Article

Thermodynamic Analysis on the Aging of THPP, ZPP and BKNO₃ Explosive Charges in PMDs

Kyung Min Kim¹, Sung Il Choi¹, Ki Heon Eom¹, Gil Hwan Ahn², Jong Gyu Paik³, Byung Tae Ryu³, Yong Ha Kim¹ and Yong Sun Won¹,*

¹ Department of Chemical Engineering, Pukyong National University, Busan 48547, Korea; koko4846@naver.com (K.M.K.); csii515@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

Received: 19 November 2018; Accepted: 9 January 2019; Published: 10 January 2019

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 BKNO₃) 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 > BKNO₃ (4100 >> 3260 > 3050 K), and it was decreased by aging as follows: ZPP >> BKNO₃ > 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 (BKNO₃)

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: BKNO₃ (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 H₂O and O₂, 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$_2$O. 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$_2$O 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](Image)

**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$_2$O) 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$_2$O 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 (H₂O and O₂), 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, H₂O was added by the same amount (0.05 to 0.20 mole by 0.05), while the levels of O₂ 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.

\[
\text{TiH}_2 + 0.75 \text{KClO}_4 \rightarrow 0.75 \text{KCl} + \text{TiO}_2 + \text{H}_2\text{O}
\]  (1)

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 O₂ than H₂O.

![Figure 2. Flame temperature decrease of THPP correlated with the levels of oxygen sources (H₂O or O₂).](image-url)
We then investigated the extent of metal pre-oxidation in explosive charges following the addition of H$_2$O and O$_2$. 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 TiO$_2$ (s) at low temperatures (such as 298 K), regardless of the amount of added oxygen source. It does not imply spontaneous TiO$_2$ (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 H$_2$O and O$_2$ 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 (H$_2$O or O$_2$) due to the oxidation of TiO (s) to TiO$_2$ (s or l). The amount of TiO (s) was, however, generally higher with H$_2$O addition. A reducing environment was created by the presence of three moles of hydrogen: one mole derived from TiH and two moles from H$_2$O. Thus, the pre-oxidation of THPP explosive charge by the extra oxygen source was enhanced by O$_2$ addition. The decrease in flame temperature by pre-oxidation (or the loss of explosive energy) was accordingly more significant with O$_2$ addition.

Table 1. Compositional changes in TiO$_x$ species determined by equilibrium calculations at the flame temperatures calculated under given conditions for H$_2$O and O$_2$ 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 | 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:

$$\text{Zr} + 0.5 \text{KClO}_4 \rightarrow \text{ZrO}_2 + 0.5 \text{KClO}$$ \hspace{1cm} (2)

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 H$_2$O addition and remained negligible with O$_2$.

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 H$_2$O and O$_2$, 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 ZrO$_2$ (s or l). The amount of ZrO (s) was, however, higher with O$_2$ addition, compared with THPP. It was found that the additional oxygen sources were also consumed to generate radicals such as KO and ClO via O$_2$ addition (see upper part in Table 2). The H and OH radicals were generated by the decomposition of added H$_2$O (see lower part in Table 2). Thus, pre-oxidation of ZPP by the additional oxygen source was promoted by H$_2$O 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.

![Flame temperature decrease of ZPP correlated with respect to the amount of oxygen sources (H₂O or O₂) added.](image)

**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 ZrO₂ 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 |
|-----------------------|----------|------|------|------|------|
| **H₂O addition**      |          |      |      |      |      |
| ZrO₂ (s)              | 0.1080    | 0.1000 | 0.0908 | 0.0812 | 0.0720 |
| ZrO (s)               | 0.0696    | 0.0525 | 0.0393 | 0.0292 | 0.0217 |
| ZrO₂ (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 |
| **O₂ addition**       |          |      |      |      |      |
| ZrO₂ (s)              | 0.1080    | 0.1137 | 0.1171 | 0.1189 | 0.1198 |
| ZrO (s)               | 0.0696    | 0.0597 | 0.0526 | 0.0471 | 0.0457 |
| ZrO₂ (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 BKNO₃ were robust to the aging effects, despite their lower explosive powers.

![Image of flame temperature decrease comparison](image_url)

**Figure 4.** Comparison of the flame temperature decrease with H₂O addition among THPP, ZPP, and BKNO₃.

### 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 H₂O 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 BKNO₃ demonstrated that the explosive power followed the order of ZPP >> THPP > BKNO₃; however, the explosive power decrease by aging occurred in the order of ZPP >> BKNO₃ > 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.

**Author Contributions:** Conceptualization, Y.S.W.; methodology, K.M.K., S.I.C., and K.H.E.; software, K.M.K., S.I.C., and K.H.E.; validation, Y.H.K.; formal analysis, K.M.K., S.I.C. and K.H.E.; investigation, K.M.K., S.I.C., and K.H.E.; resources, Y.S.W.; data curation, K.M.K., S.I.C. and K.H.E.; writing—original draft preparation, Y.S.W.; writing—review and editing, Y.S.W.; visualization, K.M.K., S.I.C., and K.H.E.; supervision, J.G.P.; project administration, G.H.A.; funding acquisition, B.T.R.

**Funding:** This research received no external funding.

**Acknowledgments:** This work was supported by the Agency for Defense Development under the Precise Energy Release for the Pyrotechnic Mechanical Device program and the BB21 + Project in 2018.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.
References

1. Paik, J.G.; Ryu, B.T.; Kwon, M. A Study on Acceleration Aging Characteristics of B-KNO₃ Igniter. Korean Chem. Eng. Res. 2014, 52, 166–174. [CrossRef]

2. Le, A.Q.; Sun, L.Z.; Miller, T.C. Detectability of Delaminations in Solid Rocket Motors with Embedded Stress Sensors. J. Propul. Power 2013, 29, 299–304. [CrossRef]

3. Hosseini, S.G.; Pourmortazavi, S.M.; Hajimirasadeghi, S.S. Thermal Decomposition of Pyrotechnic Mixtures Containing Sucrose with either Potassium Chlorate or Potassium Perchlorate. Combust. Flame 2005, 141, 322–326. [CrossRef]

4. Risha, G.A.; Kuo, K.K. An Investigation of the Performance of a Boron/Potassium-Nitrate Based Pyrotechnic Igniter. Propellants Explos. Pyrotech. 2006, 31, 311–317.

5. Sorensen, D.N.; Quebral, A.P.; Baroody, E.E.; Sanborn, W.B. Investigation of the Thermal Degradation of the Aged Pyrotechnic Titanium Hydride/Potassium Perchlorate. J. Therm. Anal. Calorim. 2006, 85, 151–156. [CrossRef]

6. Lee, J.S.; Lin, L.K.; Lin, C.H.; Chen, P.J.; Huang, C.W.; Chang, S.S. A Study of Zirconium/Potassium Perchlorate Primer Mixture. Thermochim. Acta 1990, 173, 211–218. [CrossRef]

7. Moore, J.E.; Son, S.F.; Sivathanu, Y.R.; Lim, J. Experimental Characteristics of Particle Dynamics within Solid Rocket Motors Environments; Technical Paper (PA #09154); Air Force Research Laboratory: Dayton, OH, USA, 2009.

8. Danali, S.M.; Palaiah, R.S.; Raha, K.C. Developments in Pyrotechnics (Review Paper). Defence Sci. J. 2010, 60, 152–158. [CrossRef]

9. Conkling, J.A.; Mocella, C. Chemistry of Pyrotechnics: Basic Principles and Theory; CRC Press: New York, NY, USA, 2010.

10. Lee, J.R.; Chia, C.C.; Kong, C.W. Review of Pyroshock Wave Measurement and Simulation for Space Systems. Measurement 2012, 45, 631–642. [CrossRef]

11. Babar, Z.; Malik, A.Q. Synthesis of Micro Porous Barium Nitrate with Improved Ignition Reliability as a Reliable Pyrotechnic Oxidant. J. Saudi Chem. Soc. 2014, 18, 707–711. [CrossRef]

12. Kuwahara, T.; Kubota, N. Role of Boron in Burning Rate Augmentation of AP composite propellants. Propellants Explos. Pyrotech. 1989, 14, 43–46. [CrossRef]

13. De Klerk, W.P.C.; Colpa, W.; van Ekeren, P.J. Ageing Studies of Magnesium–Sodium Nitrate Pyrotechnic Compositions. J. Therm. Anal. Calorim. 2006, 85, 203–207. [CrossRef]

14. Eom, K.H.; An, H.Y.; Kim, K.M.; Ahn, G.H.; Paik, J.G.; Ryu, B.T.; Won, Y.S. Equilibrium Analysis on the Aging of a BKNO₃ Igniter. J. Nanosci. Nanotechnol. 2017, 17, 7685–7688. [CrossRef]

15. Yang, L.C. Reaction Rate Analysis for Selected Solid-to-Solid-Reaction Pyrotechnic Compositions. In Proceedings of the 48th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Atlanta, GA, USA, 30 July–1 August 2012.

16. Kong, T.K.; Won, Y.S.; Ryu, B.T.; Ahn, G.H.; Im, D.J. Mathematical Modeling of ZrKClO₄ Nano Particle Energy Release. J. Nanosci. Nanotechnol. 2017, 17, 8372–8377. [CrossRef]

17. Lee, J.; Choi, K.; Ryu, S.U.; Ahn, G.H.; Ryu, B.T.; Won, Y.S. Aging Mechanism of Zirconium Potassium Perchlorate Propellant in Pyrotechnic Mechanical Devices. NanoSci. Nanotechnol. Lett. 2018, 10, 735–740. [CrossRef]

18. Lee, J.; Kim, T.; Ryu, S.U.; Choi, K.; Ahn, G.H.; Paik, J.G.; Ryu, B.; Park, T.H.; Won, Y.S. Study on the Aging Mechanism of Boron Potassium Nitrate (BKNO₃) for Sustainable Efficiency in Pyrotechnic Mechanical Devices. Sci. Rep. 2018, 8, 11745–11754. [CrossRef] [PubMed]

19. Kim, K.M.; Lee, J.; Choi, S.I.; Ahn, G.H.; Paik, J.G.; Ryu, B.T.; Kim, Y.H.; Won, Y.S. A Combined Study of TEM-EDS/XPS and Molecular Modeling on the Aging of THPP, ZPP, and BKNO₃ Explosive Charges in PMDs under Accelerated Aging Conditions. Energies 2018, 12, 151. [CrossRef]

20. Thermo-Calc Software SSUB5 SGTE Substances Database Version 5.1. Available online: https://www.thermocalc.com/academia/researchers/how-to-cite-thermo-calc-products/ (accessed on 20 March 2016).