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Thermodynamic Analysis on the Aging of THPP, ZPP and BKNO_3 Explosive Charges in PMDs

Kyung Min Kim ¹, Sung Il Choi ¹, Ki Heon Eom ¹, Gil Hwan Ahn ², Jong Gyu Paik ³,
Byung Tae Ryu ³, Yong Ha Kim ¹ and Yong Sun Won ^{1,*}

¹ Department of Chemical Engineering, Pukyong National University, Busan 48547, Korea; koko4846@naver.com (K.M.K.); csi515@naver.com (S.I.C.); astralmoon@naver.com (K.H.E.); yhkim@pknu.ac.kr (Y.H.K.)

² Defence R&D center, Hanwha Corporation, Daejeon 34068, Korea; gil9980@hanwha.com

³ Agency for Defense Development, Daejeon 34183, Korea; paikjg@add.re.kr (J.G.P.); btryu@add.re.kr (B.T.R.)

* Correspondence: yswon@pknu.ac.kr; Tel.: +82-51-629-6431

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Abstract: The aging of explosive charges in pyrotechnic mechanical devices (PMDs) significantly affects the reliability of their performance. Aging decreases the explosive power of explosive charges via pre-oxidation by external sources of oxygen. In this study, the flame temperature was calculated based on the amount of added oxygen source, and the effect of aging was quantified in terms of the performance of explosive charges. Three primary explosive charges (THPP, ZPP, and BKNO_3) were selected, and the explosion was assumed to have occurred in a closed adiabatic system. The flame temperature decreased with increasing oxygen addition, suggesting that the aging decreased the pressure exerted by the PMDs. The explosive power decreased in the following order: ZPP >> THPP > BKNO_3 (4100 >> 3260 > 3050 K), and it was decreased by aging as follows: ZPP >> BKNO_3 > THPP (802 >> 219 > 95 K per mole of added water). As a result, ZPP is appropriate for the generation of the huge thrust of PMDs despite its increased susceptibility to aging, while THPP is superior for reliable PMD performance.

Keywords: Aging; Pyrotechnic Mechanical Devices (PMDs); Flame Temperature; Thermodynamic Analysis; Titanium Hydride Potassium Perchlorate (THPP); Zirconium Potassium Perchlorate (ZPP); Boron Potassium Nitrate (BKNO_3)

1. Introduction

Pyrotechnic mechanical devices (PMDs) convert the energy of explosive charges into mechanical energy in military and aerospace applications [1]. The precision and reliability of PMDs is very important, and therefore, aged PMDs are periodically scrapped due to unreliable long-term performance of the aged explosive charges in PMDs. The study investigating the aging of explosive charges is thus critical in efforts designed to extend the shelf-life of PMDs and further reduce the military defense budget [2,3]. The three widely used explosive charges in PMDs include the following: BKNO_3 (boron potassium nitrate), [4] ZPP (zirconium potassium perchlorate), [5] and THPP (titanium hydride potassium perchlorate) [6]. They occur as mixtures of metallic fuels, oxidizers, and polymer binders [7–9]. External shocks, such as electric arcs, generate a large amount of heat instantaneously via rapid oxidation of metal and generation of increased pressure for the propulsion of PMDs [10–12]. Meanwhile, external factors such as temperature and humidity affect the properties of explosive charges [13]. Exposure to sources of oxygen such as H_2O and O_2 , in particular, leads to pre-oxidation between the metal and oxidizer and decreases the explosive power of PMDs in the long run. Thus, storage under high humidity to prevent undesirable explosions during the fabrication of PMDs

contributes to aging. Although the explosive charges are dried after the fabrication of PMDs, they would have already been exposed to a considerable amount of H_2O . In addition, the explosive charges are exposed to air due to imperfect sealing of the chamber of PMDs.

We have already proposed an approach based on the thermodynamic analysis of the flame temperature to investigate the effect of oxygen sources (H_2O or O_2) on the aging of $BKNO_3$. The rationale of the approach is presented in Figure 1 [14]. Explosive charges are aged by oxygen sources in an open system during the fabrication of PMDs and storage. As the explosion is triggered, the system can be regarded as closed in an instant time lapse following the event. The closed system consists of several sub-processes: an adiabatic process in which the huge energy generated by the oxidation reactions between the metal and the oxidizer is utilized in heating reaction products and the phase transition of condensed matter into gases, the expansion (or increased kinetic energy) of gaseous species for the propulsion of mechanical gadgets in PMDs, and heat loss through the metal casing. The kinetic barriers of primary oxidations and subsequent reactions may be ignored because the huge energy generated by the explosion may overcome the barriers easily. Thermodynamically, the concept of “adiabatic flame temperature” is a good indicator of energy released by an explosion. We also reported that the pressure exerted by PMDs is correlated to the flame temperature of the system [15,16]. The decrease in flame temperature suggests that the resulting gaseous products are less energetic and thereby weakens the propulsion of PMDs.

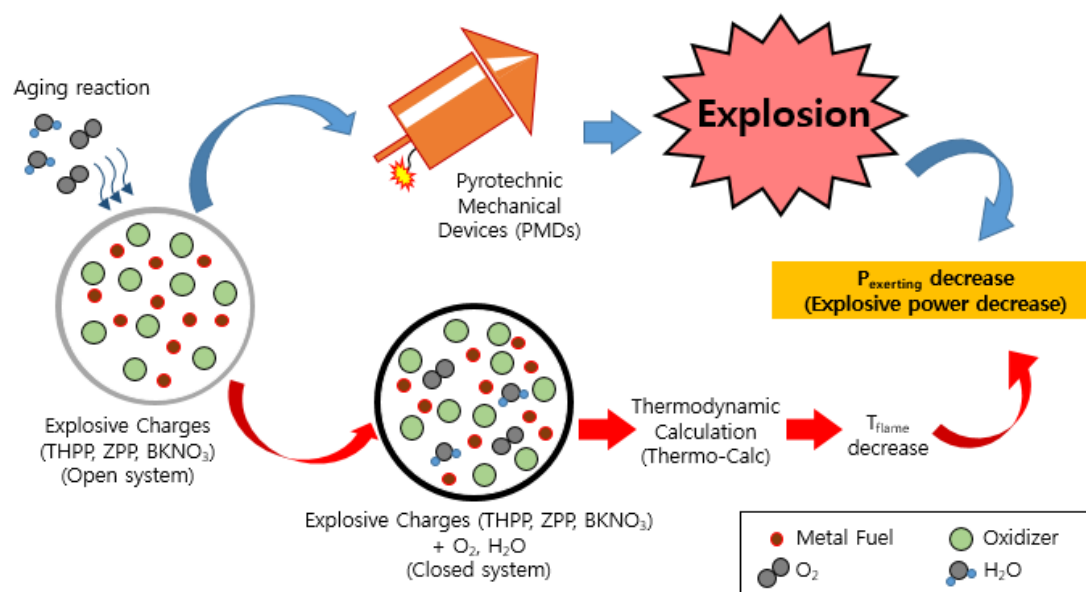


Figure 1. Schematic representation of the thermodynamic analysis of the aging of explosive charges.

Meanwhile, we conducted our experimental study on the aging of $BKNO_3$ and ZPP by exposing them to water vapor (H_2O) in an accelerated aging condition with high RH (relative humidity) [17,18]. DSC (differential scanning calorimetry)-based thermal analysis confirmed the reaction (or explosive) energy decrease with the duration of exposure to a highly humid atmosphere, and TEM (transmission electron microscopy)-EDS (energy dispersive spectroscopy) specified the gradual growth of an oxide layer on the surface of B and Zr—metallic fuels of $BKNO_3$ and ZPP, respectively. Then, the relative robustness of $BKNO_3$, ZPP, and THPP to aging was reported based on our experimental works and a complementary computational kinetic study [19].

In this study, we adopted the same approach [14] used in our previous study for two other explosive charges (ZPP and THPP). The flame temperature was calculated with respect to the amount of added oxygen source (H_2O or O_2) to illustrate the sensitivity of explosive charges to thermodynamic aging. Finally, the aging effect of the three primary explosive charges (THPP, ZPP, and $BKNO_3$) was compared.

2. Materials and Methods

Thermodynamic calculations were carried out using the CALPHAD (CALculation of PHase Diagrams) method using a commercial software known as ‘Thermo-Calc’ [20]. In this method, the elements are defined for a given system initially, and the thermodynamic properties of all the available species comprising defined elements are collected from a database as forms of Gibbs energies. In this study, the SSUB5 substance database was used. The SSUB5 is one of the largest SGTE (Scientific Group Thermodata Europe) databases, containing 5580 pure condensed compounds and gaseous species. The parameters of the mathematical models were evaluated by optimizing the model fit to the collected information. The calculation algorithm for equilibrium analysis was summarized in our previous study by a flowchart [14]. The adiabatic flame temperature was defined as the final temperature of the system raised by the combustion of explosive charges in a closed adiabatic state (Thermo-Calc. Example #22).

To investigate the aging effect of explosive charges by oxygen sources (H_2O and O_2), the flame temperature was calculated by increasing the amount of oxygen source delivered into pure explosive charges. The calculation was based on a stoichiometric ratio of 1 mole of metal component to the amount of oxidizer. The amount of oxygen element added to the system was then increased from 0.05 to 0.20 mole by an increment of 0.05. In other words, H_2O was added by the same amount (0.05 to 0.20 mole by 0.05), while the levels of O_2 were halved because it has two moles of oxygen.

3. Results and Discussion

3.1. Aging of THPP Explosive Charge by Oxygen Sources

The explosion reaction of THPP is represented as follows.



The calculation (also denoted as ‘pure THPP’) is thus based on 1 mol of Ti, 2 moles of H, 0.75 mole of K and Cl, and 3 moles of O. The decrease in flame temperature is shown in Figure 2 based on the oxygen amount added to the system. The decrease was more sensitive following exposure to O_2 than H_2O .

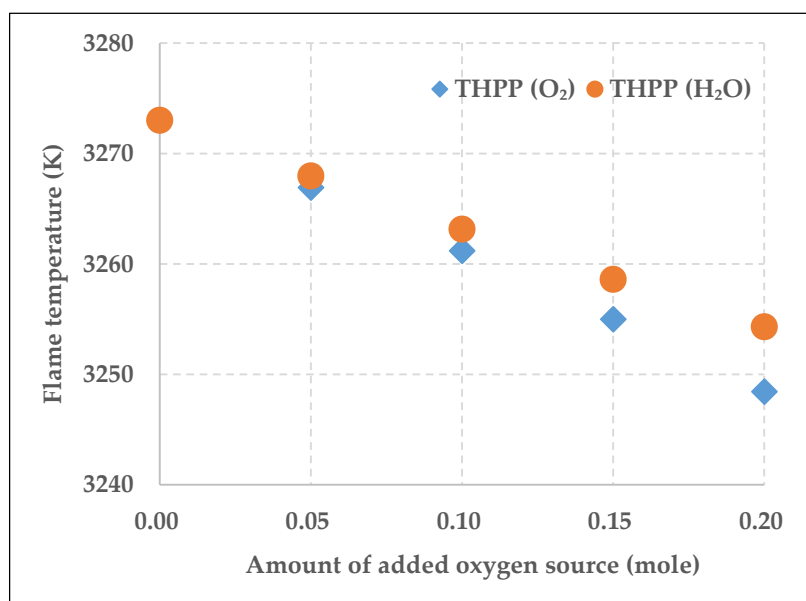


Figure 2. Flame temperature decrease of THPP correlated with the levels of oxygen sources (H_2O or O_2).

We then investigated the extent of metal pre-oxidation in explosive charges following the addition of H₂O and O₂. Thus, equilibrium calculations were introduced to alter the composition, as summarized in Table 1. Equilibrium calculations propose the most stable phases under given conditions. For example, Ti exists mostly as TiO₂ (s) at low temperatures (such as 298 K), regardless of the amount of added oxygen source. It does not imply spontaneous TiO₂ (s) formation at low temperatures. However, the oxidation of metal is extremely favorable even at low temperatures if kinetic barriers are overcome by the energy supply (ignition) or aging. To compare the relative extent of Ti pre-oxidation with H₂O and O₂ addition, calculations were conducted at temperatures as high as the flame temperatures under the given conditions. The amount of TiO (s) was decreased by the addition of oxygen sources (H₂O or O₂) due to the oxidation of TiO (s) to TiO₂ (s or l). The amount of TiO (s) was, however, generally higher with H₂O addition. A reducing environment was created by the presence of three moles of hydrogen: one mole derived from TiH and two moles from H₂O. Thus, the pre-oxidation of THPP explosive charge by the extra oxygen source was enhanced by O₂ addition. The decrease in flame temperature by pre-oxidation (or the loss of explosive energy) was accordingly more significant with O₂ addition.

Table 1. Compositional changes in TiO_x species determined by equilibrium calculations at the flame temperatures calculated under given conditions for H₂O and O₂ addition. The initial composition for equilibrium calculation is 1 mol of Ti, 2 moles of H, 0.75 mole of K and Cl, and 3 moles of O plus added moles of O, and the temperature and pressure for equilibrium calculation are the calculated flame temperatures shown in Figures 1 and 2, respectively.

Added O Amount (mole)		Pure THPP	0.05	0.10	0.15	0.20
H ₂ O addition	TiO ₂ (s)	0.1721 mole	0.1716	0.1712	0.1709	0.1707
	TiO (s)	0.0140	0.0137	0.0133	0.0130	0.0127
	TiO ₂ (l)	0.8214	0.8134	0.8151	0.8158	0.8163
O ₂ addition	TiO ₂ (s)	0.1721	0.1729	0.1734	0.1737	0.1738
	TiO (s)	0.0140	0.0134	0.0128	0.0122	0.0116
	TiO ₂ (l)	0.8214	0.8134	0.8135	0.8138	0.8143

3.2. Aging of ZPP Explosive Charge by Oxygen Sources

The explosive reaction of ZPP is represented as follows:



The calculation denoted by ‘pure ZPP’ is based on 1 mol of Zr, 0.05 mole of K and Cl, and 2 moles of O. The flame temperature decrease is shown in Figure 3 with respect to the oxygen amount added to the system. Interestingly enough, the decreasing effect was observed only with H₂O addition and remained negligible with O₂.

Using the same approach, the compositional changes of ZrO_x species were determined by equilibrium calculations as summarized in Table 2. Again, to determine the relative oxidative ability of H₂O and O₂, calculations were conducted at the flame temperatures under the given conditions. In fact, we found that the oxygen permeated the Zr metal surface with time in accelerated aging experiments under high humidity (not shown here), suggesting that kinetic barriers were overcome by Zr oxidation under aging [15]. However, with increasing exposure to oxygen sources, the amount of ZrO (s) gradually decreased via conversion to ZrO₂ (s or l). The amount of ZrO (s) was, however, higher with O₂ addition, compared with THPP. It was found that the additional oxygen sources were also consumed to generate radicals such as KO and ClO via O₂ addition (see upper part in Table 2). The H and OH radicals were generated by the decomposition of added H₂O (see lower part in Table 2). Thus, pre-oxidation of ZPP by the additional oxygen source was promoted by H₂O addition.

Accordingly, the decrease in flame temperature was steeper with H₂O addition. The Zr pre-oxidations with O₂ addition probably competed with the oxidation of K and Cl elements.

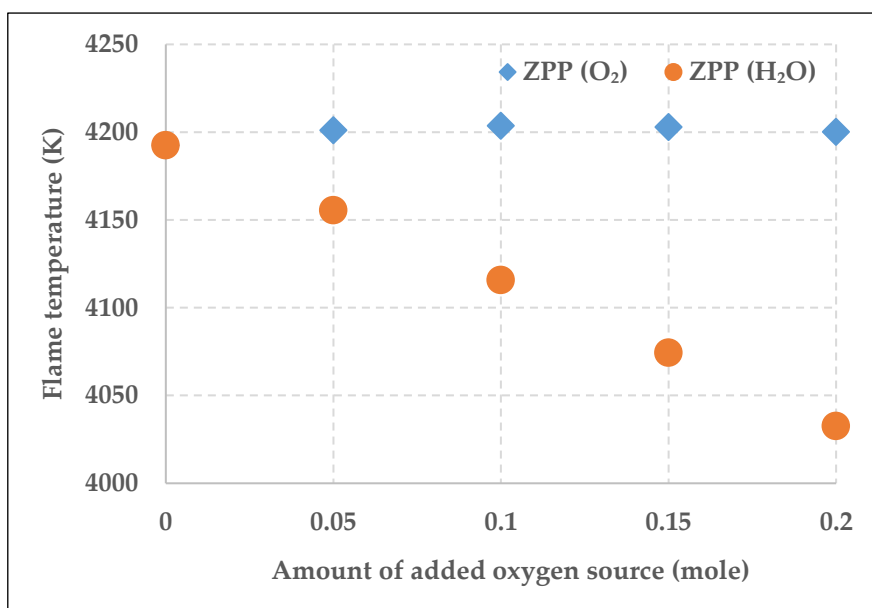


Figure 3. Flame temperature decrease of ZPP correlated with respect to the amount of oxygen sources (H₂O or O₂) added.

Table 2. Compositional changes of ZrO_x species based on equilibrium calculations at the flame temperature at specific H₂O and O₂ addition. The initial composition for equilibrium calculation is 1 mol of Zr, 0.05 mole of K and Cl, and 2 moles of O plus added moles of O, and the temperature and pressure for equilibrium calculation are the calculated flame temperatures shown in Figures 1 and 3, respectively.

Added O Amount (Mole)		Pure ZPP	0.05	0.10	0.15	0.20
H ₂ O addition	ZrO ₂ (s)	0.1080 mole	0.1000	0.0908	0.0812	0.0720
	ZrO (s)	0.0696	0.0525	0.0393	0.0292	0.0217
	ZrO ₂ (l)	0.8222	0.8437	0.8698	0.8895	0.9036
	KO (rad)	0.0078	0.0099	0.0117	0.0133	0.0146
	ClO (rad)	0.0004	0.0005	0.0005	0.0006	0.0007
O ₂ addition	ZrO ₂ (s)	0.1080	0.1137	0.1171	0.1189	0.1198
	ZrO (s)	0.0696	0.0597	0.0526	0.0471	0.0457
	ZrO ₂ (l)	0.8222	0.8264	0.8302	0.8339	0.8374
	H (rad)		0.0763	0.1446	0.2050	0.2580
	OH (rad)		0.0123	0.0267	0.0427	0.0600

3.3. Comparison of the Aging Effect Among THPP, ZPP, and BKNO₃

As mentioned in the introduction, the most probable source for the aging of explosive charges is water vapor (H₂O) during the PMD fabrication under high humidity. Thus, the decrease in flame temperature was compared with H₂O addition among the three primary explosive charges—THPP, ZPP, and BKNO₃, as shown in Figure 4. The flame temperature ranges were 4100 ± 80 K, 3260 ± 12 K, and 3050 ± 30 K for ZPP, THPP, and BKNO₃, respectively, based on the amount of H₂O added to 0.2 mole. The explosive power thus decreased in the order of ZPP >> THPP > BKNO₃, because higher energy was released at elevated flame temperatures. Meanwhile, the flame temperature decreased (or explosive power decreased) in the following order: 801.90 K, 219.28 K, and 95.28 K per mole of added H₂O for ZPP, BKNO₃, and THPP, respectively. Although energy was utilized to heat the derivatives of

added oxygen sources, resulting in a decrease in the flame temperature, substantial differences in the slope indicate that additional oxygen sources certainly contributed to the thermodynamic changes in the system. In summary, the decrease in the explosive power of ZPP was very sensitive to the aging effect of water vapor. By contrast, THPP and BKNO_3 were robust to the aging effects, despite their lower explosive powers.

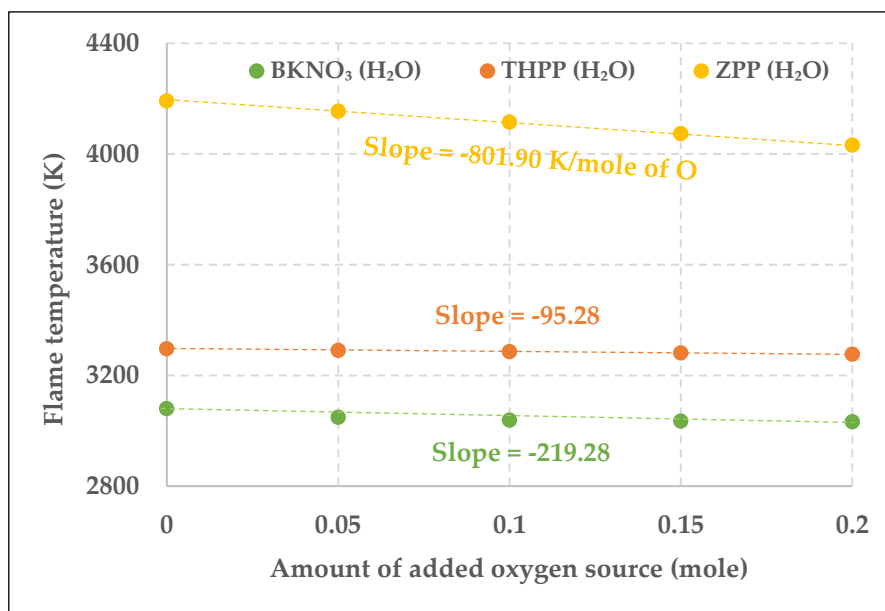


Figure 4. Comparison of the flame temperature decrease with H_2O addition among THPP, ZPP, and BKNO_3 .

4. Conclusions

The decrease in flame temperature following the addition of oxygen sources into the system was effectively used to evaluate the aging of explosive charges in PMDs in this and in our previous studies. The aging is mainly attributed to exposure to water vapor during the PMD fabrication under high humidity. With increasing H_2O addition to THPP and ZPP explosive charges, the flame temperature decreases (or the explosive power decreased) in general as a result of pre-oxidation of explosive charges. The comparison of THPP, ZPP, and BKNO_3 demonstrated that the explosive power followed the order of $\text{ZPP} \gg \text{THPP} > \text{BKNO}_3$; however, the explosive power decrease by aging occurred in the order of $\text{ZPP} \gg \text{BKNO}_3 > \text{THPP}$. Thus, THPP may represent an appropriate choice for the reliable retention of PMD performance with time, compared with ZPP, which is very sensitive to aging. In other words, it is recommended to increase the ratio of THPP in explosive charge mixtures to extend the shelf-life of PMDs and further reduce the military defense budget.

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