研究論文

Sensitivities of zirconium and its mixture with lead dioxide

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1 Introduction

Zirconium (designated as Zr) when mixed with an oxidizer has been utilized as a fuel igniter, etc., of pyrotechnic devices because of its high reactivity and heat of reaction. However, as a mixture or even as a powder, many accidents involving spontaneous ignition and explosions, etc., have been reported during the treatment of pulverizing, drying, sieving, weighing, mixing and so on[1]. Especially, it is well known to have a high sensitivity for friction and static electricity[2].

In this study, the sensitivities of the zirconium powder and its mixtures with lead dioxide (PbO_2) were evaluated using thermal analysis, an ignition sensitivity test, an electrostatic sensitivity test, a friction sensitivity test, a drop hammer test, etc. Also, the effect of drying conditions on the sensitivities was also discussed.

2 Experimental

2.1. Materials

The sample of zirconium (Zr) was obtained from a commercial supplier while stored in water. This was dried under two different conditions. One was at 25℃ for 24 hours in an argon atmosphere and designated as Zr (1) which had a mean particle diameter of 0.61 μm. The other designated as Zr (2) was treated under 100 ℃ for 2 hours in air and had the same particle size.

Lead dioxide having a β shaped crystal structure was obtained from a commercial supplier. It had an mean particle diameter of 0.78 μm and its content was determined to be 97.5 wt% based on its active oxygen.

After weighing, the zirconium and lead dioxide by passing them through a sieve (total weight is under 100 mg) were carefully mixed in a dry box equipped with a protective board to avoid any blast and combustion products projectiles caused by an unexpected explosion. The compositions of the mixtures were determined based on the following stoichiometric reaction equation (1).

$$Zr + PbO_2 \rightarrow Pb + ZrO_2 \qquad (1)$$

The prepared mixtures have the compositions of zirconium/lead dioxide = 16/84 by weight (1/2 by mole), 28/72 (equimolar, stoichiometric composition), 43/57 (2/1), 53/47 (3/1) and 60/40 (4/1).

2.2. Analysis of surface properties

The particle morphology was observed using a Nippon Denshi Scanning Electron Microscope, JSM-2. X-ray photoelectron spectroscopy (ESCA) was performed with a Nippon Denshi ESCA JPS-90S.

2.3. Thermal analysis

Thermal analysis was performed using a Rigaku Simultaneous DTA-TG Analyzer TAS-200, in which the sample weight was 5 mg and the heating rate was 20℃/min. under air or argon. Moreover, a handmade DTA analyzer made to be operated using an atmosphere with limited oxygen was also used in order to avoid air oxidation.

2.4. Sensitivity tests

The drop hammer test was performed using the Drop Hammer Tester from the Kuramoti Scientific Instrumentation Production Co., Ltd., according to The Japan Explosives Society Standard [3]. Friction sensitivity was measured using a BAM Friction Sensitivity Tester from the Kuramoti Scientific Instrumentation Production Co., Ltd., according to the Japanese Industry Standard JIS K 4810[4]. The electrostatic sensitivity test was carried out using an electrostatic sensitivity tester having a fixed electrode which was designated

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by the Japanese Explosives Society Standard ES-25 [5].

2.5. Ignition test

The ignition test was carried out according to the Krupp method in an atmosphere of argon. After the mixture of 100 mg was pressed at 6t /cm^2, the pellet was divided into 5 mg pieces.

3. Results and discussion

3.1. Surface properties of zirconium and lead dioxide powder

Fig.1 (a) and (b) shows the appearance of the zirconium (Zr (1)) and lead oxide powder based on a SEM photograph. The surface of the zirconium specimen was smooth and the average particle diameter was 0.61 μm consisting of particles like 0.2~5 μm based on the particle size distribution measurement. Fig.2 shows the ESCA spectra of the zirconium 3d electron (a) and oxygen 1s electron (b) for the powders of Zr (1) and Zr (2). The zirconium and oxygen were confirmed to exist on their surface. However, after etching with an argon ion beam for 10 min, the peak in the spectra ranging from 183~191 electron volts was ascribed to the oxide shifted to the lower binding energy side due to the metal itself [6]. This suggested that the surface oxide layer is not so strong, and is easily destroyed by a mechanical treatment.

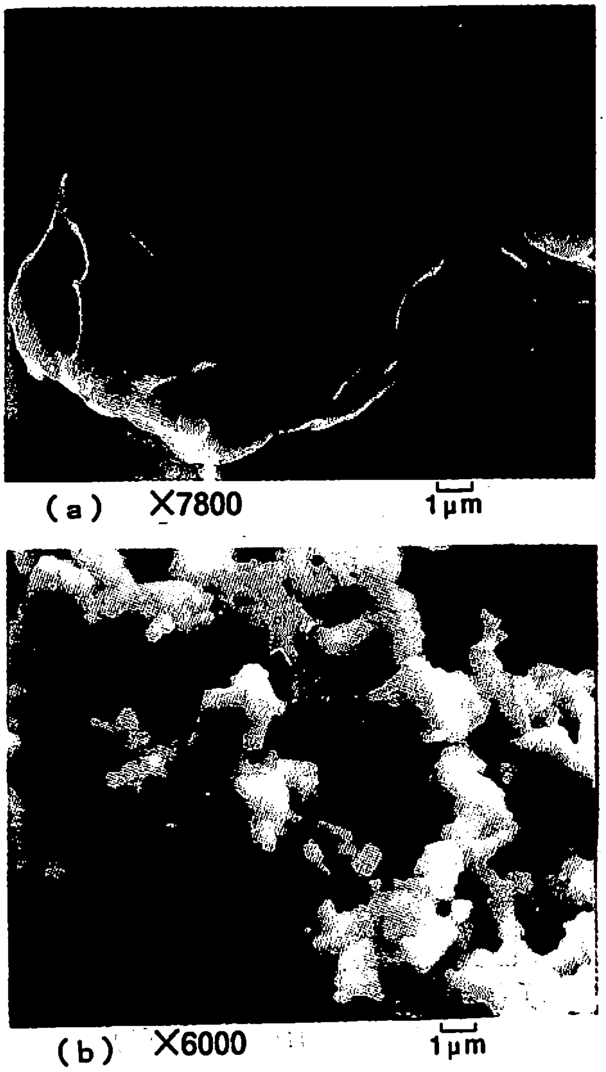

Fig.1 SEM photographs of zirconium (Zr (1))(a) and lead dioxide powder(b)

As previously stated, the lead dioxide used in this study has a β type crystalline structure. This lead dioxide looks like a single crystal (Fig.1 (b)) and has an average particle diameter of 0.78 μm and consisted of particles from 0.3~6 μm.

3.2. Thermal reaction of zirconium, lead dioxide and their mixtures

The results of the thermal analysis of zirconium and lead dioxide are shown in Fig.3. Zirconium powder was oxidized in air in the temperature range of 220 ~600℃. The oxidation of zirconium by oxygen gas is described by Eq.2.

$$Zr + O_2 \rightarrow ZrO_2 \qquad (2)$$

According to Eq. (2), a complete oxidation causes a 35.1% weight increase. However, Zr (1) showed an increase in weight of 31% based on the precise TG investigation, thus indicating that zirconium was oxidized upon drying. Zr (2) also showed a similar weight increase of 30% and had the same average particle diameter as Zr (1).

Fig.4 shows the results of the thermal analysis of the various mixtures of zirconium with lead dioxide in

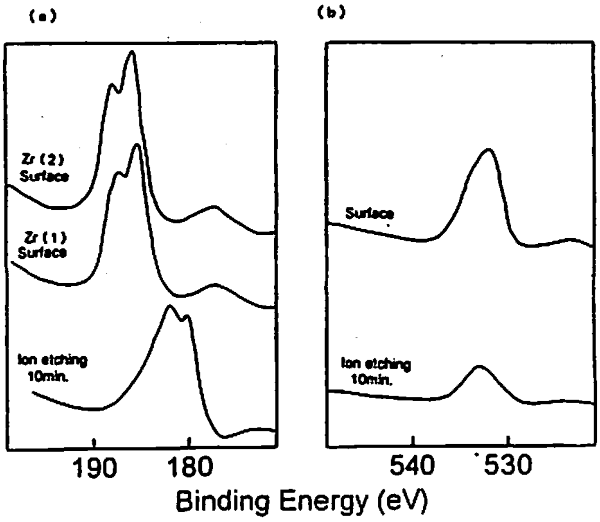

Fig.2 ESCA spectra of zirconium 3d electron (a) and oxygen 1s electrons.

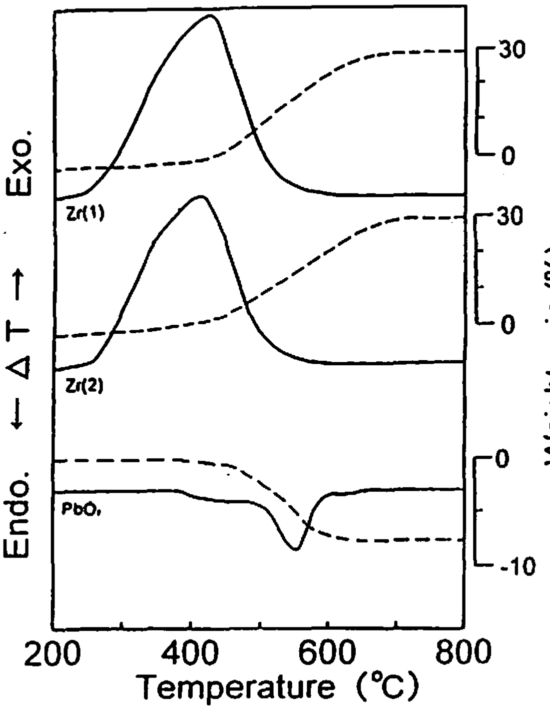

Fig. 3 Thermal analysis of zirconium and lead dioxide in air

air. All the mixtures caused an exothermic reaction in the temperature range from 230 to 650℃. As the decomposition of lead dioxide commenced at 370 ℃, it can be concluded that oxygen in the air also reacted. That is, zirconium in the mixture was oxidized by oxygen in the gas phase or absorbed on the metal surface during the course of the reaction. In contrast to air, the results at reduced pressure below 0.1 Torr obtained using the handmade apparatus showed a violent exothermic reaction as traced in Fig.5 for Zr (1) and in Fig 6 for Zr (2). This is interpreted as follows. In the case of the experiments in air, zirconium in the mixture was gradually oxidized before its reaction with lead dioxide and made the oxidized layer. This oxidized layer acted as a resistance to the oxidation reaction by lead dioxide. On the other hand, zirconium in an atmosphere free of oxygen was scarcely oxidized before the reaction which caused a violent reaction at the temperature where the decomposition of lead dioxide once commenced. Moreover, comparing Zr (1) and Zr (2), Zr (1) had a higher reactivity than Zr (2) thus causing an exothermic reaction at the somewhat lower temperature of 21 ~34 ℃.

3.4. Sensitivities of zirconium and its mixture with lead dioxide

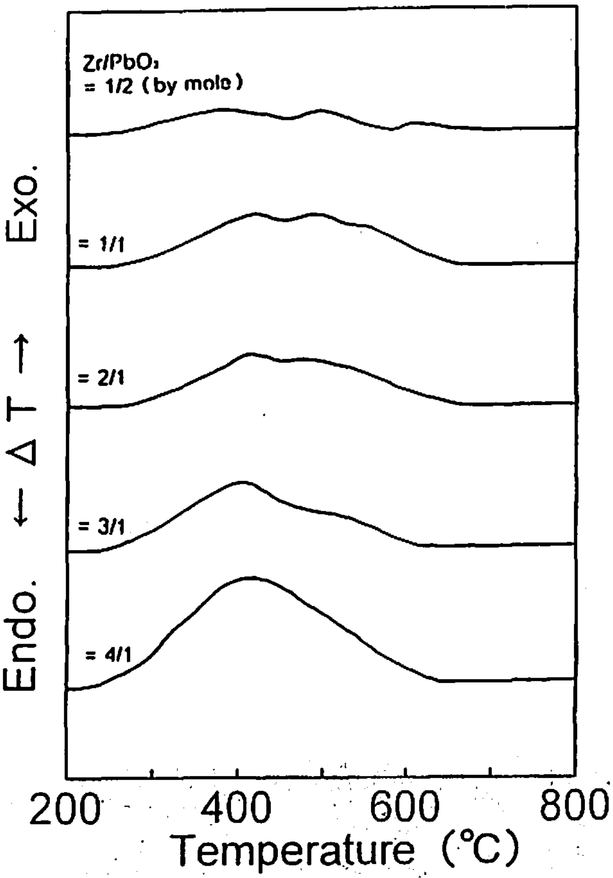

Fig. 4 Thermal analysis of the mixtures of zirconium with lead oxide in air

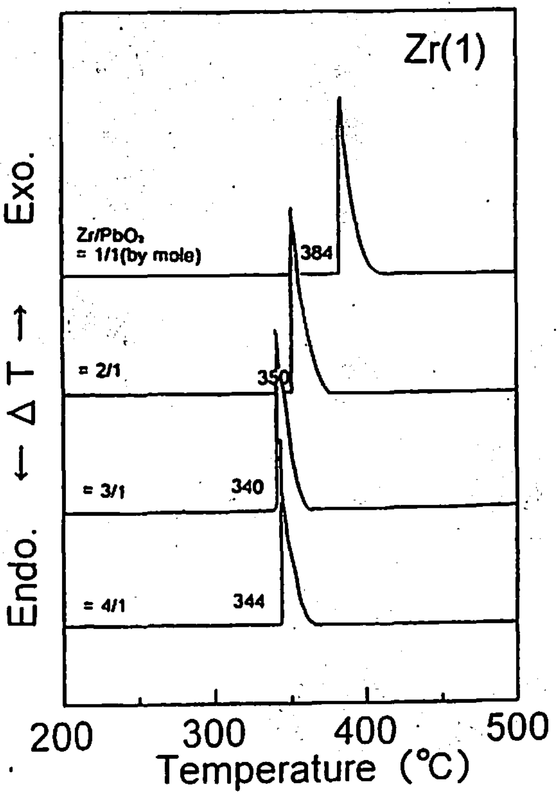

Fig. 5 DTA analysis of the mixtures of zirconium (Zr (1)) with lead dioxide under reduced pressure below 0.1 Torr

Every composition of zirconium and lead dioxide mixture violently exploded accompanied by a loud explosive sound in the friction sensitivity test. The results of the friction sensitivity test for the mixture of zirconium with lead dioxide are shown in Fig.7. The vertical axis is the load which causes one firing among 6 trials of the test. For Zr (1), the mixture of Zr/PbO_2 = 53/47 gave the most sensitive value of 0.6 kgf which corresponded to that of the primary explosive diazodinitrophenol (DDNP). Though the stoichiomeric composition contained 28% zirconium, the maximum sensitivity corresponded to a fuel rich composition and the sensitivity had a tendency to increase as the proportion of zirconium increased. In the case of the thermal reactivity, Zr (1) had a higher reactivity than Zr (2). With regard to the friction sensitivity, the mixture of Zr (1) was more sensitive than that of Zr (2) for all the compositions.

Zirconium itself was insensitive in the friction sensitivity test. However, the electrostatic sensitivity test, not only the mixture but also zirconium metal itself caused a firing because of the oxidation with the oxygen in air. Zr (1) and its mixture also showed the higher sensitivity compared to Zr (2) for the electrostatic sensitivity test using zirconium metal and the mixtures. Fig.8 shows the relation between the composition and the ignition energy which caused one firing during two trials (50% ignition energy) of the test.

The electrostatic sensitivity of zirconium and its mixture has a characteristic feature with regard to the composition. That is, the larger the zirconium content, the more sensitive the mixture, and the maximum sensitivity was obtained for the zirconium metal. There was a slight difference between the electrostatic sensitivity and the friction sensitivity. This is because oxygen in the air participated in the former different from that in the latter.

The drop hammer test was carried out for the mixture which contained Zr (1) and Zr (2). However, all the compositions caused a misfiring. Therefore, these compositions were concluded to be stable against an impact.

3.5 Ignitability of zirconium and its mixture with lead dioxide

The results of the ignition delay test were in good agreement with the following Arrhenius type equation (3).

$$\ln \tau = Ea/RT + C \qquad (3)$$

where τ is the ignition delay time and Ea is the parameter of the temperature dependence of ignition delay or the activation energy for ignition.

Table 1 shows the lowest ignition temperature (T_L) and the activation energy for the ignition of zirconium

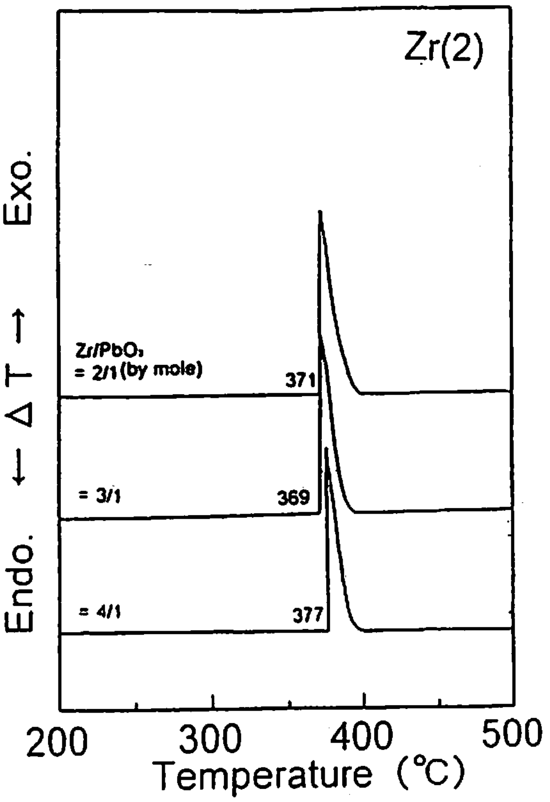

Fig. 6 DTA analysis of the mixtures of zirconium (Zr (2)) with lead dioxide under reduced pressure below 0.1 Torr

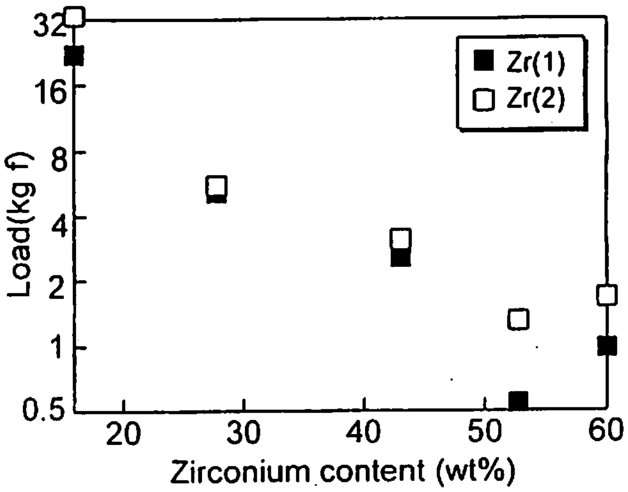

Fig. 7 Friction sensitivity test for the mixture of zirconium with lead dioxide

Table 1 The lowest ignition temperature (T_L) and the activation energy for the ignition of zirconium and its mixture with lead dioxide

Zr/PbO_2	T_L(℃) Zr(1)	Zr(2)	Ea (kJ / mol) Zr(1)	Zr(2)
16 / 84	340	360	44.6	62.3
16 / 84	300	320	44.3	59.9
16 / 84	299	310	41.6	53.2
16 / 84	310	305	41.7	56.7
16 / 84	290	300	41.7	53.7
100 / 0	285	295	41.1	51.4

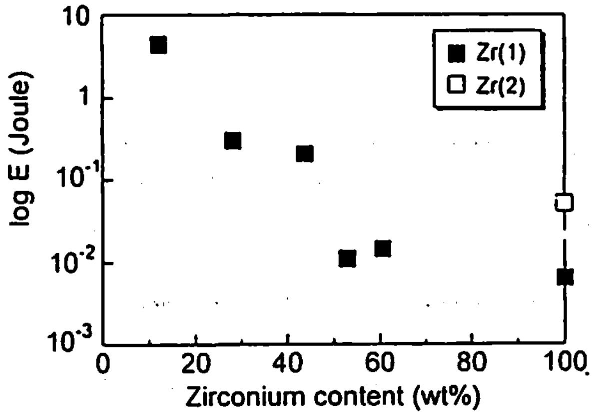

Fig. 8 The relation between the composition and the ignition energy which caused a 50% ignition

and its mixture with lead dioxide. Ignitability showed the same tendency as the electrostatic sensitivity, and zirconium metal had the lowest minimum ignition temperature and activation energy for ignition. Moreover, Zr (1) and its mixture also showed the higher ignitability and a smaller activation energy for ignition.

4. Conclusion

The surface of the zirconium powder was covered by a thin oxide layer and its reactivity differed from the conditions of dehydration. The mixture of zirconium with lead dioxide caused an intense exothermic reaction under reduced pressure.

Friction sensitivity and electrostatic sensitivity are affected by the surface properties and the composition of the mixtures, and the higher the zirconium content, the more sensitive they become. The mixtures of zirconium with lead dioxide misfired in the drop hammer test.

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ジルコニウムおよびその二酸化鉛混合物の各種感度

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乾燥方法の異なるジルコニウムを用いて，ジルコニウムおよびその二酸化鉛との混合物の各種感度を，表面分析，熱分析，発火待ち試験，落つい感度試験，摩擦感度試験，静電気感度試験などを行って検討し，以下の結果が得られれた。

ジルコニウム表面は薄い酸化物層に覆われ，その反応性は乾燥方法によって異なった。ジルコニウムの二酸化鉛との混合物は，空気中では緩慢な酸化反応を起こすが，減圧下では激しい発熱反応を起こした。

ジルコニウムの二酸化鉛との混合物は静電気や摩擦には高い感度を示し，混合物中のジルコニウム量が多いと高い感度を示した。また，混合物のこれらの感度はジルコニウムの活性によって異なった。しかし，この混合物は落つい感度試験では不爆であった。

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