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Experimental confirmation of the model for microcracking during lithium charging in single-phase alloys

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Abstract

Indentation fracture toughness measurements yielded a K_{IC} for $Li_{4.4}Sn$ equal to 0.8 ± 0.2 MPa $m^{1/2}$. From K_{IC}, a critical crack length of 0.005 nm was determined for the stress generated due to the volume expansion as a result of Li charging into the $Li_{4.4}Sn$ alloy. The critical crack length was in excellent agreement with the predicted critical grain size for microcracking. This suggests that the model for predicting the critical grain size for microcracking during Li charging into brittle single-phase alloys is correct. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Recently, Wolfenstine [1] developed a model for predicting the critical grain size for microcracking during Li charging into brittle single-phase Li alloys for example, $Li_{4.4}Sn$. The basic concept of the model is that the alloys will crack when the strain energy generated due to the volume expansion as a result of Li insertion exceeds the energy required for the creation of new fracture surfaces. The model predicts a critical grain size, d_{crit}, grain size below which fracture will not occur, that is less than the unit cell size for a majority of brittle single-phase alloys.

The predictions were based on estimated values for many of the material's parameters (i.e., surface energy) since, no published data exists for a majority of the single-phase Li alloys. Consequently, how realistic are the predictions? It is the purpose of this paper to determine if the theoretical predictions are consistent with experimental results for a typical brittle single-phase Li alloy, $Li_{4.4}Sn$. The following paragraph outlines how this will be accomplished.

Fracture toughness, K_{IC}, is an intrinsic material property and for the case of a brittle material is related to the applied stress, σ, and the critical crack size, c_{crit}, by the following relation [2–5]:

$$K_{IC} = \sigma (\pi c_{crit})^{1/2} \quad (1)$$

When $\pi (\sigma c)^{1/2} > K_{IC}$, brittle fracture occurs, where c is the crack size. Thus, the critical crack size corresponds to the largest crack size the material can tolerate and not exhibit brittle fracture for a given value of applied stress. From Eq. (1), it is observed that if K_{IC} and σ are known, then this allows for a determination of the critical crack size. The value of σ, tensile stress generated due to the volume expansion as a result of Li charging, is given as follows [1]:

$$\sigma = \frac{E}{3(1-2\nu)} \frac{\Delta V}{V_o} \quad (2)$$

Where ΔV is the volume change, V_o is the initial volume, ν is Poisson's ratio and E is the elastic modulus. ΔV and V_o are known for $Li_{4.4}Sn$ [6,7]. An experimental value of E for $Li_{4.4}Sn$ that was determined using an acoustic technique will be used [8]. Since, ν for a ceramic material is typically between 0.20 and 0.30 [2–5], a value of 0.25 will be used. K_{IC} for $Li_{4.4}Sn$ will be experimentally determined using an indentation technique [2,9–13]. Since both K_{IC} and σ are known, primarily based on experimental data, it is then possible to determine c_{crit} for

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$Li_{4.4}Sn$. If the previous theoretical predictions are correct, then, $c_{crit} \approx d_{crit}$. It is the goal of this paper to determine if this is true.

2. Experimental

A $Li_{4.4}Sn$ alloy was chosen as representative of a typical brittle single-phase Li alloy anode material. The $Li_{4.4}Sn$ alloy was prepared by mixing the appropriate amounts of Li (rod; Cypress-Foote Mineral) and Sn (powder; Aldrich) in a Mo crucible. The Li–Sn mixture was heated at 800°C for 0.5 h in a glove box having an oxygen concentration and moisture level of less than 1 ppm to form a molten alloy. The molten alloy was rapidly quenched onto a stainless steel cooling plate. Several of the smaller solid pieces were crushed and ground using a mortar and pestle in the glove box. These powders were sealed in capton for X-ray diffraction studies. Some of the larger chunks were mounted and polished for fracture toughness measurements. The samples were cold-mounted in the glove box. They were rough polished using SiC paper with mineral oil as the lubricant. Final polishing was done using 1.0 and 0.3 μm Al_2O_3 powder suspended in mineral oil. The samples were indented immediately after polishing. The time the samples were exposed to the ambient atmosphere was kept to a minimum to prevent a reaction with the moisture and oxygen in the air. If such reactions occurred, the sample was not indented but, repolished to remove the reaction layer prior to indentation.

Measurements of room temperature fracture toughness were made using the indentation technique [9–13]. For fracture toughness, a total of five indents per sample were made at 5 kg with a Vickers indenter. The indentation crack lengths were measured immediately after unloading. Fracture toughness was evaluated using the following relation for median cracks [13].

$$K_{IC} = C_v\left(P/C_o^{3/2}\right)(E/H)^{1/2} \quad (3)$$

where C_v (= 0.016) is a material independent constant for a Vickers produced radial median crack, H is the measured hardness, P is the load, and C_o is the crack dimension. Hardness was measured at different indentations than those used for the fracture toughness determination. The elastic modulus of the alloy was determined using an ultrasonic technique [8]. Crack propagation was examined using optical microscopy.

3. Results and discussion

X-ray diffraction revealed that the Li–Sn alloy was single-phase $Li_{4.4}Sn$. A typical Vickers indentation in the $Li_{4.4}Sn$ alloy is shown in Fig. 1. From Fig. 1, several important points are noted. Firstly, the cracks emanating

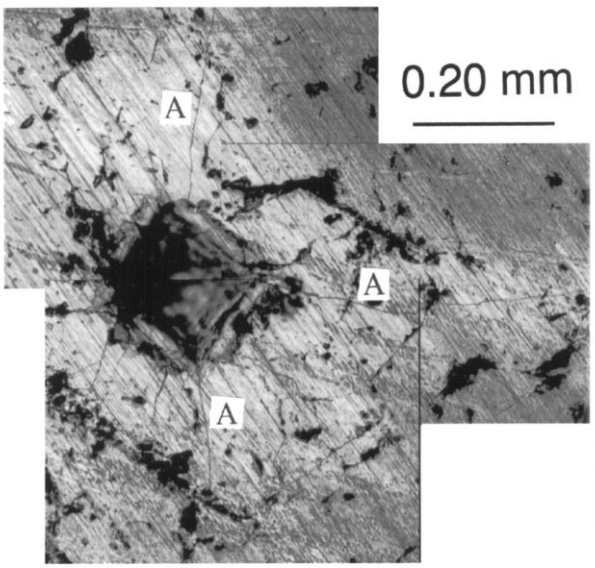

Fig. 1. Indentation crack pattern in $Li_{4.4}Sn$.

from the corners of the indent (marked A) are the ones that are used to determine C_o in Eq. (3). Secondly, these cracks are long and straight, indicative of a very brittle material [2,9–13].

The values of H, P and C_o determined from the indentation measurements along with E determined from acoustic measurements are listed in Table 1. K_{IC} for $Li_{4.4}Sn$ determined using the data in Table 1 and Eq. (3) is 0.8 ± 0.2 MPa $m^{1/2}$. The K_{IC} for $Li_{4.4}Sn$ can be compared to K_{IC} values for other single-phase ceramics, which range from 0.5 to 6.0 [2–5]. K_{IC} values for the ideal brittle material, glass, are close to unity [2–5]. Thus, the K_{IC} results confirm the microstructural observations that $Li_{4.4}Sn$ is indeed a very brittle material.

The volume change, $\Delta V/V_o$, from Sn to $Li_{4.4}Sn$ is 2.59 per atom of Sn [6,7]. Inserting this value into Eq. (2) with $E = 120$ GPa from Table 1 and $\nu = 0.25$, yields a value for $\sigma = 2.1 \times 10^5$ MPa. Inserting $K_{IC} = 0.8$ MPa $m^{1/2}$ and $\sigma = 2.1 \times 10^5$ MPa into Eq. (2) and rearranging yields c_{crit} for $Li_{4.4}Sn \approx 0.005$ nm. The $c_{crit} \approx 0.005$ nm value can be compared to the critical grain size, $d_{crit,} \approx 0.002$ nm that was predicted for $Li_{4.4}Sn$ [1]. From the comparison, it can be observed that c_{crit} for $Li_{4.4}Sn$ is in excellent agreement with the predicted d_{crit} for $Li_{4.4}Sn$. This result suggests that the model for predicting the critical grain size for microcracking during Li charging into brittle single-phase Li alloys is correct. To conclusively confirm the model, data from a host of Li alloys is required.

It is important to note that both the model and experimental data reveal a grain size below which fracture will not occur, that is less than the unit cell size for a majority

Table 1
Experimental values for $Li_{4.4}Sn$

P (kg)	5
H (GPa)	25.8 ± 1.5
C_o (μm)	322 ± 27
E (GPa)	120 ± 19

of brittle single-phase alloys. For example, the size of a Sn unit cell is ≈ 0.5 nm compared to $d_{crit} \approx 0.002$ nm and $c_{crit} \approx 0.005$ nm. This reiterates what was previously stated [1]; decreasing the particle and/or grain size alone will not solve the mechanical instability problem in brittle single-phase Li alloys. More likely, potential solutions to solve the mechanical instability problem involve a composite approach which includes: (i) incorporating the Li-alloys within a ductile Li-ion conducting metal or polymer matrix or (ii) surrounding the alloys within a matrix which places them under compressive stresses, which prevents microcrack formation.

4. Conclusions

(1) Indentation fracture toughness measurements yielded a K_{IC} for $Li_{4.4}Sn$ equal to 0.8 ± 0.2 MPa $m^{1/2}$.

(2) From K_{IC}, a critical crack length of 0.005 nm was determined for the stress generated due to the volume expansion as a result of the Li charging in $Li_{4.4}Sn$.

(3) The critical crack length is in excellent agreement with the predicted critical grain size for microcracking. This suggests that the model for predicting critical grain size for microcracking during Li charging into brittle single-phase alloys is correct.

(4) Decreasing the particle and/or grain size alone will not solve the mechanical instability problem in brittle single-phase Li alloys anodes.

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