Simultaneous measurements of acoustic emission and differential thermal analysis for different KClO₄ samples

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Abstract

Simultaneous measurements of acoustic emission (AE) and differential thermal analysis (DTA) were made for three types of $KClO_4$ samples (powders, dendrite crystals and one single crystal) using a home-made AE–DTA apparatus. Sensors of resonated frequency 140 KHz, 500 KHz, 1 MHz and 1.5 MHz were used. Irrespective of the type of sample, $KClO_4$ gives low and high temperature AE peaks at temperatures of 180–330°C and 560–640°C respectively. Scanning electron micrograph observation showed that the low temperature AE peak results from the break-up of large particles (crystals) and/or liquid release from their surfaces. The AE signals due to the transition of $KClO_4$ from orthorhombic to cubic form overlap with the low temperature peak and become more appreciable with increasing resonance frequency of the sensor. The high temperature AE peak consists of three peaks, a, b and c. The lower temperature part (560–590°C) of peak a is attributed to a precursory event of the melting. Peaks a and b, which suggest a two-step decomposition, exhibit different frequency dependencies. Peak c, due to the solidification of molten KCl product, does not vary with the type of sample. In the case of a single crystal, an independent intense peak appears as the precursory event of the melting at 550–590°C.

INTRODUCTION

In previous papers [1–3], the authors have described a new apparatus for simultaneous measurements of acoustic emission (AE) and differential thermal analysis (DTA) and its successful application to the detection of structural and mechanical changes during dehydration, phase transition and decomposition of several salts. It has been demonstrated that the AE technique is a useful and sensitive method for following rapid decomposition as well as dehydration and phase transition, and for recording some mechanical event occurring during heating which cannot be detected by

DTA [2]. For example, the AE measurements of the $KClO_4$ powders with a 140 kHz resonance frequency sensor gave one broad peak and three sharp peaks at temperatures of 200–340 °C and 560–630 °C respectively. It was found that the low temperature AE peak results from some mechanical change occurring in the particles prior to the phase transition of $KClO_4$ and that the three high temperature AE peaks are associated with the melting of $KClO_4$ and its subsequent decomposition to KCl [1,2]. Furthermore, it was shown that the low temperature AE peak is greatly reduced when the particle size is decreased and that the two lower temperature peaks of the three sharp ones tend to overlap as the sample mass is decreased [3].

The origin of the mechanical event occurring in the $KClO_4$ particles before transition was, however, not explained. A different sample of $KClO_4$ gave rise to another AE peak at temperatures of 80–160 °C, although both the low and high temperature peaks appear similar [1]. The AE experiments with a sensor having a frequency higher than 140 kHz showed that the three high temperature peaks are reduced in a different way by increasing the frequency of the sensor. It is interesting now to examine the influence of two factors on the low and high temperature AE peaks: the types of $KClO_4$ samples and the sensors. This paper, as part of an experimental programme on the measurement of the thermal decomposition of perchlorates by simultaneous AE–DTA, reports on the AE peaks occurring during heating of the $KClO_4$ samples, and on (i) the influence of three sample types (three different powders, dendrite crystals and one large single crystal), (ii) the influence of the sensor resonated at a frequency higher than 140 kHz, and (iii) the origin of the low temperature AE signals.

EXPERIMENTAL

Three kinds of powdered $KClO_4$ samples were used, supplied from Kanto Chem. Co., Inc. (designated K sample), Nacalai Tesque Inc. (N sample) and Wako Pure Chem. Ind. (W sample). Dendrite crystals of $KClO_4$ were grown by allowing the saturated solution at 60 °C to stand at room temperature. A flat bottomed sample holder was used for AE measurement of the dendrite crystals which were positioned in it as a single layer. When the flat bottomed holder is used, DTA curves are not obtained [2]. A large transparent single crystal, 4.3 mm × 3 mm × 3 mm in size, in the form of a deformed octahedron, was grown by stepwise cooling from 45 °C of the saturated solution of $KClO_4$ at an average rate of 0.5 °C h^{-1}. The reference material used was α-Al_2O_3 powder. The sample and reference materials were placed in two fused silica holders, fitted with caps. Alumel–chromel thermocouples were used for recording the heating temperature and DTA signal. A heating rate of 5 °C min^{-1} was used. A fused silica rod, fixed at the bottom of the sample holder, acts as the waveguide. A piezoelectric sensor, resonated at a frequency of 140 kHz, 500 kHz, 1 MHz or 1.5 MHz, was attached at the end

of the rod. The acoustic waves generated in the sample are transmitted through the rod to its end where they are converted by the sensor to electrical signals in the form of voltage amplitude–time traces. The traces are discriminated at predetermined levels of voltage (designated the threshold) by an AE tester. The discriminated waves are finally converted to two output parameters, the event count rate and the cumulative event count. The details of this apparatus were reported elsewhere [2].

RESULTS AND DISCUSSION

Figure 1 shows the simultaneous AE–DTA curves for the three kinds of $KClO_4$ powders heated to 640°C. The DTA curves (EXP 1–3, (A)) show almost the same thermal changes. The endothermic peak at 280–330°C is due to the transition from the orthorhombic to the cubic phase. The endothermic/exothermic peaks at 585–630°C are due to the melting of $KClO_4$ and its subsequent decomposition to KCl. All three samples display the two main AE features (EXP 1–3, (C)); one broad peak at 170–310°C (low temperature peak) and three sharp peaks, a, b and c, at 560–630°C
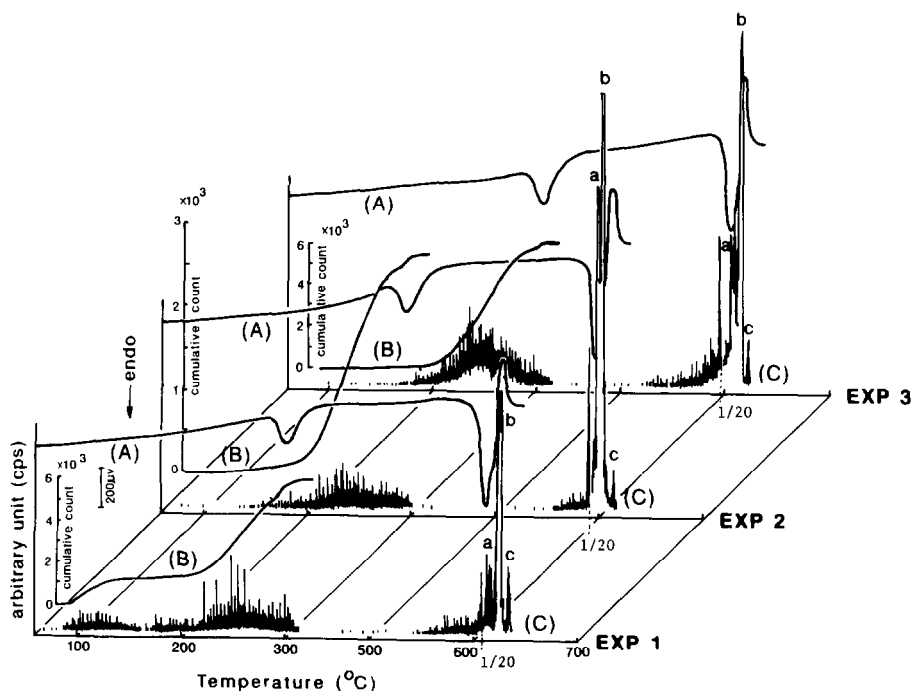

Fig. 1. Simultaneous AE–DTA curves obtained during heating of three kinds of $KClO_4$: EXP 1, K sample (400 mg); EXP 2, N sample (390 mg); EXP 3, W sample (400 mg). (A), DTA curve; (B), cumulative count curve; (C), count rate curve. Heating rate, 5°C min^{-1} in air. The threshold is raised at the broken lines, the intensity being reduced to 1/20.
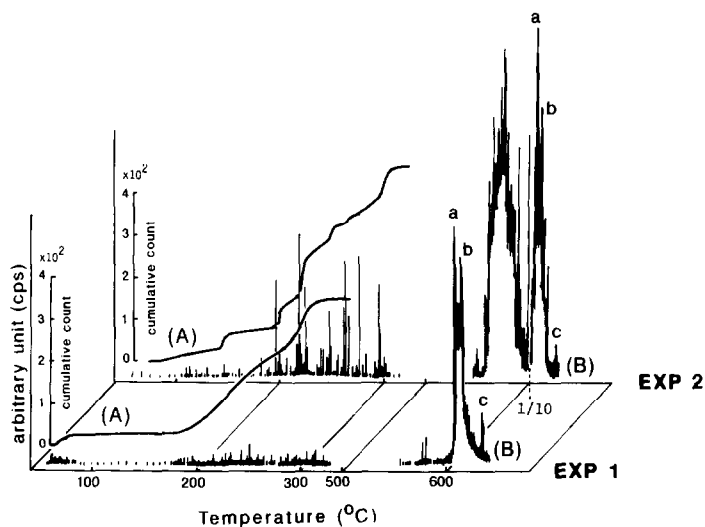
Fig. 2. AE measurement of dendrite crystals and one single crystal of KClO$_4$: EXP 1, dendrite crystals (64 mg); EXP 2, one single crystal (53 mg). (A), cumulative count curve; (B), count rate curve. Heating rate, 5 °C min^{-1} in air. The threshold is raised at the broken lines, the intensity being reduced to 1/10.

(high temperature peak). The K sample has another broad AE peak (below the low temperature peak) at temperatures of 80–160 °C (EXP 1 (C)). The cumulative count curves of the three samples show a slight rise above around 290 °C when the phase transition begins, as found in the DTA curves. Thus this rise results from the signals emitted by the transition. The AE signals cease at 320 °C after the transition is complete, but start again at 540 °C, 560 °C or 530 °C, in the K, N or W samples, respectively, which is much lower than the initiation temperature of the melting (around 590 °C). The signals emitted before the melting are associated with the break-up of the particles as a precursory event of the melting. The signals gradually increase in intensity, become more intense at the endothermic peak, and continue to the inflexion temperature of the endothermic/exothermic peak (peak a). Peak b of high intensity begins at the inflexion temperature and terminates at around the exothermic peak temperature. Peaks a and b suggest a two-step decomposition of molten KClO$_4$, as reported in the previous paper [3]. Peak c corresponds to the solidification of the molten KCl product which is not detected by DTA.

Figure 2 shows the cumulative count curves (curve (A)) and count rate curves (curve (B)) obtained by heating the dendrite crystals (EXP 1) and one single crystal (EXP 2). The dendrite crystals give the low and high temperature AE peaks in a manner similar to that of the powdered samples. A small peak occurring at 60–80 °C may be attributed to desorption of the water adsorbed on the crystal surfaces. A steep rise in the temperature range

280–320 °C of curve (A) arises from the transition, because the temperature range agrees with that of the transition determined from the DTA curve (Fig. 1 (A)). The cumulative count due to the transition is greater in the dendrite crystals (about 2 counts mg^{-1}) than in the powdered samples (less than 1 count mg^{-1}), because of the large size of the dendrite crystals. Of the high temperature AE peaks, peak a is more intense than peak b. Peak b trails towards peak c. As already explained, the two peaks a and b are attributed to the two-step decomposition, and peak c to the solidification of the molten KCl product. In the case of one single crystal (Fig. 2, EXP 2), the AE mode of the low temperature peak is different from that in the dendrite and powdered samples. The rate count curve (EXP 2(B)) is composed of separate intense AE signals, particularly at temperatures of 190–310 °C, leading to the stepwise cumulative count curve (EXP 2(A)). The last rise on curve (A) at temperatures of 290–310 °C is due to the transition, as explained for the dendrite crystals. No signal is emitted after the transition is complete. Signals restart rapidly at 550 °C, reach a maximum at around 570 °C and then decrease before melting. As a result, an independent intense peak is formed, which corresponds to the lower temperature part of peak a occurring in the powdered samples and dendrite crystals below 590 °C. Peaks a and b, due to the two-step decomposition of molten KClO$_4$, occur consecutively at temperatures of 595–620 °C, overlapping as described in the previous paper [3], and peak c is also observed. It is concluded from the above AE results (Figs. 1 and 2) that irrespective of the sample source and form, KClO$_4$ samples show the low temperature peak and the three high temperature peaks, a, b and c: the first includes signals due to the transition and the last includes the lower temperature portion of peak a arising from a precursory event of the melting (an independent intense peak for one large single crystal). In the K sample and dendrite crystals, a peak below the low temperature peak is observed below 160 °C.

The AE peaks shown in Figs. 1 and 2 were obtained by measurement with a 140 kHz resonance frequency sensor. The cumulative count and count rate curves measured with different kinds of sensor are shown in Fig. 3: the resonance frequencies of 500 kHz, 1 MHz and 1.5 MHz are used. The curves (Fig. 1, EXP 1(A) and (B)) obtained at 140 kHz are shown again in Fig. 3. The AE peak which falls below 160 °C is large at 500 kHz frequency, but decays abruptly at 1 MHz and is not detected at 1.5 MHz. There is little change in the low temperature peak at frequencies between 140 and 500 kHz, but the peak decreases at 1 and 1.5 MHz. The peak due to the structural transition around 290 °C, which overlaps with the low temperature peak, becomes more appreciable with increasing frequency, as indicated by the steep rise from around 290 °C (see arrow) on curve (A). Thus the peak below the low temperature peak, and the low temperature peak, including the signals due to transition, exhibit different frequency dependences. The signals generated prior to melting (the lower temperature part of
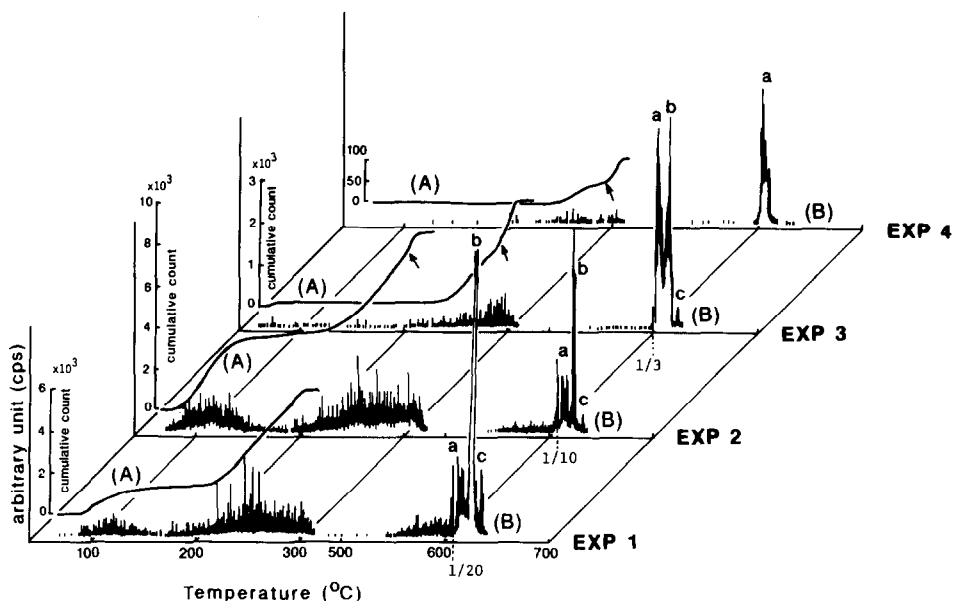
Fig. 3. AE measurement of KClO₄ powders with sensors of different resonance frequencies. EXP 1, 140 kHz; EXP 2, 500 kHz; EXP 3, 1 MHz; EXP 4, 1.5 MHz. (A), cumulative count curve; (B) count rate curve; K sample, 400 mg. Heating rate, $5°C$ min^{-1} in air. The threshold is raised at the broken lines, the intensity being reduced to the values indicated.

peak *a*) decrease with increase in frequency and are not detected at 1.5 MHz. Peaks *a* and *b* are also reduced by increasing the frequency; peak *b* shows a stronger decay tendency than peak *a* and is hardly detected at 1.5 MHz. Peak *c* gradually decreases at frequencies above 500 kHz and is not detected at 1.5 MHz.

As described above, the low temperature peak and the peak below it are observed in the K sample. Repeated heating experiments to different temperatures were carried out, and a small portion of the samples thus obtained was examined by scanning electron microscopy (SEM) to establish the origin of the two peaks. Figure 4 shows the AE curves and SEM micrographs of the samples obtained by heating to the temperatures corresponding to the arrow on the DTA curve. As-received samples are seen to consist of large, separate particles of 100–300 μm size (micrograph (a)). On heating to the completion temperature (190°C) of the lowest peak (curve (A)), each particle becomes angular as a whole and large grooves appear between the particles (micrograph (b)). Thus, this peak, below the low temperature peak, can be correlated with the formation of grooves or angulation of the particles. On reheating the samples obtained after the first heating experiment, this peak is greatly reduced and the low temperature peak appears as the main peak (curve (B)). The SEM observation (micrograph (c)) of the samples obtained after curve (B) shows that small particles emerge from the
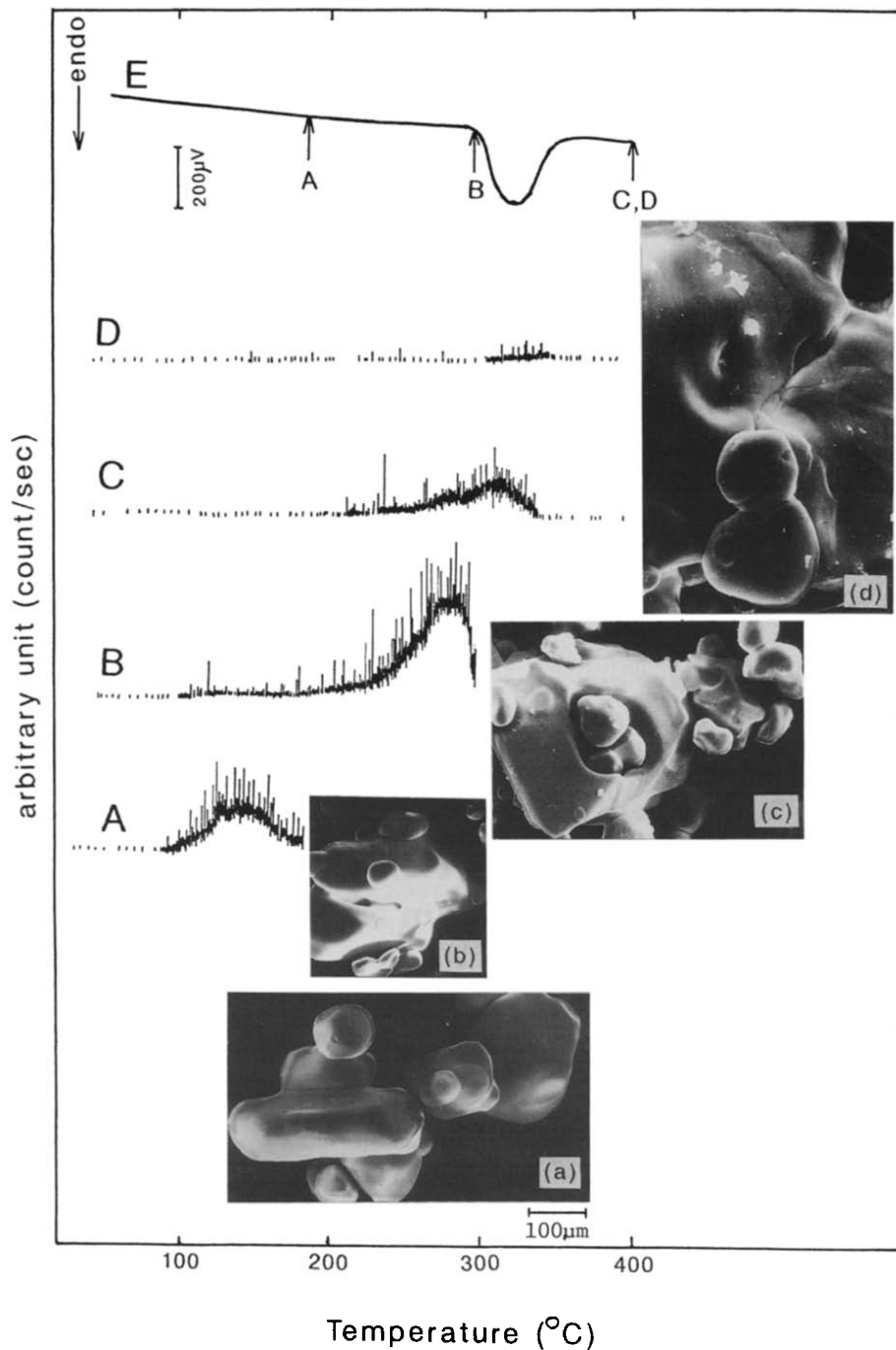
Fig. 4. AE measurement and SEM micrographs of the KClO$_4$ samples heated to different temperatures: A–D, count rate curve; E, DTA curve. (a)–(d), SEM micrographs: (a) original sample; (b) the sample heated to 190°C; (c) the sample heated to 290°C; (d) the sample heated to 400°C; K samples (600 mg). Heating rate, 5°C min^{-1} in air.

large particles owing to loss of part of their surface skin and that cracking on the surface of some small particles occurs. The emergence of small particles hidden under the skin indicates the release of fluids from the surface skin of the large particles. This is supported by the TG result from the as-received samples which shows a weight loss of 0.2 wt.% at temperatures of 240–307°C, which covers the low temperature peak seen on curve (B). Clark and Garlick [4] have also reported that AE signals are emitted from $KClO_4$ at 130–250°C arising from microcracking and release of fluid inclusions. Thus the low temperature peak is assumed to result from the break-up of the surface skins of large particles and cracking on the surface of small particles. Signals due to the structural transition are observed when the low temperature peak disappears (curve (C)). The SEM observation of the samples obtained after transition show many microcracks on the surfaces of the small particles (micrograph (d)). It is found that several repeated heating experiments diminish the low temperature peak and finally extinguish all the peaks.

ACKNOWLEDGEMENT

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