Journal of Alloys and Compounds 434–435 (2007) 542–545

www.elsevier.com/locate/jallcom

Mechanical alloying of lithium-base systems

K.N. Ishihara [*], F. Kubo, K. Irie, K. Shichi, E. Yamasue, H. Okumura

Graduate School of Energy Science, Kyoto University, Yoshida Honmachi, Sakyo, Kyoto 606-8501, Japan

Abstract

Mechanical alloying (MA) is one of the most suitable methods to produce alloys with various elements such as refractory, low melting and high vapor pressure materials. The high energy vibrating ball milling was performed under an argon atmosphere both at room temperature and at liquid nitrogen temperature. Small pieces of Li metal and powders of Al, Si and Fe were used as starting materials. In the case of Al–Li, the stable intermetallic compound, β-AlLi, is formed after 10 h of milling. When lithium is milled with silicon at the low temperature, powder is obtained without formation of any compound, while for the milling at room temperature the formation of metastable $Li_{21}Si_8$ is detected by X-ray diffractometry. As for the Fe–Li system, which is immiscible even in a liquid state, evidence of alloying is not observed. The results are explained in terms of the heat of mixing and the mutual diffusivity in these systems. The surface activation of the milled powder will be discussed in terms of the nitrogen reactivity of each milled alloy system.

Keywords: Nitride materials; Metals and alloys; Mechanical alloying; Phase transitions; X-ray diffraction

1. Introduction

Mechanical alloying (MA) is one of the most suitable methods to produce alloys with various elements such as refractory, low melting and high vapor pressure materials [1,2]. There are many reports of formation of various materials utilizing the MA method. For the case of lithium-base alloys, though the lithium ion battery is very popular, MA has been investigated for several systems including C–Li [3] and Li–Mg [4] alloys. It is well known that lithium reacts with nitrogen to form nitride even at a room temperature. If lithium becomes more reactive than the bulk form, it may be useful as a nitrogen absorption material. We reported that the activity of an element in a metastable solid solution produced by mechanical alloying is enormously increased for the case of immiscible systems [5,6]. Moreover, the lithium element is the lightest metal. It is interesting to know whether a metastable solid solution including lithium is obtained, and whether a new light alloy can be obtained. The purpose of this work is to show how lithium forms alloys during MA with aluminum, silicon and iron. Especially, the characteristics for Li–Fe system, which is immiscible even in a liquid state, will be discussed.

2. Experimental procedure

Small pieces of Li metal and powders of Al (99.9%, 150 mesh), Si (99.9%, 45 μm) and Fe (99.9%, 53 μm) were used as starting materials. The high energy vibrating ball milling was performed under an argon atmosphere at room temperature (and for some Li–Si at a liquid nitrogen temperature). In total, about 10 g of samples was used. No process control agent (PCA) was used for Li–Si, Fe–Li, and 1 g of carbon powders was used to prevent the samples from adhering to the surface of vessel and balls for Al–Li. The ball to power ratio was 10. For the nitrogen gas absorption, the sample was put into the test tube under an argon atmosphere. Then, the test tube is evacuated and filled with nitrogen gas. The amount of nitrogen absorption is measured by change of pressure and sample weight.

The microstructure of specimen is observed using scanning electron microscopy, SEM (JSM-5800) with energy dispersive X-ray analysis (EDAX). Differential scanning calorimeter, DSC (Perkin-Elmer lambda 700) and differential thermal analysis with thermal gravity DTA/TG (Rigaku) were used for thermal analysis.

3. Results

3.1. Al–Li system

The stable intermetallic compound, β-AlLi, is formed after 10 h of milling for 60% Li sample, as shown in Fig. 1. At the same time, small amount of LiOH and Al was detected by X-ray diffractometry. Up to 50 h of milling, the constituent phases are not changed. After β-AlLi formation, the reaction with nitrogen was not observed.

---

[*] Corresponding author. Tel.: +81 75 753 5464; fax: +81 75 753 5464.
E-mail address: ishihara@energy.kyoto-u.ac.jp (K.N. Ishihara).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.08.170

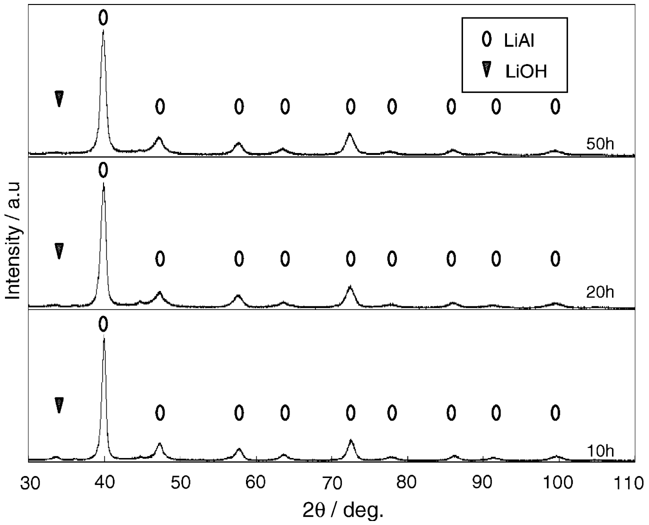

Fig. 1. X-ray diffraction patterns of Al–60%Li samples milled for 10 h, 20 h and 50 h.

3.2. Si–Li system

For the Si–25%Li and Si–50%Li samples, powder samples were not obtained after 1 h milling. The powder form sample was obtained for Si–17%Li milled for 30 min and 60 min. The formation of metastable $Li_{21}Si_8$ [7] is detected by X-ray diffractometry as shown in Fig. 2. When lithium is milled with silicon at low temperature, the powder sample is obtained without formation of any compound.

The reactivity of the milled powders with nitrogen was investigated at room temperature (RT) for the samples, since the metallic lithium is known to react with nitrogen at room temperature. It is found, as shown in Fig. 3, that the reaction kinetics is drastically enhanced due to the milling process (especially for the low temperature (LT) milling), but also that the reactivity is reduced when an intermetallic compound phase is formed, due to consumption of pure lithium.

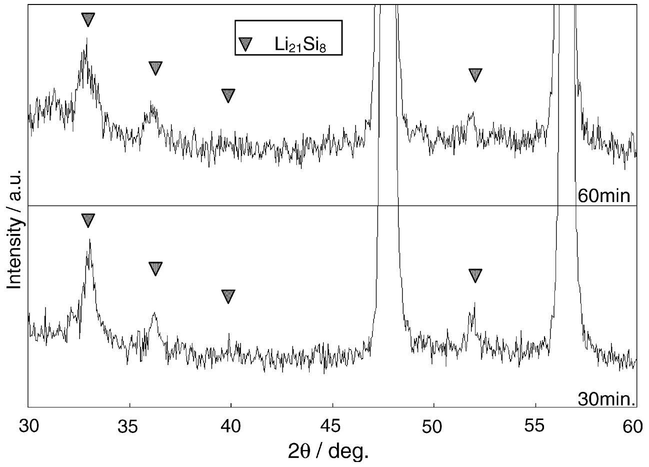

Fig. 2. X-ray diffraction patterns for Si–17%Li sample milled for 30 min and 60 min at room temperature.

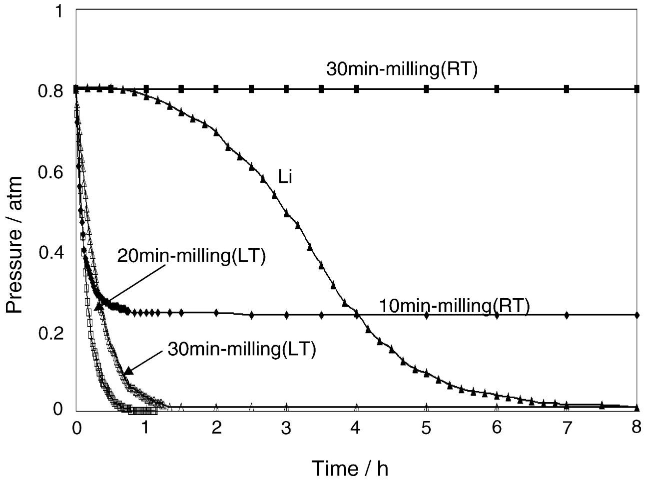

Fig. 3. The change of nitrogen gas pressure by the formation of lithium nitride for pure lithium and mechanical alloyed Si–17%Li samples. RT and LT indicate room temperature and low temperature, respectively.

3.3. Fe–Li system

For the Fe–Li system with the Li concentration higher than 20%, the samples could not be obtained in powder form after milling. Then, in this work, 15.3% Li sample will be reported. The results of the nitrogen absorption experiment were shown in Fig. 4. In the case of bulk lithium, it takes about 40 min to start the reaction with nitrogen gas, while the sample milled for 10 min exhibits a much faster reaction. The longer-milled samples, however, do not show the clear reaction, which is similar to the case of Si–Li system.

Fig. 5 shows the SEM image of the sample milled for 1 h. It is difficult to detect lithium atoms under SEM/EDX measurements since the atomic number is small. We then focused on the oxygen atoms, which cover the lithium phase as lithium oxide, since oxidation occurred during handling the sample in the air for

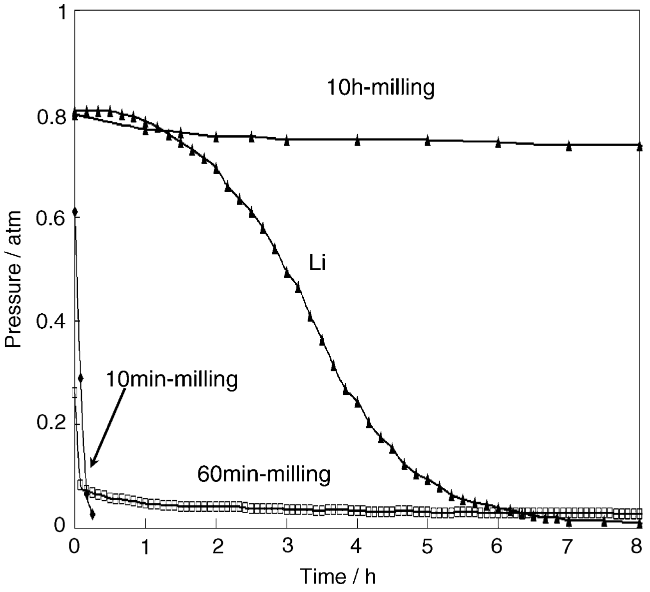

Fig. 4. The change of nitrogen gas pressure by the formation of lithium nitride for pure lithium and mechanical alloyed Fe–15.3%Li samples.

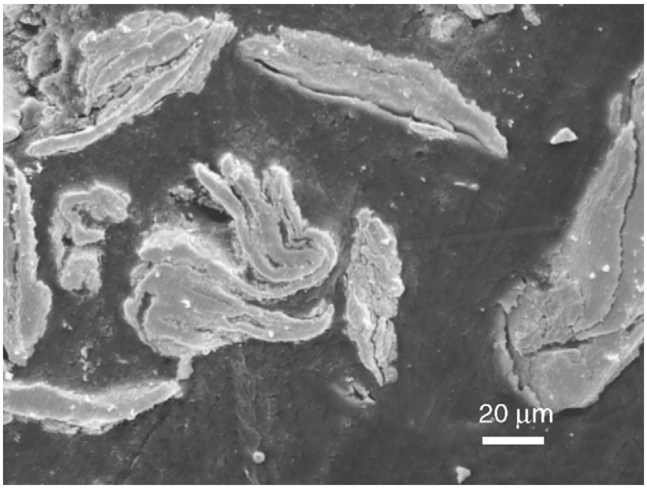

Fig. 5. SEM image of Fe–15.3%Li sample milled for 1 h. Layered structures are seen.

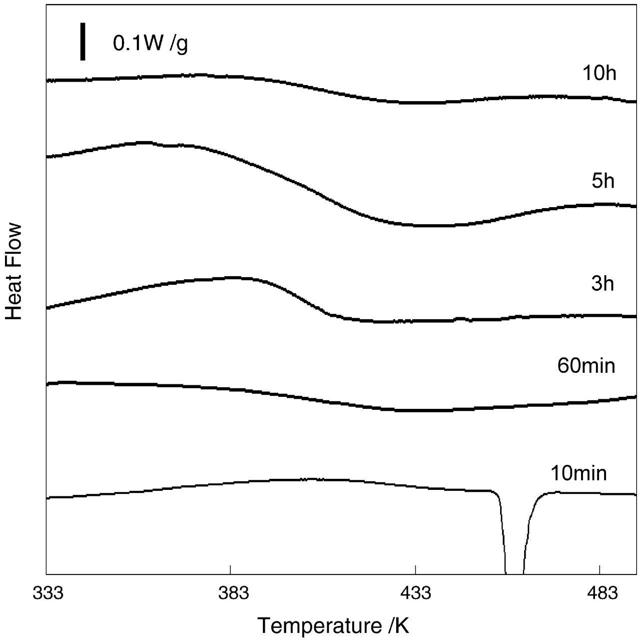

Fig. 6. DSC thermograms of Fe–15.3% for various milling times.

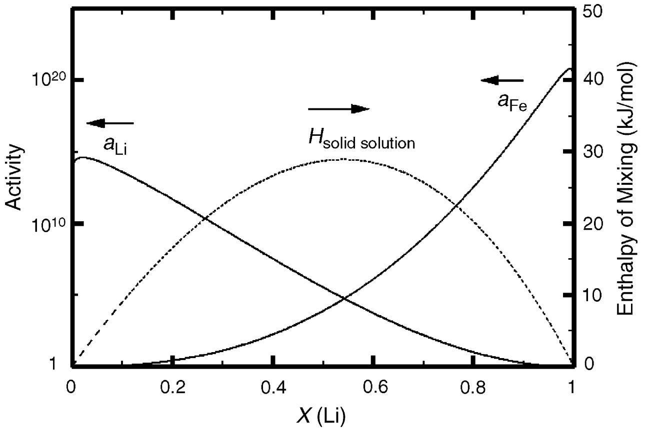

Fig. 7. Activity of Li and Fe, and excess enthalpy of mixing for hypothetical solid solution of Fe–Li system, calculated by Miedema's model.

the SEM/EDX. The formation of laminar structure consisting of oxygen rich area and the iron rich area was confirmed by the EDX analysis. The so-called 'kneading effect' is clearly seen in this sample as is often observed for a general milling process.

4. Discussions

From the above results, it is concluded that for the system exhibiting intermetallic compounds as thermodynamically stable phases, a preferable compound is formed by mechanical alloying. When the compounds are formed, the nitrogen absorption cannot be observed anymore. In this section, the case of Fe–Li system, which is immiscible even in a liquid state, is particularly discussed in terms of the Li reactivity. The reason why the lithium did not react to nitrogen gas in the longer-millied samples can be thought that the small lithium particle is put in iron matrix and does not contact to the atmosphere. In order to confirm this, DSC experiment was performed. If the pure lithium exists in the sample, the melting can be detected as endothermic peak at around 454 K. However, all the samples after 1 h milling did not indicate a clear endothermic peak as shown in Fig. 6. Only very broad exothermic peak is seen around 373 K. The magnetizations are also measured using a vibrating sample magnetometer, VSM. The saturation magnetization in each sample did not decrease the value. It suggests that the environment of iron atoms does not change, and iron and lithium do not contact in an atomistic level. These results strongly suggest that the lithium does not exist in iron matrix microscopically or macroscopically.

Fig. 7 shows the calculated activity of Li in hypothetical Fe–Li solid solution using Miedema's model [8,9], where the structural enthalpy is neglected. It is suggested that if the solid solution is formed at the investigated composition, the order of activity is about 10^{12}. As proceeding of the mechanical alloying process, the lithium becomes very active. Thus, for the short-time-milled samples, the fast reaction with nitrogen gas was seen. However, since the longer the milling time is, the more active the lithium becomes, the lithium forms oxide and/or hydroxide very easily if it contacts to the air and/or water vapor. Furthermore, since the free energy of the lithium in the surface region is smaller than that in the bulk, the Gibbsian segregation may be seen. It is reported that this effect is observed in the Cu–Li system, which is also immiscible [10]. It is reported that the partial solid solution phase was formed for Fe–Bi [11], Fe–In [12] which is similar to Fe–Li system in terms of immiscibility and those large different melting temperatures. However, the mixing enthalpy is not so large positive. In this study, all the experiments were carefully performed in an argon atmosphere. Nevertheless, a small amount of impurity is enough to attack the lithium atoms, which exist in the surface of powders.

5. Conclusion

Mechanical alloying was performed on Al–Li, Si–Li and Fe–Li systems with the following results:

(1) The intermetallic compound β-AlLi was formed for milling period longer than 10 h, in the case of Al–60%Li.
(2) When lithium is milled with silicon at liquid nitrogen temperature, powder sample is obtained without formation of any compound, while for the milling at room temperature the metastable $Li_{21}Si_8$ phase is formed.
(3) Fe–Li system, which is immiscible even in the liquid state, the evidence of alloying is not observed. The results can be explained in terms of the heat of mixing and the mutual diffusivity in these systems.

Acknowledgement

This research was partially supported by Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Scientific Research (B), 17360369, 2005.

References

[1] F. Ahou, Y.T. Chou, E.J. Lavernia, Mater. Trans. 42 (2001) 1566.
[2] K. Uenishi, K.F. Kobayashi, S. Nasu, H. Hatano, K.N. Ishihara, P.H. Shingu, Z. Metallkd. 83 (1992) 132.
[3] D. Guerard, R. Janot, J. Phys. Chem. Solids 65 (2004) 147.
[4] J. Huot, S. Bouaricha, S. Boily, J.-P. Dodelet, D. Guay, R. Schulz, J. Alloys Compd. 266 (1998) 307.
[5] K.N. Ishihara, S. Diaz de la Torre, T. Hosoe, A. Yamamoto, P.H. Shingu, in: H. Hennen, T. Oki (Eds.), First International Conference on Processing Materials for Properties, Hawaii, 1993, pp. 667–670.
[6] S.D. De la Torre, A. Yamamoto, K.N. Ishihara, P.H. Shingu, T. Hirato, Y. Awakura, Mater. Sci. Forum 179–181 (1995) 237.
[7] R.A. Sharma, R.N. Seefurth, J. Electrochem. Soc. 123 (1976) 1763.
[8] F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, Cohesion in Metals Transition Metal Alloys, North-Holland, 1988.
[9] H. Bakker, Enthalpy in Alloys, Miedema's Semi-Empirical Model, Trans Tech Publications, 1998.
[10] B. Baretky, W. Echstein, R.P. Schorn, J. Nucl. Mater. 224 (1995) 50.
[11] N. Lyakhov, T. Grigorieva, A. Barinova, S. Lomayeva, E. Yelsukov, A. Ulyanov, J. Mater. Sci. 39 (2004) 5421.
[12] T.Yu. Kiselva, A.A. Novakova, T.F. Grigorieva, A.P. Barinova, J. Alloys Compd. 383 (2004) 94.