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# A Combined Study of TEM-EDS/XPS and Molecular Modeling on the Aging of THPP, ZPP, and BKNO<sub>3</sub> Explosive Charges in PMDs under Accelerated Aging Conditions

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**Abstract:** The aging mechanism of explosive charges in pyrotechnic mechanical devices (PMDs) is pre-oxidations of their fuels (TiH<sub>2</sub> for THPP, Zr for ZPP, and B for BKNO<sub>3</sub>) by external oxygen. The effect of water on the aging of explosive charges was thus investigated by TEM-EDS/XPS and DFT-based molecular modeling under accelerated aging with 71 °C and 100% relative humidity. The formation of oxide shell and its thickness on the surface of fuels by the aging were observed by TEM-EDS. It failed to detect any oxide on the surface of TiH<sub>2</sub> (no sign of Ti-O peaks in XPS) regardless of the aging time, while the thickness of oxide shell increases linearly with the time for ZPP and is saturated at a certain point for BKNO<sub>3</sub>. It suggested that THPP is highly robust to aging compared to the others (the order of THPP >> BKNO<sub>3</sub> > ZPP). Then, DFT-based vacuum slab calculations visualized the diffusion of oxygen from the surface of fuels into the interior, confirming that the activation barrier for the oxygen diffusion is much lower for Zr and B than TiH<sub>2</sub> (37, 107, and 512 kcal/mol for Zr, B, and TiH<sub>2</sub>, respectively), in agreement with experimental results.

**Keywords:** aging; Pyrotechnic Mechanical Devices (PMDs); Vacuum Slab Calculation; Titanium Hydride Potassium Perchlorate (THPP); Zirconium Potassium Perchlorate (ZPP); Boron Potassium Nitrate (BKNO<sub>3</sub>)

# 1. Introduction

Pyrotechnic mechanical devices (PMDs) convert the explosive power (or pressure) of explosive charges into mechanical force to ignite the serial explosion of the bomb or rocket [1]. The three primary explosive charges used in fields are boron potassium nitrate (BKNO<sub>3</sub>), zirconium potassium perchlorate (ZPP), and titanium hydride potassium perchlorate (THPP) [2–4]. However, the aging of those explosive charges has rarely been studied intensively, although it significantly affects the long-term performance (or stability) of PMDs [5,6].

Recently, we have studied how the aging of BKNO<sub>3</sub> and ZPP is affected by internal and external factors [7,8]. It turned out that internal factors such as spontaneous pre-reactions have no effect, but pre-oxidations of fuels (B and Zr) by external oxygen source is the key aging mechanism of



explosive charges. According to AKTS (advanced kinetics and technology solutions) simulations, any spontaneous pre-reaction such as laminac (a polymer binder used for integrating metal and oxidizer in explosive charges) decomposition would not occur in less than 500 years even at a storage temperature of 120 °C [7,8]. Meanwhile, TEM (transmission electron microscopy)-EDS (energy dispersion spectroscopy) and XPS (X-ray photoelectron spectroscopy) studies confirmed the formation of oxide shells on the surface of fuels and their growth with time under accelerated aging conditions [7,8]. A substantial decrease of relative heat (18% and 40% for BKNO<sub>3</sub> and ZPP, respectively) was also detected by DSC (differential scanning calorimetry) measurements for 16-week aged samples under accelerated aging conditions, confirming that the aging of explosive charges is mostly affected by extra oxygen sources, such as moisture [7,8]. In addition, thermodynamic calculations of B by extra oxygen source, complied with experimental results [9,10]. However, the growth of oxide shells with time was different between B and Zr, suggesting that the extent of aging depends on the materials of explosive charges [7,8].

In this study, we employed the same TEM-EDS and XPS study for THPP finally to compare the extent of aging by time among three explosive charges (BKNO<sub>3</sub>, ZPP, and THPP) and proposed which one is the most robust to the aging and why. DSC measurements were used complementarily. Furthermore, DFT (density functional theory)-based computational calculations with the vacuum slab model were introduced to support our TEM-EDS/XPS studies by the calculated energetics of oxygen diffusion from the surface of fuels (TiH<sub>2</sub> for THPP, Zr for ZPP, and B for BKNO<sub>3</sub>) of explosive charges to the interior.

#### 2. Materials and Methods

#### 2.1. TEM-EDS and XPS Study under Accelerated Aging Conditions

THPP samples (30.0 wt% of TiH<sub>2</sub>, 65.0 wt% of KClO<sub>4</sub>, and 5.0 wt% of VitonB) were provided from Hanwha Corp. (Daejeon, Korea) and aged under accelerated aging conditions at 71 °C in 100% RH (relative humidity) for up to 16 weeks; for reference, BKNO<sub>3</sub> consisted of 23.7 wt% of boron, 70.7 wt% of KNO<sub>3</sub>, and 5.6 wt% Laminac and ZPP 52.0 wt% consisted of Zirconium, 43.0 wt% of KClO<sub>4</sub>, and 5 wt% of VitonB. Then, the samples for TEM-EDS studies were prepared by immersing TEM meshes into ethanol containing suspended aged TiH<sub>2</sub> particles. After being dried in air, the TEM meshes were used for TEM imaging, elemental mapping, and EDS analysis by a Titan G2 ChemiSTEM Cs probe (FEI Company, Eindhoven, The Netherlands) with an acceleration voltage of 200 kV. XPS spectra were obtained using a MultiLab 2000 with monochromated Al K $\alpha$  X-rays and a hemispherical analyzer with a pass energy of 30 eV. The THPP samples were prepared on conductive copper tape. Background subtraction was performed using a Shirley background and MonoXPS.

#### 2.2. DSC Measurements

DSC measurements were performed using a DSC 4000 (PerkinElmer, Waltham, MA, USA). The heats of reaction were measured as the samples were heated to 550  $^{\circ}$ C at a scanning rate of 2  $^{\circ}$ C/min. A slow heating rate could generate thermodynamic information with a sufficient relaxation time.

#### 2.3. DFT-Based Computational Calculation

The vacuum slab model was employed to calculate the energetics of oxygen diffusion from the surface of fuels (TiH<sub>2</sub> for THPP, Zr for ZPP, and B for BKNO<sub>3</sub>) into the interior [11,12]. The calculated activation (or kinetic) barrier was then compared to evaluate the extent of surface oxidation with time among three explosive charges. Firstly, supercells are constructed by  $2 \times 2 \times 2$  expansion from the primitive cells of fuels in literatures; simple rhombohedral B (space group R-3m), hexagonal closed packed Zr (P63/mmc), and cubic TiH<sub>2</sub> (Fm-3m) structures [13–15]. Secondly, (100) surfaces were cleaved out from the supercells and vacuum slabs were built with a sufficiently large vacuum thickness

of 5 Å to avoid any artificial effect from the upper and lower slabs [11]. Thirdly, an oxygen atom (or radical) is placed on the cleaved surface and the optimized geometry of the corresponding local minimum was located. The energy of this geometry was used as a baseline for the energetics of oxygen diffusion. In every calculation, the fractional coordinates of all the layers were fixed because the coordinate relaxation is considered to have limited effect for the comparison of the energetics and the computation time was also a factor. Finally, the energetics was constructed by moving the position of oxygen atom into the interior and calculating the corresponding energy in every step. Although extra oxygen sources, such as water, have to be decomposed into oxygen atoms (or radicals) on the surface prior to the subsequent oxygen diffusion, our concern was on the kinetics of the growth of oxide shells and thus the decomposition step was not counted here.

DFT calculations for the energetics were carried out using the CASTEP program suite in Materials Studio (Accelrys Inc., San Diego, CA, USA) [16]. The DFT exchange-correlation potential used in the calculations was the generalized gradient approximation (GGA) along with the PW91 (Perdew-Wang) functional [17]. Core and valence electron interactions were considered using on-the-fly generation (OTFG) ultrasoft pseudopotentials and a plane-wave basis set with a cutoff energy of 381 eV [18]. The tolerance for energy convergence was set to as low as  $5.0 \times 10^5$  eV/atom to speed up the calculations.

### 3. Results and Discussion

## 3.1. Oxide Shell Formation

The formation of oxide shells on the surface of  $TiH_2$  particles stored in accelerated aging conditions was monitored by TEM-EDS characterizations. However, it failed to observe any oxide layer on the surface regardless of the duration of accelerated aging conditions, completely different from B and Zr in our previous studies. Figure 1a shows the TEM-EDS result for the 8-week sample, where atomic contents were characterized across the surface of a  $TiH_2$  particle from the vacuum to the interior of the particle. There is no oxygen peak surge on the surface, unlike in B and Zr particles [7,8]. It is all the same for the pristine and 16-week aged samples, suggesting that THPP is highly robust to the aging by extra oxygen source. XPS spectra showed no trace of Ti-oxide more clearly (see Figure 1b). Only Ti-hydride peaks are present. The decrease of relative peak intensity of Ti-hydride peaks depending on the duration of accelerating aging proposes a possibility of physical surface deformation such as local metal coagulation.



**Figure 1.** TEM-EDS (**a**) and XPS (**b**) characterizations of THPP under accelerated aging conditions for 8 weeks. Unlike BKNO<sub>3</sub> and ZPP, the formation of an oxide layer on the surface was not detected, regardless of the duration of accelerated aging.

Quantitative heat analysis by using DSC measurements was carried out as well. As shown in Figure 2, there are endothermic peaks at 300 °C linked with the crystal structure change of KClO<sub>4</sub> from orthorhombic to face-centered cubic and exothermic peaks related to combustion reactions from 350 to 550 °C [19]. To consider the error in weighing highly energetic materials, relative heat released was calculated by the ratio of exothermic heat to endothermic heats; 51.9, 49.9, and 49.0 for the pristine, 8-week, and 16-week aged samples, respectively. A 6% decrease was measured for the 16-week sample, compared to 18% and 40% decreases for BKNO<sub>3</sub> and ZPP, respectively [7,8]. In accordance, the thickness of oxide shells with the duration of aging shows different behavior among explosive charges as shown in Figure 3. While the thickness of oxide shell increases linearly with the duration for Zr and is saturated at a certain point for B, there is no change for TiH<sub>2</sub>. The combination of these two results (DSC results and the thickness change of oxide shells), suggests that the aging effect is negligible in THPP compared to BKNO<sub>3</sub> and ZPP, in the order of ZPP (high) > BKNO<sub>3</sub> >> THPP (negligible).



**Figure 2.** DSC profiles of THPP under accelerated aging conditions. The relative heat released rarely changed with the duration of accelerated aging.



**Figure 3.** The thickness change of oxide shell vs. aging time. The aging effect has the order of ZPP >> BKNO<sub>3</sub> > THPP [7,8].

#### 3.2. Computational Interpretation of Oxygen Diffusion

Figure 3 shows the change of oxide shell thickness with the duration of accelerated aging for the three explosive charges. It is apparent that ZPP experiences performance degradation when exposed to water for a long time because oxygen keeps penetrating into the interior of Zr, allowing growth of oxide shells by pre-oxidation. Pre-oxidation means the pre-consumption of explosive power, leading to the decreased power of aged explosive charges [9,10]. On the contrary, THPP is superbly robust to aging. Because pre-oxidations are in the regime of kinetics, the comparison of barriers for the oxygen diffusion into the interior (in other words, activation energies for the oxygen diffusion) among the three explosive charges could give quantitative support for experimental results.

Figure 4 shows constructed vacuum slab systems. The baseline is the energy when the oxygen atom (or radical) is in the most stable surface position. At first glance, the B structure is too dense for oxygen penetration (see Figure 4c) compared to Zr and TiH<sub>2</sub>, although the chemical affinity of oxygen to B, Zr, or Ti will be counted later by calculations. Meanwhile, the Ti matrix (see Figure 4b) seems to be as spacious as that of Zr (see Figure 4a), but the presence of interstitial hydrogen atoms probably inhibits the diffusion of oxygen atoms.



**Figure 4.** Constructed vacuum slab systems (side view) and their dimensions for Zr(a),  $TiH_2(b)$ , and B (c).

Figure 5 presents the calculated energetics for the oxygen penetration into the interior of Zr, TiH<sub>2</sub>, and B. Especially, Figure 5a visualizes how the energy calculation was done according to the position of penetrating oxygen as an example. Along with the baseline position (the 1st point in Figure 5a), we detected a local minimum in the vacancy just underneath the surface (the 6th point in Figure 5a). Thus, in the journey from the baseline to the local minimum inside, the energy related to the position of penetrating oxygen increases due to the neighboring Zr atoms and decreases at a certain point down to that of the internal local minimum. The energy increases again for further penetration. The anomalous energy increase (the 7th point in Figure 5a) probably resulted from the small depth of constructed vacuum slab. Meanwhile, it is noted that the local minimum inside is quite stable for Zr, compared to TiH<sub>2</sub> and B (the 6th points in Figure 5a-c), favored by the presence of spacious vacancies in Zr matrix and the chemical affinity of oxygen to Zr. From the energetics in Figure 5, the activation energies were estimated as ~37, ~512, ~107 kcal/mol for Zr, TiH<sub>2</sub>, and B, respectively. It means that oxygen penetration into the interior is almost impossible for TiH<sub>2</sub>. The order of estimated activation energies (TiH<sub>2</sub> >> B > Zr) are consistent with the findings in Figure 3. In this calculation, the absolute accuracy of calculated values is limited due to the usage of rather simplified calculation model and scheme. But it has its rationale to compare the values calculated by the same methodology because any inaccuracy will be cancelled out in comparison.



Figure 5. Calculated energetics for oxygen penetration into the inside of Zr (a), TiH<sub>2</sub> (b), and B (c).

# 4. Conclusion

We investigated how susceptible three explosive charges (BKNO<sub>3</sub>, ZPP, and THPP) are to aging with an extra oxygen source (i.e., water). The presence of an oxide shell on the surface of THPP and its thickness change with the duration of accelerated aging were monitored by TEM-EDS, but no sign of oxide formation was detected. XPS also confirmed the presence of Ti-hydride, but without any Ti-oxide. Compared to BKNO<sub>3</sub> and ZPP in our previous studies, THPP is highly robust to aging (the order of THPP >> BKNO<sub>3</sub> > ZPP). A minor decrease of relative heat released from DSC measurements for THPP indicated the same conclusion as well.

Meanwhile, the energetics of oxygen diffusion from the surface of explosive charges into the interior were obtained by DFT-based molecular modeling using the vacuum slab model. The calculated activation barrier for oxygen diffusion is much lower for ZPP and BKNO<sub>3</sub> compared to THPP (the order of ZPP < BKNO<sub>3</sub> << THPP), suggesting that ZPP is the most susceptible to the pre-oxidation (or the aging) by an extra oxygen source.

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