Short communication

Young's modulus of polycrystalline $Li_{22}Si_5$

J.B. Ratchford [a,*], B.E. Schuster [b], B.A. Crawford [c], C.A. Lundgren [a], J.L. Allen [a], J. Wolfenstine [a]

[a] U.S. Army Research Laboratory, Adelphi Laboratory Center, 2800 Powder Mill Road, Adelphi, MD 20783, United States
[b] U.S. Army Research Laboratory, Aberdeen Proving Grounds, MD 21005, United States
[c] Nanomechanics Incorporated, Analytical Services Laboratory, 105 Meco Lane, Suite 100, Oak Ridge, TN 37830, United States

ABSTRACT

In order for Li–Si alloys to be used in Li-ion batteries as anodes, knowledge of their mechanical properties, such as Young's moduli, is crucial. Young's modulus of polycrystalline $Li_{22}Si_5$ was determined from nanoindentation testing. The value of Young's modulus was 35.4 ± 4.3 GPa. This value is approximately one-half of the predicted value based on density functional theory calculations. This difference was not a result of the testing procedure or microstructural variables.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Many researchers have investigated alternative electrode materials to graphite that would significantly increase the anode capacity of lithium-ion batteries [1–5]. Li–Si alloys are potential alternatives, in particular $Li_{22}Si_5$, which has a capacity 10 times (4200 mAh g^{-1}) greater than graphite (372 mAh g^{-1}) [1–5]. However, the capacities of Li–Si alloys decrease with cycling as a result of substantial volume changes with Li-ion addition/removal that cause the alloy to fracture. In order to solve the fracture problem, knowledge of the mechanical properties for the alloy is required; in particular, Young's modulus [6,7]. For example, Cheng and Verbrugge [6] have stated "Experiments and theoretical calculations are also urgently needed to provide material parameters, such as Young's modulus E and effective surface energy γ_{eff} that are seldom available, for quantitative predictions of fracture and decripitation of lithium-ion battery electrodes."

Values of Young's moduli for the Li–Si alloys were unknown until the very recent predictions of Shenoy et al. [7] that were based on density functional theory (DFT). For example, Shenoy et al. [7] predicted that Young's modulus for a polycrystalline $Li_{22}Si_5$ alloy was ~78 GPa. However, no experimentally measured value exists to verify this predicted value. Therefore, the objective of this study was to experimentally determine the value of Young's

modulus for polycrystalline $Li_{22}Si_5$ using nanoindentation testing.

2. Experimental

To synthesize polycrystalline $Li_{22}Si_5$, stoichiometric amounts of silicon powder and lithium granules were mixed and then pelletized. The pellet was placed inside a molybdenum crucible. The crucible containing the pellet was heated from 20 to 800 °C over the course of 40 min and then held at 800 °C for an additional 30 min. The sample was then heated at 450 °C for 16 h to ensure its homogeneity before it was slowly cooled to 20 °C [9]. All syntheses were performed in glove box filled with argon, which contained less than 1 ppm oxygen and 1 ppm water.

To determine the phase purity of $Li_{22}Si_5$, ~100 mg of the sample was removed from the center of the crucible, ground into fine powder, and analyzed by X-ray diffraction. Because the alloy is sensitive to ambient moisture, the sample was hermetically sealed with Kapton film. Inductively coupled plasma-mass spectrometry (ICP-MS) was used to confirm the weight percentage of lithium in the synthesized $Li_{22}Si_5$. To prepare samples of polycrystalline $Li_{22}Si_5$ for mechanical testing and microstructural analysis, granules of the sample were removed from the center of the crucible, then cold mounted and polished using standard metallographic techniques. Because the alloy is water reactive, the papers/clothes were lubricated with mineral oil instead of water. The surfaces of the granules were fine polished until a mirror finish was obtained. To determine the grain size of the alloy, an etching solution was developed. The composition of this solution was 0.2% by mass water and 0.3% by
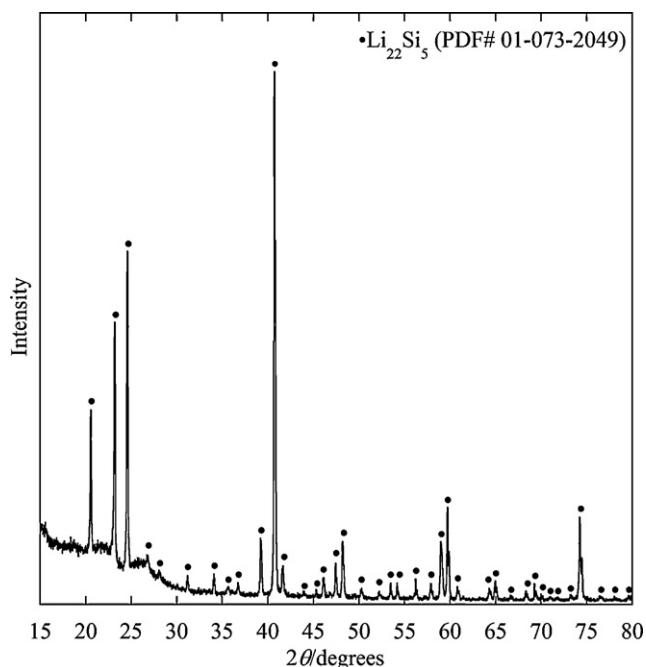
Fig. 1. X-ray diffraction pattern produced from a powder sample of the $Li_{22}Si_5$ alloy.

mass hydrochloric acid diluted with hexane. The grain size was measured using the linear intercept method [10].

Nanoindentation testing was used to determine Young's modulus, because it is a routine and convenient method that measures mechanical properties from small volumes of materials [11–17]. Young's modulus was determined from the load–displacement curve during unloading using the Oliver–Pharr method [11,17]. A Berkovich diamond indenter, specified with at least a 30 μm working depth, was used to indent homogeneous regions of the sample's surface under mineral oil. Each test was performed using a transducer, which had a maximum force of 500 mN, and force and displacement resolutions of 50 nN and 0.01 nm, respectively. Twenty tests were performed on each $Li_{22}Si_5$ sample. A standard reference material of fused silica was used to calibrate the instrument and quantify the effect of mineral oil on the indentation response. Optical microscopy was used to investigate the possibility of pile-up around the contact impressions after indentation.

3. Results and discussion

The X-ray diffraction pattern in Fig. 1 shows that the alloy is polycrystalline. The amorphous background in the 15–30° range is an artifact of the Kapton® tape. The position of the diffraction peaks that match those from the International Centre of Diffraction Data's powder diffraction file for $Li_{22}Si_5$ (PDF# 01-073-2049) are marked with bullets in Fig. 1. Fig. 1 shows that the positions of the diffraction peaks from the alloy agree perfectly with those from the powder diffraction file. Furthermore, the diffraction peaks shown in Fig. 1 are also in excellent agreement with those for $Li_{22}Si_5$ made by Zhou et al. [18]. These results suggest that the material is single phase $Li_{22}Si_5$.

The weight percentage of lithium in the $Li_{22}Si_5$ alloy obtained using ICP-MS was $52.5 \pm 1.1\%$. The expected weight percentage of the alloy is 52.1%. Using the upper bound of the measured Li weight percentage ($\sim$54%) and the Li–Si phase diagram [8], in conjunction with the lever rule [20], one finds that the maximum possible amount of second phase is 6 vol% βLi.

Optical microscopy of the fine polished surface revealed no porosity and no second phases. The grain structure of polycrys-

Table 1
Young's moduli of samples measured by nanoindentation.

Sample	Young's modulus (GPa)
$Li_{22}Si_5$	35.4 ± 4.3
Fused silica	71.2 ± 1.6
Fused silica[a]	71.7 ± 1.6
Fused silica[a,b]	74.0 ± 0.3

[a] Without mineral oil.
[b] Measured by ultrasonic spectroscopy.

talline $Li_{22}Si_5$ is fairly equiaxed, with a grain size of 25 ± 3 μm as shown in Fig. 2. The elemental and microstructural analyses confirm the X-ray diffraction results, that the alloy is predominately single phase $Li_{22}Si_5$.

Young's moduli of polycrystalline $Li_{22}Si_5$ and fused silica that were measured using nanoindentation are listed in Table 1. From Table 1 several important points can be made. Firstly, mineral oil did not affect the measurement as one sees that Young's moduli of the fused silica with and without mineral oil are the same. Secondly, the value of Young's modulus of the fused silica samples measured by nanoindentation is in very good agreement with the value determined by a different technique, ultrasonic spectroscopy. This result is in good agreement with recent reports, which have shown excellent agreement between Young's modulus determined using nanoindentation testing and values obtained using ultrasonic spectroscopy on the following brittle materials: Pyrex glass and Al_2O_3 [12], Cr_3Si [15], Y_2O_3 [13], and $Ce_{0.9}Fe_{3.5}Co_{0.5}Sb_{12}$ and $Co_{0.95}Pd_{0.05}Te_{0.05}Sb_3$ [16]. Therefore, we expect that the value of Young's modulus for polycrystalline $Li_{22}Si_5$ measured using nanoindentation is the true property of the alloy.

Table 1 shows that the average value of Young's modulus for polycrystalline $Li_{22}Si_5$ is 35 ± 4.3 GPa, which is between the measured values for polycrystalline lithium (4.9 GPa from tension [20] or 8.0 GPa from ultrasonic spectroscopy [21]) and polycrystalline silicon (202 GPa from nanoindentation [22]). This result is expected because, in a first approximation, Young's modulus directly scales with melting temperature [19]. The melting (peritectic) temperature of $Li_{22}Si_5$ is = 901 K, which is higher than the melting temperature of lithium ($T_m = 453$ K) and lower than the melting temperature of silicon ($T_m = 1687$ K) [8].

This experimental value of Young's modulus can be compared to the very recent prediction by Shenoy et al. [7]. Shenoy et al. [7] predicted Young's modulus for polycrystalline $Li_{22}Si_5$ to be $\sim$78 GPa by applying a Hill averaging scheme to single-crystal elastic constants determined from DFT calculations. The predicted value is
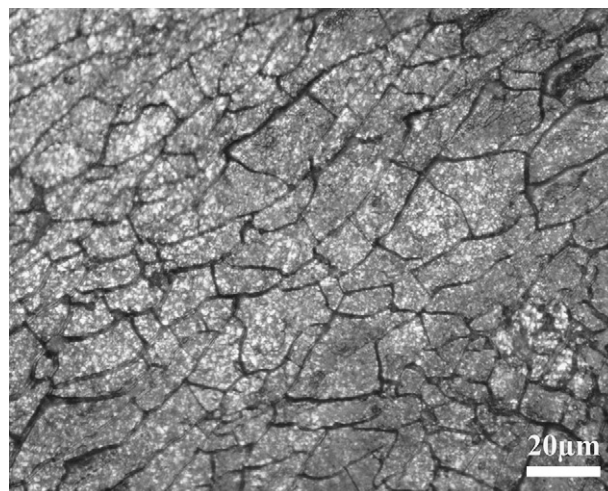

Fig. 2. Optical image of an etched sample of polycrystalline $Li_{22}Si_5$.

significantly higher than the measured value; 2.2 times the measured value. Furthermore, Shenoy et al. [7] predicted Young's modulus for polycrystalline Li to be ~20 GPa, which is 2.5–4 times the measured values [20,21]. Thus, it appears that for the $Li_{22}Si_5$ alloy and Li DFT overestimated the value of Young's modulus. In addition, the DFT calculations by Shenoy et al. [7] also predicted Poisson's ratio for crystalline $Li_{22}Si_5$ to be ~0.08. This is a low value as compared those of other Li alloys which range from ~0.2 to 0.4 [23].

Another example of this is for the case of a Li–Al alloy, LiAl. Young's modulus for LiAl was predicted by Uesugi et al. [24] to be 77 GPa for a polycrystalline material using the Voigt–Reuss–Hill averaging scheme applied to single-crystal elastic constants determined from DFT calculations. The measured value of Young's modulus for polycrystalline LiAl using ultrasonic spectroscopy was 45 GPa [23]. The predicted value is 1.7 times the measured value, similar to the case for polycrystalline $Li_{22}Si_5$. Uesugi et al. [24] suggested that a possible reason for the difference between the predicted value and the measured value of Young's modulus for LiAl was a result of strong texturing within the measured material as compared to the isotropic properties used in the calculations. From Fig. 2, the optical micrograph reveals that the microstructure of $Li_{22}Si_5$ is fairly equiaxed. Therefore, it is likely that texturing cannot explain the difference between the predicted and measured value of Young's modulus for polycrystalline $Li_{22}Si_5$.

Other possible reasons for the difference in the measured and predicted value could be a result of the microstructure of polycrystalline $Li_{22}Si_5$. It has been shown that Young's modulus can be influenced by microstructural variables, such as a mixture of phases, grain size, and porosity [25–31]. The upper bound of Young's modulus from the Voigt model, E_V, and lower bound of Young's modulus from the Reuss model, E_R, for a mixture of two phases can be calculated using Eqs. (1) and (2), respectively [19]:

$$E_V = E_{Li_{22}Si_5}f_{Li_{22}Si_5} + E_{\beta Li}f_{\beta Li} \tag{1}$$

$$\frac{1}{E_R} = \frac{f_{Li_{22}Si_5}}{E_{Li_{22}Si_5}} + \frac{f_{\beta Li}}{E_{\beta Li}} \tag{2}$$

where $E_{Li_{22}Si_5}$ and $E_{\beta Li}$ are Young's moduli for $Li_{22}Si_5$ and βLi, respectively, and $f_{Li_{22}Si_5}$ and $f_{\beta Li}$ are the relative volume fractions of the two phases. For our material, in the worst case, the alloy is 94 vol% $Li_{22}Si_5$ and 6 vol% βLi. If one considers this composition with the predicted values of Young's modulus from Shenoy et al. [7], then from Eqs. (1) and (2), one would calculate $E_V = 75$ GPa, and $E_R = 67$ GPa, respectively. These values are significantly higher than the measured value 35.4 ± 4.3 GPa. Therefore a mixture of two phases cannot explain the difference between the predicted and measured values of Young's modulus for polycrystalline $Li_{22}Si_5$. The grain size of our material is 25 ± 3 μm. In this grain size regime, Young's modulus is not influenced by grain size [26,28,30,31]. Optical microscopy shows that the alloy is 100% dense. Therefore porosity did not affect the measured value of Young's modulus [25–27,29–31]. It is apparent from the above arguments that microstructural variables cannot account for the difference between the predicted and measured values of Young's modulus for polycrystalline $Li_{22}Si_5$.

One other possible reason for the difference between the measured and predicted value could be a result of pileup around contact impressions made during nanoindentation [32,33]. Bolshakov and Pharr [32] showed that significant pileup caused the elastic modulus to be overestimated by as much as 50%. However, optical microscopy of the $Li_{22}Si_5$ surface around the contact impressions showed that pileup did not occur. Furthermore, if excessive pileup had occurred in polycrystalline $Li_{22}Si_5$, the measured value of Young's modulus would have been even lower than the measured value of 35.4 ± 4.3 GPa [32]. Therefore, pileup cannot explain the

difference between the predicted and measured values for Young's modulus for polycrystalline $Li_{22}Si_5$.

The above results suggest that the difference between the experimentally measured value of Young's modulus and the predicted value by Shenoy et al. [7] using DFT calculations cannot be explained by the testing procedure or microstructural variables. Because of this discrepancy, and the significant difference between the predicted value of Young's modulus for Li using DFT calculations and the experimental value, we believe that the measured value of Young's modulus for polycrystalline $Li_{22}Si_5$ using nanoindentation represents a more realistic value than the predicted value by Shenoy et al. [7] based on DFT.

4. Conclusion

Polycrystalline $Li_{22}Si_5$ was synthesized. The single-phase purity of the alloy was confirmed by X-ray diffraction, ICP-MS and optical microscopy. Young's modulus for polycrystalline $Li_{22}Si_5$ was determined from nanoindentation testing. The value of Young's modulus was 35.4 ± 4.3 GPa. This value is approximately one-half of the predicted value based on density functional theory calculations. This difference was not a result of the testing procedure or microstructural variables.

Acknowledgements

References

[1] J.M. Tarascon, M. Armand, Nature 414 (2001) 359–367.
[2] U. Kasavajjula, C.S. Wang, A.J. Appleby, J. Power Sources 163 (2007) 1003–1039.
[3] A.S. Arico, P. Bruce, B. Scrosati, J.M. Tarascon, W. Van Schalkwijk, Nat. Mater. 4 (2005) 366–377.
[4] W.J. Zhang, J. Power Sources 196 (2011) 13–24.
[5] C.M. Park, J.H. Kim, H. Kim, H.J. Sohn, Chem. Soc. Rev. 39 (2010) 3115–3141.
[6] Y.T. Cheng, M.W. Verbrugge, Electrochem. Solid State Lett. 13 (2010) A128–A131.
[7] V.B. Shenoy, P. Johari, Y. Qi, J. Power Sources 195 (2010) 6825–6830.
[8] H. Okamoto, J. Phase Equilib. Diffus. 30 (2009) 118–119.
[9] C.J. Wen, R.A. Huggins, J. Solid State Chem. 37 (1981) 271–278.
[10] G.F. Vander Voort, Metallography: Principles and Practices, McGraw-Hill, Inc., 1984.
[11] W.C. Oliver, G.M. Pharr, J. Mater. Res. 7 (1992) 1564–1583.
[12] M. Radovic, E. Lara-Curzio, L. Riester, Mater. Sci. Eng. A 368 (2004) 56–70.
[13] I.C. Albayrak, S. Basu, A. Sakulich, O. Yeheskel, M.W. Barsoum, J. Am. Ceram. Soc. 93 (2010) 2028–2034.
[14] H. Bei, E.P. George, Acta Mater. 53 (2005) 69–77.
[15] H. Bei, E.P. George, G.M. Pharr, Scripta Mater. 51 (2004) 875–879.
[16] R.D. Schmidt, J.E. Ni, E.D. Case, J.S. Sakamoto, D.C. Kleinow, B.L. Wing, R.C. Stewart, E.J. Timm, J. Alloys Compd. 504 (2010) 303–309.
[17] W.C. Oliver, G.M. Pharr, J. Mater. Res. 19 (2004) 3–20.
[18] G.-T. Zhou, O. Palchik, I. Nowik, R. Herber, Y. Koltypin, A. Gedanken, J. Solid State Chem. 177 (2004) 3014–3020.
[19] C.R. Barrett, W.D. Nix, A.S. Tetelman, The Principles of Engineering Materials, Printice-Hall, Inc., 1973.
[20] P.W. Bridgman, Proc. Am. Acad. Arts Sci. 57 (1922) 40–66.
[21] W.M. Robertson, D.J. Montgomery, Phys. Rev. 117 (1960) 440–442.
[22] B. Bhushan, X.D. Li, J. Mater. Res. 12 (1997) 54–63.
[23] K. Kuriyama, S. Saito, K. Iwamura, J. Phys. Chem. Solids 40 (1979) 457–461.
[24] T. Uesugi, Y. Takigawa, K. Higashi, Mater. Trans. 46 (2005) 1117–1121.
[25] J. Kovacik, J. Mater. Sci. Lett. 18 (1999) 1007–1010.
[26] H.S. Kim, M.B. Bush, Nanostruct. Mater. 11 (1999) 361–367.
[27] S.L. Dole, O. Hunter, C.J. Wooge, J. Am. Ceram. Soc. 60 (1977) 488–490.
[28] I. Yamai, T. Ota, J. Am. Ceram. Soc. 76 (1993) 487–491.
[29] R.M. Spriggs, J. Am. Ceram. Soc. 45 (1962) 454–455.
[30] R. Chaim, M. Hefetz, J. Mater. Sci. 39 (2004) 3057–3061.
[31] R.E. Fryxell, B.A. Chandler, J. Am. Ceram. Soc. 47 (1964) 283–291.
[32] A. Bolshakov, G.M. Pharr, J. Mater. Res. 13 (1998) 1049–1058.
[33] T.Y. Tsui, W.C. Oliver, G.M. Pharr, J. Mater. Res. 11 (1996) 752–759.