

Communication

Effect of Sn on the Dehydrogenation Process of TiH₂ in Al Foams

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The study of the dehydrogenation process of TiH₂ in aluminum foams produced by the powder metallurgy technique is essential to understanding its foaming behavior. Tin was added to the Al foam to modify the dehydrogenation process and stabilize the foam. A gradual decomposition and more retention of hydrogen gas can be achieved with Sn addition resulting in a gradual and larger expansion of the foam.

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The production of metal foams by the powder metallurgy technique requires the proper mixture of a metal or alloy and blowing agent powders. Then, this mixture is compressed to high densities, and finally the densified product (called precursor) goes through a heat treatment (above the alloys melting temperature) where the blowing agent releases gas that the molten metal matrix traps. As the heat treatment is interrupted, the metal solidifies and the foam is obtained.^[1] In order to produce good metallic foams, with the powder metallurgy technique, the decomposition of the blowing agent has to be synchronized with the melting of the metal or alloy.^[2] For the foaming process of Al, TiH₂ is the most commonly used blowing agent as it has the closest decomposition temperature range at about 723 K to 923 K (450 °C to 650 °C) to the melting of Al at 933 K (660 °C).^[3]

According to the Ti-H phase diagram in Figure 1, solid TiH₂ (δ) can contain 2.06 to 4.05 wt pct H. With increasing temperature, TiH₂ can be unstable and evolve to TiH_x (β) and Ti (α) with releasing H₂ gas.^[4] Although TiH₂ can theoretically be dehydrogenated to pure Ti at high temperature and low pressure, it has been reported that TiH₂ is degenerated to nonstoichiometric TiH_x (β) phase over a wide temperature range between 688 K and 898 K (415 °C to 625 °C) at ambient pressure^[5] with weight loss of about 2.0 to 2.5 wt pct. However, this

decomposition temperature is still lower than the Al melting temperature, and this mismatch of temperature still should be overcome. The ways to reduce the mismatch are (1) to increase the decomposition temperature of TiH₂ and (2) to decrease the melting temperature of Al.

To increase the TiH₂ decomposition temperature, heat treatments (oxidation) of TiH₂ were investigated under various atmospheres (air, argon, and nitrogen) to create an oxide layer on the surface of the hydride that acts as a diffusion barrier.^[2,5-8] The application of a Ni coating on the hydride was studied to delay the dehydrogenation onset during the foaming process.^[9] Furthermore, isothermal X-ray diffraction and thermal analysis on different particle sizes were performed to better understand the dehydrogenation of TiH₂.^[3,10]

To decrease the melting temperature of the Al matrix, Al was alloyed with melting point depressant elements. The wrought Al alloys commonly used for this purpose are the 2xxx and 6xxx series, which contain mainly Mg and Cu or Mg and Si, respectively. Casting alloys employed for metal foams are often combinations of Al-Si-Mg-Cu-Zn, which give a large solidification range. For example, Al-7 wt pct Si-Mg (A356) or Al-9 wt pct Si-3 wt pct Cu allows foaming at lower temperature in the semisolid state.^[11,12]

Regardless of the efforts for matching the decomposition temperature of TiH₂ and melting temperature of Al matrix, the foaming behavior of Al alloys should be further improved: although high maximum expansion can be reached, the metal foam stability is quite low (in most cases, foam collapses within less than 30 seconds), due to pore coalescence and metal drainage.^[11-13]

In order to enhance foam stability and obtain higher expansions, a new alloying element (Sn) was investigated in the present study. Kennedy reported that good densification of the powder mixture is required to retain a high amount of hydrogen, as high compaction density can seal interconnected porosity.^[14] Sn proved to be beneficial in the extrusion of Pb-Sn powder mixtures at a temperature near the melting point of Sn at 505 K (232 °C) during the production of Pb-Sn foams.^[15] Also, Sn additions can modify the surface tension of Al, the surface tension of the cell walls, therefore, generating more stable pores. This would be similar to the effect of surfactants in liquid foams.^[16] Surprisingly, it was found that the addition of Sn can easily control the dehydrogenation process of TiH₂ in the Al foam, to achieve maximum foam expansion and enhance the foam stability.

To study the effect of Sn on the dehydrogenation of TiH₂, Al powders containing 1 wt pct TiH₂ were hot compacted with and without additional Sn (3 wt pct) powder into a cylindrical shape (0.71 cm in height and 2 cm in diameter) under an uniaxial load of 550 MPa at 573 K (300 °C), above the Sn melting temperature. The particle sizes of Al, TiH₂, and Sn powders were all less than 44 μ m, and the purities of the powders were more than 99 pct. The average size of TiH₂ powders was about 15 to 18 μ m. The precursors were placed on an alumina plate in a Lindberg/Blue M furnace preheated at 998 K (725 °C). The foaming of the precursor was

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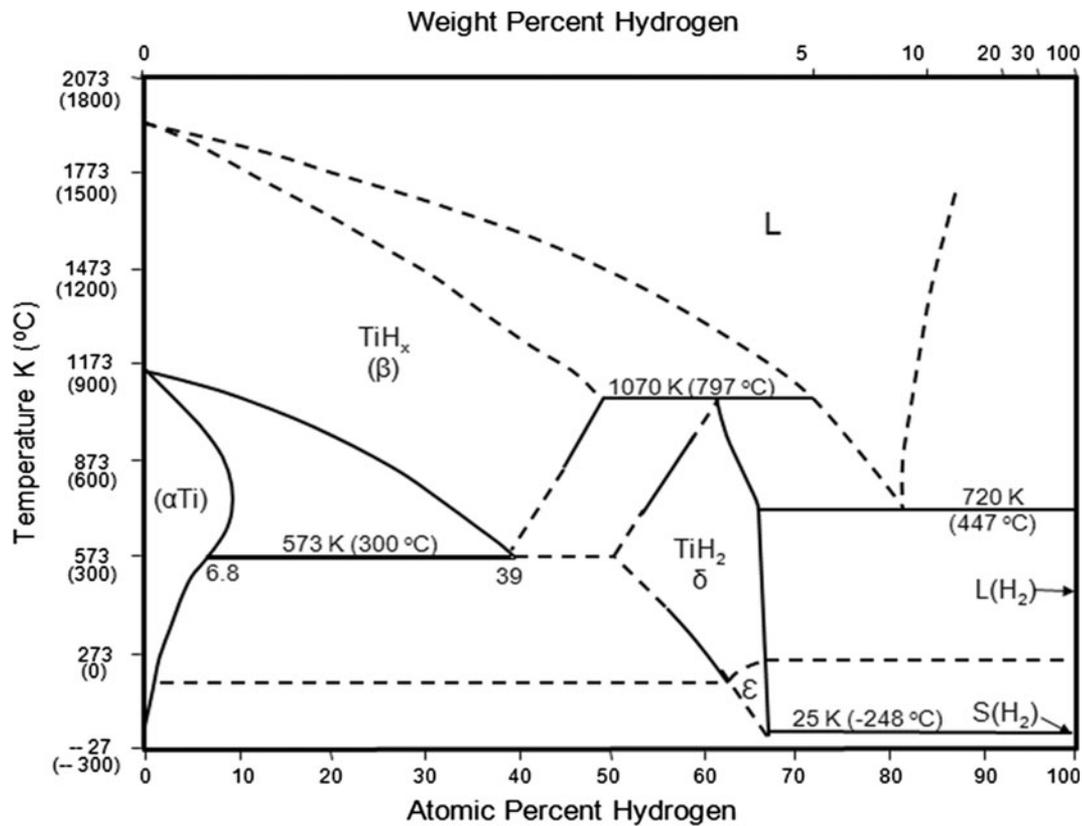


Fig. 1—Ti-H phase diagram.^[4]

interrupted after a certain time by quenching the samples in air. Microstructural characterizations with scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were carried out on the sectioned foams.

To understand the difference in the decomposition behavior of TiH_2 in Al and Al-3 wt pct Sn foam, the morphology of the remaining TiH_x was examined. Typical SEM morphologies of TiH_2 in Al and Al-3 wt pct Sn foams with foaming time are presented in Figure 2. EPMA was used to confirm the Ti-Al phase on the surface of the TiH_x particle, identified as TiAl_3 intermetallic. In the case of pure Al foam, thin TiAl_3 layer formed on the surface of TiH_x until 12 minutes without any rupture. Then, abrupt rupture of the TiAl_3 layer was observed after 12 minutes, and the amount of TiAl_3 was suddenly increased. In the case of Al-3 wt pct Sn foam, continuous TiAl_3 layer was observed until 9 minutes. After 1 minute, small fragments of ruptured TiAl_3 layer were observed around the TiH_x . The amount of TiAl_3 particles increased gradually with foaming time. It should be noted also that the size of TiAl_3 fragments in pure Al foam was larger than that in Al-3 wt pct Sn foam.

As it is very difficult to ascertain the exact decomposition amount of TiH_2 , this was determined from SEM images of the remaining Ti hydride particles in the foams. That is, the extent of the decomposition was calculated as

Degree of decomposition (pct)

$$= \frac{\text{area of surrounding TiAl}_3}{\text{area of surrounding TiAl}_3 + \text{area of TiH}_x} * 100$$

The amount of unreacted TiH_x (pct) (100 – degree of decomposition) with foaming time is plotted in Figure 3. Each point in the figure is an average value of more than 10 Ti hydride particles of the mean size (15 to 18 μm). The estimated thermal history of the metallic foam was also plotted in Figure 3; because the decomposition behavior of TiH_2 is highly dependent on temperature, it is important to know the thermal histories of the Al and Al-Sn foams. The decomposition of pure Al foams increased slowly up to 12 minutes and showed an abrupt increase at 12 minutes. On the other hand, the decomposition of Al-3 wt pct Sn foams increased slowly until about 8 minutes, and then a large but gradual decomposition occurred between 9 and 12 minutes. After 15 minutes, the remaining Ti hydride (TiH_x (β) phase) was less than 20 pct of an original TiH_2 . Thus, the presence of Sn certainly led to a gradual and earlier decomposition of TiH_2 .

The expansion behavior of Al and Al-3 wt pct Sn foams at 998 K (725 °C) is presented in Figure 4 along with the decomposition behavior of TiH_2 . The foam expansions were determined using the Archimedes principle. As can be seen, in Figure 4, the foam expansion of Al-3 wt pct Sn foam is directly related to

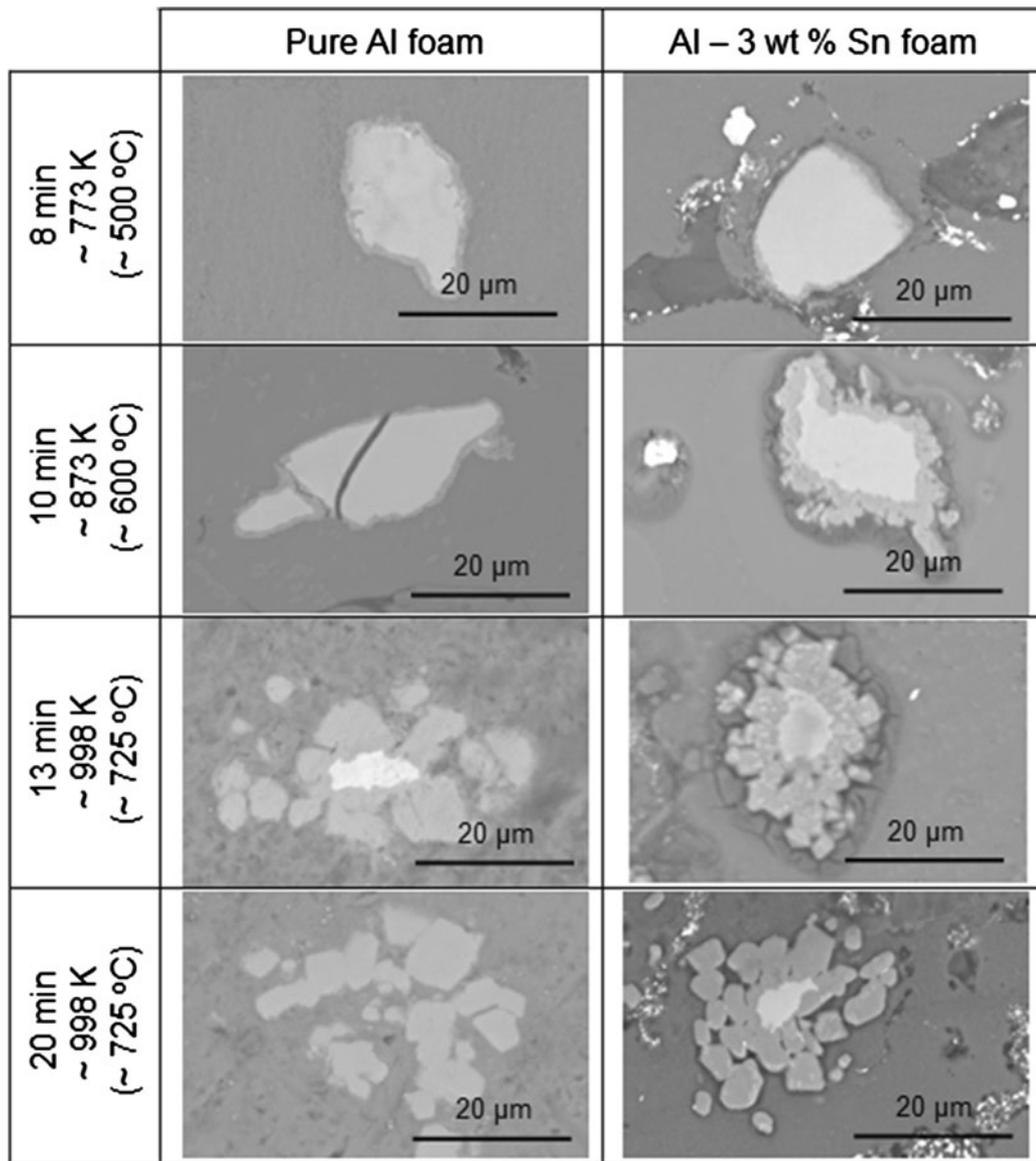


Fig. 2—Evolution of typical morphologies of TiH_2 (SEM-backscattered image) in pure Al and Al-3 wt pct Sn foams with foaming time.

the decomposition behavior of TiH_2 . That is, the gradual and large expansion of the foam occurred between 9 and 11 minutes when a large decomposition of TiH_2 took place. Pure Al foam showed a maximum expansion at 11 minutes, which is coincident with the melting temperature of Al. The maximum expansion of the Al foam (250 pct) is lower than that of Al-3 wt pct Sn foam (400 pct). In addition, while the Al foam collapsed after maximum expansion at 11 minutes, Al-3 wt pct Sn foam was stable for a long time.

Based on the present experimental results and the thermodynamic behavior of the Al-Sn system, the effect of Sn on the decomposition behavior of TiH_2 can be explained. The schematic diagram of the microstructural evolution of TiH_2 in Al and Al-Sn foams during the foaming process is depicted in Figure 5. In the case of pure Al foam, TiH_2 can react with solid Al to produce a thin solid layer of $TiAl_3$ around TiH_2 (reaction 1). Although the self-decomposition reaction of TiH_2 to

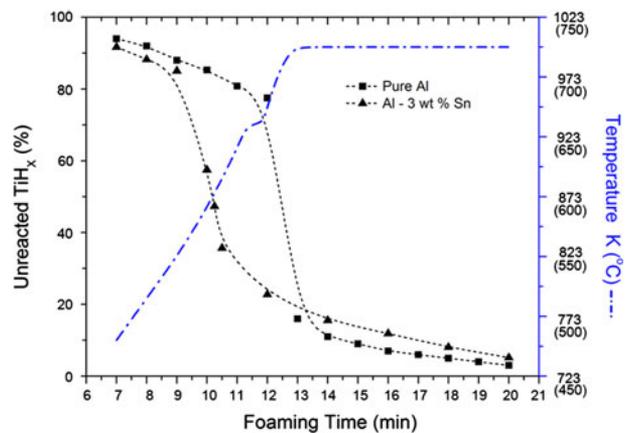
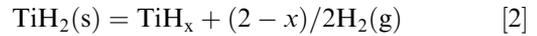


Fig. 3—Relationship between TiH_2 decomposition (100 pct-unreacted TiH_2 pct) for pure Al and Al-Sn foams along with the estimated thermal history.

TiH_x (reaction 2) can occur between 723 K (450 °C) and 923 K (650 °C) under ambient pressure, the decomposition is not observed for Al foam in this temperature range. This seems to be induced by the high pressure exerted on the TiH₂ (covered by TiAl₃) by the surrounding solid Al matrix (pressed to 550 MPa), which can effectively increase the decomposition temperature of TiH₂. Therefore, it is expected that H₂ (g) pressure can build up inside the TiAl₃ layer at the temperature range of 723 K and 923 K (450 °C and 650 °C), as depicted in Figure 5. Immediately after melting of the Al

matrix, when the hydrogen pressure generated by the self-decomposition reaction (reaction 2) can overcome the suppressed pressure of the Al matrix, H₂ (g) can be released with the abrupt rupture of TiAl₃ layer. According to the present experimental results in Figures 2 through 4, the rupture of TiAl₃ layer was not observed until the melting of Al at 12 minutes. At 12 minutes, the abrupt rupture of TiAl₃ and drastic decomposition of Ti hydride were observed. Unfortunately, H₂ (g) released during this abrupt decomposition of Ti hydride cannot be effectively retained in liquid Al matrix. The Al foam collapsed due to the drainage of liquid Al and bubble bursting with increasing temperature.



In the case of Al-3 wt pct Sn foam, Sn-rich liquid can already form above 505 K (232 °C). As TiH₂ is in contact with Sn-rich liquid saturated with solid Al, the formation of the solid TiAl₃ layer can be promoted due to a faster diffusion of Al *via* liquid Sn (reaction 3) up to about 823 K (550 °C). Similarly to the pure Al foam scenario, a certain pressure of H₂ (g) can build up inside the TiAl₃ layer by reaction 2. Once the temperature reaches about 823 K (550 °C), the amount of liquid Sn-Al can increase steeply and subsequently relieve the surrounding pressure on TiH₂ (TiAl₃) because the liquid medium can be deformable. Therefore, the solid TiAl₃ layer can be ruptured, releasing H₂ (g). Of course, after

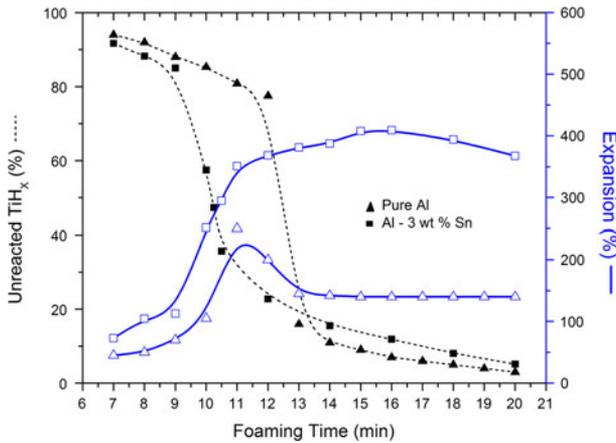


Fig. 4—Relationship between TiH₂ decomposition (100 pct-unreacted TiH₂ pct) and foam expansion during the foaming process for pure Al and Al-Sn foams.

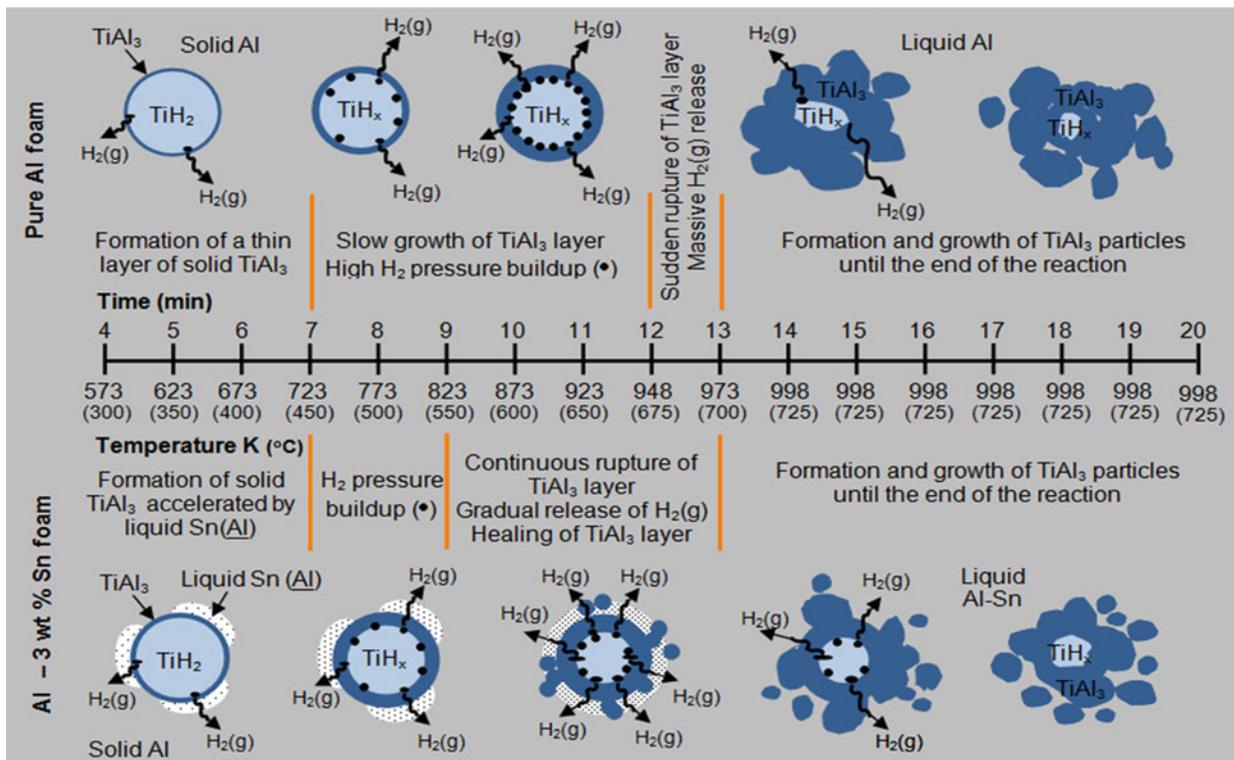
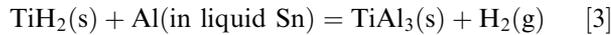


Fig. 5—Schematic diagram of the decomposition process of TiH₂ in pure Al and Al-Sn foams.

the rupture of the TiAl₃ layer, its recovery (formation of TiAl₃) can easily occur by the presence of liquid Al (in Sn). This rupture/recovery process can be continued with a gradual release of H₂ (g). In the present study, this process can be observed between 9 and 12 minutes. Moreover, this explanation can explain the smaller size of the TiAl₃ fragment in Al-Sn foam than in pure Al foam.



Because H₂ (g) can be gradually released from low temperature to 933 K (660 °C) and liquid Al-Sn can be formed even below 933 K (660 °C) (*i.e.*, about 5 and 15 wt pct of the Al-Sn foam is liquid at 873 K and 903 K (600 °C and 630 °C), respectively), a relatively high amount of H₂ (g) can be retained in the Al-Sn foam, which in turn increases its expansion. The Al-Sn foam showed about 360 pct expansion at 12 minutes and further expanded to 410 pct at 16 minutes. Furthermore, the addition of Sn can significantly increase the foam stability (durability) of Al foam. This can be explained as a result of surface energy modification of the cell wall by Sn, which is discussed in detail elsewhere.^[17]

In summary, the gradual and larger expansion of Al foam can be achieved with Sn addition. This results from the formation of Sn-rich liquid below the melting temperature of Al, which can promote a gradual and earlier decomposition of TiH₂ and help to retain more H₂ (g) in the Al foam.

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REFERENCES

1. J. Banhart: *Progr. Mater. Sci.*, 2001, vol. 46 (6), pp. 559–632.
2. B. Matijasevic and J. Banhart: *Scripta Mater.*, 2006, vol. 54 (4 SPEC ISS), pp. 503–08.
3. M.T. Malachevsky and C.A. D'Ovidio: *Scripta Mater.*, 2009, vol. 61 (1), pp. 1–4.
4. H. Okamoto: *J. Phase Equilib.*, 1992, vol. 13 (4), pp. 443–43.
5. B. Matijasevic-Lux, J. Banhart, S. Fiechter, O. Gorke, and N. Wanderka: *Acta Mater.*, 2006, vol. 54 (7), pp. 1887–1900.
6. A.R. Kennedy: *Scripta Mater.*, 2002, vol. 47 (11), pp. 763–67.
7. D. Lehmus and G. Rausch: *Adv. Eng. Mater.*, 2004, vol. 6 (5), pp. 313–30 and 275.
8. F. von Zeppelin, M. Hirscher, H. Stanzick, and J. Banhart: *Compos. Sci. Technol.*, 2003, vol. 63 (16), pp. 2293–2300.
9. P.M. Proa-Flores and R.A.L. Drew: *Adv. Eng. Mater.*, 2008, vol. 10 (9), pp. 830–34.
10. V. Bhosle, E.G. Baburaj, M. Miranova, and K. Salama: *Mater. Sci. Eng. A*, 2003, vol. 356, pp. 190–99.
11. D. Lehmus and M. Busse: *Adv. Eng. Mater.*, 2004, vol. 6 (6), pp. 391–96.
12. F. Baumgartner, I. Duarte, and J. Banhart: *Adv. Eng. Mater.*, 2000, vol. 2 (4), pp. 168–74.
13. I. Duarte and J. Banhart: *Acta Mater.*, 2000, vol. 48 (9), pp. 2349–62.
14. A.R. Kennedy and S. Asavavisithchai: *Mater. Sci. Forum*, 2002, vols. 396–402, pp. 251–58.
15. A. Irretier and J. Banhart: *Acta Mater.*, 2005, vol. 53, pp. 4903–17.
16. Q. Xu, M. Nakajima, S. Ichikawa, N. Nakamura, P. Roy, H. Okadome, and T. Shiina: *J. Coll. Interface Sci.*, 2009, vol. 332, pp. 208–14.
17. L.Y. Aguirre-Perales, I.-H. Jung, and R.A.L. Drew: *McGill University*, unpublished research, Montreal, 2011.