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A STUDY ON THE THERMAL DECOMPOSITION OF $KClO_4$ AND $NaClO_4$ BY ACOUSTIC EMISSION THERMAL ANALYSIS

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SUMMARY

This paper describes the first application of simultaneous measurements of acoustic emission (AE) and differential thermal analysis (DTA) to the thermal decomposition of $KClO_4$ and $NaClO_4.H_2O$. It was found that AE technique successfully follows rapid decomposition and phase transition of the salts. In the case of $KClO_4$, two extra AE signals were detected at 100 - 200 ° and 200 - 300 °C at which no thermal effect was observed on DTA curve.

INTRODUCTION

It is well known that when a solid is subjected to certain levels of stress, discrete acoustic wave packets are generated. The phenomenon of such sound generation in materials is termed the acoustic emission (AE). The pioneering studies of solid state reactions using AE technique were carried out by Lønvik, who investigated the thermal decomposition of minerals, the transformation of silica minerals and the melting of salts using this techique, which was named thermosonimetry (ref. 1). However, further studies of solid state reactions by AE technique have not been reported. The authors have designed a new apparatus which can measure simultaneously DTA and AE curves during the thermal decomposition of solids. This paper describes the first application of the AE-DTA technique to the thermal decomposition of $KClO_4$ and $NaClO_4.H_2O$.

EXPERIMENTAL PROCEDURE

The samples are as-received powders of $KClO_4$ and $NaClO_4$ (KANTO Chem. Co. Ltd. Japan), which are used without any further treatment. α-Al_2O_3 powder is used as the reference material. The sample and reference material are put in two fused silica holders (15 mm^{ϕ} x 15 mm) fitted with a cup. The holders are placed symmetrically in the electric furnace. A fused silica rod (8 mm^{ϕ} x 240 mm) is attached to the bottom of the sample holder. A 140 kHz resonance frequency piezo-electric sensor is contacted at the end of the rod. The acoustic

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waves generated in the sample holder are transmitted through the rod to the end where they are detected and converted to electric pulses, and recorded as counts per second by an AE TESTER (NF ELECTRONIC INSTRUMENTS 9501). DTA curves are also recorded by the chromel-alumel thermocouple. The tip is located in a 10 mm length cavity at the top of the sample cup. The details of AE-DTA equipment will be reported elsewhere.

RESULTS AND DISCUSSION

Figure 1 shows the results of simultaneous AE-DTA measurement for the thermal decomposition of $KClO_4$. According to the previous work (ref. 2), the endothermic peak at 300 - 340 °C on DTA curve is due to the transition of $KClO_4$ from the orthorhombic to cubic form. The endothermic and exothermic effect at 600 - 660 °C is due to the melting of $KClO_4$ and its subsequent decomposition to KCl. On AE curve (AE-1), three peaks are seen at 100 - 200 °C, 200 - 300 °C and 560 - 660 °C. The scale of AE counting rate is reduced to 1/20 above 610 °C. It is seen from DTA and AE curves that the first AE peak at 100 - 200 °C on AE-1 curve does not have any corresponding DTA signals at these temperatures and second AE peak at 200 - 330 °C is at lower temperatures compared with DTA peak (300 - 340 °C) due to the phase transition of solid $KClO_4$. As seen from curves AE-1 and AE-2, the two lower temperature peaks on AE-1 curve are greatly decreased in their counting rate by re-heating of the sample after a previous heating up to 400 °C, but the weak AE signals survive at 300 - 340 °C on AE-2 curve which correspond to the phase transition of $KClO_4$. These facts suggest that two peaks below 330 °C on AE-1 curve are caused by the extra events occurring in fresh particles which cannot be detected by DTA technique. The initiation (560 °C) of the higher-temperature AE peak (560 - 660 °C) is about 40 °C lower than the starting temperature (600 °C) of the endothermic DTA peak of the melting. This indicates some mechanical events occurring in particles just before the melting. At higher temperatures above 630 °C where DTA curve shows the exothermic peak due to the decomposition, two very intense peaks a and b, and one weak peak c are observed on AE-1 curve. The weak peak c is considered to be due to the solidification of molten KCl formed by the decomposition, which is not detected by the DTA. Thus, the peaks a and b suggest that the decomposition (oxygen evolution process) of $KClO_4$ is two steps reaction in the molten state. Figure 2 shows the results of simultaneous AE-DTA measurement for the thermal decomposition of $NaClO_4.H_2O$. The DTA result coincides with that reported by Devlin et. al.(ref. 3), who showed that decomposition of $NaClO_4.H_2O$ is accompanied by four endothemic and one exothermic peaks as follows: dehydration of $0.2H_2O$ at 55 - 80 °C and $0.8\ H_2O$ at 155 - 200 °C, phase transition of the orthorhombic to cubic form at 305 - 330 °C and melting at 485 °C followed by the exothermic decomposition. On curve AE-1, AE signals begin at 90 °C and intensify with the loss of $0.8H_2O$. AE

signals appearing at 300 - 330 °C which correspond to the phase transition are very weak. At higher temperatures, the thermal processes, which include melting and decomposition, generate six AE peaks above 450 °C. Peak a is apparently due to the melting. Intense peaks b and c are observed at temperatures at which no obvious DTA signal is observed (485 - 550 °C). Subsequently, two sharp, well resolved peaks d and e occur at temperatures corresponding to the exothermic DTA peak due to the decomposition (peaks d and e sometime overlapped each other). Peak f is probably due to the solidification of molten NaCl. These results make it possible to postulate that four peaks b, c, d and e are associated with the decomposition processes of $NaClO_4$; the latter two peaks are due to two steps oxygen evolution. AE-2 curve is the result of re-heating of the sample after a previous heating up to 400 °C, showing that the dehydrated $NaClO_4$ still continues to emitt the signals up to 300 °C.

It is shown that the acoustic emission method is a useful technique for following rapid reactions or explosions such as the decomposition of $KClO_4$ and $NaClO_4$, especially when combined with DTA.

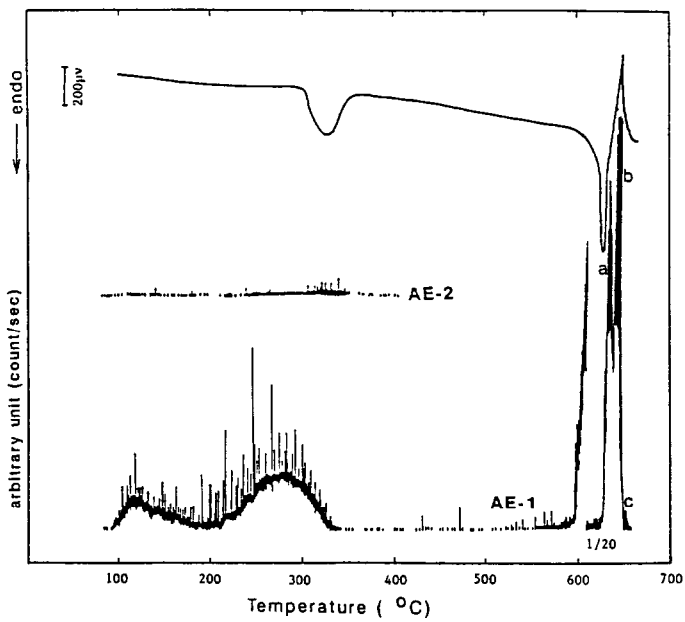

Fig. 1. The simultaneous AE-DTA measurement for decomposition of $KClO_4$. Curve AE-1: heating up to decomposition, curve-2: re-heating of sample previously heated to 400 °C on curve AE-1, heating rate: 5 °Cmin^{-1}, in air, sample weight: 1 g. The scale of counting rate is 1/20 above 620 °C.

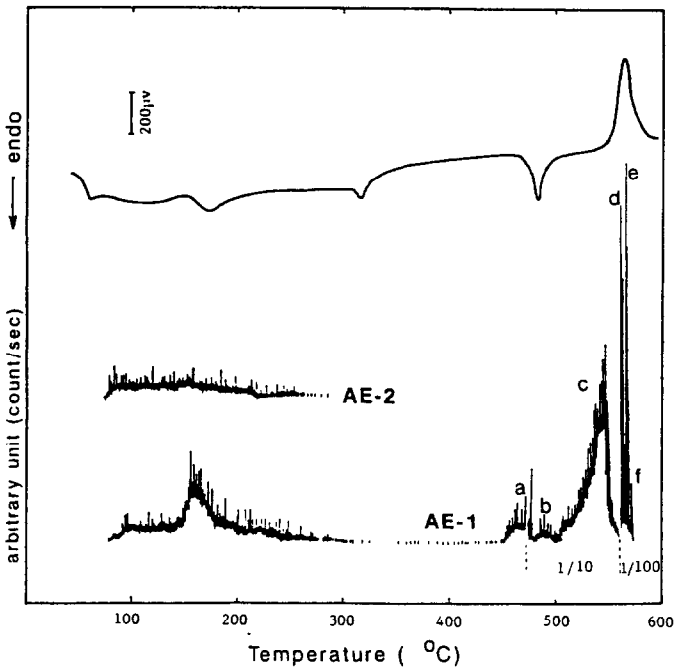

Fig. 2. The simultaneous AE-DTA measurement for decomposition of $NaClO_4.H_2O$. Curve AE-1: heating up to decomposition, curve-2: re-heating of sample previously heated to 400 °C on curve AE-1, heating rate: 5 °Cmin^{-1}, in air, sample weight: 600 mg. The counting rate was changed from 1/1 to 1/10 at 480 - 560 °C and 1/100 above 560 °C.

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