
**METALLURGY
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Study of the Process of Dissociation of Lithium Carbonate in the Presence of Aluminum Powder

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Abstract—The results of a study of the dissociation process of lithium carbonate in vacuum in the presence of aluminum powder are presented. It is revealed that at a process temperature of 700°C, the degree of dissociation achieves ~60% and the thermal decomposition of lithium carbonate retards. It follows from the phase diagram of the Li_2CO_3 – Li_2O system that an increase in the temperature leads to the appearance of a liquid phase. On the basis of the experimental data with the use of the half-division method, a maximum rate of heating from 700 to 740°C of $0.33 \pm 0.02^\circ\text{C}/\text{min}$ is determined at which there is no formation of the low-melting eutectic between the carbonate and lithium oxide. The partial micromelting does not affect the mechanical properties of the briquette. The selected temperature mode provides the uniform thermal decomposition of lithium carbonate over the whole mass of the briquette, which minimizes the possibility of contacts between the carbonate and lithium oxide. Under these conditions, the time of the total degree of dissociation is 2 h. A decrease in the heating rate leads to an increase in the duration of the dissociation process, while its increase leads to the partial melting of the briquette. Aluminum plays the role of an inert additive accelerating the dissociation process at the stage of dissociation.

Key words: lithium carbonate, aluminum powder, dissociation, the half-division method, thermodynamic analysis, Erofeev–Kolmogorov equation, high-temperature vacuum device.

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Increased interest in lithium is explained by the successful use of its compounds in the implementation of some technological processes in various branches of industry, including nuclear industry and metallurgy of rare and nonferrous metals. In recent years the application of metal lithium in the manufacture of new aluminum alloys has attracted special attention as an effective alloying component that increases the level of physicomechanical characteristics. Construction Li-doped Al alloys are considered base materials for the development of fifth-generation aircraft. In connection with this, the development of effective technologies or the improvement of existing technologies for obtaining metal lithium is a topical problem now.

In recent years, the methods of obtaining lithium by the aluminothermic reduction of its aluminates in vacuum have been developed at the Moscow Institute of Steel and Alloys [1]. In this case, the metallothemic method is more environmentally safe and less waste-producing compared with the electrolytic method. However, it has disadvantages such as a low Li content in starting raw materials (lithium monoaluminate and pentolithium aluminate). To increase the productivity of reduction apparatuses, it is necessary

to use a compound more enriched by lithium–lithium oxide, which can be obtained by the thermal dissociation of lithium carbonate:



In addition, the aluminum powder is introduced into the charge for the subsequent aluminothermic reduction of lithium oxide:



Thus, two processes are combined in one apparatus, namely, the dissociation of lithium carbonate and the reduction of lithium oxide by aluminum. For this reason, the losses of the valuable metal and the consumption of electric power decrease.

In this article we present the results of studies on the process of dissociation of lithium carbonate in the presence of aluminum powder in vacuum.

The thermodynamic analysis of reaction (1) showed that a carbon dioxide pressure of 0.1 MPa (1 atm) (Fig. 1) is achieved at $t = 1323^\circ\text{C}$. However, it seems impossible to obtain Li_2O at atmospheric pressure, since the melting point of Li_2CO_3 is 733°C . In addition, lithium carbonate forms low-melting eutectic with lithium dioxide ($t_m = 705^\circ\text{C}$) (Fig. 2). This

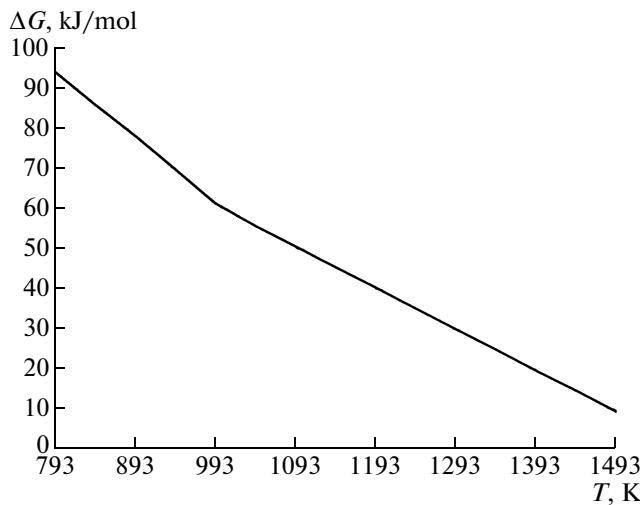


Fig. 1. Dependence of change of the Gibbs energy on the temperature of the thermal dissociation of lithium carbonate.

eutectic possesses high corrosion activity with respect to virtually all metals, including platinum.

Performing the dissociation process of lithium carbonate under the conditions of a dynamic vacuum makes it possible to lower the temperature of the complete dissociation due to the removal of the gaseous product of reaction (1) from the reaction region.

The temperature dependence of the standard Gibbs energy of reaction (1) can be described by the following equations:

at $t < 705^\circ\text{C}$ (i.e., below the melting point of the low-melting eutectic)

$$\Delta G_T^0 = 224.304 - 0.161 T, \quad (3)$$

and at $t \geq 705^\circ\text{C}$

$$\Delta G_T^0 = 160.813 - 0.101 T. \quad (4)$$

Using the dependence

$$\Delta G_T^0 = -RT \ln K_e = -RT \ln P_{\text{CO}_2}, \quad (5)$$

where ΔG_T^0 is the change of the Gibbs energy, kJ/mol ; R is the universal gas constant, $\text{kJ}/(\text{mol K})$; T is the temperature, K ; K_e is the equilibrium constant of reaction (1); and P_{CO_2} is the equilibrium pressure of carbon dioxide, Pa ; we can determine the value of P_{CO_2} at the specified temperature and the atmospheric pressure ($P = 1 \text{ atm}$). For example, at $t = 650$ and 700°C , the equilibrium pressure of CO_2 is 7.9 and 35.3 Pa , respectively (or 5.4×10^{-2} and 0.27 mmHg).

The performed analysis showed that, in the case of implementing dissociation at $t = 700^\circ\text{C}$, the necessary rarefaction can be implemented by the application of only a mechanical forevacuum pump; while at 650°C , diffusion pumps are required.

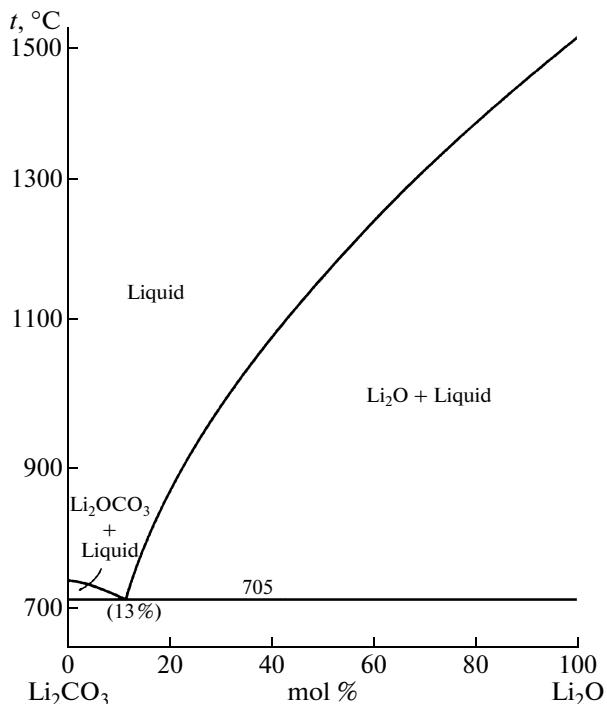


Fig. 2. Phase diagram of the Li_2CO_3 - Li_2O system.

As starting materials, we used powders of lithium carbonate (TU (Technical Specifications) 950308-08-94) and aluminum of the PA-4 grade (GOST (State Standard) 5592-71). After careful mixing, the charge was briquetted by using a hydraulic press with loading of 240 MPa. We used a steel compression mold 10 mm in diameter. After pressing, we obtained briquettes 5.5–5.8 mm in height and 0.56–0.58 g in weight.

The dissociation of lithium carbonate in the presence of the aluminum powder was studied on a VE-0.35-16-V high-temperature vacuum installation with automatic recording of the duration of the process and the change of the sample weight (Fig. 3).

The obtained kinetic curves have a sigmoid form that is characteristic of the decomposition reactions of solid substances with the liberation of a gaseous product [2, 3].

The dissociation reaction of lithium carbonate is a typical topochemical reaction and can be described by the Erofeev-Kolmogorov equation [4]:

$$\alpha = 1 - \exp[-K\tau^n]. \quad (6)$$

where α is the degree of dissociation, K is the constant of the reaction rate, τ is the time, and n is the reaction order.

The kinetic curves for the reaction (1) are given in Fig. 4 for various heating rates in a temperatures range of 650–700°C.

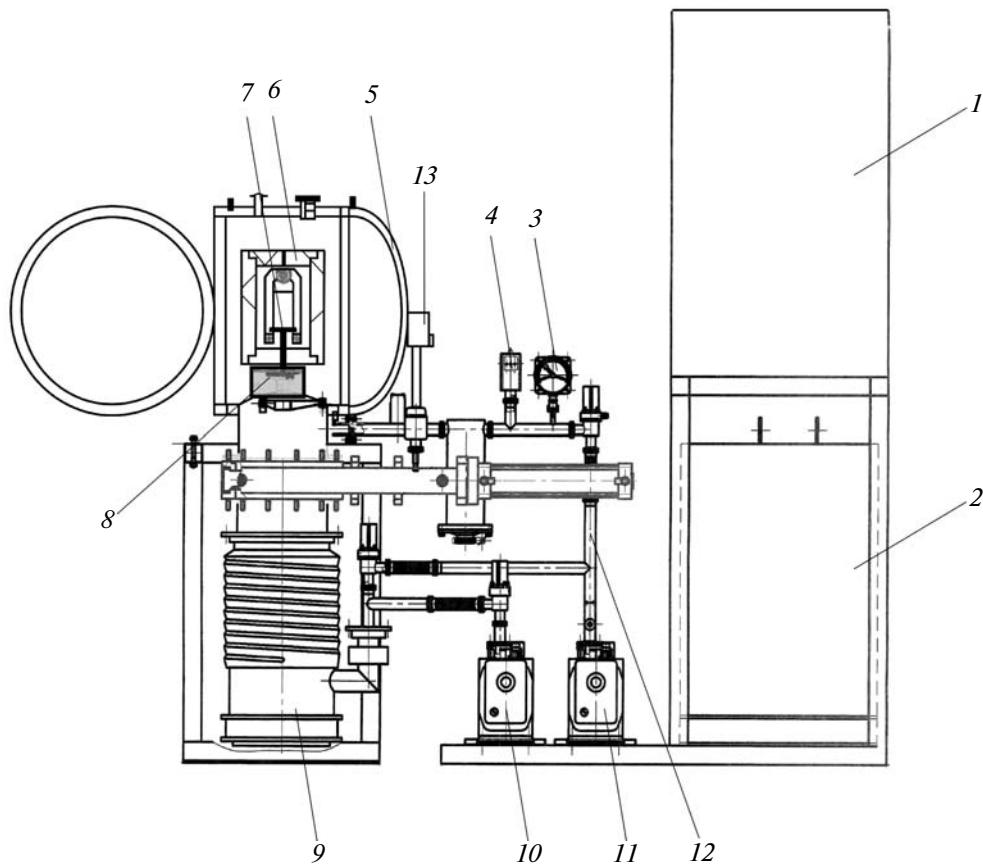


Fig. 3. Schematic image of high-temperature vacuum installation. (1) box of electroautomatics; (2) transformer; (3) vacuum pressure gauge; (4) Pirani linear vacuum gauge; (5) water-cooled case; (6) thermal block in assembly; (7) little table; (8) facility for weight measurement; (9) diffusion pump; (10, 11) vacuum pumps; (12) pipes nipples of the vacuum system; (13) modular converter.

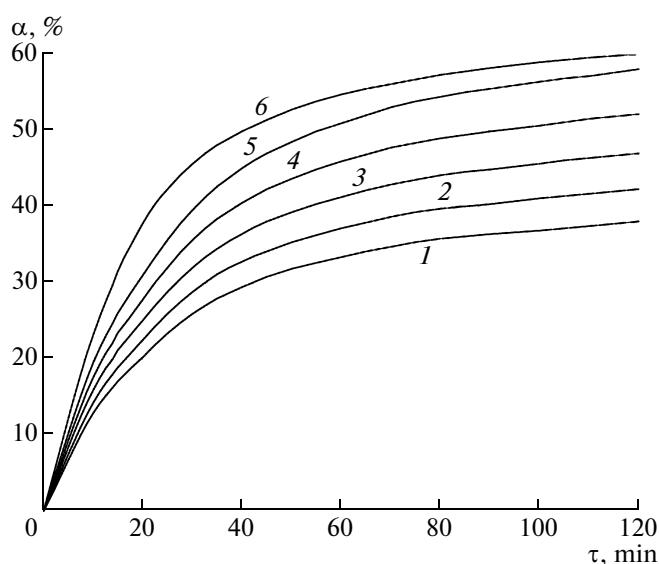


Fig. 4. Kinetic curves of the process of dissociation of lithium carbonate t : (1) 650, (2) 660, (3) 670, (4) 680, (5) 690, and (6) 700°C.

Using the dependence

$$\ln \frac{K(T_1)}{K(T_2)} = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \quad (7)$$

where $K(T)$ is the constant of the reaction rate at the specified temperature and E_a is the activation energy of the dissociation process of lithium carbonate, the experimental value $E_a = 77.72$ kJ/mol was determined. It follows from this fact that the dissociation process of lithium carbonate takes place in the diffusion region. The degree of dissociation was $\alpha = 60\%$ at $t = 700^\circ\text{C}$ and the holding time was 2h.

With the further increase in the process duration, the thermal decomposition of lithium carbonate retards.

We can assume that an increase in the process temperature will result in an increase in the value of α . From the phase diagram (see Fig. 2), it is evident that an increase in temperature results in the appearance of a liquid phase. However, its insignificant amount should not affect the mechanical properties of the briquette.

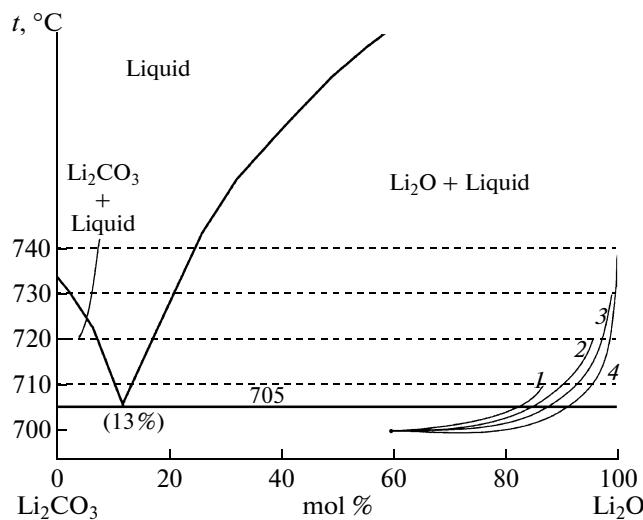


Fig. 5. Temperature dependence of the phase composition at various heating rates v : (1) 0.17, (2) 0.33, (3) 0.5, and (4) 0.67 °C/min.

In Fig. 5, the temperature dependence of the phase composition is presented at various heating rates. The results of experiments show that the 100% degree of dissociation is achieved at $t = 740^\circ\text{C}$ for 1 h.

Using the half-division method [2, 5] (in our case, this is the time interval from 0 to 3 h), the optimum rate of heating from 700 to 740°C was determined without the formation of low-melting eutectic between the carbonate and lithium oxide (Fig. 6). This rate is $0.33 \pm 0.02^\circ\text{C}/\text{min}$, and the time of the completed dissociation is 2 h. A decrease in the heating rate (v) increases the duration of the dissociation process, while its increase results in partial melting of the briquette (Fig. 6b).

Under the specified conditions of dissociation, the low-melting eutectic is not formed due to the experimental selection of the temperature mode of heating, which provides the following:

(i) the uniform thermal decomposition of lithium carbonate;

(ii) the minimization of contact between lithium carbonate, its oxide, and the aluminum powder; for this reason, in places where the particles are in contact, only micromelting is observed and complete or partial melting is absent (Fig. 7).

Figure 8 shows the change in the phase structure of the briquette in the interval t from 700 to 740°C at $v = 0.33^\circ\text{C}/\text{min}$. In this case, the liquid phase does not form, since the appearance of new phases determined by the phase diagram of the Li_2CO_3 - Li_2O system (see Fig. 5) depends on the rate of their formation by the solid-phase way of sintering [6].

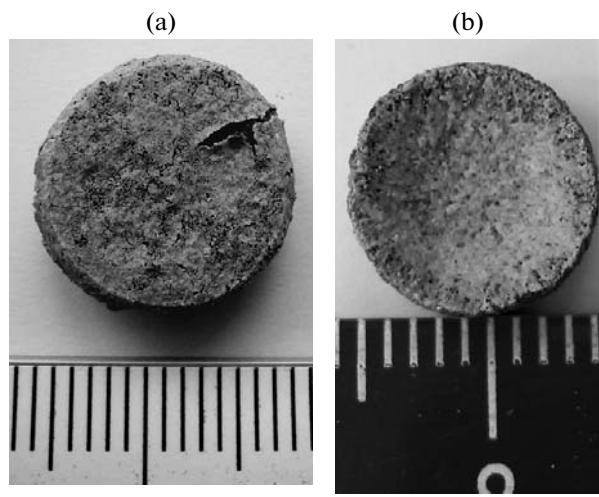


Fig. 6. Appearance of the briquette after sintering at various heating rates v : (a) 0.33 ± 0.02 and (b) $0.38 \pm 0.02^\circ\text{C}/\text{min}$.

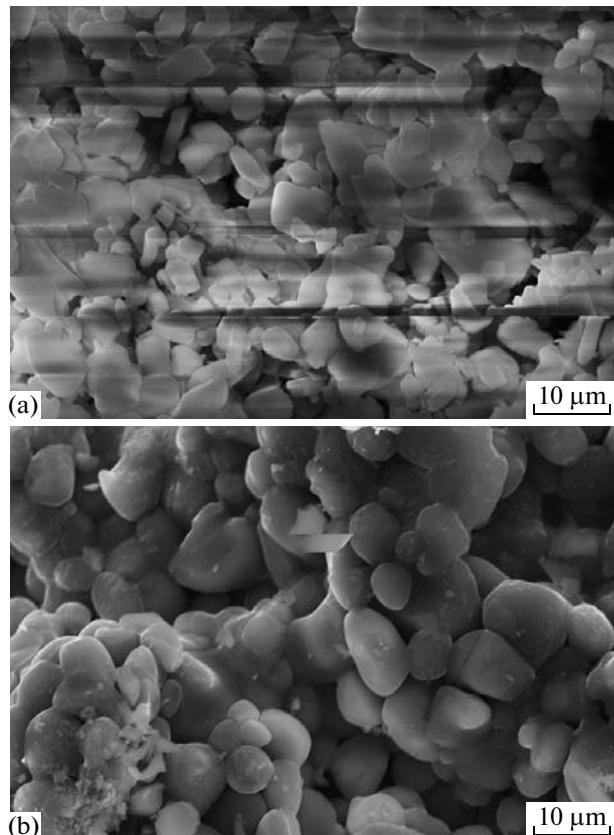


Fig. 7. Microphotograph of (a) the starting briquette and (b) after sintering.

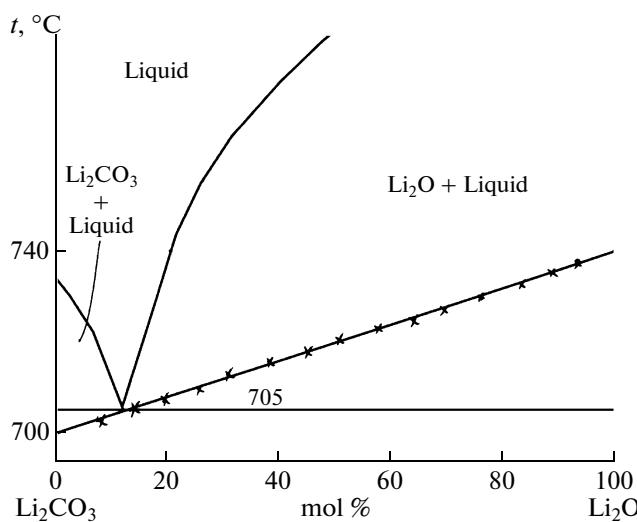


Fig. 8. Change of phase composition at a heating rate of $0.33^{\circ}\text{C}/\text{min}$.

CONCLUSIONS

A new way of obtaining lithium oxide from its carbonate is suggested. Due to the experimental data obtained with the use of the half-division method, a maximum heating rate from 700 to 740°C of $0.33 \pm 0.02^{\circ}\text{C}/\text{min}$ at which there is no formation of low-melting eutectic between the carbonate and lithium oxide, is determined. The time of the complete dissociation is 2 h. A decrease in the heating rate results in an increase in the duration of the dissociation process, and its increase results in partial melting of the briquette.

The selected temperature mode of heating prevents the appearance of low-melting eutectic due to the uni-

form thermal decomposition of lithium carbonate; in addition, the contacts between lithium carbonate, its oxide, and the aluminum powder are minimized (only micromelting is observed in the places of contact between the particles; complete or partial melting is not observed).

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