The changes of thermodynamic reactions of a NASA standard initiator due to hygrothermal aging

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1 Introduction

When energetic materials are in storage for a long period of time, their performance degradation may occur due to various factors such as oxidization, hydrolysis, chemical or structural deformations. Various studies have investigated on accelerated aging of energetic materials to obtain their aging effects and estimate the lifespan of aged samples in reduced time [1, 2]. In addition, relative humidity (RH) should be considered essentially in aging analyses to replicate the aging influences in real environments. Although propellant or explosive substances are kept hermetically sealed, during the sealing process, they cannot help exposing to external environment [3]. Furthermore, the sealing system may get degraded when the device is stored for a longer period of time. Thus, the current study involves the effect of aging on energetic materials, which varied with both RH and temperature conditions, to provide various and detailed results reflecting the actual environment.

The aging analysis is conducted for Zirconium Potassium Perchlorate (ZPP), which is utilized universally as a NASA Standard Initiator (NSI) [4]. ZPP consists of zirconium (Zr) as a fuel, potassium perchlorate ($KClO_4$) as an oxidant, and Viton b as a binder. A prior study has investigated on ZPP to reveal an extreme humidity effect on aging alone [5]. The present research utilized various RH (0, 30%, 70%, and 100%) aging conditions for ZPP samples. The authors also provide surface analysis that shows chemical variations in both fuel (Zr) and oxidants ($KClO_4$) by utilizing X-ray photoelectron spectroscopy (XPS). Moreover, the thermal analysis and reaction kinetics are extracted from differential scanning calorimetry (DSC). The extracted reaction kinetics is also utilized in simulating a trend of reaction progress for ZPP aged under various conditions. The simulation result matches well with the conducted experimental results. Thus, it can be derived that high-RH conditions induces significant performance degradation of ZPP materials.

2 Experimental details and kinetics calculations

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2.1 Materials

Simply mixed ZPP materials, a powder form, consist of 52 wt% Zr (Rockwood Lithium, ~2 μm, USA), 42 wt% $KClO_4$ (Barium & Chemical Inc., ~6 μm, USA), 5 wt% Viton b ($[-C_7H_2F_{12}-]_n$, Dupont, USA) and 1 wt% graphite. Prior to conducting the DSC experiment, each sample sifted through a 200 mesh size (75 μm) particle sieve. The utilized ZPP samples were aged at 71°C following aerospace guidelines [2], at various RH levels for different aging periods. Henceforth, each sample will be referred by labels represented in Table 1.

Table 1: Sample list and aging conditions under which ZPP samples were aged.

Sample label	Aging conditions		Utilized for XPS	Aging type
	Relative humidity	Aging duration		
0	-	-	O	Unaged
1	0%	4 months	O	Thermal
2	0%	8 months	O	Thermal
3	30%	2 weeks	O	Hygrothermal
4	30%	8 weeks	O	Hygrothermal
5	70%	2 weeks	O	Hygrothermal
6	70%	8 weeks	O	Hygrothermal
7	100%	2 weeks	O	Hygrothermal
8	100%	4 weeks	O	Hygrothermal
9	100%	6 weeks	-	Hygrothermal

2.2 XPS study

Ultra-high-vacuum (UHV) AXIS-SUPRA (Kratos, UK) was employed to measure the ZPP mixtures' chemical bonding state, relative quantification, and detailed XPS spectra. This apparatus was equipped with micro-focused monochromatic Al Kα X-ray sources (1486.6 eV) and a hemispherical analyzer (WX-600). The base pressure in sample analysis chamber and load lock chamber was less than $5*10^{-10}$, and $5*10^{-8}$ torr, respectively.

2.3 DSC study and peak deconvolution method

The DSC experiments were carried out using DSC-3+ instrument from Mettler Toledo. The materials were heated from 30 to 600 °C under slow heating rates (1, 2, 3, and 4 °C/min) and 85 ml/min flow of nitrogen atmosphere to observe the thermal reaction process. At least three replicates were performed for each sample, and required sample weight of about 2-3 mg was predicted, which can inhibit the heating rate effect. The materials were distributed evenly over the bottom of a standard 40 μL pierced aluminium pan to avoid concentrated heat inside the pan, and were sealed. To provide a reasonable kinetic analysis, DSC data were collected following the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee's recommendations [6].

The overlapping exothermic reactions can be separated into sub-reactions using the Fraser-Suzuki function, installed in Advanced Kinetics and Technology Solutions (AKTS) software program [7]. The peak deconvolution method was applied to the reaction rate-temperature relationship of ZPP samples, heated at 3°C/min, which was obtained from the kinetic analysis.

2.4 Reaction kinetics calculations based on Friedman-isoconversional method

In the present study, the activation energy was calculated by utilizing the AKTS software program. The kinetic parameters such as activation energy (E_α) and pre-exponential factor (A_α) were obtained using the Friedman-isoconversional method [8]. The current study restricted the range of reaction progress (α) between 0.2-0.8 in order to reflect a range where high accuracy of calculation is included.

3 Results

3.1 XPS-DSC analysis

Figure 1(a) represents the variation of fuel composition. In XPS results, zirconium dioxide (ZrO_2) signals (182.20 and 184.50 eV) are presented instead of Zr signal because Zr is spontaneously covered with a thin oxide layer when it is exposed to an external environment due to its reactive and sensitive characteristics [9]. The XPS result shows an increase of ZrO_2 signals in aged samples, signifying that ZPP can be affected by either oxygen in air or oxidants when it undergoes aging process. The ZrO_2 content increased rapidly with the RH level.

In the case of surface analysis of oxidant (Fig. 1(b)), a small portion of potassium chlorate ($KClO_3$) was identified even though the unaged ZPP sample composed of $KClO_4$ with high purity (≥ 99%). Therefore, the relationship between $KClO_3$ (206.50 eV) and $KClO_4$ (208.70 eV) is addressed in the present study. As Fig. 1(b) shows, the composition of $KClO_4$ also varied according to each RH condition. In thermal aged case, $KClO_4$ decomposed into $KClO_3$, while in hygrothermal aged cases, different patterns are noticed. In the case with 30% RH, no significant effect on ZPP composition is observed when compared to the unaged sample, while in cases of 70% and 100% RH, both $KClO_4$ and $KClO_3$ indicate rapid decomposition.

The difference in DSC thermograms is also clearly discerned between the unaged (Fig. 2(a)) and aged ZPP samples (Fig. 2(b)). The sample #0 consists of one endothermic peak and broad exothermic peaks. The endothermic reaction at 300°C indicates the phase transition of $KClO_4$ [1]. The exothermic reactions around 350~500°C represent combustion reaction between the fuel and oxidizer [10]. Meanwhile, in Fig. 2(b), the sample #9 shows a new exothermic peak around 500°C. This reaction results from the hygrothermal aging effect, which causes an increased amount of ZrO_2 that cannot function as a reducing agent. Thus, the decomposition of remaining $KClO_4$ [1] in sample #9 is represented as this peak by DSC thermograms.

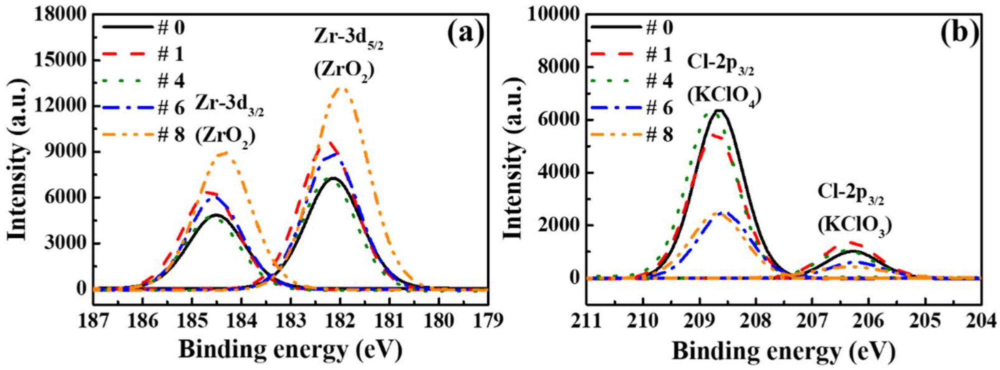

Figure 1. XPS results of ZPP samples: (a) fuel (Zr), and (b) oxidants.

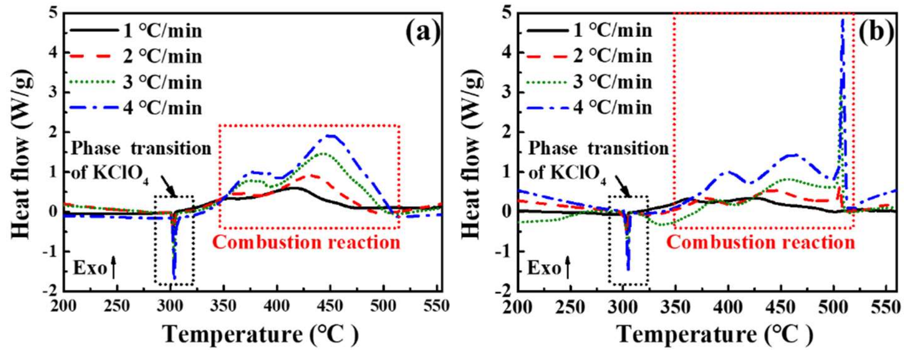

Figure 2. DSC results of ZPP samples: (a) unaged ZPP (sample #0) and (b) hygrothermally aged ZPP (sample #9).

3.2 Peak deconvolution analysis on the basis of DSC thermograms

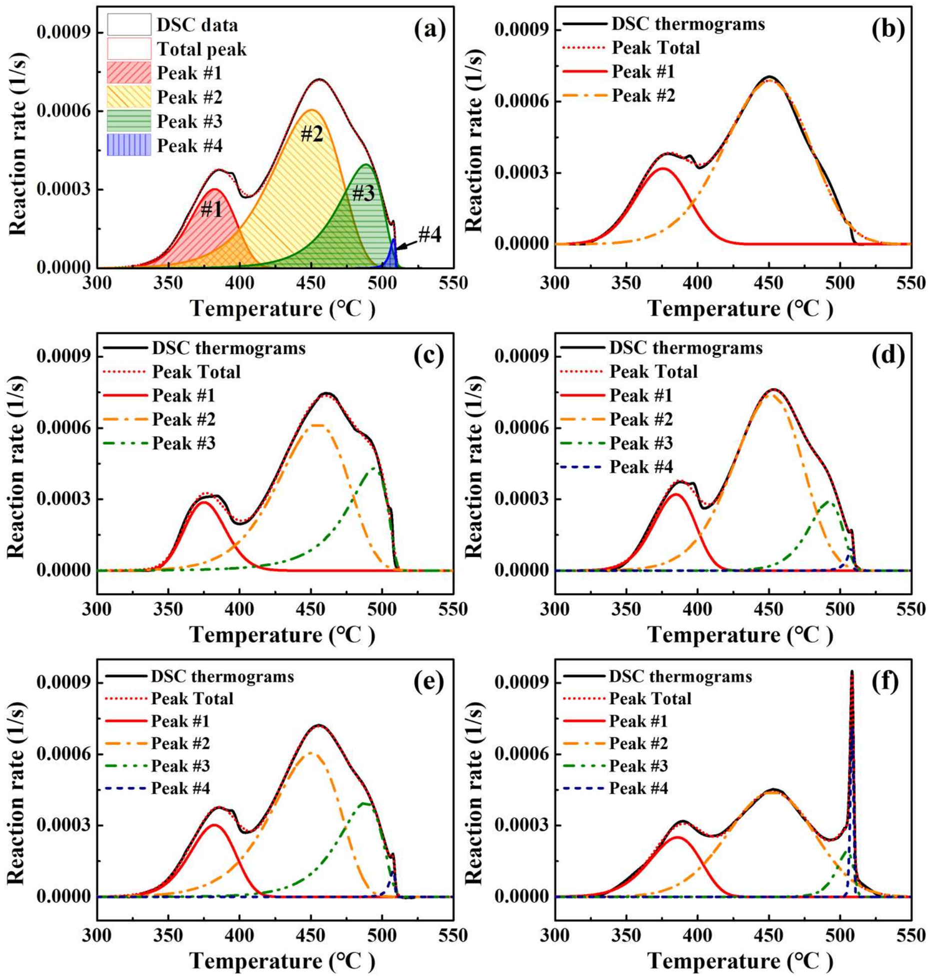

Figure 3. Peak deconvolution results of ZPP samples: (a) an illustration of overall reaction composition, (b) unaged, (c) thermal aging (0% RH), (d) 30% RH condition, (e) 70% RH condition, and (f) 100% RH condition.

To examine the detailed aging effects on exothermic reactions, peak deconvolution analysis is performed. Based on previous studies, the whole combustion reaction of ZPP is considered to be comprised of four sub-reactions [1, 10, 11], namely combustion reactions among Viton b, Zr, $KClO_3$ and $KClO_4$ (Peak 1), combustion reactions among Zr, $KClO_3$ and $KClO_4$ (Peak 2), $KClO_3$ decomposition reaction (Peak 3), and $KClO_4$ decomposition reaction (Peak 4) as shown in Fig. 3(a). Figure 3 shows the results for unaged, thermal and hygrothermal aged cases. The thermal aged case consists of three exothermic reactions (Peaks 1, 2 and 3). Among these reactions, $KClO_3$ decomposition (Peak 3) stood out in comparison with sample #0. This result concurs with the XPS result (Fig. 1(b)). In Figs. 3(d-f), all four exothermic reactions are noticed and composes the combustion process of hygrothermally aged ZPP. Figures 3(d) and 3(e), ZPPs aged under 30% and 70% RH conditions, show results nearly analogous to the thermal aged case. With 100% RH condition, however, it is remarkably different. Here, the remaining $KClO_4$ decomposition, as a result of considerably increased ZrO_2 content, is particularly magnified.

3.3 Reaction kinetics based on Friedman-isoconversional analysis and simulation of the ZPP reaction progress

Figure 4(a) shows both the heat of reaction (ΔH) with errors, range of E_α and an average E_α value for all ZPP samples. The ΔH decreased as the aging period increased while E_α indicated an opposite trend. Even though hygrothermally aging was applied to ZPP samples for only a few weeks, the reaction enthalpy values are similar to those of thermal aging cases. Thus, it is fairly likely that the RH level leads to a significant decrease in the heat of reaction. E_α of samples aged under low-RH condition for a longer period decreased continually. As can be seen in Fig. 1(b), this can be attributed to $KClO_3$, an intermediate reaction product, which is more reactive and sensitive than $KClO_4$ [12]. Under high-RH conditions (Samples #5-9), E_α tends to increase with each RH level. The increasing trend can be derived from aging effect, namely the growth of ZrO_2, which is in a stable state resulting from the insensitive ZPP.

Figure 4(b) shows the reaction progress from unreacted ($\alpha = 0$) to completely reacted ($\alpha = 1$) cases, calculated based on the kinetic parameters obtained from DSC experiments. The Arrhenius equation that is solved for various aging cases can be represented as,

$$\frac{d\alpha}{dt} = A_\alpha \exp(-\frac{E_\alpha}{RT_\alpha}) \quad (1)$$

where R, T_α are the universal gas constant and temperature (K) at the corresponding α, respectively.

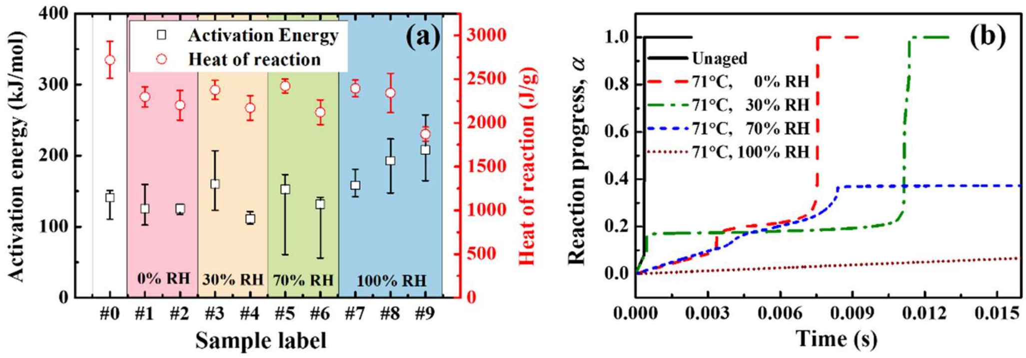

Figure 4. (a) Variation in activation energy values and heats of reaction for various aging types, and (b) the calculated reaction of each representative ZPP samples for each aging type.

In this simulation of constant volume reaction for ZPP, specific heat and density under constant pressure are taken as 250 J/kg-K and 4600 kg/m^3, respectively. The samples are ensured to ignite promptly at 1100 K, a preheated value, and observed to progress into a complete reaction. As represented, a more delayed conversion rate is observed at extreme hygrothermal aged samples. Especially, 70% RH condition caused a misfire or incomplete reactions at about 35% conversion, and 100% RH case failed to react.

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