state. For the foam, the lack of macroscopic specimen dimension change and the observed radial reaction front within the struts indicate that the volume change is solely accommodated by an increase in strut wall thickness within the foam. Applying Eq. (2) with dimensions given in Table 1 to an aluminized 80 ppi foam, and assuming no internal aluminizing ( $d_i = d_i'$ ) with  $R = 2.3$  for stoichiometric NiAl, the calculated increase in wall thickness is about  $4.5 \mu\text{m}$ . Alternately, assuming that all aluminization occurs from the internal surface of the struts ( $d_o = d_o'$ ), the expected increase in wall thickness is about  $7.5 \mu\text{m}$ . This range of  $4.5\text{--}7.5 \mu\text{m}$  compare well to the wall thickness increase of  $8 \pm 2 \mu\text{m}$  measured on an aluminized 80 ppi specimen with NiAl composition.

The ratio  $R$  also represents the factor by which the relative density of the foam increases after aluminization, provided the macroscopic dimensions of the foam specimen are unchanged, as observed in the present

study. For example, the 80 ppi nickel foams (with initial relative density of 3.5%) are predicted to exhibit a relative density of 8.1% after aluminization to stoichiometric NiAl, in good agreement with the measured value of 7.7% (the calculated porosity over the whole composition range of NiAl ranges from 7 to 10%). The 20 ppi nickel foams (with initial relative density of 2.2%) homogenized to Ni<sub>3</sub>Al composition is predicted to show a relative density of 3.0%.

#### 4.3. Porosity

Voids in the partially aluminized nickel wires and tubes are due to the Kirkendall effect, which is pronounced in the Ni–Al system [17]. Their coalescence separated the outer Al-rich shells from the inner Ni-rich core, thus preventing global equilibrium upon homogenization. A similar effect was observed in Ref. [19], where an infiltrated material consisting of individual nickel spheres within an aluminum-rich matrix was annealed at 1473 K: intermetallic formation initially took place by interdiffusion between the matrix and the spheres, but the diffusion flux was prematurely interrupted by the formation of Kirkendall-induced gaps separating completely the spheres from the matrix. In our case, each region can however be single phase and free of concentration gradients after homogenization, since the Ni and the NiAl phases have large solubilities for Al and Ni, respectively. Furthermore, Fig. 1c illustrates that for the aluminization conditions used here, wires with at most  $\sim 100$   $\mu\text{m}$  radius can be aluminized and homogenized to form NiAl. Aluminization for higher depths may require different homogenization temperatures or an intermediate pore densification step. The single-step aluminization process described by Das et al. [13] could also solve the porosity problem caused by homogenization of Ni<sub>2</sub>Al<sub>3</sub>, since that process produces NiAl as the main phase, with little or no expected Kirkendall porosity.

It follows from the above experiments that tubes (or, for foams, hollow struts) with wall thickness less than about 100  $\mu\text{m}$  should be amenable to full aluminization to NiAl: assuming aluminization from the outer surface only, Kirkendall pores migrating with the Ni<sub>3</sub>Al/Ni interface will disappear at the inner surface of the tube or strut, before they can coalesce into a circumferential gap preventing diffusion as in Fig. 1c. Fig. 2b supports this prediction, as it shows that nickel tubes with 25  $\mu\text{m}$  wall thickness exhibited Kirkendall pores located at the inner surface of the tube. In contrast, the 80 ppi nickel foam for which aluminizing was taking place from both the inner and outer surfaces of the hollow foam strut is expected to show Kirkendall porosity midway within the wall thickness of the strut, where the last nickel region exists (Fig. 4a). The observed lack of porosity (Fig. 4c) can be explained by the very thin strut wall

thickness (6  $\mu\text{m}$ ) preventing the accumulation of significant Kirkendall pore volume.

Another source of porosity originates from the as-processed 20 ppi nickel foam (Fig. 5a). While these pores may shrink during aluminization by sintering and by the addition of aluminum, they may also grow by incorporating Kirkendall vacancies during the subsequent homogenization to NiAl. Fig. 5b shows no significant differences in pore size and volume fraction in the 20 ppi foam with average Ni<sub>3</sub>Al composition, most probably because the Kirkendall effect is not as pronounced as for the NiAl composition.

#### 4.4. Aluminide foams for high-temperature applications

The present results demonstrate that pack-aluminization followed by homogenization, is a simple method to synthesize nickel–aluminide foams. The process maintains the highly-structured, complex geometry of the nickel foam (hollow struts, open cells) while increasing the foam relative density by a factor of 1.4–2.3 for Ni<sub>3</sub>Al and NiAl. Nickel–aluminide foams with different architectures and porosities should be amenable to fabrication by this new process. Also, additional alloying elements (e.g. boron in Ni<sub>3</sub>Al or zirconium in NiAl [20,21]) could be added by diffusion before, during or after aluminization and homogenization. The process can further be applied to produce foams of other technologically-relevant aluminides (e.g. iron, cobalt, titanium, platinum and ruthenium).

Two limitations preventing full aluminization are apparent for the conditions studied here. First, Kirkendall pores accumulate at the moving Ni/Ni<sub>3</sub>Al boundary and coalesce into large gaps preventing mass flow for aluminization depths greater than about 100  $\mu\text{m}$ . Thus, the largest wall thickness of foams which can be fully aluminized is about 100  $\mu\text{m}$ , or twice this amount if aluminization can occur from within the hollow strut. Second, local variations in strut wall thickness lead to corresponding variations in composition, which over short ranges can be smoothed by homogenization. For NiAl, these composition variations are usually less significant, as this phase has a broad range of composition over which creep properties do not vary significantly. For foams with target compositions of Ni<sub>3</sub>Al, however, the narrow range in which Ni<sub>3</sub>Al exists will lead to two-phase regions (Ni/Ni<sub>3</sub>Al or NiAl/Ni<sub>3</sub>Al) where the strut wall thickness deviates from average. Even though the strut thickness deviation problem could be solved by using nickel foams made by CVD which gives a very uniform thickness, the CVD process itself significantly limits the maximum foam strut thickness as well as the maximum macroscopic dimension of the foam. Another route to fabricate a nickel foam with no variation in strut thickness is to use nickel wires or tubes of uniform diameters. Cellular nickel structures can then be produced by



standard techniques used to make ceramic fiber preforms (pressing of chopped fibers, stacking of woven fabrics or 3D weaving of continuous fibers), lightly pre-sintered if necessary, and finally aluminized as discussed in the present paper. We finish this discussion by noting that full aluminization of the nickel foams may not be desirable in all cases. For instance, a partially-aluminized foam with an outer strut surface consisting of oxidation- and corrosion resistant nickel aluminides and an inner strut region of tough nickel (or nickel alloy) may have better structural performance than a single-phase aluminide foams.

## 5. Conclusions

The pack-aluminizing process used to create aluminide coatings on the surface of nickel and nickel-base alloys has been used to synthesize nickel aluminide foams from commercially-available nickel foams with 96–98% porosity. Using a high-activity pack, 80 and 20 ppi nickel foams were aluminized at 1273 K for times ranging from 0.5 to 4 h; after aluminization the foams presented a range of aluminide phases, which were subjected to a subsequent homogenization treatment at 1273 K. This resulted in a single-phase NiAl structure for 80 ppi foams, but single-phase Ni<sub>3</sub>Al foams could not be produced from 20 ppi nickel foams, due to the narrow range of solubility in this phase and the broad range of wall thickness in the original nickel foam.

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