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THE REACTION OF TERNARY MIXTURES OF SODIUM NITRATE, DIBORON TRIOXIDE AND SILICA

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The reaction and the thermal changes of the ternary system $NaNO_3$–B_2O_3–SiO_2 have been investigated by means of high-temperature thermogravimetry, derivative thermogravimetry, microscopy, differential thermal analysis, gas chromatography, X-ray diffractometry and IR spectrometry. The combination of these techniques provides information on the reaction process. The major reactions which take place in this system are as follows: several sodium borates are preferentially formed in a liquid-phase reaction after $NaNO_3$ and B_2O_3 melt, with the generation of O_2, NO and N_2. SiO_2 does not take part in the reaction below 550°. Sodium borates with $B/Na = 9$ to 1 are formed successively with the generation of O_2 and NO as the temperature increases. The reaction products around 700° are mixtures of borates and silicates. Borosilicates are formed above 750°.

The investigation of the formation of borosilicates from $NaNO_3$, B_2O_3 or H_3BO_3, and SiO_2 is important in the preparation of multicomponent glass materials for optical-wave guides [1], in the vitrification of radioactive wastes from nuclear reactors [2], etc. Systematic studies on the glass formation process when $NaNO_3$ is used as sodium source are rare in the literature. The reactions of two binary systems ($NaNO_3$–B_2O_3 and $NaNO_2$–B_2O_3) have first been investigated to facilitate the analysis of the reactions which take place in the ternary system. The reason why $NaNO_2$ is dealt with is that it is formed during the course of heating of $NaNO_3$. Studies on two other binary systems ($NaNO_3$–SiO_2 and $NaNO_2$–SiO_2) are also of use for the analysis of the reactions of this ternary system and have been discussed elsewhere [3, 4].

Experimental

Materials

Reagent-grade $NaNO_3$, $NaNO_2$, B_2O_3 (from Wako Pure Chemical Ind., Ltd.) and SiO_2 (α-quartz, from Kyoritsu Yogyo Genryo Ltd.) were ground to below 100 mesh and were dried in an oven. These chemicals were mixed by dry blending for each run.

Apparatus and procedure

The investigation was performed by the simultaneous measurement of TG, DTA, DTG and gas chromatography, by the analysis of solid reaction products, and by observations with a high-temperature microscope. For the simultaneous measurement, a thermobalance (Rigaku Denki Co., Ltd.), a differentiator (Rikadenki Kogyo Co., Ltd.), and a GC-2C gas chromatograph (Shimadzu Seisakusyo, Ltd.) were used. All measurements were carried out in an argon atmosphere (flow rate 50 $cm^3 min^{-1}$). The gases formed were introduced into the gas chromatograph every two minutes and the amounts of O_2, N_2 and NO formed were determined; silica gel and molecular sieve 5A were used as the column-packing reagents [5].

The solid reaction products were identified by X-ray diffractometry and IR spectrometry. The amounts of nitrate and nitrite ions were determined by ion-exchange chromatography (Dionex model 10).

Results and discussion

Observation with a high-temperature microscope

Figure 1 shows microphotographs of B_2O_3 and a mixture of B_2O_3 and $NaNO_3$ during the course of heating. The B_2O_3 used in this work was amorphous and began to melt around 400°, which was about 60° lower than the literature value [6]. It was a viscous liquid above 450°. $NaNO_3$ melts at 308°, irrespective of the presence of B_2O_3 or SiO_2. Vigorous gas evolution was observed around 420° and 600° in the $NaNO_3$–B_2O_3 system. The gas evolution around 420° occurred immediately after the melting of B_2O_3, and that around 600° occurred during the precipitation of solid products from the liquid. On the other hand, pure $NaNO_3$ decomposes above 500° with the generation of O_2 and NO [3, 4]. The decrease of the thermal decomposition temperature in this system indicates that the decomposition of $NaNO_3$ is accelerated by the coexistence of liquid B_2O_3, which is an acidic oxide.

In the $NaNO_2$–B_2O_3 system, the gas evolution began around 380°, and was more vigorous than that in the $NaNO_3$–B_2O_3 system at 420°. This suggests that $NaNO_2$ is less thermally stable than $NaNO_3$. Pure $NaNO_2$ gradually decomposes above 430° [7].

SiO_2 reacts with nitrate or nitrite above 550°, irrespective of the presence of B_2O_3.

Reaction of sodium nitrate with diboron tiroxide

Figure 2 shows the TG and DTG curves and the behaviour of gas formation in the reaction of $NaNO_3$ with B_2O_3. The reaction in this system are clearly classified into two steps (Step I: $< 500°$, and Step II: $> 500°$). The gases formed in Step I were O_2, N_2 and NO, and in Step II O_2 and NO.

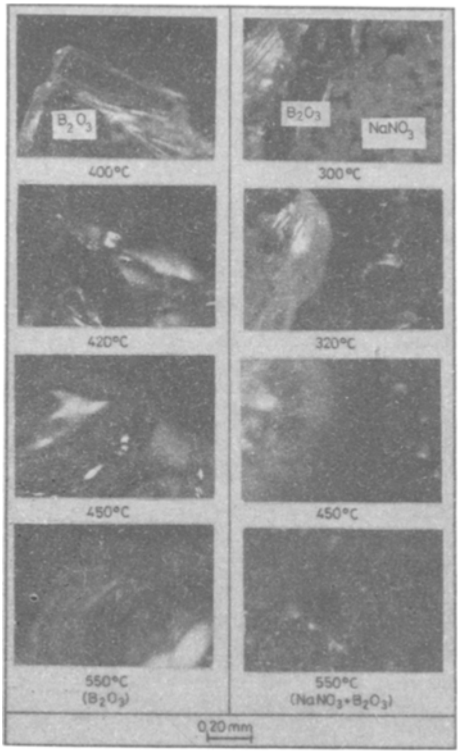


Fig. 1 High-temperature microphotographs of B_2O_3 and ($NaNO_3$ + B_2O_3). Heating rate: 10° min^{-1} in vacuo

Figure 3 shows the X-ray diffraction patterns of the reaction products in Step I (450°) and in Step II (670°). At 450°, the diffraction lines of $Na_2O \cdot B_2O_3$, $Na_2O \cdot 4\,B_2O_3$, α-$Na_2O \cdot 9\,B_2O_3$ and β-$Na_2O \cdot 9\,B_2O_3$ were observed in addition to those of $NaNO_3$, irrespective of the initial composition. No additional lines of compounds such as $NaNO_2$ were observed in these patterns. At 670°, the x values of the reaction products, $Na_2O \cdot x\,B_2O_3$, agreed with those of the initial mixtures. $Na_2O \cdot 4\,B_2O_3$ was formed even from the samples with $x > 4.0$, but the content of $Na_2O \cdot 9\,B_2O_3$ in the mixtures at 450° increased with increase in the B/Na ratio. The fraction of weight loss, α, in Fig. 2 at 500° corresponds to the formation of a mixture of $Na_2O \cdot 9\,B_2O_3$ and $Na_2O \cdot 4\,B_2O_3$ in Step I. The generation of N_2 was observed when $Na_2O \cdot 9\,B_2O_3$ was formed. Therefore, the reaction in Step I probably consists of the following concurrent reactions rather than the successive reaction to form $Na_2O \cdot 4\,B_2O_3$ via $Na_2O \cdot 9\,B_2O_3$:

$$2\,NaNO_3 + 9\,B_2O_3 = Na_2O \cdot 9\,B_2O_3 + 5/2\,O_2 + N_2 \qquad (1)$$

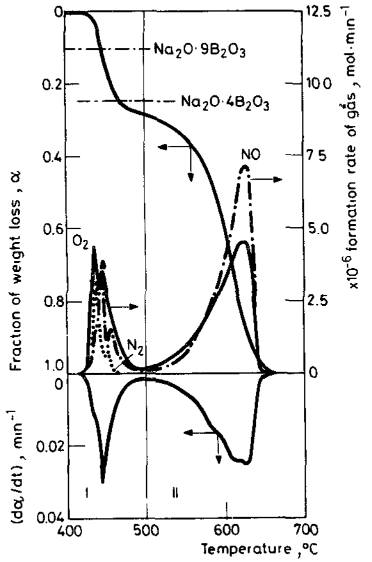


Fig. 2 TG and DTG curves and behaviour of gas formation in the reaction of $NaNO_3$ and B_2O_3. Sample: B/Na = 1.0 (0.2 mmol $NaNO_3$ + 0.1 mmol B_2O_3)

$$2\ NaNO_3 + 4\ B_2O_3 = Na_2O \cdot 4\ B_2O_3 + 3/2\ O_2 + 2\ NO \qquad (2)$$

The formation of O_2 and NO in Reaction 2 is readily explainable by assuming intermediates such as $NaNO_2$ and Na_2O_2, as was discussed in previous papers [4, 7]. It has been found that pure $NaNO_3$ decomposes to form O_2, N_2 and Na_2O above 680° and the activation energy and the frequency factor of this reaction are 243 kJ mol^{-1} and 26.7 in ln (K°/min^{-1}), respectively [4]. The apparent activation energy and the frequency factor of Reaction 1 for the sample with B/Na = 2.0 were 408 kJ mol^{-1} and 63.2 in ln (K°/min^{-1}). These values, and especially the frequency factor, are much greater than those for the thermal decomposition of $NaNO_3$. This indicates that the melting of B_2O_3 results in an increase in reactivity.

In Step II, $Na_2O \cdot B_2O_3$ is formed by the reaction of $NaNO_3$ with $Na_2O \cdot 4\ B_2O_3$ and $Na_2O \cdot 9\ B_2O_3$ in the mixture with B/Na = 1.0. Although the reaction of $NaNO_3$ with B_2O_3 takes place in the liquid phase, the initial grain size of the B_2O_3 affects the reaction in Step I. The reaction proceeds faster as the grain size becomes smaller. This is probably due to the fact that the liquid B_2O_3 is too viscous to mix with liquid $NaNO_3$.

The reactions are more complicated in mixtures of composition B/Na > 1.0. Figure 4 shows an "isothermal plot" of α values at several temperatures against the composition. If the reaction is successive or the weight loss of a particular reaction is predominant, the presence of stable intermediates is indicated by the converging lines

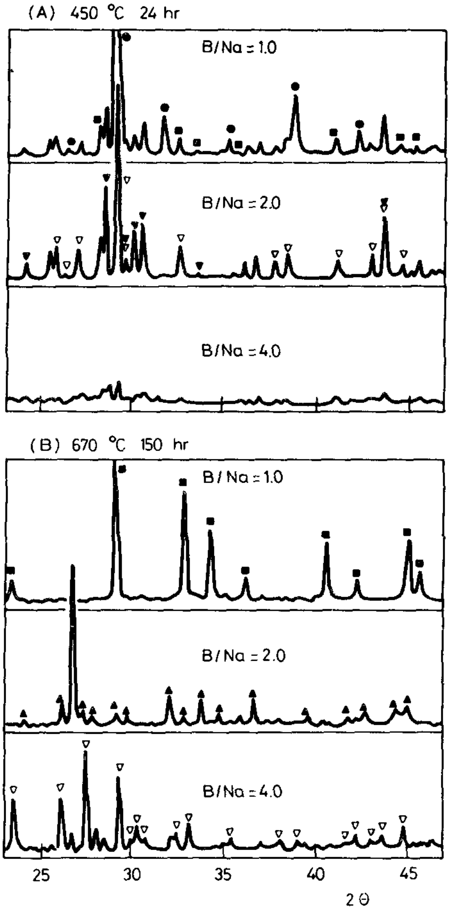
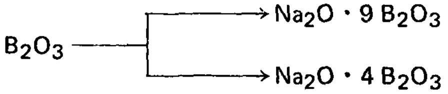


Fig. 3 Reaction products of $NaNO_3$ and B_2O_3 in argon atmosphere at 450° for 24 hr (A) and 670° for 150 hr (B). ●: $NaNO_3$, ■: $Na_2O \cdot B_2O_3$, ▲: $Na_2O \cdot 2\,B_2O_3$, ▽: $Na_2O \cdot 4\,B_2O_3$, ▼: $Na_2O \cdot 9\,B_2O_3$

in Fig. 4 (shaded region). It is assumed from Fig. 4 that the compounds with $x = 5, 4, 2.5, 2$ and 1 are stable. Another more detailed "isothermal plot" in the temperature range from 400 to 450° indicates that the compound with $x = 9$ is also stable. The path by which the reaction takes place is concluded to be as follows:

(Step I)



$$B_2O_3 \longrightarrow \begin{cases} Na_2O \cdot 9\,B_2O_3 \\ Na_2O \cdot 4\,B_2O_3 \end{cases} \qquad (3)$$

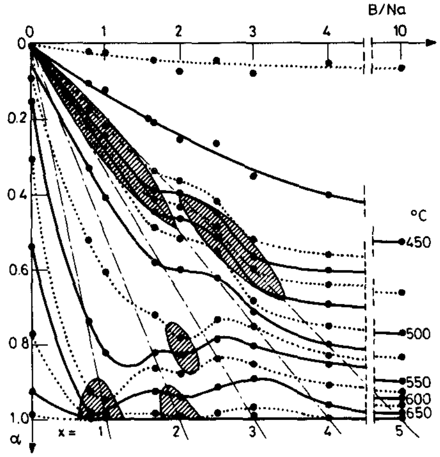


Fig. 4 "Isothermal plot" of TG curves in the system $NaNO_3$–B_2O_3. x indicates the value in $Na_2O \cdot xB_2O_3$

(Step II)

$$\left.\begin{array}{l} Na_2O \cdot 9\,B_2O_3 \text{ —— } (Na_2O \cdot 5\,B_2O_3) \text{ —— } Na_2O \cdot 4\,B_2O_3 \\ Na_2O \cdot 4\,B_2O_3 \text{ ———————————————————— } \end{array}\right] \longrightarrow \tag{4}$$

$$\longrightarrow (Na_2O \cdot 2.5\,B_2O_3) \longrightarrow (Na_2O \cdot 2\,B_2O_3) \longrightarrow Na_2O \cdot B_2O_3$$

The internal compounds with $x = 1.0$ and 4.0 should be more stable than the others because the distance between the lines was narrow around $x = 1.0$ to 4.0.

Reaction of sodium nitrite with diboron trioxide

Figure 5 shows the TG and DTG curves and the behaviour of gas formation in the $NaNO_2$–B_2O_3 system. The Figure clearly indicates that there are three weight loss steps in the TG curve, (Step I′, II′ and III′). The weight loss in this system begins at about the same temperature (380°) as for the $NaNO_2$–SiO_2 system. Below 420°, the reaction in this system occurs between liquid $NaNO_2$ and solid B_2O_3 with the generation of NO and a trace amount of N_2. It was found by X-ray diffractometry that $NaNO_3$ was formed below 400°, but no borates were formed. The reaction in Step I′ may be the same as the first step reaction in the $NaNO_2$–SiO_2 system [7]:

$$2\,NaNO_2 = Na_2O_2 + 2\,NO \tag{5}$$

$$Na_2O_2 + NaNO_2 = Na_2O + NaNO_3 \tag{6}$$

In Step II′, which accompanies the melting of B_2O_3, only $Na_2O \cdot 4\,B_2O_3$ was formed. The reaction in Step II′ is shown in Eq. 7:

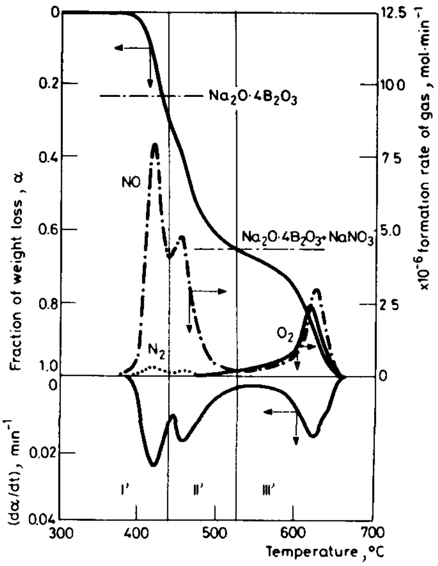


Fig. 5 TG and DTG curves and behavior of gas formation in the reaction of $NaNO_2$ and B_2O_3. Sample: B/Na = 1.0 (0.2 mmol $NaNO_2$ + 0.1 mmol B_2O_3). Heating rate: 2.5° min^{-1} in argon atmosphere

$$Na_2O + 4\ B_2O_3\ (\text{liquid}) = Na_2O \cdot 4\ B_2O_3 \tag{7}$$

Only 65% of theoretical amount of NO was formed below 530°, a value quite close to that estimated on the assumption that $NaNO_2$ decomposes to form an equimolar mixture of $NaNO_3$ and Na_2O (0.67).

In Step II', the reactions of $NaNO_3$ with $Na_2O \cdot 4\ B_2O_3$ to form borates progress by the same path as Step II in the $NaNO_3$–B_2O_3 system. The molar ratio of O_2 to NO formed above 550° was 0.80, agreeing well with the value of 0.75 for the thermal decomposition of $NaNO_3$:

$$2\ NaNO_3 = Na_2O + 3/2\ O_2 + 2\ NO \tag{8}$$

Reaction of sodium nitrate, diboron trioxide and silica

Figures 6 and 7 show the DTA and TG curves for the reaction of ternary mixtures of $NaNO_3$, B_2O_3 and SiO_2. In Fig. 6, the endothermic peak at 575° is the transition of α- to β-quartz. The areas of the endothermic peaks around 450° and 620° increase with the increase of the B/Na ratio in the initial mixture. This suggests that $NaNO_3$ reacts only with B_2O_3 below 550°, while above 550° it reacts with SiO_2. This is supported by the fact that only $Na_2O \cdot 4\ B_2O_3$ and a trace amount of $Na_2O \cdot 9\ B_2O_3$ were formed below 550°, while no silicates were formed. At 670°, the reaction products were a mixture of borates and α- and β-$Na_2O \cdot 2\ SiO_2$. Two steps of weight

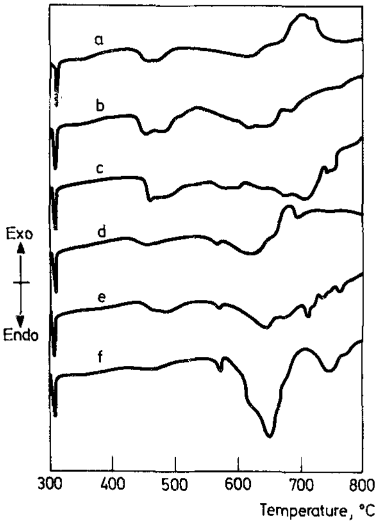


Fig. 6 DTA curves of the system $NaNO_3$–B_2O_3–SiO_2. The composition Na:B:Si is 3:2:1 (a), 2:2:1 (b), 1:3:1 (c), 2:1:2 (d), 1:2:2 (e) and 1:1:3 (f)

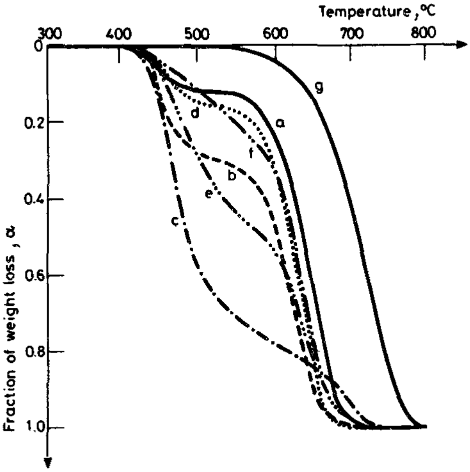


Fig. 7 TG curves of the system $NaNO_3$–B_2O_3–SiO_2 (a–f) and of the decomposition of $NaNO_3$ (g). The composition of (a) to (f) is identical with Fig. 6

loss are observed in the TG curves. The reactions in this system consist of two steps: that at 450° is the reaction of $NaNO_3$ with B_2O_3 expressed by Eq. 3, and the other at around 650° is the concurrent reactions to form borates and silicates. In the first step, the fraction of weight loss for the samples with the same B/Na ratio is 0.27 (*b* in Fig. 7: 570°) and 0.25 (*f* in Fig. 7: 525°). These values are close to the value of 0.28 (500°) for the reaction of Step I in the $NaNO_3$—B_2O_3 system (see Fig. 2). It is found from Figs 2 and 7 that the reaction in Step I becomes more sluggish when the system contains a great amount of SiO_2. SiO_2 plays a role as a diluent. The reaction path to form silicates is expressed by Eq. 9:

$$SiO_2 \longrightarrow \alpha\text{-}Na_2O \cdot 2\,SiO_2, \beta\text{-}Na_2O \cdot 2\,SiO_2 \longrightarrow Na_2O \cdot SiO_2 \qquad (9)$$

Borosilicates were formed from the mixture of borates and silicates.

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Zusammenfassung — Die Reaktionen und die thermische Veränderung des ternären Systems $NaNO_3$—B_2O_3—SiO_2 wurde mittels Hochtemperatur-Mikroskopie, TG, DTG, DTA, Gaschromatographie, Röntgendiffraktometrie und IR-Spektrometrie untersucht. Die Kombination dieser Methoden liefert Informationen über den Reaktionsprozess. Verschiedene Natriumborate werden vorzugsweise durch Flüssigphasenreaktion von $NaNO_3/B_2O_3$-Schmelzen unter Freisetzung von O_2, NO und N_2 gebildet. Siliciumdioxid nimmt unterhalb 550° an der Reaktion nicht teil, bildet jedoch mit geschmolzenem Natriumnitrat Silikate bei Temperaturen über 550°. Natriumborate mit B/Na-Verhältnissen von 9—1 werden mit steigender Temperatur unter Entwicklung von O_2 und NO gebildet. Bei Temperaturen um 700° werden Mischungen von Boraten und Silikaten als Reaktionsprodukte erhalten. Borsilikate werden über 750° gebildet.

Резюме — С помощью высокотемпературной микроскопии, ТГ, ДТГ, ДТА, газовой хроматографии, рентгеновской диффрактометрии и ИК спектроскопии были исследованы реакции и термические изменения тройной системы $NaNO_3$—B_2O_3—SiO_2. Эти комбинированные методы позволили получить информацию о реакционных процессах. После плавления нитрата натрия и окиси бора, из жидкофазной реакции предпочтительно образуются несколько боратов натрия с выделением кислорода, азота и окиси азота. Кремний ниже 550° в реакцию не вступает. Выше 550° он вступает в реакцию с расплавленным нитратом натрия, образуя силикаты. Последовательно образуются бораты натрия с отношением B:Na = 9—1 с выделением кислорода и окиси азота по мере увеличения температуры. При температуре около 700° продуктами реакции является смесь боратов и силикатов. Боросиликаты образуются выше 750°.