Ni-Mo-Cr Foams Processed by Casting Replication of Sodium Aluminate Preforms**

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The casting replication method, where a liquid metal is infiltrated in a bed of space-holder powders which are subsequently removed by dissolution, has been used primarily for aluminum and magnesium foams,[1–6] because the low melting points of these metals allows the use of inexpensive salts with high water solubility, such as NaCl. There is interest in using the replication casting method for metals with higher melting temperature with greater strength at ambient and elevated temperature. In particular, Ni-base superalloy foams are attractive for applications where creep, oxidation and corrosion resistance are needed together with a low density and high specific area, *e.g.*, for structural applications in engines, and as catalyst support and heat exchangers.[7] However, creating Ni-superalloy foams by casting replication necessitates a space-holder material with high melting point and chemical inertness with the melt. These requirements are usually incompatible with that of high solubility in aqueous solutions needed for easy removal, so that to date no such material has been identified in the metallic foam literature.

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Prior work on processing of open-cell Ni-superalloy foams has thus concentrated on powder metallurgy routes, where metal powders are combined with low-melting space-holders which are removed early during the sintering processes at low temperatures. As shown by Bram *et al.*[8] Hastalloy (X and C) and Inconel (600 and 625) foams with 20–40 % relative density can be fabricated by mixing pre-alloyed powders with carbamide or ammonium hydrogen carbonate powders, which are removed by burning out at temperatures below 200 °C. Powders forming the foam struts, however, are only partially densified after 1 h of sintering at 1300 °C. A similar approach was adopted by Quadbeck *et al.* who fabricated Inconel 625 foams (25–50 % relative density) with polyoxymethylene as a space-holder.[9] To improve the densification of the pre-alloyed powder, liquid phase sintering was employed. While foam struts became almost fully dense, distortion and slumping of the foams were found problematic, and a tight control of optimum sintering temperatures, which were in turn sensitive to impurity contents, was required to achieve sound products.

A different fabrication process was explored by Queheillalt *et al.*[10] who created cellular Inconel 625 with low relative densities (1–4 %) by electron-beam vapor deposition of the alloy on a polymer foam template, followed by sintering with or without additional low-melting braze deposited in a fluidized bed. Queheillalt *et al.*[11] later produced cellular Inconel 625 (7–11 % relative density) by co-depositing in a fluidized bed Inconel powders with 10 vol.% brazing Ni-Cr-P powders on a carbon foam template, followed by sintering. The low-melting braze material improved the sintering of the alloyed powders, leading to better densification of foam struts but at the expense of altered alloy composition and microstructure. However, the presence of a carbon core within the metallic struts may be undesirable in terms of corrosion, carburization and burning resistance.

It is apparent that the existing fabrication techniques for Ni-superalloy foams, which rely on solid-state consolidation processes, suffer from the low sinterability of Ni-base alloys, which is inherently associated with their low diffusivity and high creep strength. Additionally, powder pre-alloying, sintering or vapor deposition processes can be time-consuming and expensive. The casting replication method for such foams would solve the above problems, but it is dependent on the identification of an appropriate space-holder.

In this work, we demonstrate that sodium aluminate (NaAlO$_2$) can be used successfully as space-holder for the

casting of Ni-base alloy foam by the replication method. The foam microstructure and mechanical properties are compared to those for Ni-base foams processed by different routes, and to analytical models for strength and stiffness of metallic foams.

Material Selection

The nickel-base alloy J5 (Ni-22.5Mo-12.5Cr-1Ti-0.5Mn-0.1Al-0.1Y, in wt.%) was selected for this study. This alloy, with a liquidus temperature of 1350 °C and a density of 8.6 g/cm^3, was recently developed by Jablonski and Alman[12] for solid-oxide fuel cell (SOFC) interconnect applications, because it exhibits a thermal expansion coefficient lower than most other Ni-base alloys (which is critical to minimize thermal mismatch with the ceramic components of the cell), high creep strength, and good oxidation resistance (which results from chromia rather than alumina formation). The cast J5 alloy ingot used in this work was provided by the National Energy Technology Laboratory (Albany, OR).

Sodium aluminate (NaAlO$_2$ or Na$_2$O·Al$_2$O$_3$) was selected as space-holder because it possesses a series of properties useful for the present application. First, NaAlO$_2$ exhibits a melting point (1650 °C)[13] well above the casting temperature of J5 or any other Ni-superalloy; the melting point is however relatively low for an oxide, suggesting that it can be easily sintered, which is of importance for the space-holder to be continuous and thus removable after casting. Second, NaAlO$_2$ is highly stable thermodynamically, and does not form mixed oxides with the elements found in J5, indicating that chemical reaction with the melt is unlikely. Third, NaAlO$_2$ has good solubility in water and acids, of importance for the removal step.[13,14] Finally, it is inexpensive and commercially available, as it is commonly used in water treatment and construction applications.[14,15] However, the wettability of NaAlO$_2$ with liquid J5 is unknown: some wetting is needed for infiltration to occur at low pressures, a necessity given the high processing temperatures making high-pressure infiltration impractical. We note that two of the highest melting halides, BaF$_2$ and SrF$_2$, have been recently used as space-holders for high-temperature infiltration of Zr-based amorphous alloys.[16,17] BaF$_2$ exhibits a melting point (1368 °C) too low for Ni-base foam production; SrF$_2$ has a high enough melting point (1473 °C) but its solubility in water is low, making space-holder removal possible only in acids.[16,17] Both salts are also more expensive than NaAlO$_2$ and produce corrosive fluoride solutions in acids, which may corrode the metallic foam concurrently with the space-holder removal.

Results

After sieving to the size range of 355–500 µm, the NaAlO$_2$ particles are of uniform size and shape, and exhibit facetted surfaces (Fig. 1). Following the pre-firing step, the NaAlO$_2$ particles were found to be only lightly sintered to one another without reaction with the alumina crucible. The bulk density
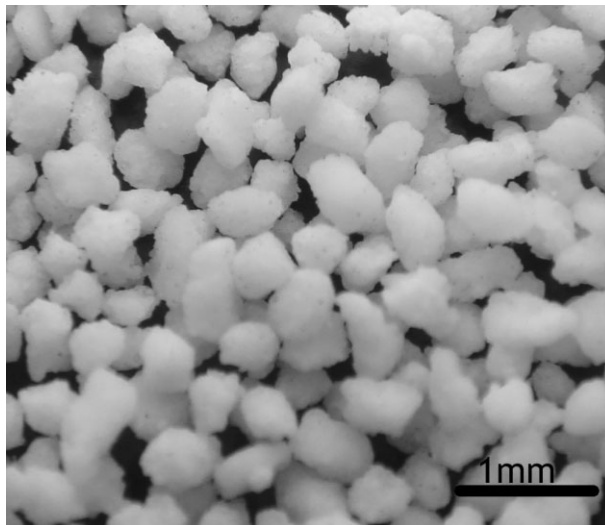

Fig. 1. Sieved NaAlO$_2$ particles with 355-500 µm size.

of the pre-fired particles was determined to be 1.0 g/cm^3 by measuring the mass and dimensions of the sintered preform, corresponding to 36 % of the theoretical NaAlO$_2$ density (measured as 2.8 g/cm^3 by helium pycnometry of loose powders).

Despite the modest infiltration pressure employed here, the J5 alloy appeared to wet adequately both alumina crucible and the NaAlO$_2$ particles without the presence of any adverse reaction, resulting in good infiltration of the alloy into the preform. After infiltration, the volume of the composite section matched that of the original preform, indicating that no densification of the NaAlO$_2$ preform took place during the infiltration process. The density of the solidified J5-NaAlO$_2$ composite was measured as 5.0 g/cm^3.

Despite the good solubility of NaAlO$_2$ in water,[13,14] leaching of the space-holder from the infiltrated samples was very slow in pure water, with only a few percent of the space-holder removed after 15 h immersion of a 8 × 4 × 4 mm^3 specimen. This was determined to be due to the formation of a tacky substance resulting from the reaction of NaAlO$_2$ with water, which obstructed the pores at the surface of the specimen. Using a 10 % HCl aqueous solution with sonication (which raised the bath temperature to about 60 °C) resulted in complete removal of NaAlO$_2$ after 8 h, as determined from pycnometer measurement. This was confirmed in a separate HCl dissolution test with sonication performed on a much larger disc-shape J5-NaAlO$_2$ composite (with height and diameter of 6 and 27 mm, respectively) for which complete NaAlO$_2$ removal was achieved after about one day.

The dissolution rates in hydrochloric acid are much higher for NaAlO$_2$ than for J5, so that the space-holder can be removed with minimal dissolution of the metal. In a separate experiment performed on a 50 g specimen of monolithic J5, the dissolution rate of J5 in a 10 % HCl aqueous solution was measured as 0.2 mg/cm^2·h, corresponding to a slow penetration rate of 0.2 µm/hr. This was confirmed in another experi-

ment, where a fully leached $8 \times 4 \times 4$ mm^3 foam with 48 % relative density lost only 0.4 % of its mass after 14 h sonication in 10 % HCl.

Figure 2 shows a polished cross-section of the leached J5 replicated foam, illustrating that the pores are distributed fairly uniformly in the material, and that the pore size and shape are similar to those of the space-holder particles (Fig. 1). A second phase, expected to be molybdenum-rich precipitates as reported in Ref.[12] can also be observed in the J5 matrix (Fig. 2). The density of leached rectangular $8 \times 4 \times 4$ mm^3 specimens varied in the range of 3.8–4.1 g/cm^3, with an average density of 4.0 g/cm^3 corresponding to a relative density of 46 %.

Figure 3 presents the compression stress-strain curves for a monolithic and the porous J5 specimen with relative density of 47 %. The elastic moduli are 180 and 44 GPa, respectively, and the 0.2 % compressive yield strengths are 367 and 119 MPa respectively. The monolithic sample exhibits strong strain hardening, while the foam, as expected, is character-

ized by a plateau with the stress increasing slowly to ~ 250 MPa at a strain of 48 %, beyond which localized crumbling of the foam, associated with a slight drop in stress, were observed.

Discussion

Processing

As reviewed in the Introduction, casting replication of Ni-alloy foams has not been used to date due to lack of suitable space-holders. NaAlO$_2$ exhibits an unusual combination of properties for an oxide – or indeed any ceramic – making it well suited as space-holder for Ni-alloys: (i) moderate melting point, high enough to prevent melting at the infiltration temperature but low enough to allow for sintering of a preform with relatively coarse powders; (ii) very high chemical stability, preventing reaction with liquid or solid J5; (iii) adequate wetting by liquid J5, allowing preform infiltration at low pressure; (iv) high solubility in acidic solutions, permitting rapid removal after infiltration. Two additional properties are also useful: (v) low cost; and (vi) low toxicity as oxide or as salt after reaction with HCl. While points (ii) and (iii) would need to be verified when using other alloys, NaAlO$_2$ seems a promising space-holder material for replication of foams with other Ni-base alloys, as well as other metals (*e.g.*, Fe, Co, Cu, Pd, Ag, Au) and their alloys with a casting temperature below 1650 °C.

With the packing density of the preform particles of 36 %, the expected volume fraction of the alloy in the as-infiltrated material is 64 % if complete infiltration had been achieved. However, based on the measured density of the infiltrated J5-NaAlO$_2$ composite (5.0 g/cm^3), the pore volume fraction in the infiltrated composite is calculated as 18 %, corresponding to a metal volume fraction of 46 %. After dissolution, the foam relative density is directly measured to be 46 %, in agreement with the above calculation. This implies that liquid J5 only partially infiltrates the NaAlO$_2$ preform at the low infiltration pressure (< 1 atm) used here, indicating that wetting in this system is moderate. Partial wetting may be apparent in incomplete struts or walls (five examples are highlighted in Fig. 2), which may however also represent sintered necks between NaAlO$_2$ particles. Incomplete infiltration was also reported for pure Al infiltrated into NaCl preforms to produce Al foams,[1] and for a Zr-based alloy infiltrated into BaF$_2$ preforms to create amorphous metallic foams.[17] The volume fraction of J5 in the composite (and thus the relative density of the foam) can thus be increased to about 64 % by using higher infiltration pressures, or possibly even higher by densifying the preforms further through a judicious choice of particle size and size distribution. Conversely, lower infiltration pressures will lead to J5 foams with lower relative densities than the present value of 36 %. Alternatively, chemical dissolution/milling of the foams can be used to decrease foam relative density, as demonstrated in Zr foams[17] and Al foams.[18]
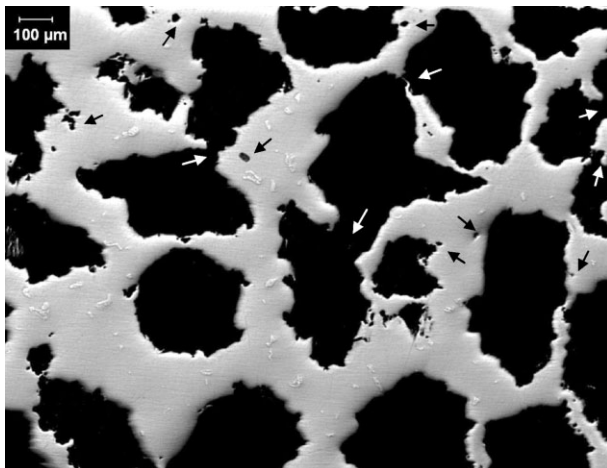

Fig. 2. Metallographic cross-section of J5 replicated foam (46 % relative density) after space-holder removal. White arrows indicate open channels between pores, due to sintering necks or incomplete infiltration, and black arrows point to some small pores in foam struts/walls which may be due to solidification shrinkage.
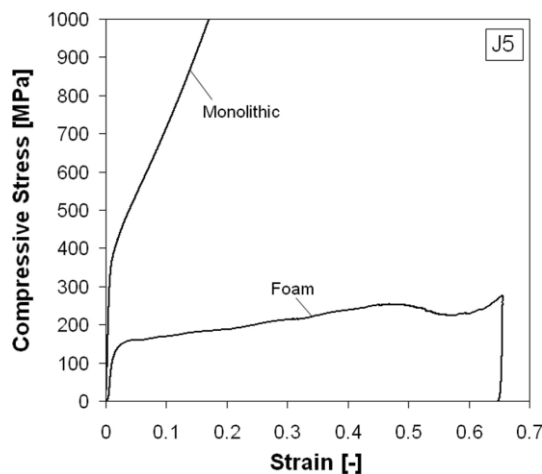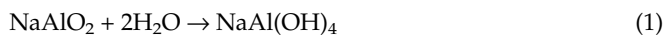

Fig. 3. Compressive stress-strain curves of monolithic and foamed J5 (47 % relative density). The unloading portion of the foam curve is due to test interruption.

Pure water was found to be ineffective at leaching $NaAlO_2$ from the infiltrated composite, most probably due to the formation of sodium tetrahydroxoaluminate $NaAl(OH)_4$ by the reaction:

$$NaAlO_2 + 2H_2O \rightarrow NaAl(OH)_4 \tag{1}$$

The tacky material, which was found to clog the pores thus preventing rapid removal of the space-holder, is believed to be a highly concentrated $NaAl(OH)_4$ aqueous solution. On the other hand, reaction of $NaAlO_2$ with HCl promotes the formation of different, more soluble products according to:

$$NaAlO_2 + 4HCl \rightarrow NaCl + AlCl_3 + 2H_2O \tag{2}$$

The high solubilities in water of sodium and aluminum chlorides (approximately 36 and 46 g/l, respectively[19]) explain the faster leaching kinetics of $NaAlO_2$ from the foams.

Compared to previous Ni-base foams processed by different methods reviewed in the Introduction,[8–11] the present Ni-base replicated foams produced by liquid metal replication are distinct in the following ways. First, the structure of the space-holder preform is replicated well without macroscopic distortion or slumping. Second, the foam struts/walls and nodes are nearly fully dense, with only a very few pores (marked with black arrows in Fig. 2) which may have been due to solidification shrinkage. This nearly fully-dense structure is distinct to those created by partial powder densification and is expected to improve the mechanical properties of the present foams. Third, the present foams consists of relatively thin struts or walls connected by relatively large nodes where mass is concentrated, unlike the previous reticulated, low-density foams, where nodes and struts/walls are much more similar in size. Finally, the 46% relative density of the present replicated foams is at the higher end of the values previously reported for Ni-base foams.[8–11] The latter two effects (mass concentration at nodes and high relative density) lead to high strengths, as discussed in the following section.

Mechanical Properties

The compressive yield strength σ and Young's modulus E of the replicated J5 foam (normalized by the values for the monolithic alloy) are plotted as a function of relative density ρ/ρ_s in Figures 4 and 5. Also shown in these figures are data for the powder-metallurgy Ni-base foams reviewed in the Introduction and predictions from the Gibson-Ashby equations:[20]

$$\sigma = C_\sigma \sigma_s \left(\frac{\rho}{\rho_s}\right)^{3/2} \tag{3}$$

$$E = C_E E_s \left(\frac{\rho}{\rho_s}\right)^2 \tag{4}$$
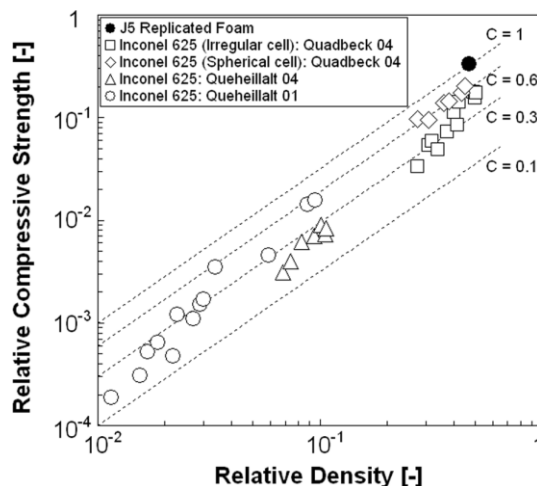

Fig. 4. Relative compressive strength for the present J5 foam and various Ni-base foams [9–11] as a function of relative density. The Gibson-Ashby relationship for foam strength (Eq. 3) is also plotted with a range of C_a values. The strengths of solid J5 and of solid Inconel alloys studied by Quadbeck et al. and Queheillalt et al. are respectively 367, 356, and 414 MPa.
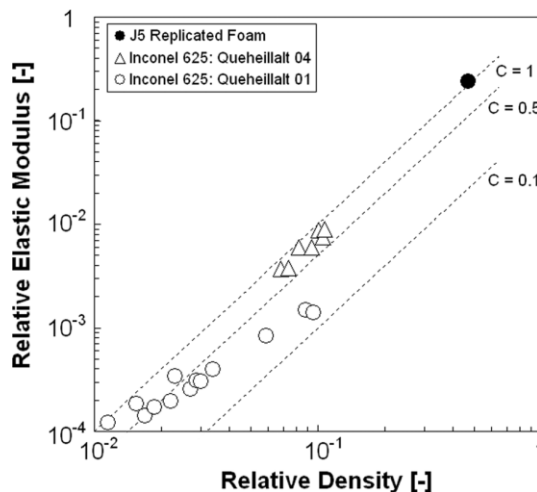

Fig. 5. Relative Young's modulus for the present J5 foam and various Ni-base foams [9–11] as a function of relative density. The Gibson-Ashby relationship for foam modulus (Eq. 4) is also plotted with a range of C_E values. The moduli of solid J5 and of solid Inconel studied by Queheillalt et al. are respectively 180 and 208 GPa.

where the subscript 's' refers to the solid material, and the scaling parameters $C_\sigma \approx 0.3$ and $C_E \approx 1$ are determined from experimental data on open-cell foams.[20] Predictions for a range of values for C_σ and C_E are shown in Figures 4 and 5.

Figure 4 seems to indicate that, for the strength of existing Inconel 625 foams, the value of C_σ increases steadily from $C_\sigma \approx 0.15$ for the lowest-density foams to $C_\sigma \approx 0.7$ for the highest density foams (*i.e.*, the exponent 3/2 in Eq. 3 may in fact be higher). This apparent trend in relative strength may instead reflect different levels of strut densification, which is lowest for the low-density foams[10,11] and highest for the high-density foams produced by liquid-phase sintering.[9] Also, cell shapes have an effect on strength: for the same range of Inconel relative densities, $C_\sigma \approx 0.4$ and 0.6 for irregular and spherical cells, respectively.[9] With $C_\sigma \approx 1$, the relative

strength of the J5 replicated foam is about twice that of the powder-metallurgy Inconel 625 foams[9] with the same relative density. This may be attributed to stronger nodes and struts/walls (due to lack of defects) in the cast J5 foam, and to higher mass concentration at the nodes of the J5 foam delaying plastic hinging (which is assumed to control foam yield in Eq. 3). Further experiments on replicated foams with different relative densities will need to be carried out to confirm this hypothesis.

Figure 5 indicates that the elastic moduli of the low-density Inconel foams ($\rho/\rho_s < 0.1$[10, 11]), and the present higher-density J5 foams follow, for the most part, Equation 4 with $C_E \approx 0.4$–1. Again, the highest value $C_E = 1$ is achieved for the present J5 foam, possibly reflecting the full level of densification of the struts/walls. Equation 4 with $C_E \approx 1$ is found empirically to apply for a very broad range of relative densities (i.e., $\rho/\rho_s \approx 0.01 – 1$[20]) and cell architecture, so stiffness seems to be less sensitive to strut defects or cell shape than strength.

Conclusions

The casting replication method was used to create an open-cell foam from the nickel-base alloy J5 (Ni-22.5Mo-12.5Cr-1Ti-0.5Mn-0.1Al-0.1Y, in wt.%) recently developed for solid-oxide fuel cell interconnects. Preforms of lightly sintered powders of sodium aluminate ($NaAlO_2$) were infiltrated at low pressure by liquid J5 without observable chemical reaction. The $NaAlO_2$ phase was then removed by dissolution in a 10 % HCl solution, resulting in J5 foams with average relative density of 46 %. Sodium aluminate is thus an excellent candidate for creation of nickel foams from other nickel alloys (and other high-melting metals) by the low-pressure casting replication method. The relative strength of the cast J5 foams is found to be superior to that of foams produced by powder metallurgy methods, probably because the struts/walls and nodes are nearly fully dense. The relative stiffness of the J5 foam follows general scaling laws for open-cell foams.

Experimental

$NaAlO_2$ powders (-45 mesh; technical grade) were procured from Alfa Aesar (Ward Hill, MA). Because these powders were too fine for the present application, they were cold pressed to 125 MPa into pellets, sintered at 1500 °C for 1 h in air, crushed and sieved in the range of 355-500 µm. The sieved $NaAlO_2$ particles were transferred to a cylindrical-shaped alumina crucible (ID = 20 mm) and lightly sintered in air at 1500 °C for 3 h to achieve a small degree of bonding between particles.

Subsequently, a J5 ingot was inserted into the crucible, with an alumina disc used as spacer for separating melt from $NaAlO_2$ in case there may have been some slow chemical reaction. The system was heated to 1450 °C at a heating rate of 7 °C/min, and maintained under high vacuum at this temperature for 1 h to insure complete melting of the ingot. The furnace was then pressurized with argon at a low pressure of 0.08 MPa, thus infiltrating the melt into the pores of the preform which remained under vacuum due to the seal formed by the liquid metal wetting the crucible. Three minutes after infiltration, the specimen was furnace-cooled, while maintaining the gas pressure for about 30 min, at which time the alloy had solidified. The as-cast J5/$NaAlO_2$ composite was machined into parallelepiped 8 × 4 × 4 mm³ specimens from which the space-

holder was removed by dissolution in a bath of ultrasonically-agitated distilled-water with or without 10 % HCl. The density and porosity of the resulting J5 foam samples were determined by helium pycnometry and Archimedes water displacement measurements, and their microstructures were examined by optical and scanning electron microscopes on mounted and polished, unetched cross-sections.

All 8 × 4 × 4 mm³ specimens were heat-treated by homogenizing at 1100 °C for 4 h under argon, followed by annealing at 850 °C in air for 4 h. The specimens were water-quenched after each step. The majority of these specimens were used for creep testing (to be reported in a separate publication), but one as-leached specimen was subjected to uniaxial compressive testing at ambient temperature, performed at an initial strain rate of 10^{-3} s^{-1}, with strain measured by cross-head displacement after machine compliance correction. The Young's modulus was determined ultrasonically by measuring the speed of transverse and longitudinal sound waves transmitted through the specimen at a frequency of 5 MHz.

[1] J. F. Despois, A. Marmottant, L. Salvo, A. Mortensen, *Mater. Sci. Eng. A* **2007**, *462*, 68.

[2] Y. Conde, J. F. Despois, R. Goodall, A. Marmottant, L. Salvo, C. S. Marchi, A. Mortensen, *Adv. Eng. Mater.* **2006**, *8*, 795.

[3] J. F. Despois, A. Mortensen, *Acta Mater.* **2005**, *53*, 1381.

[4] A. Pollien, Y. Conde, L. Panbaguian, A. Mortensen, *Mater. Sci. Eng. A* **2005**, *404*, 9.

[5] Y. Yamada, K. Shimojima, Y. Sakaguchi, M. Mabuchi, M. Nakamura, T. Asahina, T. Mukai, H. Kanahashi, K. Higashi, *J. Mater. Sci. Lett.* **1999**, *18*, 1477.

[6] Y. Zhao, F. Han, T. Fung, *Mater Sci. Eng. A* **2004**, *364*, 117.

[7] J. Banhart, *Prog. Mater. Sci.* **2001**, *46*, 559.

[8] M. Bram, C. Stiller, H. P. Buchkremer, D. Stover, H. Baur, *Adv. Eng. Mater.* **2000**, *2*, 196.

[9] P. Quadbeck, J. Kaschta, R. F. Singer, *Adv. Eng. Mater.* **2004**, *6*, 635.

[10] D. T. Queheillalt, D. D. Hass, D. J. Sypeck, H. N. G. Wadley, *J. Mater. Res.* **2001**, *16*, 1028.

[11] D. T. Queheillalt, Y. Katsumura, H. N. G. Wadley, *Scr. Mater.* **2004**, *50*, 313.

[12] P. D. Jablonski, D. E. Alman, *Int. J. Hydrogen Energy* **2007**, *32*, 3705.

[13] D. R. Lide, *CRC Handbook of Chem. and Phys.*, CRC PRESS, Boca Raton **1999**.

[14] M. Kabsch-Korbutowicz, *Desalination* **2005**, *185*, 327.

[15] M. D. Andersen, H. J. Jakobsen, J. Skibsted, *Cem. Concr. Res.* **2004**, *34*, 857.

[16] A. H. Brothers, R. Scheunemann, J. D. DeFouw, D. C. Dunand, *Scr. Mater.* **2005**, *52*, 335.

[17] A. H. Brothers, D. C. Dunand, *Acta Mater.* **2005**, *53*, 4427.

[18] Y. Matsumoto, A. H. Brothers, S. R. Stock, D. C. Dunand, *Mater. Sci. Eng. A* **2007**, *447*, 150.

[19] J. Burgess, *Met. Ions in Solutions*, ELLIS HORWOOD, Chichester **1978**.

[20] L. J. Gibson, M. F. Ashby, *Cellul. Solids*, CAMBRIDGE UNIVERSITY PRESS, Cambridge **1997**.