

Effect of milling on the reactivity of lead dioxide

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In order to clarify the surface reactivity of β -PbO₂, thermal analysis, surface analysis and kinetic analysis of the reaction of β -PbO₂ with an aqueous solution of hydrazine were performed and the following results were obtained.

The reaction rate of β -PbO₂ with an aqueous solution of hydrazine was affected by its surface reactivity. Kinetic analysis of the reaction of β -PbO₂ with hydrazine shows that the Avrami-Erofeev equation represents well a sigmoidal type of fractional reaction vs. time curves for β -PbO₂ without milling, and that a surface reaction-controlled shrinking unreacted-core model is in good agreement with the experimental results for milled β -PbO₂. Correlation between these results and surface reactivity of β -PbO₂ are discussed.

1. Introduction

Lead dioxide has long been used as an oxidant in pyrotechnic compositions, but pyrotechnic engineers found that its activities as an oxidizer were often different from its sources. This is because lead dioxide has a high activity for absorbing reactive gases, losing oxygen and acquiring some energy to change near its surface. For example, the modifications, which include tetragonal lead dioxide (β -PbO₂) and orthorhombic (α -PbO₂), have a very similar standard free energy of formation¹⁾. In addition, a significant structural changes between the α -form and β -form are known to easily occur during mechanical treatment^{2,3)}.

We proposed that the surface reactivity of lead dioxide as an oxidizer in pyrotechnic compositions could be estimated by the activity of lead dioxide in its reaction with an aqueous solution of hydrazine^{4,6)}. In this paper, the effect of milling on the surface properties of β -PbO₂ and the reaction mechanisms of lead dioxide with aqueous hydrazine were discussed in order to clarify the surface properties of the lead dioxide.

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2. Experimental

2.1 Materials

The sample of β -PbO₂ was obtained from a commercial supplier and contained 97.5 wt% lead dioxide determined from its active oxygen.

Mechanical treatment was performed using a laboratory vibro-mill (Tsutsui Scientific Instrumentation Co., Ltd.) consisting of a ceramic container and 15 ceramic grinding balls. The vibrational frequency was 100 rpm and grinding time ranged up to 100 hours.

2.2 Analysis

Active oxygen was determined by iodometry. Particle size was measured using a Horiba Centrifugal Particle Size Analyzer CAPA-500. Specific surface area was determined by a Shimadzu Automatic Surface Area Analyzer 2200. Thermal analysis was performed with a RIGAKU DTA-TG simultaneous analyzer in an argon flow. TEM analysis and electron diffraction were performed using a Nippon Densi Analytical JEM 200 B transmission electron microscope.

2.3 Reaction of lead dioxide with aqueous hydrazine

50 ml of a 20% aqueous solution of hydrazine was mixed with 1 g of β -PbO₂ in a reaction vessel which was maintained at a constant temperature and equipped with a magnetic stirrer. In order to determine the reaction rate, the volume of nitrogen gas evolved by the reaction of β -PbO₂ with hydrazine was measured with time using gas

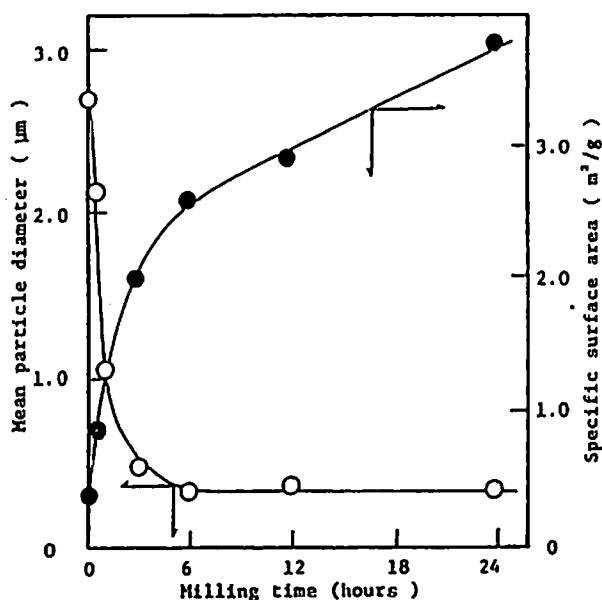


Fig. 1 Effect of milling on surface area and mean particle diameter of β - PbO_2
 ○; mean particle diameter
 ●; specific surface area

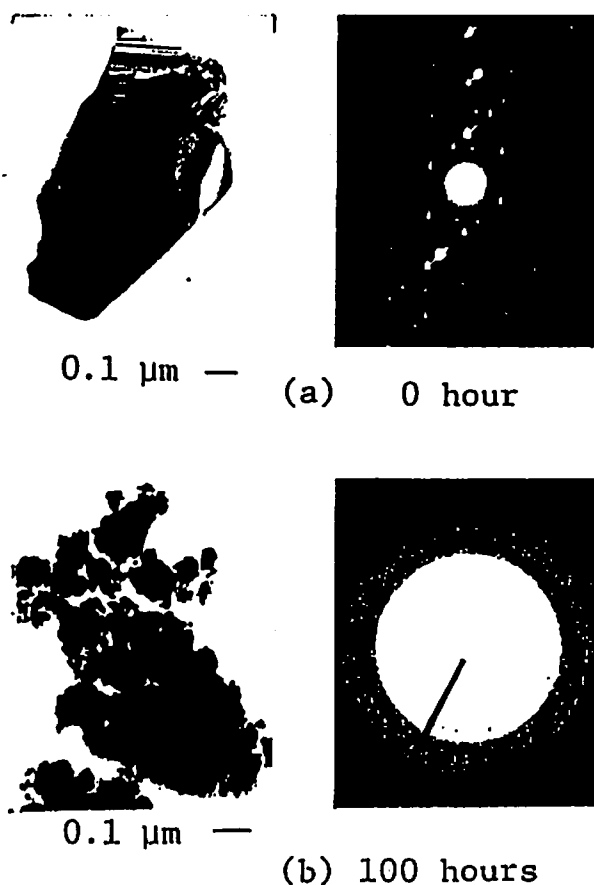


Fig. 2 TEM photographs and electron diffraction patterns of milled β - PbO_2

burette. From preliminary experiments, the rotating speed was determined to be 90 rpm, because of a constant reac-

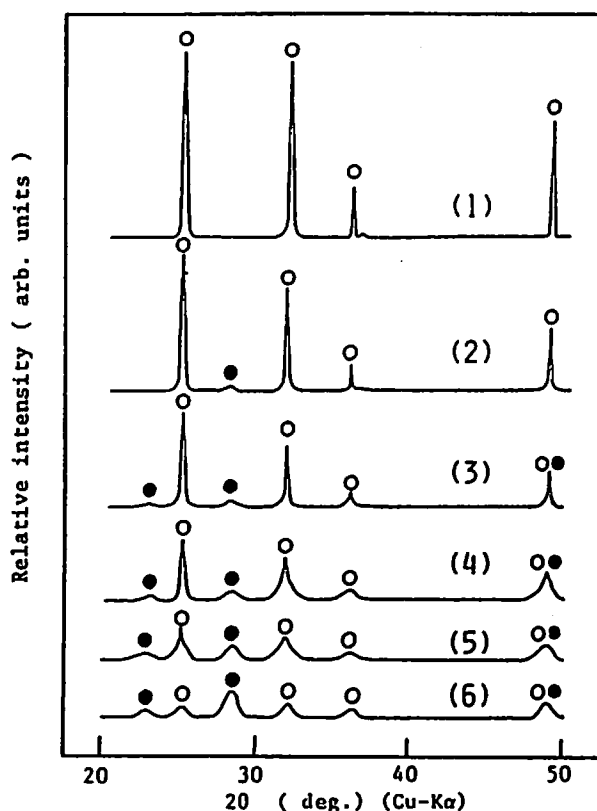


Fig. 3 Effect of milling on X-ray diffraction patterns of β - PbO_2
 Milling time; (1) 0 hr (without milling), (2) 3 hrs, (3) 12 hrs, (4) 24 hrs, (5) 50 hrs, (6) 100 hrs,
 ●; α - PbO_2 , ○; β - PbO_2

tion rate above a rotating speed of 70 rpm, although the gas evolution rate increased as the rotating speed increased up to 70 rpm.

3. Results and Discussion

3.1 Effect of milling on surface properties and thermal reactivities of lead dioxide

Fig. 1 shows the effect of milling on the mean particle diameter and the specific surface area of β - PbO_2 . Mean particle diameter markedly decreased up to a milling time of 6 hours and thereafter shows a constant value of about $0.68 \mu\text{m}$. On the other hand, specific surface area gradually increased with milling time and does not attain a maximum value. TEM images (Fig. 2) shows that though the β - PbO_2 without milling looks like a single crystal, milled β - PbO_2 consisted of opaque polycrystalline particles, which are primary particles that aggregate to form secondary particles. A large specific surface area compared with a constant particle size implies that fine primary particles formed during milling begin to have surface heterogeneity, an amorphous phase and many cracks along with grain boundaries. The electron diffraction patterns

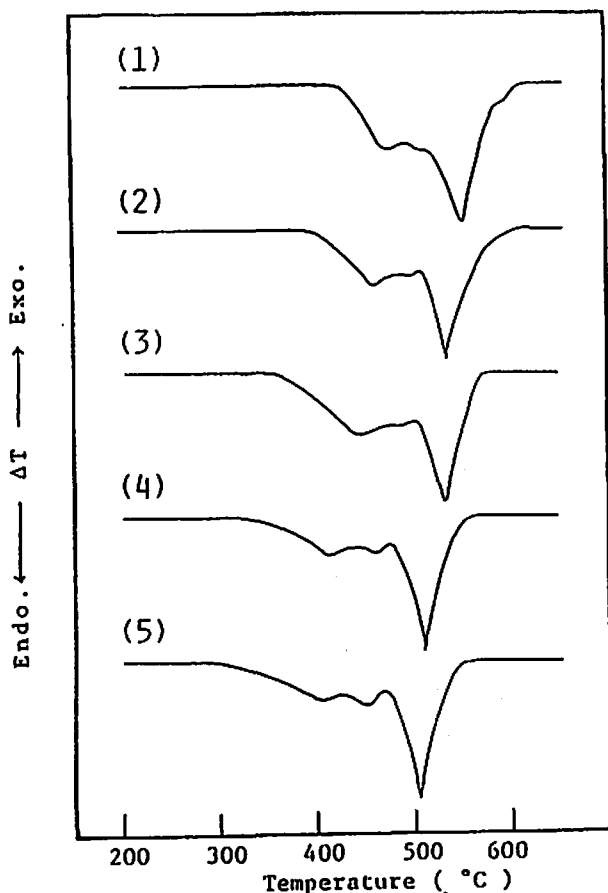


Fig. 4 DTA curves of β - PbO_2 and milled β - PbO_2 in argon milling time; (1) 0 hr, (2) 1 hr, (3) 3 hrs, (4) 12 hrs, (5) 24 hrs

in Fig. 2 showed that β - PbO_2 without milling was a single crystal but that milled β - PbO_2 had a polycrystalline or amorphous structure. This implies that mechanical energy consumed causes a structural destruction of the particle as well as subdividing.

X-ray powder diffraction data in Fig. 3 indicated that milling above 3 hours causes the formation of α - PbO_2 . By using quantitative X-ray analysis, Schrader et al. reported that 90 % of β - PbO_2 is transformed to α - PbO_2 after 80 hours of milling²⁾. Senna also reported ca. 60 % β - α transformation over 20 hours of vibro-milling⁵⁾. In this experiment, milling over a period of 12 hours caused a loss of 8 % of active oxygen and a change in the diffraction intensities, decreasing to 25 % of their initial value.

DTA curves of β - PbO_2 milled and without milling are shown in Fig. 4. The temperature at which the decomposition commenced (decomposition temperature) varied with milling time. That is, milling of β - PbO_2 over 24 hours lowered the decomposition temperature by ca. 100 °C as compared with β - PbO_2 without milling.

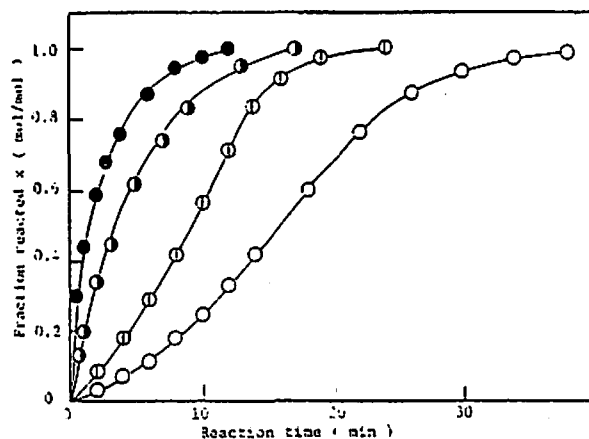
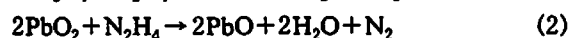
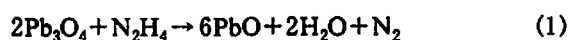


Fig. 5 Effect of milling of β - PbO_2 on its isothermal reaction with an aqueous solution of hydrazine at 10 °C
Milling time ○; 0 hr (without milling), ⊙; 1 hr, ⊕; 6 hrs, ●; 24 hrs

3.2 Reaction of lead dioxide with an aqueous solution of hydrazine

Lead oxides which contained active oxygen reacted quantitatively with an aqueous solution of hydrazine by evolving nitrogen gas. By analysing the reaction, especially the initial reaction, we proposed that the surface reactivity of lead dioxide and red lead could be estimated by their activities with aqueous hydrazine. Reactions of red lead or lead dioxide with an aqueous solution of hydrazine are described by the following chemical equations (1) and (2).



In this experiment, the amount of nitrogen gas evolved by the reaction of β - PbO_2 with an aqueous solution of hydrazine agreed well with the amount calculated from equation (2) within an experimental error of $\pm 5\%$. The extent of the reaction at any time or the fractional reaction (x) for equation (1) or (2) can be determined from the amount of evolved nitrogen gas divided by its final amount.

Fractional reaction vs. time (t) curves for the reaction of β - PbO_2 milled and without milling are shown in Fig. 5. The initial reaction rate, obtained from the reciprocal of the reaction time required to attain a given fractional reaction was found to increase with increasing milling time and corresponded well to the reactivity of the thermal decomposition, although a quantitative comparison was not made in this experiment. Figs. 6 and 7 show the fractional reaction vs. time curves for β - PbO_2 milled (12 hours) and

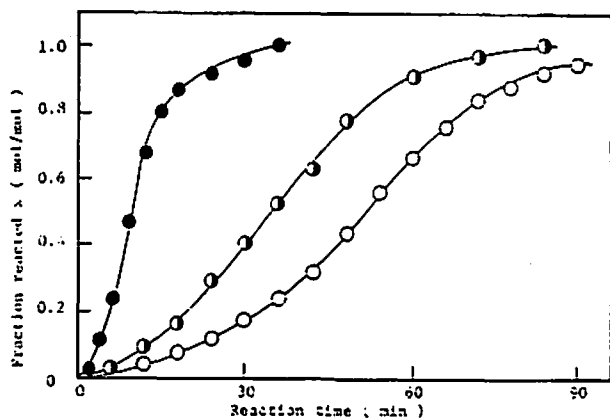


Fig. 6 Isothermal reaction of β - PbO_2 (without milling) with an aqueous solution of hydrazine
Reaction temperature \bullet ; 20°C, \circ ; 10°C, \circ ; 0°C

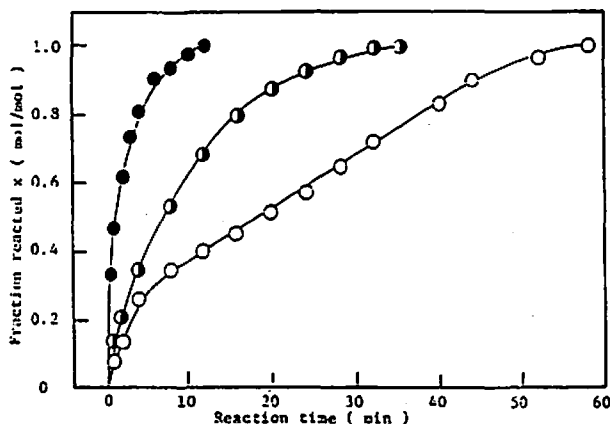


Fig. 7 Isothermal reaction of milled β - PbO_2 (12 hrs) with an aqueous solution of hydrazine
Reaction temperature \bullet ; 20°C, \circ ; 10°C, \circ ; 0°C

without milling at 0, 10 and 20 °C. β - PbO_2 without milling had a small reaction rate during the initial stage of the reaction and showed a sigmoidal shape for the x - t curves. On the other hand, milled β - PbO_2 showed a large reaction rate during the initial stages of the reaction and the reaction rate decreased linearly as the reaction proceeded.

The Avrami-Erofeev equation or autocatalytic rate equation represents well a sigmoidal type of fractional reaction vs. time curve. The results for Fig. 6 are in good agreement with the Avrami-Erofeev equation (3), as is shown in Fig. 8.

$$x = 1 - \exp(-Bt^k) \quad (3)$$

On the other hand, the results of Fig. 7, which deals with milled β - PbO_2 , fit well with a surface reaction-controlled shrinking unreacted-core model represented by equation (4).

$$kt = 1 - (1-x)^{1/3} \quad (4)$$

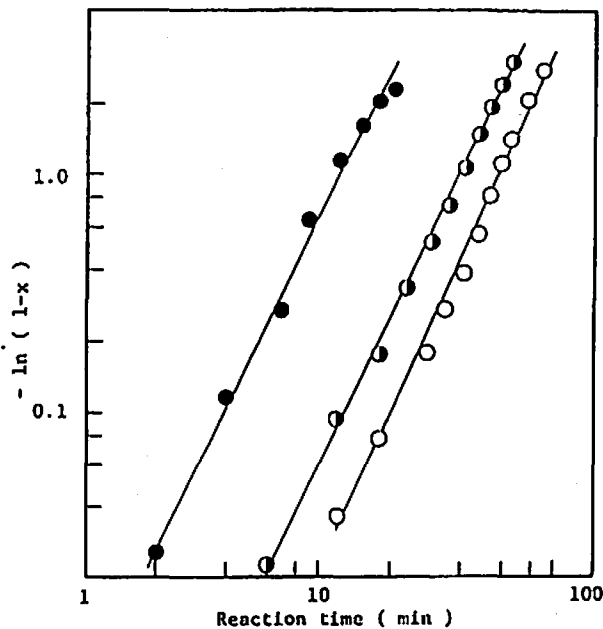


Fig. 8 Avrami-Erofeev plots for the reaction of β - PbO_2 (without milling) with an aqueous solution hydrazine
Temperature \bullet ; 20°C, \circ ; 10°C, \circ ; 0°C

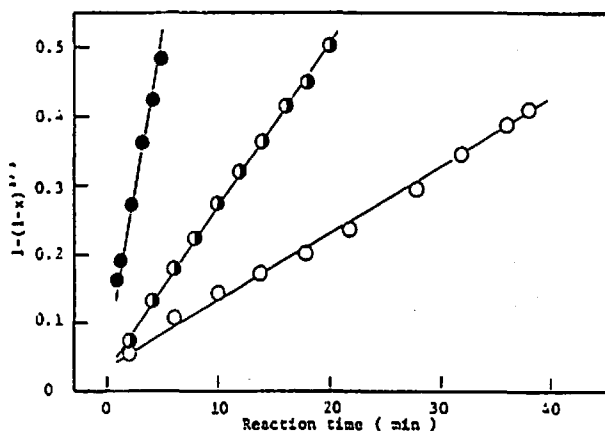


Fig. 9 Plots of a surface reaction-controlled shrinking unreacted-core model in the reaction of milled β - PbO_2 with an aqueous solution of hydrazine
Temperature \bullet ; 20°C, \circ ; 10°C, \circ ; 0°C

As previously stated, milling of lead dioxide increased surface heterogeneity such as the amorphous phase in the neighborhood of the surface and produced many cracks along with grain boundaries on the lead dioxide. Because this surface heterogeneity results in surface activation of the lead oxide, both its thermal reactivity and reactivity with hydrazine increase with increasing milling time. It is found out from the results of Fig. 6 and Fig. 7 that the mechanisms for the reaction of lead dioxide with an aqueous solution of hydrazine differ with the milling time. This can be interpreted as follows.

From the TEM observations it was found out that β -

PbO₂ without milling was like a single crystal, while milled β -PbO₂ consisted of fine primary particle aggregating to form secondary particles. Therefore, the surface layer of milled lead dioxide has an enormous number of active sites which become germ nuclei to start the reaction. The rate determining step for the reaction with aqueous hydrazine is a surface reaction step of lead dioxide with reactant hydrazine which has diffused to the surface of the unreacted core. On the contrary, lead dioxide without milling has fewer active sites on its surface because of its cleanliness around the surface layer and this causes the nucleation step to be rate determining. Though the initial reaction being slower, a feature of the reaction of β -PbO₂ which was milled for 6 hours resembled to that for 12 hours. But β -PbO₂ milled for 1 hour reacted autocatalytically like as that without milling. On the other hand, β -PbO₂ milled for from 2 to 4 hours showed an intermediate reaction feature between autocatalytic and surface reaction controlled.

The thermal reaction of a pyrotechnic composition which contains metallic oxide as an oxidizer usually proceeds in the solid state because of its high melting point compared with oxysalts. Lead dioxide in pyrotechnic mixtures which are brought about in thermally induced circumstances also causes a thermal reaction with reducing agents in the solid state. Surface reactivity as will be described later has a remarkable effect on the solid state reaction, especially in the early stage of its reaction.

The solid state reaction is affected by surface reactivity, which depends upon both the intimacy of contact and surface heterogeneity of the ingredients. The former mainly depends on particle size which is generally considered as an index of the surface reactivity. The latter depends on crystallinity, disorder, oxygen deficiency, contamination, adsorbed gases, etc. in the vicinity of the surface, and also affects the reaction because of its high instability. But it is difficult to determine separately the effect of particle size or surface heterogeneity on surface reactivity.

As previously stated, vibro-milling also caused an increase in surface heterogeneity by accumulating mechanochemical energy on the surface layer in addition to an increase in surface area. Estimation of surface reactivity

of lead dioxide by the kinetic analysis of its reaction with aqueous hydrazine is an excellent method to evaluate the surface properties because this method makes it possible to estimate the total surface reactivity of lead dioxide as an oxidizer in a pyrotechnic composition. This method can be used to evaluate the effect of particle size and surface heterogeneity on surface reactivity at the same time.

4. Conclusion

The reaction rate of β -PbO₂ with an aqueous solution of hydrazine is affected by its surface reactivity. Kinetic analysis shows that when β -PbO₂ that has not been milled is used, the Avrami-Erofeev equation can well represent a sigmoidal type of fractional reaction vs. time curves. When β -PbO₂ is milled a diffusion-controlled shrinking unreacted-core model is in good agreement with the experimental results.

When β -PbO₂ is vibro-milled, mechanical energy is partly used for reducing particle size and partly for accumulation in the surface layer which results in an increase in surface heterogeneity. Surface heterogeneity results in production of many germ nuclei of the reaction of β -PbO₂ with aqueous hydrazine solution. In this case, vibro-milled β -PbO₂, which has many reaction nuclei on its surface reacts with aqueous hydrazine shrinking from the surface to the core. On the other hand, β -PbO₂ without milling shows a small reaction rate in the initial state of the reaction because of a scarcity of germ nuclei to start the reaction.

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二酸化鉛の反応性に及ぼす粉碎の影響

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市販の二酸化鉛を粉碎して、表面物性の異なる種々の試料を調製した。この試料について、表面物性、熱分解およびヒドラジン水溶液との反応などについての検討から、以下の結論を得た。

二酸化鉛はヒドラジン水溶液と反応すると、窒素を発生しながら分解する。β型の二酸化鉛とヒドラジン水溶液との反応の速度はその表面物性により影響された。速度解析から、粉碎しない二酸化鉛の反応性はAvrami-Erofeev式に従って起こり、反応率-時間曲線はS字型を示した。一方、粉碎した試料では初期に高い反応活性を示し、表面反応律速の未反応核モデルに良く適合した。以上の結果とβ型の二酸化鉛の表面活性の相関について議論した。

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