

Mechanical Milling of Lithium with Metal Oxide and its Reactivity with Gases

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Abstract

Li reacts with N₂ at room temperature. In order to activate Li, the mechanical milling of Li with stable metal oxide, namely, Al₂O₃ and MgO, using a high energy vibrating ball mill was performed. In the case of Li-MgO system, it reacts with N₂, but hardly reacts with O₂. The reaction with N₂ generally produces Li₃N, while for some vigorous reactions the Mg₃N₂ is produced as the major phases. In the case of Li-Al₂O₃ system, reactivities with both N₂ and O₂ are high. The difference is explained in terms of the reaction mechanism and the Li state.

Keywords : Li-MgO system, Li-Al₂O₃ system, nitrogen absorption, mechanical milling, Mg₃N₂

1. Introduction

Li is known as one of active metals, reacting with N₂ at room temperature (RT). However, it takes more than half an hour, for the case of a bulk Li, before reacting with N₂ at RT, and it hardly reacts with O₂. The mechanical milling (MM) is of great value for creating a finely mixed specimen, which is expected to promote the gas absorption and activation. When the MM is carried out on the Li-Al and Li-Si systems^[1-2], the reactivity with N₂ is markedly reduced due to the formation of intermetallic compounds. But, for the milling of the Li-Fe system using the Fe powder oxidized on the surface, the reactivity is promoted, since the surface oxide is seemingly reduced by Li at the early stage of the MM and the mixture of the iron oxide and the lithium oxide with Fe and Li powders promotes the progress of the milling process.

It is then suggested that in order to obtain activated finely-divided Li the stable and hard metal oxide be useful in consideration of the effective milling process. The MgO and Al₂O₃ are selected on considering the formation energies^[3], where the MgO is more stable than Li₂O near RT, which is slightly more stable than Al₂O₃. The purpose of this study is to investigate the milling process of Li-MgO and Li-Al₂O₃ alloy systems, particularly by focusing on the state of Li, and the reaction characteristics with N₂ and O₂.

2. Experimental Procedure

The small pieces of Li of 98 % purity, MgO of 99.99% (BET surface area of 21 m²/g) and Al₂O₃ powder of 95 % (0.58 m²/g) were used as the starting materials. About 6-8g of the sample mixture with the initial Li contents of 3.33-14.69 wt% for Li-MgO and 3.29-6.73 wt% for

Li-Al₂O₃ was measured in a glove box under an Ar atmosphere, and put in a ball mill vial with stainless steel balls (3.68g/piece). The MM was performed using a high energy vibrating ball mill with water jacket (NEV-MA8, Nisshin Giken). The ball-to-powder weight ratio was about 10, and no process control agent was used. As for the gas absorption experiment, the sample was first put into a quartz tube (inner vol.: 20cc) under an Ar atmosphere, followed by evacuation and filling of gases such as N₂ (6N), O₂ (6N) at RT. The absorbed amount of each gas was estimated from changes in both the sample weight and the inner pressure, where the latter was measured using capacitance manometer. The morphology of the sample was observed using SEM (JSM-5800 type-C, JEOL). The single-point BET specific surface area measurements were performed, where the measurements of Li-containing samples were carried out after sufficient exposure to air (Flowsorb III 2300, Micromeritics). Powder XRD with Cu-K_α radiation was performed utilizing RINT2000 (Rigaku) with the specimen airtight attachment under Ar atmosphere. The state of ⁷Li nucleus was observed using NMR (Unity Inova 4000, Varian). The Li content in the sample was measured using the ICP-AES (Nippon Jarrell-Ash ICAP-575 MarkII).

3. Results and Discussion

The recovery yield for the Li-MgO samples after MM for 1h is over 92% for 3.33-7.93wt%Li samples (Li content confirmed with ICP), but is reduced to 63-73% for the 14.69wt%Li sample, with the actual Li content of about 13wt%Li due to adherence of Li on the balls and the vial. As for the Li-Al₂O₃ system the recovery yield is only examined for the 5.88wt%Li sample and is 50-60%. The

recovered samples are in a powder form for the former system, while are in both powder and granular forms for the latter (granules of 0.5-1.2 mm in diameter).

The features and morphologies of both samples are essentially not changed after MM for 1 hour, but the surface of the flake or the granule becomes slightly roughened for both cases ((b) and (d)), which appears consistent with the observed BET results (around 25 and 2 m²/g, respectively).

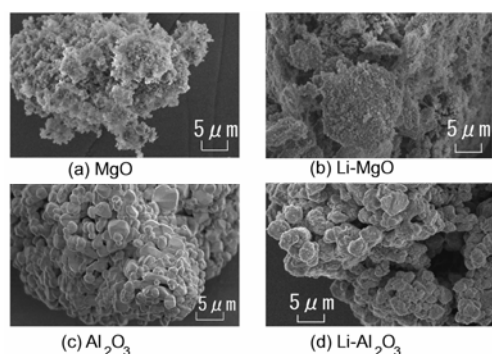


Fig. 1. SEM images of (a) MgO, (b) 1h milled Li-MgO, (c) Al₂O₃ and (d) 1h milled Li-Al₂O₃.

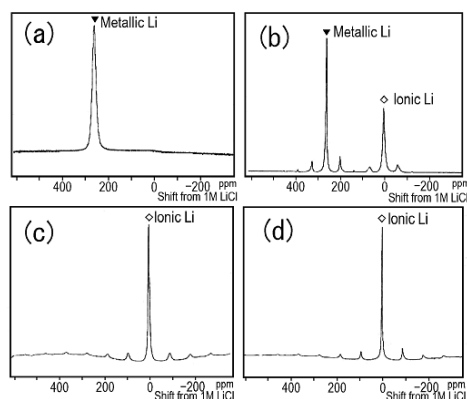


Fig. 2. ⁷Li NMR spectra of (a) Li-MgO [static method], (b) Li-Al₂O₃, (c) Li-MgO after N₂ absorption, (d) Li-Al₂O₃ after N₂ absorption [(b)-(d) : MAS method].

The NMR spectrum of Li in the milled Li-MgO sample (Fig. 2(a)) shows that the Li atoms exist only as a metallic state, suggesting the chemical stability of MgO during the milling with Li. On the other hand, for the milled Li-Al₂O₃ (Fig. 2(b)) the existence of both metallic and ionic Li atoms is shown, suggesting that about a half (48.2%) of all Li atoms form pseudo bond with Al₂O₃ at the contact interface or replace Al atoms inside the Al₂O₃ during the milling process. There is also a possibility that the Li atoms even deprive the Al₂O₃ of its oxygen to form the Li₂O phase during MM, but the amount of nitrogen that reacts with the sample after the milling eliminates the possibility, since the Li₂O is much more stable than Li₃N. The results are

self-consistent on considering the thermodynamic order of the stability among the oxides such as Li₂O, Al₂O₃ and MgO. All the metallic Li for both samples become ionic after the N₂ absorption experiment (Fig. 2(c), (d)), indicating that all the Li metal is consumed during the reaction.

For both systems the reactivities of the milled powder with N₂ are drastically enhanced as compared with the bulk Li metal. In the case of 14.69%Li-MgO the N₂ pressure drops from 66000 Pa to 1000 Pa in 10 sec and to 50 Pa in 60 sec. It also reacts with N₂ at 10000 Pa (or even 300 Pa), reducing to 100 Pa in 15 sec and to 15 Pa in 30 sec. It absorbs 8.0-8.6 wt% of nitrogen per own weight (70-75 cc/g) when it is completely reacted. The Li-MgO sample hardly reacts with O₂, where the O₂ pressure drops from 62000 Pa to only 60000 Pa even after 24h exposure (and, from 10100 Pa to 9900 Pa after 12h). On the other hand, the milled Li-Al₂O₃ reacts with both N₂ and O₂. In the case of 5.88Li-Al₂O₃, it absorbs 3.2-3.7 wt% of nitrogen per own weight (27-32 cc/g). The reaction with O₂ is faster than the reaction with N₂, suggesting a faster reaction kinetics of Li with oxygen than with nitrogen. The results suggest there is a characteristic oxidization mechanism for the Li-Al₂O₃ system compared with the bulk Li and the Li-MgO system. Both milled alloys, unlike the bulk Li, react with air, indicating that the mixture of N₂ and O₂ complicates the reaction mechanism.

As for the 14.69%wtLi-MgO sample, it vigorously reacts with N₂ to produce Mg₃N₂ and Li₂O besides ordinary Li₃N formation. Because of the high Li content and the milled state a large amount of heat appears generated at the early stage of the reaction, greatly enhancing the reaction kinetics and even changing the reaction path. According to the thermodynamic consideration [3], the reaction is expressed as follows: 3MgO + N₂ + 6Li → Mg₃N₂ + 3Li₂O.

4. Conclusion

MM of Li with MgO and Al₂O₃ greatly activates the Li reactivity. The milled Li-MgO system reacts with N₂, but hardly reacts with O₂. The Li-MgO system with high Li content (14.69wt%Li) vigorously reacts with N₂ to produce Mg₃N₂ and Li₂O besides Li₃N. In the case of Li-Al₂O₃ system, the reactivities with both N₂ and O₂ are high. The characteristic oxidation mechanism of the Li-Al₂O₃ system is self-consistently explained on considering the special state of the Li atoms after the milling process.

5. References

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