

## REACTIONS OF BINARY AND TERNARY ALKALI METAL CARBONATE MIXTURES WITH ALUMINIUM OXIDE

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Reactions of binary and ternary alkali metal carbonate mixtures with aluminium oxide were studied by means of a derivatograph under different conditions. Reaction products were identified by X-ray diffraction.

In the presence of binary and ternary carbonate mixtures containing  $\text{Li}_2\text{CO}_3$  the product was always  $\alpha$ -lithium metaaluminate, transforming to the  $\gamma$ -form at higher temperatures, while using only  $\text{Li}_2\text{CO}_3$  the orthodialuminate could be obtained too.

The reactions between aluminium oxide and alkali metal carbonates have been studied by several authors with different aims. Bartuska [1], Gál [4], Hummel and co-workers [5, 6], La Ginestra and co-workers [7], Maslova and Lileev [9], Semenov [13] and Soóki-Tóth [12] used lithium carbonate as the reagent, while Erdey and Gál [2], Gál and co-workers [3, 4], Maslova [10] and Semenov and Zabolotskii [15] worked with sodium and potassium carbonates.

In these investigations the reactivity of the alkali metal carbonates with aluminium oxide decreases in the order  $\text{Li}-\text{Na}-\text{K}$ . The product of the reaction in the 1 : 1 mixture of lithium carbonate and aluminum oxide is lithium metaaluminate. Lithium metaaluminate has two known modifications; the  $\alpha$  modification undergoes transformation into the  $\gamma$ -modification [5, 6, 8, 12, 13, 16]. The compound is chemically stable below  $1200^\circ$ . In binary (lithium and sodium carbonates) and ternary (lithium, sodium and potassium carbonates) systems of alkali metal carbonates neither sodium nor potassium ions can substitute those of lithium [10, 15]. In our present work we describe some studies giving new information about reactions in solid and molten phases between aluminum oxide and alkali metal carbonates.

### Experimental

$\gamma$ -aluminum oxide was used as the other reactant, ensuring favourable conditions for the study of the chemical reaction owing to its structure and particle size (the average particle size was 0.3 micrometer). Analytical grade materials were used. The studied mixtures were blended in water and then dried. The water remaining in the sample (bound by adsorption or as water of crystallization) left

below 400° in every case. These thermal effects did not influence the possibilities of evaluation of the investigations.

In the studied mixtures physical and chemical changes take place, causing changes of enthalpy and generally of the weight. Thus, dynamic thermal analysis methods are suitable for following them.

Chemical and physical processes were studied as a function of temperature by means of a derivatograph [1] in air and carbon dioxide (15 l/h) at atmospheric pressure from room temperature up to 1000°. Samples of 100–500 mg were measured in platinum or carborundum crucible. The heating rate was 10°/min.

Materials produced in the reaction, and components which had been in excess at the beginning, were identified by means of an X-ray diffractometer.

### Results

Depending on the particle size, the ratio of mixing and the temperature reached, the chemical reactions described by the following equations can proceed between the alkali metal carbonates and aluminum oxide:

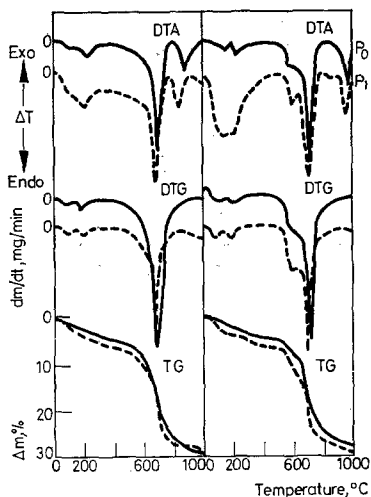
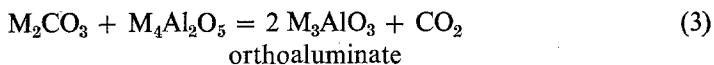
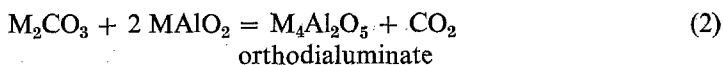
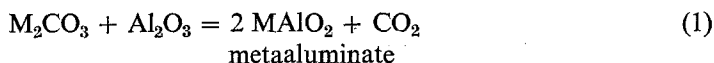


Fig. 1. Thermal curves of the reaction between lithium carbonate and aluminium oxide

P<sub>0</sub> – Li<sub>2</sub>CO<sub>3</sub> + γ-Al<sub>2</sub>O<sub>3</sub> 1.0 : 1.0

P<sub>1</sub> – Li<sub>2</sub>CO<sub>3</sub> + γ-Al<sub>2</sub>O<sub>3</sub> 1.1 : 1.0

Formation of lithium metaaluminate [1] was investigated in a 1 : 1 lithium carbonate-aluminium oxide mixture in air and CO<sub>2</sub> atmospheres (see Fig. 1, compositions given in molar ratio).

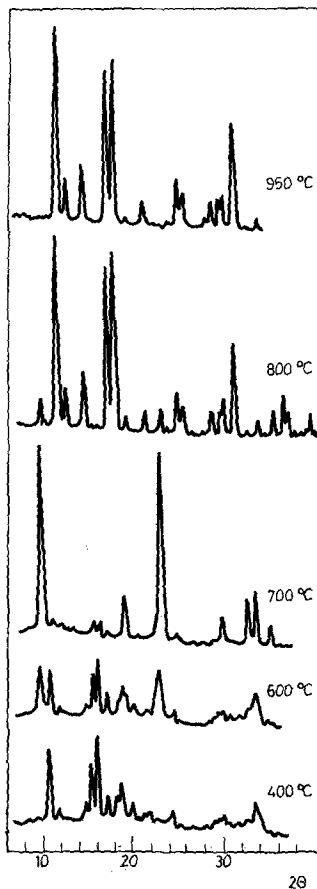


Fig. 2. X-ray diffractograms of mixtures containing  $\text{Li}_2\text{CO}_3$  and  $-\text{Al}_2\text{O}_3$  after isothermal reaction

The chemical reaction started on the surface of the solid material at about 500° in both cases, but in the carbon dioxide atmosphere the chemical process was repressed and became slower. (At a molar ratio of 1.1 : 1.0 a new DTG peak appeared.) Only as a result of further heat transport did it become as rapid as in air.

At 700° lithium carbonate melted, causing an endothermic peak in the DTA curve; the chemical reaction went on between the solid and molten phases and became complete only at about 950° producing  $\gamma$ -lithium metaaluminate.

In the range of temperature employed lithium metaaluminate has two known

polymorphic forms: the  $\alpha$ -modification, stable at low temperatures and the  $\gamma$ -modification, stable at high temperatures [2].

Analysis of the DTA curves and the X-ray diffractograms (Fig. 2) of the samples examined isothermally in air at 400, 600, 700, 800 and 950° (an isothermal run lasted 30 minutes) established that the first product of reaction is  $\alpha$ -lithium metaaluminate, which undergoes a monotropic transformation to  $\gamma$ -lithium metaaluminate (Fig. 1, DTA peaks at 880, 850, 970 and 960°).

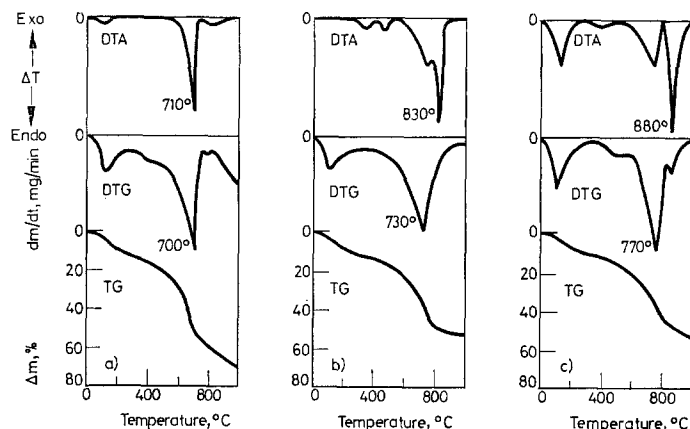


Fig. 3. Reaction of alkali carbonates and aluminium oxide in air

- a -  $\text{Li}_2\text{CO}_3 + \gamma\text{-Al}_2\text{O}_3$  2 : 1
- b -  $\text{Na}_2\text{CO}_3 + \gamma\text{-Al}_2\text{O}_3$  2 : 1
- c -  $\text{K}_2\text{CO}_3 + \gamma\text{-Al}_2\text{O}_3$  2 : 1

A study was made of how reactions (1) and (2) run in 2 : 1 mixtures of lithium, sodium or potassium carbonate and  $\gamma$ -aluminum oxide. In the thermal curves shown in Fig. 3, obtained in air up to 900°, it is easy to see that the reaction started in the solid phase in all three cases. The maximum rate of reaction was reached before the melting of the alkali metal carbonate. When the alkali metal carbonate melted the reaction became slower. In the case of lithium carbonate, besides lithium metaaluminate the orthodialuminate could also be identified, but with sodium and potassium carbonates the formation of the metaaluminate was not complete.

The conditions of the reaction were very different in mixtures containing lithium and sodium carbonates or lithium, sodium and potassium carbonates of eutectic composition in excess of the amount necessary for lithium metaaluminate formation [1].

In the thermoanalytical experiments the equivalent mixture of lithium and sodium carbonates melted at 495° (see Fig. 4a and b) while the mixture of 43.5 molar % lithium carbonate, 31.5 molar % sodium carbonate and 25 molar % potassium carbonate melted at 400° (Fig. 5).

When only lithium carbonate was present (Fig. 1), the reaction started in the solid phase and became a reaction between solid and melt phases only at about 700°. On the other hand, when more alkali metal carbonate was present this already melted before the start of the reaction (Fig. 5), or at the same time (Fig. 4). In the binary alkali metal carbonate samples the molten phase appears in increasing amounts in the order  $B_1, B_2, B_3, B_4$ , as shown by the peak areas of the melting endotherms.

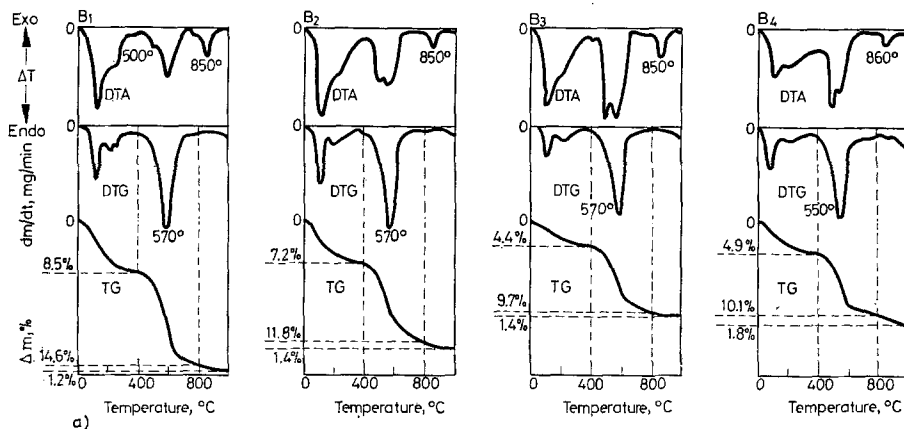


Fig. 4a. Reaction of binary carbonate mixtures with aluminium oxide in air

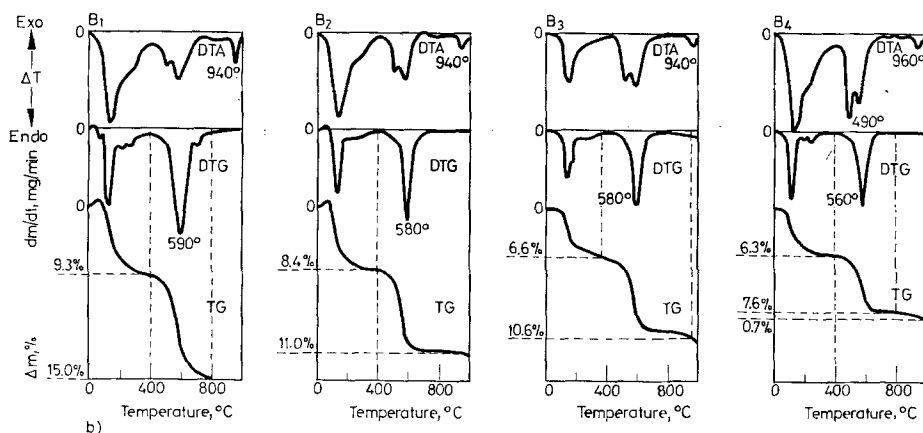
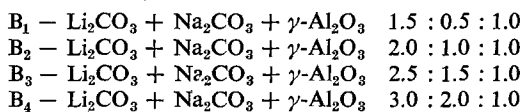


Fig. 4b. Reaction of binary carbonate mixtures with aluminium oxide in carbon dioxide (15 l/h) Composition are the same as in Fig. 4a

Every sample was measured with a derivatograph in air and carbon dioxide atmospheres under the same experimental conditions. In both air and carbon dioxide atmospheres below 350–400° the aluminium oxide and the alkali metal carbonates present in the mixture lost the water of adsorption, and the sodium carbonate lost the water of crystallization, too.

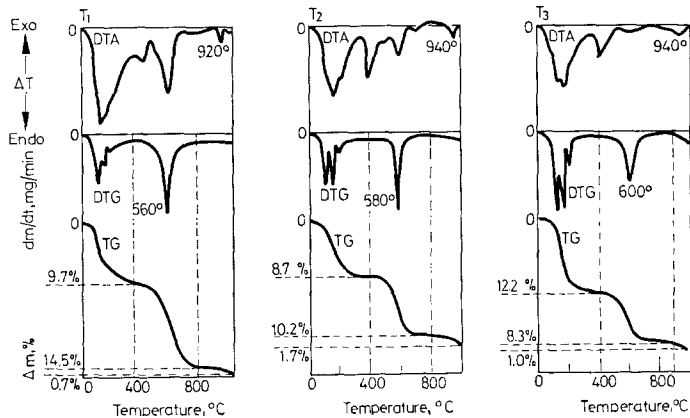


Fig. 5. Reaction of ternary carbonate mixtures with aluminium oxide in air

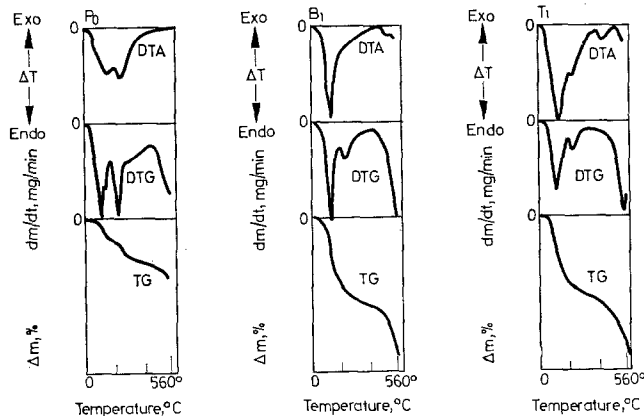
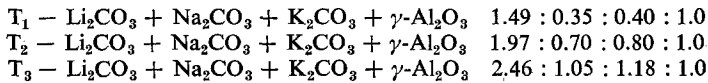
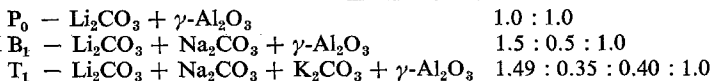


Fig. 6. Comparison of the reaction of lithium carbonate and carbonate mixtures with aluminium oxide in air



At about 500° the alkali metal carbonates melted and at the same time the chemical reaction started, yielding  $\alpha$ -lithium metaaluminate (Fig. 6, B<sub>1</sub>). By comparing the curves obtained in air, it can be concluded that the chemical reaction started at about the same temperature in the mixtures, but the rate of the process increased as the amount of alkali metal carbonate increased. The maximum rate of the reaction process shifted to lower temperatures, as is shown by the DTG peaks at 570–550°.

The curves obtained in carbon dioxide atmosphere are identical with those obtained in air up to the melting of the alkali metal carbonates. The maximum of the reaction rate shifted by 10–20° to higher temperatures (see the DTG curves).

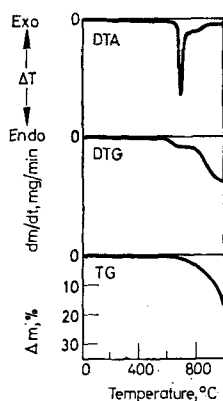


Fig. 7. Thermal decomposition of lithium carbonate in air

The important difference between the results obtained in air and carbon dioxide is in the temperatures of the maximum rate of the lithium metaaluminate crystal modification transformation.

In the DTA curves the endothermic effect appeared at 850° and at 940–950° in air and in carbon dioxide respectively.

The ternary series contained an increasing amount of melt in the order  $T_1$ ,  $T_2$ ,  $T_3$ . The mixture of the three alkali metal carbonates melted at 400°, but the chemical reaction did not start at this temperature. As in the case of the binary series, the reaction started only at about 500°, and reached its maximum rate at 560–600°. With increasing amount of the molten phase ( $T_1 - T_3$ ), the DTG peak indicating the maximum reaction rate shifted to higher temperature values: 560, 580, 600°.

For the range of composition studied, it was found that the starting temperature of the chemical reaction does not depend primarily on the phase of the alkali metal carbonate present but on the nature of the alkali metal carbonate. The rate of the starting reaction, however, is greatly influenced by the phase of the reactants. X-ray diffraction analysis of dynamically and isothermally processed samples

showed the product of the chemical reaction to be lithium meta-aluminate even in the presence of two or three alkali metal carbonates and a lithium carbonate excess. Aluminate of higher alkali metal content could not be identified.

In three mixtures of different composition, after starting at 560° the reaction was frozen and the crystallographic compositions of the samples were identified X-ray diffraction.

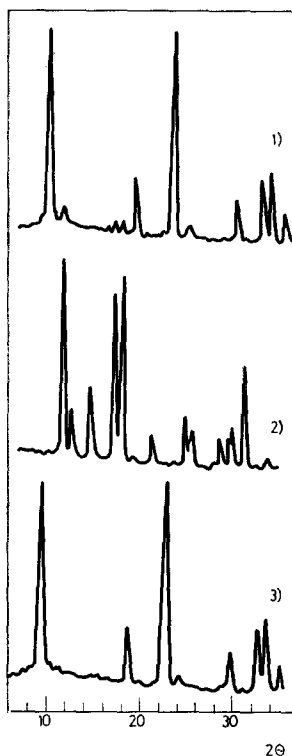


Fig. 8. X-ray diffractograms of  $\text{Li}_2\text{CO}_3 + \gamma\text{-Al}_2\text{O}_3$  mixture after

- 1 — 60 minutes in  $\text{CO}_2$  at 850 °C
- 2 — 60 minutes in air at 850 °C
- 3 — 60 minutes in air at 700 °C

It was found that, even at the starting temperature of the primary product of the reaction between lithium carbonate and  $\gamma$ -aluminum oxide is  $\alpha$ -lithium metaaluminate. On further heating, the  $\alpha$ -lithium metaaluminate transformed into  $\gamma$ -lithium metaaluminate.

Analysis of the thermoanalytical curves clearly showed that the temperature of the modification transformation is closely connected with the thermal dis-



sociation of lithium carbonate. The thermal dissociation expressed by the following equation starts even before the melting of lithium carbonate (Fig. 7):



In the case of measurements in carbon dioxide atmosphere the temperature of the decomposition shifts to higher values. This therefore makes it possible for the  $\alpha$ -modification (stable at low temperatures) to exist at higher temperatures (Fig. 8). In air reaction (4) becomes more and more intensive above 700°, owing to the dissociation of the  $\text{Li}_2\text{O}$  remaining in the melt. More and more oxide ions are formed, and this lowers the temperature of the polymorphic transformation.

Figure 8 shows X-ray diffractograms of samples containing lithium carbonate and  $\gamma$ -aluminum oxide in a 1 : 1 molar ratio. The samples were heated from room temperature up to the desired value, and the reaction was frozen in after an isothermal period of one hour.

### Literature

1. M. BARTUSKA, *Silikaty*, 4 (1960) 147.
2. L. ERDEY and S. GÁL, *Talanta*, 10 (1963) 23.
3. S. GÁL, J. SIMON and L. ERDEY, *Proc. III. Anal. Chem. Conf., Budapest, Vol. 2 (1970)* 243.
4. S. GÁL, *Thermal Analysis Proc. Third ICTA, Davos Vol. 2 (1971)* 559.
5. F. A. HUMMEL, *J. Am. Ceram. Soc.*, 34 (1951) 235.
6. F. A. HUMMEL, B. S. R. SASTRY, and D. WOTRING, *J. Am. Ceram. Soc.*, 41 (1958) 88.
7. A. LA GINESTRA, M. LO JACONO and P. PORTA, *J. Thermal Anal.*, 4 (1972) 5.
8. H. A. LEHMANN and H. HESSELBARTH, *Z. Anorg. Allgem. Chem.*, 313 (1961) 117.
9. E. I. MASLOVA and I. S. LILEEV, *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim.*, 1 (1958) 63.
10. E. I. MASLOVA, *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim.*, 11 (1963) 36.
11. F. PAULIK, J. PAULIK and L. ERDEY, *Z. Anal. Chem.* 100 (1958) 241.
12. G. SOÓKI-TÓTH, *Dissertation. University of Chemical Industry, Veszprém, Hungary, 1973.*
13. N. N. SEMENOV, *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim.*, 2 (1967) 156.
14. N. N. SEMENOV and T. V. ZABOLOTSKII, *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim.* 11 (1962) 70.
15. N. N. SEMENOV and T. V. ZABOLOTSKII, *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim.*, 3 (1964) 31.
16. G. SOÓKI-TÓTH, P. HORVÁTH, S. GÁL and K. TOMOR, 5th Conference on Ceramics for Electronics Liblice (CSSR) 22–24. April. 1974.

RÉSUMÉ — On a étudié à l'aide d'un Derivatograph, sous diverses conditions, la réaction de mélanges binaires et ternaires des carbonates alcalins avec l'oxyde d'aluminium. L'identification des produits formés a été effectuée par diffraction des rayons X.

Si les mélanges binaires et ternaires de carbonates contiennent du carbonate de lithium, il se forme toujours l' $\alpha$ -métaaluminat de lithium, qui, à température plus élevée, se transforme en la forme  $\gamma$ . Si la carbonate de lithium est utilisé seul, on peut obtenir aussi l'ortho-dialuminat.

ZUSAMMENFASSUNG — Die Reaktionen binärer und ternärer Alkalikarbonatmischungen mit Aluminiumoxid wurden mittels eines Derivatographen unter verschiedenen Bedingungen untersucht. Die Reaktionsprodukte wurden durch Röntgendiffraktion identifiziert.

In Gegenwart  $\text{Li}_2\text{CO}_3$ -haltiger binärer und ternärer Karbonatmischungen war das Produkt stets  $\alpha$ -Lithium-meta-aluminat, das bei höheren Temperaturen in die  $\gamma$ -Form überging, während bei Einsatz von  $\text{Li}_2\text{CO}_3$  auch Orthodialuminat erhalten werden konnte.

Резюме — Были изучены с помощью дериватографа реакции бинарных и тройных смесей карбонатов щелочных металлов с окисью алюминия в различных условиях. Продукты реакции были идентифицированы рентгено-дифракционным анализом. В случае бинарных и тройных карбонатных смесей, содержащих  $\text{Li}_2\text{CO}_3$ , продуктом реакции всегда был  $\alpha$ -метаалюминат лития, превращающийся при более высоких температурах в  $\gamma$ -форму. В то же самое время при использовании только  $\text{Li}_2\text{CO}_3$ , может быть получен также орто-диалюминат лития.