The effect of relative humidity on aging of zirconium-based energetic materials

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1 Introduction

High energy metal particles have been extensively used in standard initiators for producing hot particles to ignite other, more difficult-to-ignite materials. Zirconium (Zr) is highly reactive and thus requires great care during fabrication and storage. The chemical structure of Zr may change due to its contact with ambient moisture or oxygen during fabrication, and problems may arise during long storage. As a result, such problems cause abnormal behaviors namely decreased ignition delay time, change in activation energy, and reduction in heat of reaction [1]. There are various aging factors such as temperature, humidity, and vibration that are responsible for these behaviors. Previous studies have elucidated the cause and effects of aging by forming several accelerated aging environments [2].

In this study, naturally aged zirconium (Zr) and iron oxide (Fe₂O₃) compound, and zirconium-nickel (Zr-Ni) and potassium perchlorate (KClO₄) compound were prepared to analyze the effect of natural aging on performance behavior. Reaction kinetics were investigated using differential scanning calorimetry (DSC) and thermos-gravimetric analysis (TGA). Chemical composition changes with aging were determined using x-ray photoelectron spectroscopy (XPS). Additionally, transmission electron microscopy with energy dispersive x-ray spectroscopy (TEM-EDS) and scanning electron microscope (SEM) experiments were conducted to analyze the surface of Zr and Zr-Ni materials. Furthermore, on-going ignition delay time experiments related to aging effects is proposed.

2 Experiments and Results

2.1 Sample preparation

Three types of samples are prepared for each Zr/Fe_2O_3 and $Zr-Ni/KClO_4$ composition, to study the aging effect. The first group is pristine samples (#1, #4), the second group is 8-years naturally aged samples (#2, #5), and the last group is 8-weeks thermal aged samples at 0% RH (#3, #6). For 8-years naturally aged samples, temperature and humidity would have changed depending on the season. The prepared samples are shown in Table 1.

Туре	Sample – No.	Aging condition		
		Temperature [°C]	Relative Humidity	Aging duration
Zr/ Fe ₂ O ₃	#1	-	-	-
	#2	Seasonal	Seasonal	8 years (natural)
	#3	91 °C	0 %	8 weeks (thermal)
Zr-Ni/ KClO4	#4	-	-	-
	#5	Seasonal	Seasonal	8 years (natural)
	#6	91 °C	0 %	8 weeks (thermal)

Table. 1. Samples prepared for Zr/Fe₂O₃ and Zr-Ni/KClO₄ for aging study

2.2 Calorimetry and Gravimetry for reaction kinetics

Experimental results combining DSC and TGA show the reaction kinetics of each sample. Fig. 1 shows the results of DSC and TGA tests of non-aged samples (#1, #4). The reaction between Zr and Fe₂O₃ is known to be an exothermic reaction that forms ZrO₂ and Fe as reaction products. In this experiment, DSC results indicate two exothermic reactions. The first small exothermic reaction is attributed to initial oxidation process of Zr forming intermediate phase of α -Zr at about 388 °C, and a subsequent large heat generation part is related to oxidation of α -Zr to form ZrO₂. The results also show a good agreement between the temperature region where heat release begins and region where mass starts to increase in TGA plot. This result agrees quite well with calorimetry result of Zr reaction with oxygen [3].

The chemical reaction between Zr-Ni and KClO₄ is exothermic (Fig. 1(b), which forms ZrO_2 and NiO as reaction products, and KClO₄ is decomposed into KCl [4]. It starts to react at about 354 °C and further increases its mass forming oxides. At 474 °C, KClO₄, which does not participate in the reaction until this, now undergoes decomposition.

In conclusion, from the reaction kinetics, the performance of Zr/Fe_2O_3 and $Zr-Ni/KClO_4$ is mostly affected by Zr and Zr-Ni contents, which are main energy sources. The reduction of oxidizer is also another important factor, which can cause the deficiency of oxygen.



Fig. 1. Calorimetry and Gravimetry result for (a) pristine Zr/Fe₂O₃ sample (#1), (b) pristine Zr-Ni/KClO₄ sample (#4).

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2.3 XPS analysis for chemical composition change by aging

The XPS experiment is performed to verify the chemical composition change due to aging. The results are shown in Fig. 2. In Zr/Fe_2O_3 case, only ZrO_2 bonds are detected, and the intensity of ZrO_2 is more with 8 years naturally aged sample (#2). In thermal accelerated aged sample (#3), the increase of ZrO_2 is not critical than #2 sample, which indicates that moisture significantly influences the formation of ZrO_2 . Lglesias F.C. et al. have reported that ZrO_2 can be formed due to reaction with water at ambient temperatures [5]. This indicates that even at low temperatures, moisture can dissociate and immediately cause Zr oxidation, since Zr metal is highly reactive. Therefore, the reaction of ZrO_2 with moisture can be expressed as follows.

 $Zr+xH_2O \rightarrow ZrOx+xH_2 (0 < x \leq 2)$

The Fe₂O₃ level decreases in accelerated aged sample as well, but shows large decrease with 8 years naturally aged sample, which also indicates that moisture is important in the decomposition of Fe₂O₃. The crystal plane (0001) of Fe₂O₃ is highly susceptible to moisture, thus it accepts water molecule and changes into Fe₃O₄ [6]. The Fe₃O₄ reacts with hydrogen from dissociation of water, and becomes Fe and H₂O. The Fe is apt to bind with oxygen in the atmosphere due to its excellent reactivity, and forms FeO immediately. This is explained by the following process of Fe₂O₃ decomposition with moisture.

0001 surface of Fe₂O₃+H₂O \rightarrow Fe₃O₄

 $Fe_3O_4+4H_2 \rightarrow 3Fe+4H_2O$

 $2Fe+O_2 \rightarrow 2FeO$

In Zr-Ni/KClO₄ compound, ZrO₂ and NiO, which are chemical reaction products, are significant with 8 years naturally aged samples as shown in Fig. 2(c). This is also explained by direct effect of water on Zr and Ni. However, the effect of moisture on KClO₄ differs from Fe₂O₃. The KClO₄ and decomposed form of KClO₃ and KCl are likely to react with water to form an aqueous solution containing K⁺ and Cl⁺. At the same time, Cl⁻ acts on the surface of Zr-Ni to promote pitting corrosion [7]. If the surface is corroded and cracked, oxidation occurs more easily with external moisture and oxygen. In addition, cracked surfaces facilitate penetration of moisture and oxygen, which depletes the reactivity by forming oxide layers further deep inside the materials.

KClO₄, KClO₃, KCl + H₂O_{atmosphere} \rightarrow K⁺+Cl⁻ aqueous moiture

K⁺+Cl⁻ aqueous moiture on Zr-Ni surface \rightarrow pitting corrosion, crack and physical demolish.

As a result, the effect of natural aging is dominated more by moisture rather than temperature. The Zr/Fe_2O_3 and $Zr-Ni/KClO_4$ samples that are exposed to moisture for a long period of time forms products, such as ZrO_2 /Fe and ZrO_2 -NiO/KCl, respectively. These products are same species as chemical reaction products.



Fig. 2. XPS results confirming the chemical composition changes of #1 to #6 samples. (a) Zr, (b) Fe₂O₃ for Zr/Fe₂O₃, and (c) Zr-Ni, (d) KClO₄ for Zr-Ni/KClO₄

2.4 Surface analysis of Zr/Fe₂O₃ and Zr-Ni/KClO₄ using TEM-EDS and SEM-EDS

TEM-EDS and SEM-EDS image analysis are performed to corroborate the aging process as suggested above. TEM-EDS results on Zr surface of Zr/Fe₂O₃ compound are shown in Fig. 3. The FFT crystal structure shows that Zr layer is composed of Zr ('A' layer), α -Zr ('B' layer), m-ZrO₂ ('C' layer) and oxygen layer ('D' layer). The α -Zr layer is considerably large in 8 weeks thermal aged samples (#3). On the other hand, the m-ZrO₂ layer formation and growth of α -Zr layer and oxide layer in naturally aged sample are critical. The order of laminated layer, from the outermost: Zr— α -Zr—m-ZrO₂, is the most stable layer and m-ZrO₂ is the most thermally stable phase. The oxygen diffusion depth is deepest in sample #2 because moisture also facilitated oxygen penetration by reducing the surface density. Therefore, natural aging by moisture changes Zr to the most stable phase, and at the same time, oxygen penetrates deeply to lower its reactivity.

Natural aging of zirconium-based energetic material



Fig. 3. The results of Zr surface TEM-EDS analysis of Zr/Fe₂O₃ mixture. (a) Non-aged sample (#1), (b) 8 years naturally aged sample (#2), and (c) 8 weeks thermal aged sample (#3). The letter 'A~D' means Zr ('A' layer), α-Zr ('B' layer), m-ZrO₂ ('C' layer) and oxygen layer ('D' layer).

The Zr-Ni surface is observed by SEM analysis to confirm the aging effects on the Zr-Ni surface. The EDS results indicate that the marked surface in Fig. 4 is Zr-Ni surface. The non-aged sample (#4) shows a smooth Zr-Ni surface as shown on the left in Fig. 4, while a naturally aged sample (#5) on the right indicates a surface with rusty appearance due to surface corrosion caused by Cl⁻ solution as described in the above section. The small particles on the surface are agglomerated form of Zr-Ni particles as a result of corrosion. Therefore, SEM results in Fig. 4 further illustrates the aging process as proposed before.



Fig. 4. Zr-Ni/KClO₄ surface of Non-aged sample (#4) (left), 8-year naturally aged sample surface (right). The square box is the part where the composition analysis was performed by EDS to confirm that it is Zr-Ni surface.

3 Conclusion

Among various known factors of aging, moisture is the most important factor to deteriorate the performance of Zr/Fe₂O₃ and Zr/KClO₄. Moisture acts on Zr/Fe₂O₃ to form the most stable Zr— α -Zr—m-ZrO₂ structure and thermally stable ZrO₂ structure. In addition, it accelerates the decomposition process of Fe₂O₃, thereby reducing the performance of oxidizing agent. Moisture acts on Zr-Ni/KClO₄, ionizing KCl to K⁺ and Cl⁻, and accelerating the pitting corrosion of Zr-Ni. As a result of this, oxidation of Zr-Ni increases and cracks are formed on the surface of Zr-Ni to facilitate penetration of oxygen. Therefore, the exposure of Zr/Fe₂O₃ and Zr/KClO₄ sample to moisture decreases the reactivity significantly. The on-going heat source ignition experiment, shown in Fig. 5, will show the effect of aging on ignition delay time, ignition duration, flame shape, Go/No-go boundary for ignition and so on.



Fig. 5. Heat source ignition experiment with the 8 years natural aged ignitor(above) pristine ignitor(below)

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