SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Oxidation of Magnesium in the Systems NaClO₄–Mg–Metal Oxide (Peroxide)

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Abstract—Oxidation of magnesium in mixtures $NaClO_4 + Mg + metal oxide or peroxide has been investigated using differential thermal analysis (DTA). In the systems with peroxides <math>Na_2O_2$, Li_2O_2 , BaO_2 , CaO_2 or ZnO, magnesium oxidizes simultaneously with decomposition of $NaClO_4$ in the region $380-520^{\circ}C$, which is $100-200^{\circ}C$ below the oxidation temperature of magnesium in air. In the ternary systems with transition-metal oxides NiO, CuO, FeO, and Fe₂O₃, magnesium transforms into oxide at above $600^{\circ}C$ after sodium perchlorate had been decomposed completely. The low-temperature oxidation of magnesium occurs in the systems in which sodium chlorate is accumulated during the catalytic decomposition of $NaClO_4$.

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Magnesium is used as a fuel in solid fuel oxygen generators to maintain the self-propagating generation of oxygen during thermal decomposition of the oxygen carrier [1]. As a rule, the fire point of magnesium in oxygen ($(635 \pm 5)^{\circ}$ C [2]) is above the decomposition temperature range of the oxygen carrier. For NaClO₄ this range is 485–580°C.

Magnesium oxidizes rapidly during intense oxidant decomposition only if the oxidant decomposition temperature is higher than >600°C, as in the case of $KClO_4$ [3]. If the decomposition temperature of the oxidant is below 600°C, magnesium oxidizes only partially during oxygen generation, which is observed in the system containing $LiClO_4$ [4]. Magnesium behaves similarly in the binary systems with sodium chlorate or sodium perchlorate [5]. The investigation of the KClO₃–Mg system [6] showed that the degree of magnesium oxidation during decomposition of KClO₃ in the range 356–540°C is no higher than 7%. The main reaction of magnesium with oxygen proceeds at about ~ 600° C after the oxygen carrier has already been decomposed completely. To use magnesium as a fuel in these systems efficiently, it is necessary to determine the conditions under which metal oxidation and decomposition of the oxygen carrier proceed in the same temperature range. This will simultaneously provide a decrease in the combustion temperature of the solid oxygen source.

We previously found that, in the system with sodium chlorate and calcium peroxide or calcium oxide, magnesium transforms into magnesium oxide completely at 360–460°C [7]. The low-temperature oxidation of the metal proceeds in this ternary system under certain concentration conditions with simultaneous proceeding of all chemical transformations.

In this work, the behavior of the $NaClO_4$ -metal oxide (or peroxide) magnesium systems is investigated under heating, and the effects of Li_2O_2 , Na_2O_2 , MgO, CaO, CaO₂, BaO₂, ZnO, NiO, CuO, FeO, and Fe₂O₃ on magnesium oxidation in these systems is investigated.

EXPERIMENTAL

Sodium perchlorate NaClO₄ (pure grade) was recrystallized from an aqueous solution and dehydrated in a rotary evaporator at 300°C. The starting sodium chlorate NaClO₃ (pure grade) was twice recrystallized from an aqueous solution and dried at 110°C under atmospheric pressure. We also used a PMF-4 magnesium powder of dispersity $\sim 50 \,\mu\text{m}$. Metal oxides and peroxides, namely, Na₂O₂ (96% pure), Li₂O₂ (highpurity grade), BaO₂ (analytical grade, 85 wt % purity), MgO (analytical grade, host content 97 wt %), CuO (pure grade), ZnO (reagent grade), FeO (pure grade), Fe₂O₃ (analytical grade), and NiO (os.-ch. 10-2 grade) were used without purification. Calcium peroxide CaO_2 (96% purity) was prepared by the method described in [8]. Calcium oxide CaO was prepared by decomposing CaO₂ at 500°C.

The thermoanalytical investigation of the samples of weight 0.1–0.2 g, which were prepared by mixing the components in an agate mortar, was carried out in alundum crucibles using a Derivatograph 1500D thermal analyzer at a heating rate of 10 K/min. In solid decom-

NaClO ₄ – n NiO, where n is	Temperature, °C			
	onset of oxygen evolution	rapid oxygen evolution	exotherm peak of NaClO ₄ decomposition	
0	485	500	580	
0.01	420	445	550	
0.025	390	410	540	
0.05	370	400	500	
0.1	340	400	450	
0.2	315	400	420	
0.5	310	400	420	

Table 1. Temperature range of decomposition of $NaClO_4$ under the effect of NiO

position products, chloride ion was determined via chemical analysis according to Folhard and the sum of the Cl⁻ and ClO₃⁻ ions was determined after reduction of the ClO₃⁻ ion with sulfur oxide gas. An ADP-2-01 diffractometer (Cu K_{α} radiation) was used for X-ray powder diffraction analysis.



Fig. 1. DTA curves for (*a*) NaClO₄ and its mixtures: (*b*) NaClO₄ + 0.1NiO, (*c*) NaClO₄ + 0.4Mg, (*d*) NaClO₄ + 0.4Mg + 0.1NiO, and (*d*) NaClO₄ + NaClO₃ + 0.4Mg + NiO.

RESULTS AND DISCUSSION

Individual NaClO₄ ($T_{\rm m} = 460^{\circ}$ C) decomposes exothermally in the temperature range 485–580°C. In the course of heating of the components in the NaClO₄-Mg system, the onset decomposition temperature of sodium perchlorate decreases by 50°C as the magnesium content increases to the component molar ratio 1 : 1 while the decomposition rate increases by two orders of magnitude [5]. Magnesium oxidizes insignificantly during decomposition of perchlorate. According to our estimates, the amount of oxidized magnesium in the products after heating the mixture to 530-560°C is no higher than 2-3% of the starting one. Most of the metal transforms into oxide at $T \sim 600^{\circ}$ C. The addition of metal oxides into the mixture of NaClO₄ with magnesium variously affects both the perchlorate decomposition parameters and the magnesium oxidation.

Nickel oxide strongly catalytically affects sodium perchlorate and reduces the decomposition temperature of NaClO₄ by 100–150 °C (Table 1). In the system with magnesium, NaClO₄ decomposes at the component ratio NaClO₄ : Mg : NiO = 1 : 0.4 : 0.1 in the same temperature range as under the effect of pure NiO oxide. Magnesium virtually is not oxidized during decomposition of perchlorate in the presence of nickel oxide. The intensity of the exotherm that corresponds to oxidation of magnesium at 600°C even somewhat increases in the ternary system (Fig. 1) compared with the system containing no NiO oxide.

This fact is possibly associated with the fact that the investigated decomposition of sodium perchlorate under the effect of NiO proceeds with no formation of intermediate NaClO₃ while 5–6 mol % chlorate was formed during decomposition of NaClO₃ in the presence of Mg for the NaClO₄–Mg system [5].

We found that the addition of sodium chlorate to the mixture of perchlorate with magnesium decreases the intensity of the exotherm at 600°C, and an exotherm appears in the range 380–390°C. As the molar ratio NaClO₃/NaClO₄ = 1 is attained, the magnesium combustion peak at $T \sim 600$ °C vanishes . Magnesium oxidizes completely during decomposition of oxidants. The peak associated with magnesium oxidation at 600°C appears again as the amount of introduced chlorate decreases.

It was found previously that the partial oxidation of magnesium in the NaClO₃–Mg binary system is observed at temperatures considerably lower than the oxidation temperature of magnesium in air [5]. The exotherm at 370–390°C corresponds to this process in the DTA curve. At this step, some amount of sodium chlorate decomposes under the effect of magnesium, and NaClO₃ decomposes with no formation of intermediate NaClO₄ by the reaction NaClO₃ \longrightarrow NaCl + O₂ + MgO. The decomposition rate of NaClO₃ increases by three to four orders of magnitude in this case. Then most of NaClO₄ decomposes in a usual way via dispro-

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1

1

1

0.4

0.4

0.4

0.25

0.65

portionation to NaClO₄ in the range 400–500°C [9]. At the low-temperature stage, up to 10% magnesium transforms into MgO. Magnesium oxidizes completely at the high-temperature stage at 600-620°C after NaClO₃ has already decomposed completely.

Figure 2 shows the DTA curves for mixtures containing NaClO₄ and NaClO₃ in the molar ratio 1:1. The melting endotherm at 240°C and the exotherm at 565°C with a small shoulder at 540°C, which corresponds to the decomposition of the components, are observed in the DTA curve of the binary mixture of sodium perchlorate and sodium chlorate with no metal. The introduction of magnesium into the equimolar mixture $NaClO_4 + NaClO_3$ leads to the appearance of the exotherm peaking at 380-390°C, whose intensity varies in direct proportion to the magnesium content. This effect is accompanied by small weight loss. According to the X-ray powder diffraction data, NaCl and MgO along with the starting components are present in the products of heating of the mixture to 400°C. The decomposition of oxidants with oxygen liberation corresponds to a symmetric exotherm peaking at 550°C. The peak due to magnesium combustion at $T \sim 600^{\circ}$ C is absent. It is noteworthy that this peak is always observed when either sodium perchlorate or sodium chlorate is in excess (Table 2).

The addition of nickel oxide NiO to the equimolar magnesium-containing mixture of oxidants initially increases the intensity of the exotherm at 380°C. As the NiO content in the mixture increases, the peak temperatures of the exotherms of the low-temperature oxidation of magnesium T_1 and decomposition of oxidants T_2 decrease gradually (Table 2), and the endotherm at 410-420°C starts to manifest itself. This endotherm is attributed to melting of the NaClO₄ – NaCl eutectic. The exotherm attributed to magnesium oxidation at $T \sim 600^{\circ}$ C also starts to manifest itself. The intensity of this exotherm increases as the NiO content increases. It was shown that the decomposition temperature of sodium chlorate decreases simultaneously with an increase in its decomposition rate by a factor of 200 in the presence of nickel oxide. The NaClO₃ content in the system also drops abruptly under the effect of nickel oxide, and the molar ratio $NaClO_3/NaClO_4$ becomes much lower than unity because the decomposition rate of sodium chlorate starts to exceed the decomposition rate of sodium perchlorate.

It was found that sodium perchlorate and sodium chlorate form a complex of the composition $NaClO_3$. NaClO₄ at 190°C [11]. Taking into account that this complex affects the low-temperature oxidation of magnesium, one should expect that magnesium will oxidize during the decomposition of oxidants in the systems where the perchlorate-chlorate complex can form.

It is known that sodium perchlorate thermally decomposes to sodium chlorate by the reaction NaClO₄ -

п т 1 0 0 0.4 1 0.4 0.5 0.4 4 0.4 0 390 530 600 12 0 370 500 0.4 600 1 0.4 0.05 360 475 0.1

360

325

300

Fig. 2. DTA curves for (a) the equimolar mixture NaClO₄ + $NaClO_3$ and mixtures $NaClO_4 + NaClO_3 + Mg$ in molar ratios (b) 1 : 1 : 0.2, (c) 1 : 1 : 0.4, and (d) 1 : 1 : 0.6.

 $NaClO_3 + 0.5O_2$. Then sodium chlorate decomposes to chloride by the reaction $NaClO_3 \rightarrow NaCl + 1.5O_2$. The decomposition rate of $NaClO_3$ is higher than that of NaClO₄. Therefore, the amount of intermediate chlorate formed during the decomposition of pure perchlorate is no higher than 5–8 mol %. The content of NaClO₄ formed during the catalytic decomposition of NaClO₃ under the effect of metal oxide or peroxide varies strongly depending on the oxide nature.

To determine the degree of formation and accumulation of NaClO₃ during the decomposition of sodium

Table 2. Temperatures of the thermally induced transformations in the NaClO₄- T_1 is the temperature of ature of the second of rapid oxidation of r



nNaClO ₃ - m Mg- k NiO system, where of the first exotherm, T_2 is the temper- exotherm, and T_3 is the temperature nagnesium				
k	T_1 , °C	T_2 , °C	<i>T</i> ₃ , °C	
0		560		
0		540	590	
0	390	550		
0	385	540	600	

465

445

425

610

610



Fig. 3. Temperature dependence of the concentration of NaClO₃ formed during decomposition of NaClO₄ (*a*) with no catalyst and under the effect of (*b*) Na₂O₂, (*c*) Li₂O₂, (*d*) BaO₂, (*e*) CaO₂ or CaO, (*f*) MgO, and (*g*) ZnO.

perchlorate, the samples of the mixtures of NaClO₄ with the oxygen-containing compound of metal of the corresponding composition was heated to the temperature specified, then cooled, and the chlorate content was determined in the decomposition products. Figure 3 shows the found temperature dependence of the sodium chlorate content during the catalytic decomposition of NaClO₄ in the presence of metal oxides or peroxides. The NaClO₃ content during decomposition of perchlorate under the effect of transition metal oxides (NiO, CuO, FeO, and Fe₂O₃) is close to zero. In the ternary systems with these transition metal oxides, no formation of magnesium oxide was found during decomposition of the oxidant. Magnesium oxidizes only during the high-temperature stage at $600-635^{\circ}C$ (Fig. 4).

One of the most efficient catalysts of decomposition of NaClO₄ is sodium peroxide. It affects NaClO₃ to a lesser extent, due to which sodium chlorate accumulates during NaClO₄ decomposition in the presence of Na₂O₂, and its content attains ~50 mol % [12]. The existence of the NaClO₄ · NaClO₃ complex is most probable during the catalytic decomposition of NaClO₄ under the effect of Na₂O₂ since this peroxide favors the formation of this complex [11].

Two exotherms at 475–480°C and 515–540°C are observed in the DTA curve of the mixture NaClO₄ + $0.1Na_2O_2 + nMg$. It was previously shown that magnesium in turn affects the decomposition of NaClO₄ [5]. As the magnesium content in the ternary system increases, the peak temperature of the exotherm that corresponds to decomposition of perchlorate, gradually reduces from 540°C for n = 0.12 to 515°C for n = 0.3(Fig. 5). The peak due to rapid oxidation of magnesium is absent at $T \sim 600$ °C. The intensity of the first peak varies depending on the magnesium content. As the



Fig. 4. DTA curves for the mixtures $NaClO_4 + 0.3Mg + n$ oxide (CuO, FeO, Fe₂O₃) containing (*a*) 0.1 CuO, (*b*) 0.1 FeO, and (*c*) 0.05 Fe₂O₃.

Mg/NaClO₄ ratio increases, the intensity of the peak at 475–480°C increases. Thus starting at n = 0.175, the first exotherm, which is accompanied by a small weight loss, becomes considerably more intense than the second one. It seems likely that the exotherm at 475–480°C is associated with the involvement of magnesium into the cooperative process, due to which magnesium oxi-



Fig. 5. DTA curves for the mixtures $NaClO_4 + Na_2O_2 + Mg$ with the molar ratios (*a*) 1 : 0.1 : 0.125, (*b*) 1 : 0.1 : 0.15, (*c*) 1 : 0.1 : 0.175, (*d*) 1 : 0.1 : 0.2, and (*e*) 1 : 0.1 : 0.3.



Fig. 6. DTA curves for the ternary mixtures $NaClO_4 + 0.3Mg + n$ metal oxide (peroxide) containing (*a*) 0.05 Li₂O₂, (*b*) 0.3 MgO, (*c*) 0.3 CaO₂ (CaO), (*d*) 0.1BaO₂, and (*e*) 0.4 ZnO.

dizes at temperature 120–150°C below the temperature of rapid oxidation of magnesium in oxygen.

In the system containing lithium peroxide, magnesium completely oxidizes simultaneously with the decomposition of NaClO₄. The behavior of magnesium is similar in the case of the catalytic decomposition of sodium perchlorate under the effect of BaO₂ or CaO₂ (Fig. 6). Figure 3 shows that the highest concentration of NaClO₃, which is formed during decomposition of perchlorate under the effect of lithium, barium, and calcium peroxides, is more than 40 mol % for Li₂O₂ and about 30 mol % for BaO₂ and CaO₂.

It is noteworthy that in binary mixtures of magnesium with metal oxides or peroxides, magnesium somewhat oxidizes in the low-temperature region. However, its larger part is subjected to rapid oxidation at high temperatures. Figure 7 shows the DTA curves for the mixtures $Li_2O_2 + Mg$, $CaO_2 + Mg$, $BaO_2 + Mg$, and NiO + Mg. Up to 5–8 wt % Mg transforms into magnesium oxide on heating the mixture $Li_2O_2 + 0.3Mg$ at the low-temperature stage. The strongest exotherm at 450°C corresponds to this process. The peak temperature of the exotherm corresponding to magnesium combustion is about ~610°C.

The high-temperature peak of magnesium oxidation in the range 595–605°C is already present in the DTA



Fig. 7. DTA curves for the mixture of magnesium with $(a) \operatorname{Li}_2O_2$, $(b) \operatorname{MgO}$, $(c) \operatorname{BaO}_2$, and $(d) \operatorname{CuO}$ (NiO) in the molar ratio 0.4 : 1.

curve of the mixture NaClO₄–Mg–MgO with the molar ratio of components 1 : 0.3 : 0.3 (Fig. 6). In the CaO-containing system, in contrast to the MgO-containing system, magnesium oxidizes as in the presence of CaO₂ during the decomposition of the oxygen carrier. Compared with CaO, magnesium oxide is a weaker catalyst of decomposition of sodium perchlorate and sodium chlorate [13]. In the NaClO₄–MgO system, the highest concentration of nascent chlorate is lower by a factor of almost two than in the CaO-containing system (Fig. 3).

Under the effect of ZnO, sodium perchlorate decomposes with a somewhat larger accumulation of NaClO₃ compared with the decomposition of pure NaClO₄ (Fig. 3). On heating the mixture NaClO₄–Mg–ZnO with the ZnO content 0.4 mol per mol NaClO₄, no high-temperature stage of magnesium oxidation was found. Magnesium completely transforms into oxide below 520°C.

The investigation showed that the conditions favorable for the low-temperature oxidation of magnesium appear in the systems in which NaClO₄ is formed and accumulated during the thermal decomposition of NaClO₃. However, the presence of sodium chlorate alone is insufficient for the complete transformation of magnesium into oxide during the decomposition of oxidants. It was already mentioned above that no more than 10% Mg oxidizes in the NaClO₃–Mg binary system at 370–390°C. Only in the NaClO₃ – NaClO₄ mixture with molar ratio about unity, i.e., when the conditions are favorable for the formation of the NaClO₃ -NaClO₃ complex, does magnesium completely transform into oxide during the decomposition of oxidants.

In the presence of sodium peroxide, homogeneous decomposition of sodium perchlorate occurs. All interactions proceed in the liquid phase in this case. For other oxides, all processes occur on the oxide surface. Oxygen liberated during decomposition of the oxidant can be adsorbed by oxide either as uncharged particles or as the ions O^-,O_2^-, O_2^{2-}, etc. [14]. The adduct NaClO3 \cdot NaClO₄ has $T_m = 235^{\circ}$ C and forms a liquid phase through which the oxygen ions diffuse to magnesium. The oxide film on the magnesium surface loses its protective properties under ordinary conditions as the transition temperature is attained at which the film becomes loose (450°C) [2]. The conditions probably appear in the system NaClO₄-metal peroxide (oxide)-Mg under which the oxide film loses its protective properties at lower temperatures.

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