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THE THERMAL STABILITY OF ALKALI AND ALKALINE-EARTH METAL HYDROXIDE–NITRATE SYSTEMS

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ABSTRACT

The thermal stability of alkali and alkaline-earth metal hydroxide–nitrate systems has been investigated by thermal analysis, voltammetry and observation with a high-temperature microscope. The melts of alkali metal hydroxide–nitrate systems are thermally stable to at least 300°C above the melting temperatures. The melts have a strong oxidizing ability caused by the strong chemical interaction between hydroxide and nitrate ions. The thermal stability of strontium and barium hydroxide–nitrate systems increases at some peculiar compositions. Although nitrates of strontium and barium decompose in the solid state, the thermal decomposition of the mixtures of these hydroxide–nitrate systems is initiated via the liquid state as a result of the increase in the thermal stability of liquids.

INTRODUCTION

Fused salt mixtures of relatively low melting temperatures are important as heat-storage materials and reaction media. Binary melts of alkali metal hydroxide–nitrate systems are such materials as well as the melts of binary and ternary nitrates and hydroxides [1–4]. Physical properties, such as heat capacity, mobility of ions, electrical conductance and density, have been investigated for the melts of nitrates and hydroxides [5–12]. Redox reactions of chromium and manganese in $NaOH–NaNO_3$ melts have been reported [13–15].

The thermal stability of these melts is of interest for practical use. The thermal stability of binary systems of $NaNO_3$ with alkali metal nitrates has been investigated previously [16]. Some of the results are as follows: (1) the decomposition temperature does not decrease by the coexistence of other nitrates, while the melting temperature decreases; (2) the thermal decomposition of nitrate species in binary melts takes place independently to that of other nitrate species; and (3) the small enthalpy of mixing shows the small interaction between different ions.

The melts of hydroxide–nitrate systems are supposed to have more useful properties than the binary nitrates, because the strong ionic interaction expected in systems containing strong polar ions, such as hydroxides, often causes selectivity for particular reactions in the melts [13,14,17]. The thermal stability of hydroxide–nitrate systems has, however, been discussed in few papers. The present paper deals with the thermal stability of hydroxide–nitrate systems of alkali and alkaline-earth metals. It has been investigated by thermal analysis, the analysis of gaseous and solid reaction products, voltammetry, and observation with a high-temperature microscope.

EXPERIMENTAL

Materials

Reagent grade $NaNO_3$, KNO_3, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(NO_3)_2$ and $Ba(NO_3)_2$ (Wako Pure Chemicals) were dried in an oven at 150°C for 50 h. Carbonates on the surface of reagent grade NaOH and KOH shots (Wako Pure Chemicals) were washed off with redistilled water degassed at 90°C, and these shots were dried at 200°C for 50 h in a flow of dry nitrogen. Dehydrated samples of $Sr(OH)_2$, $Ba(OH)_2$, $Mg(NO_3)_2$ and $Ca(NO_3)_2$ were prepared from reagent grade $Sr(OH)_2 \cdot 8H_2O$, $Ba(OH)_2 \cdot 8H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$, respectively, by drying them at 150°C for 5 days in a flow of dry nitrogen. These chemicals were found to be perfectly dried by this procedure since no weight loss was observed up to 250°C. These samples were ground to below 100 mesh and mixed by dry blending in a glove box filled with dry argon. Washed and dried silica (α-quartz) was added as a diluent to the salt mixtures for thermal analysis of the decomposition.

Apparatus and procedure

DSC measurement and a simultaneous measurement of TG, DTA, DTG and EGA were performed with TG–DSC and TG–DTA units (Rigaku Denki), a differentiator (Rika Denki Kogyo), a gas chromatograph (Shimadzu Seisakusyo) and a gas sampler (Gaschro Kogyo). The gas formed was determined every 2 min. Details of the experimental conditions were discussed previously [18–21].

The melting temperatures were determined by the DSC measurement and a visual method with the high-temperature microscope illustrated in Fig. 1. Samples (10 mg) mixed in a glove box were heated on a quartz plate at a rate of 10°C min^{-1} under vacuum.

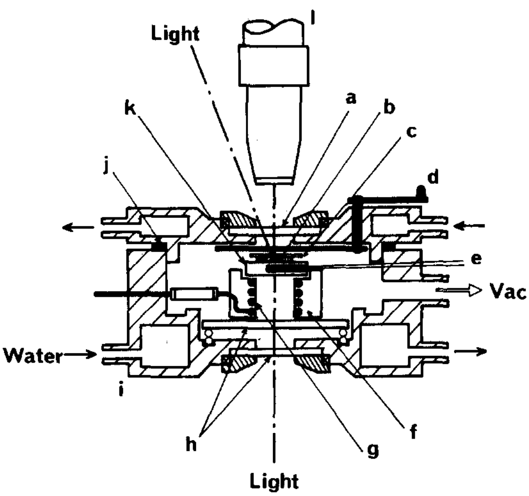

Fig. 1. High-temperature microscope. (a, h) Quartz window; (b) sample; (c) cover glass; (d) shield; (e) thermocouple; (f) heater bobbin; (g) heater; (i) aluminum body; (j) packing; (k) quartz plate; (1) microscope.

Voltammetry was carried out with the three-electrode apparatus illustrated in Fig. 2. The reference, working and counter electrodes were silver wires of 1.7, 1.7 and 15.9 cm^2 surface area, respectively. Samples for

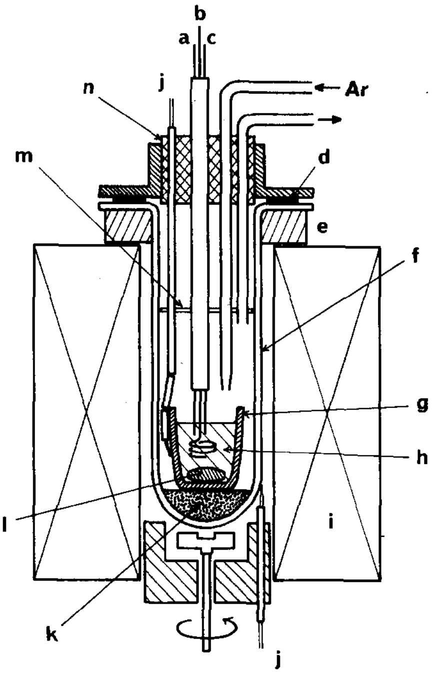

Fig. 2. Apparatus for voltammetry. (a) Silver reference electrode; (b) silver counter electrode; (c) silver working electrode; (d) packing; (e) asbestos; (f) quartz tube; (g) alumina crucible; (h) melt; (i) heater; (j) thermocouple; (k) quartz sand; (1) stirrer; (m) radiation shield; (n) silicone stopper.

voltammetry (10 g) were heated in an alumina crucible (4.3 cm ID). The melt was stirred by a magnetic stirrer.

RESULTS AND DISCUSSION

Phase diagrams of alkali metal hydroxide–nitrate systems

Figure 3 shows the phase diagram of the NaOH–$NaNO_3$ system. The solidus and liquidus temperatures were determined from the DSC curves as the lowest and highest temperatures, respectively, deviating from the baselines. The solidus temperatures were also ascertained with a high-temperature microscope. The solidus temperatures by both methods agree within 2°C.

The phase diagram obtained agreed well with those reported previously [22]. The melting point of NaOH reported by Bergman and Reshetnikov [22] is lower than that of the present work. This may be due to the contamination by water because NaOH easily absorbs water vapor.

The two maxima obtained for the liquidus temperature were at the compositions 0.33 and 0.50 mole fraction of $NaNO_3$, which correspond to the stable compounds in the system: $2NaOH \cdot NaNO_3$ and $NaOH \cdot NaNO_3$ [22].

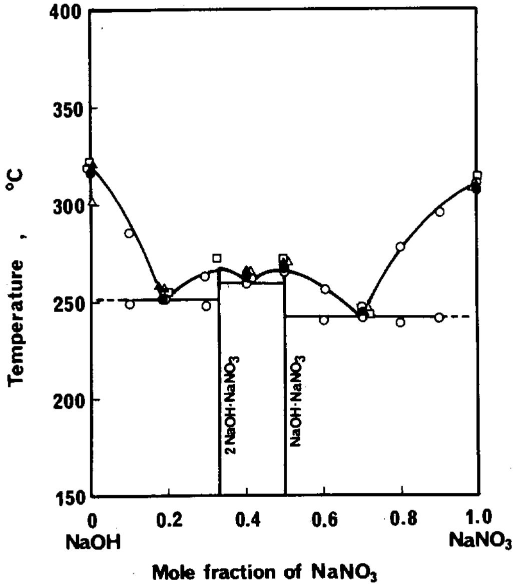

Fig. 3. Phase diagram of the NaOH–$NaNO_3$ system. (○) Present work; (△) Bergman and Reshetnikov [22]; (●) Maksimenko [22]; (▲) Diogenov [22]; (□) Janecke [22].

The phase diagram of the $KOH-KNO_3$ system was constructed by the same procedures as for the $NaOH-NaNO_3$ system. The liquidus temperature was maximum at the composition of 0.50 mole fraction of KNO_3. The eutectic temperatures were 250 and 220°C at 0.16 and 0.70 mole fraction of KNO_3, respectively.

The solidus temperatures in the $KOH-KNO_3$ system are lower than those in the $NaOH-NaNO_3$ system at any composition, while the melting points of KOH and KNO_3 are higher than those of NaOH and $NaNO_3$, respectively. Potassium ions make a greater contribution to the stabilization of liquid solutions of hydroxide–nitrate systems than do sodium ions.

The enthalpy of mixing (ΔH_{mix}), a parameter which indicates the thermal stability of solutions, takes larger negative values for systems forming more stable solutions. The following relationship is held for systems at every composition

$$\left[\Delta H^{\mathrm{ls}}_{\mathrm{mix}} - \Delta H^{\mathrm{ss}}_{\mathrm{mix}}\right]_{\mathrm{KOH-KNO_3}} < \left[\Delta H^{\mathrm{ls}}_{\mathrm{mix}} - \Delta H^{\mathrm{ss}}_{\mathrm{mix}}\right]_{\mathrm{NaOH-NaNO_3}} < 0 \qquad (1)$$

where the superscripts ls and ss indicate liquid and solid solutions, respectively.

The enthalpy of mixing is known to relate closely to the radii of component ions using Kleppa's size parameter (δ) [16,23,24]

$$\Delta H_{\mathrm{mix}} = \chi(1-\chi)(A + B\delta^2) \qquad (2)$$

where χ = mole fraction of a component, A and B = constants.

$$\delta = \frac{d_1 - d_2}{d_1 + d_2} = \frac{r(\mathrm{OH^-}) - r(\mathrm{NO_3^-})}{r(\mathrm{OH^-}) + r(\mathrm{NO_3^-}) + 2r(\mathrm{cation})/Z} \qquad (3)$$

where d = sum of ionic radii of components 1 and 2, r = ionic radii, Z = valence of cation. The size parameters of alkali and alkaline-earth metal hydroxide–nitrate systems are listed in Table 1. The size parameters have the following relationship

$$\delta(\mathrm{KOH-KNO_3}) < \delta(\mathrm{NaOH-NaNO_3}) \qquad (4)$$

TABLE 1

Size parameters of alkali and alkaline-earth metal hydroxide–nitrate systems

	Li^+	Na^+	K^+	Rb^+	Cs^+
Cation radii (nm) [25]	0.060	0.090	0.133	0.148	0.169
Size parameter	0.109	0.094	0.082	0.078	0.073
	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Cation radii (nm) [25]	0.031	0.065	0.099	0.113	0.135
Size parameter	0.136	0.124	0.114	0.110	0.105
Anion radii [26]	$r(\mathrm{OH^-}) = 0.140$ nm, $r(\mathrm{NO_3^-}) = 0.189$ nm				

The constants A and B must satisfy eqns. (5) and (6) for both eqns. (1) and (4) to hold

$$(A^{ls} - A^{ss}) < 0, \; (B^{ls} - B^{ss}) > 0 \qquad (5), (6)$$

The negative $(A^{ls} - A^{ss})$ and the positive $(B^{ls} - B^{ss})$ values mean that the interaction, irrespective of cation radii, i.e., anion–anion interaction, controls the stabilization of liquid solutions; on the contrary cation–cation and cation–anion interactions act against this stabilization. A strong chemical interaction is supposed to exist between hydroxide and nitrate ions; probably a hydrogen-bonded anion network is present.

Thermal stability of solid and liquid solutions in alkali metal hydroxide–nitrate systems

TG–DTA measurement was carried out under cooling to investigate the thermal stability of solid solutions. No weight losses in the TG curves and no peaks in the DTA curves were observed over the temperature range from just above the melting temperature to 100°C at any composition in $NaOH–NaNO_3$ and $KOH–KNO_3$ systems. The solid solutions and the compounds of $2NaOH \cdot NaNO_3$, $NaOH \cdot NaNO_3$ and $KOH \cdot KNO_3$ are stable when compared with the binary solid solutions of alkali metal nitrates [16].

The thermal stability of liquid solutions was investigated by the simultaneous measurement of TG, DTA, DTG and EGA. Figure 4 shows the DTG and DTA curves and the formation rate of O_2 gas.

For the sodium salt system, the thermal decomposition of the hydroxide–nitrate melt was initiated around 540°C (Fig. 4B), which was about 50°C higher than that of fused $NaNO_3$ (Fig. 4A). This rise in the

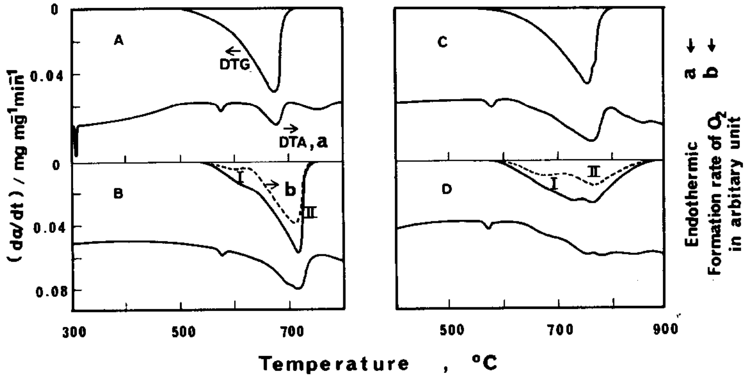

Fig. 4. DTG and DTA curves and the formation rate of O_2 during the thermal decomposition of $NaNO_3$ (A), $NaOH–NaNO_3$ (2:1 mol%) (B), KNO_3 (C), and $KOH–KNO_3$ (2:1 mol%) (D). Sample weight, 10 mg; heating rate, 5°C min^{-1}; crucible, alumina; atmosphere, Ar (50 cm^3 min^{-1}).

decomposition temperature was also observed at 0.5 mole fraction of $NaNO_3$. The DTG curve of the thermal decomposition of $NaNO_3$ (A) shows only one peak. The gases formed were O_2, NO and a trace amount of N_2. On the other hand, the DTG curve and the formation rate of O_2 indicate that the thermal decomposition of NaOH–$NaNO_3$ melts proceeds in two steps (B). An equimolar mixture of O_2 and H_2O was formed in the lower temperature region. The gases formed were O_2, NO and a trace amount of N_2 in the higher temperature region. These facts indicate that the thermal decomposition of hydroxide and nitrate is strongly correlated with each other at least in the initial decomposition process.

The practical features of the thermal decomposition of hydroxide–nitrate melts were confirmed more remarkably for the potassium salt system. For instance, the initial decomposition process is more clearly distinguished in the formation rate of O_2 (compare Fig. 4D with Fig. 4C).

The correlated decomposition of hydroxides and nitrates gives evidence to the strong chemical interaction between hydroxide and nitrate ions.

Voltammograms of the NaOH–$NaNO_3$ system

The polarized N–O bond in NO_3^- ions by OH^- ions would show high sensitivity to redox reactions compared with fused nitrates or hydroxides, even if the melts are thermally stable. Figure 5 shows the voltammograms for the melts of NaOH and the NaOH–$NaNO_3$ system. No wave appeared to 1.25 V vs. Ag electrode in the NaOH melt. The reduction wave of nitrate to nitrite appeared around 0.70 V vs. Ag (B, C and D). The silver working electrode was remarkably oxidized in NaOH–$NaNO_3$ melts after the potential sweep to 1.25 V vs. Ag, while it is scarcely oxidized in fused NaOH.

Wiaux and Claes [27] state that the two reduction waves attributed to the following reactions are observed in the voltammograms of NaOH–KOH solvent (60 : 40 mol%) at 250°C

$$NO_3^- + 2e^- \rightarrow NO_2^- + O^{2-} \tag{7}$$

$$NO_2^- + e^- \rightarrow NO + O^{2-} \tag{8}$$

Our results are quite similar to theirs. The NaOH–$NaNO_3$ melts have strong oxidizing ability, which was supposed to increase in proportion to the amount of nitrite ions formed by the decomposition of nitrate ions.

It is clear that the polarization of nitrate and nitrite ions by hydroxide ions in NaOH–$NaNO_3$ melts results in a strong oxidizing ability.

Thermal stability of alkaline-earth metal hydroxide–nitrate systems

Figure 6 shows the melting temperatures (shaded) and the decomposition temperatures of alkaline-earth metal hydroxide–nitrate systems as a function of charge density of cations ($Ze/4\pi r$), where Z, e and r are the valence of

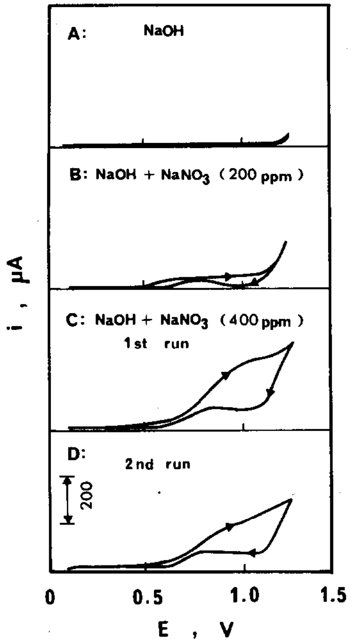

Fig. 5. Voltammograms of NaOH (A) and NaOH-NaNO$_3$ melts (B–D). Atmosphere, dry argon (100 cm^3 min^{-1}); sweeping rate, 0.01 V s^{-1}; temperature, 350°C.

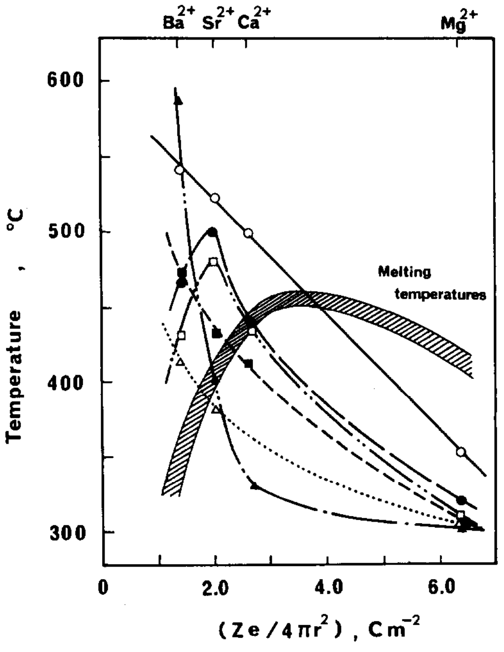

Fig. 6. Melting and decomposition temperatures of alkaline-earth metal hydroxide–nitrate system. Mole fraction of nitrate: (○) 1.00; (△) 0.90; (■) 0.67; (□) 0.50; (●) 0.33,; (▲) 0.

the cation, the charge on an electron and the radius of the cation derived from Pauling's monovalent radius, respectively. The charge density is proportional to the polarizing ability of cations. The decomposition temperatures of $M(OH_2)$ and $M(NO_3)_2$ (M = Mg, Ca, Sr and Ba) are shown in the same figure.

The melting temperatures of calcium, strontium and barium hydroxide–nitrate systems decrease with decreasing size parameter (listed in Table 1) irrespective of the composition. It is the same relationship as in the alkali metal systems. Then, the strong interaction between hydroxide and nitrate ions is present. Quite large amounts of magnesium salt mixtures decomposed below the melting temperatures in the solid state. The melting temperatures of $Mg(OH)_2$–$Mg(NO_3)_2$ might not be so accurate.

The decomposition temperatures of hydroxides and hydroxide–nitrate mixtures increase with decreasing charge density, excluding the mixtures of barium salts at 0.33 and 0.50 mole fraction of nitrate, while those of pure nitrates have an approximately linear relationship with the charge density. This linear relationship means that the thermal decomposition is initiated by the breaking of the N–O bond in NO_3^- ions polarized by cations. On the contrary, the non-linear relationships show the presence of other factors concerning the breaking of O–H and N–O bonds, e.g., the mutual polarization of hydrogen bonded OH^- and NO_3^- ions. The formation of H_2O on the decomposition of hydroxide and the hydroxide–nitrate mixtures gives evidence that the anion–anion interaction strongly relates the thermal decomposition of these materials.

It is noted from their practical use as reaction media that binary mixtures of the $Ba(OH)_2$–$Ba(NO_3)_2$ system and hydroxide-rich mixtures of the $Sr(OH)_2$–$Sr(NO_3)_2$ system form thermally stable liquid solutions having strong oxidizing ability like those of the alkali metal systems. Details of the reactions in the melts are described elsewhere [28,29].

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