Korean J. Chem. Eng., 36(3), 321-324 (2019)
DOI: 10.1007/s11814-018-0228-8

pISSN: 0256-1115
eISSN: 1975-7220

RAPID COMMUNICATION

The robustness of titanium hydride potassium perchlorate (THPP) for long-term stability of pyrotechnic mechanical devices (PMDs)

Junwoo Lee*, Hyuntae Choi*, Seyoung Lim*, Gil Hwan Ahn, Jong Gyu Paik***,
Byung Tae Ryu***, Yong Ha Kim****, and Yong Sun Won****,†**

*Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH),
Pohang, Kyoungbuk 37673, Korea
**Defence R&D Center, Hanwha Corporation, Daejeon 34068, Korea
***Agency for Defense Development, Daejeon 34183, Korea
****Department of Chemical Engineering, Pukyong National University, Busan 48513, Korea

(*Received 13 November 2018 • accepted 14 January 2019*)

Abstract−Long-term stability of the explosive charges in pyrotechnic mechanical devices (PMDs) is important in order to sustain the precision and accuracy of the explosion. We have been seeking robust materials against aging since self-generated aging by internal factors and induced aging by external factors, such as humidity (or extra oxygen source), might cause physical or chemical changes of the explosive charges to reduce their explosive power (or performance degradation). In this study, we precisely analyzed the aging properties of titanium hydride potassium perchlorate (THPP), one of the primary explosive charges. For the self-generated aging by internal factors, AKTS (advanced kinetics and technology solution) simulation using DSC (differential scanning calorimeter) profiles of different heating rates (1, 2, 4 and 8 °C/min) were used to calculate the initiation time of spontaneous reaction. The resulting initiation time at a storage temperature of 192 °C was ~200 years, demonstrating that THPP is hardly aged by itself. To investigate the induced aging by humidity, THPP samples aged under 100% RH (relative humidity) at 70 °C up to 16 weeks were characterized. Thermal analysis showed no loss of relative heat released (or no loss of explosive power) by the aging time, and almost constant reaction rate was maintained, indicating THPP is not affected by aging both thermodynamically and kinetically. This result was confirmed by direct TEM (transmittance electron microscope)-EDS (energy dispersion spectroscopy) observations as well, where no trace of oxide on the surface of titanium hydride (TiH_2) appeared regardless of the aging time.

Keywords: Aging, Explosive Charge, Pyrotechnic Mechanical Devices (PMDs), Titanium Hydride Potassium Perchlorate (THPP)

INTRODUCTION

Pyrotechnic mechanical devices (PMDs) utilize the explosive power of explosive charges to achieve mechanical force for subsequent chain explosion [1]. The origin of the explosive power is from the auto-acceleration of explosive charges in that initial exothermic reaction at one spot (often by electric-arc) triggers the whole combustion of explosive charges rapidly in the overall explosive region [2-4]. However, after a long storage period, the explosive charges (e.g., boron potassium nitrate ($BKNO_3$), zirconium potassium perchlorate (ZPP) and titanium hydride potassium perchlorate (THPP)) could be aged with their explosive power reduced. This phenomenon leads to the disposal of whole PMDs periodically, and thus the defense budget is wasted inevitably [5,6].

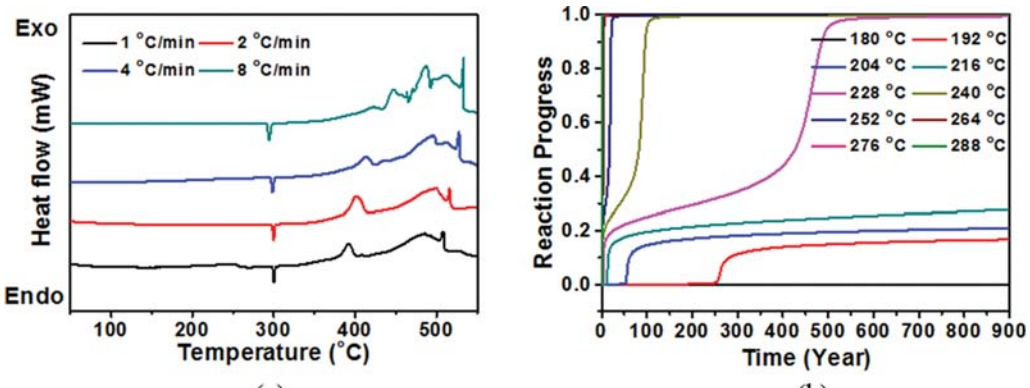
The aging phenomenon of the explosive charges, comprised of three components (metal, oxidizer, and polymer binder), can be divided into self-generated aging by internal factors [7-11] and induced aging by external factors such as humidity (or extra oxygen source) [12-16]. The self-generated aging is possibly caused by the phase separation and pre-oxidation between the metal and oxidizer, while induced aging originates from the oxidation between metal and oxygen source from exterior. The resulting physical or chemical changes of the explosive charges by time anyhow affect their performance either kinetically or thermodynamically, in other words, leading to reduced reaction rate and explosive power [17,18].

In our previous studies, we proposed an experimental methodology to evaluate the aging of $BKNO_3$ [19] and ZPP [20] quantitatively. Both explosive charges showed high stability against spontaneous aging, but there occurred the oxidation of metal component (boron in $BKNO_3$ and zirconium in ZPP) under high humidity condition, often encountered during the fabrication of PMDs to avoid any undesirable explosion. It was reflected in the formation of oxide shell on the surface of metal components by TEM (transmission electron spectroscopy)-EDS (energy dispersive spectroscopy) observations. The reduced relative heat (or explosive power) and reaction rate by DSC (differential scanning calorimetry) measurements confirmed the expected thermodynamic and kinetic aging as well.

In this study, we analyzed THPP finally in our effort to seek a robust explosive charge against aging for PMDs having long-term

---

†To whom correspondence should be addressed.
E-mail: yswon@pknu.ac.kr



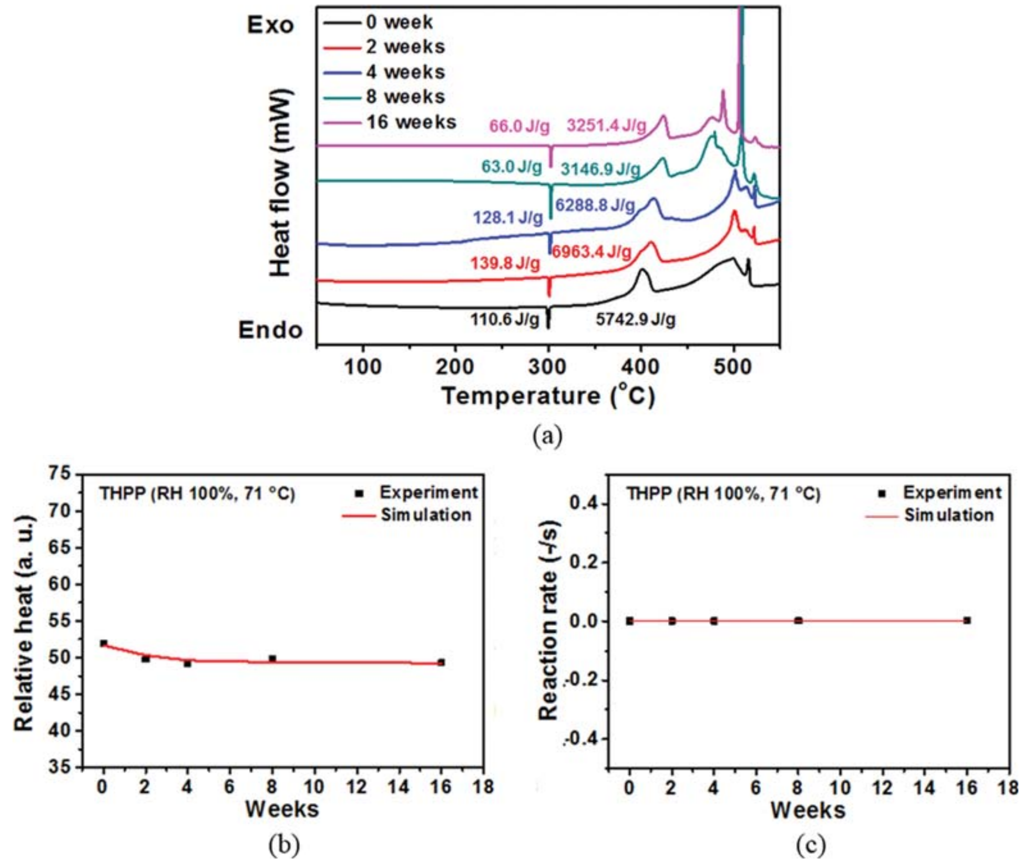
(a) (b)

Fig. 1. (a) The DSC profiles of THPP by varying the heating rate (1, 2, 4, and 8 °C/min) and (b) long-period reaction progress vs. time at various storage temperatures.

stability. We used the same methodology as in our previous studies [19,20]. The self-generated aging by internal factors and induced aging by external factors of THPP were investigated primarily by using DSC measurements and AKTS (advanced kinetics and technology solutions) simulation. The accelerated aging condition under 100% RH (relative humidity) at 70 °C was extended to 16 weeks, and the microscopic changes by time were monitored using TEM-EDS as well. At the end, we justified how robust THPP is against aging.

Table 1. Simulated initiation time vs. the storage temperature

Storage temperature (°C)	Initiation time
180	Over 900 years
192	Over 200 years
204	~56 years
216	~13 years
228	~3 years



(a)

(b) (c)

Fig. 2. (a) DSC profiles of the pristine and aged THPP samples for 2, 4, 8 and 16 weeks and (b) the corresponding relative heats and (c) reaction rates with their trend simulated by the Savizky-Golay approximation.

RESULTS AND DISCUSSION

1. Self-generated aging of THPP - DSC and AKTS Simulation

The DSC profiles of THPP demonstrate two different kinds of peaks as shown in Fig. 1(a). The endothermic peak around 300 °C indicates the transformation of the crystal structure of potassium perchlorate ($KClO_4$) from orthorhombic to FCC (face-centered cubic). The exothermic peaks between 350 and 520 °C are related to the oxidation of titanium hydride (TiH_2) with oxidizer ($KClO_4$), in other words, the explosion of THPP. The first exothermic peak of DSC data with varying the heating rate (1, 2, 4, and 8 °C/min) was then used to simulate the initiation time of the self-generated aging using AKTS program [19,20]. The resulting initiation time is illustrated in Fig. 1(b) and summarized in Table 1. The self-generated aging would not occur even in 200 years at a storage temperature of 192 °C, suggesting that self-generated aging is inconceivable considering the ambient shelf condition for THPP storage. Thus, internal factors such as metal, oxidizer, and Viton as polymer binder could not affect the chemical properties of THPP.

2. Induced aging of THPP by Analyzing Relative Heat and Reaction Rate - DSC

To investigate the effect of external factors such as humidity (or extra oxygen source) on the aging of THPP, we employed accelerated aging conditions with 100% RH at 70 °C. Considering that PMDs are soaked to avoid any undesirable explosion during the fabrication, the condition of 100% RH has its own rationale. The heat released of the aged THPP samples was quantitatively characterized by using DSC profiles shown in Fig. 2(a). The first endothermic heats of the pristine and aged samples for 2, 4, 8 and 16 weeks, which is associated with the structural transformation of $KClO_4$, are 110.6, 139.8, 128.1, 63.0 and 66.0 J/g, respectively. Meanwhile, the second exothermic heats between 350 and 520 °C for the pristine and aged samples (2, 4, 8 and 16 weeks) are 5742.9, 6963.4, 6288.8, 3146.9 and 3251.4 J/g, respectively. Since explosive charges are highly energetic mixtures, a calibrated dimensionless concept of 'relative heat' is necessary and given by the exothermic heat divided by the endothermic heat for each sample [19,20]. As summarized in Table 2, the relative heats of the pristine and aged sam-

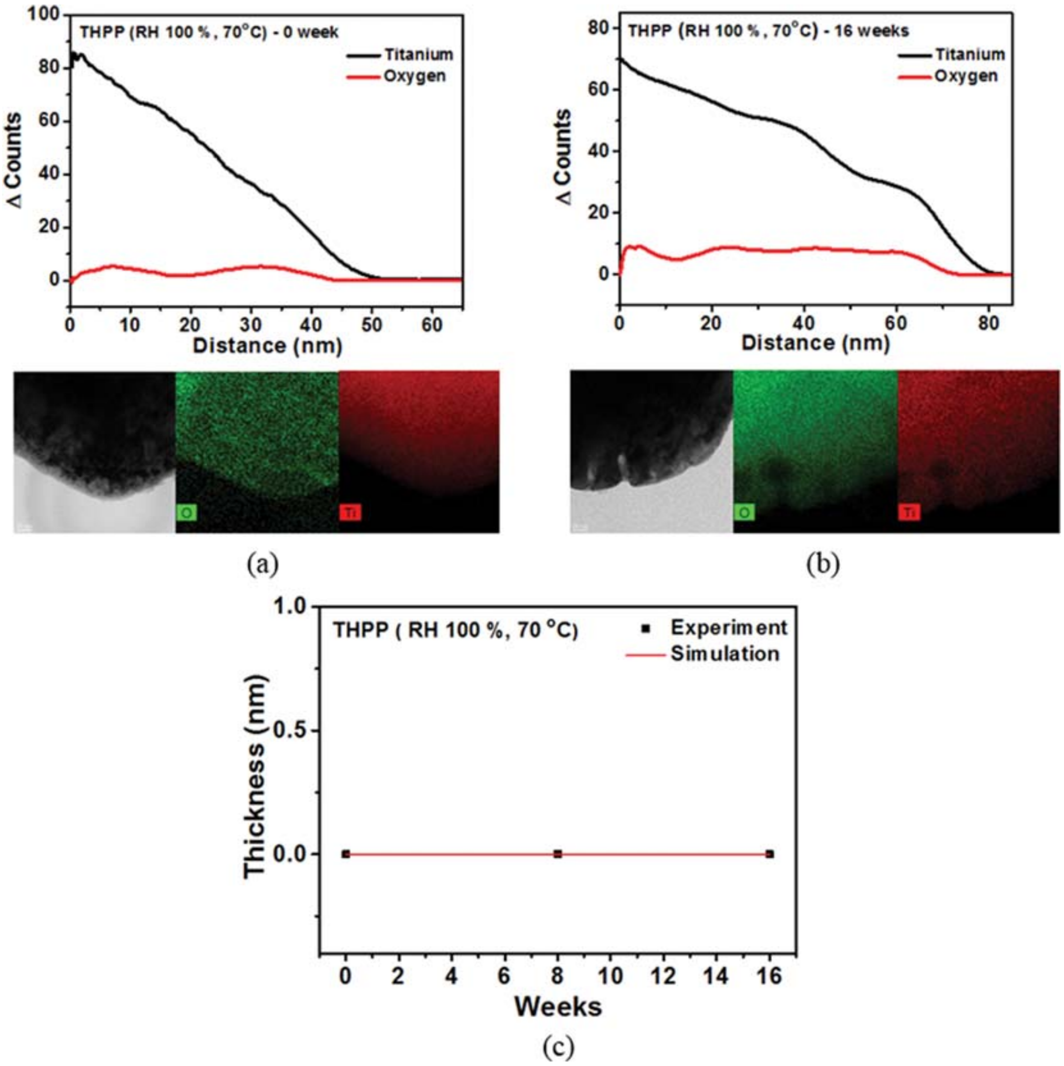


Fig. 3. TEM-EDS characterization of the (a) pristine and (b) 16 week aged THPP samples and the thickness profile simulated using the Savizky-Golay approximation.

Table 2. Relative heats and reaction rates of the pristine and aged THPP samples

Weeks	Relative heat released	Reaction rate ($\times10^{-3}$ -/s)
0	51.9	1.7
2	49.8	1.6
4	49.2	1.3
8	49.9	2.1
16	49.3	2.2

ples for 2, 4, 8 and 16 weeks are calculated 51.9, 49.8, 49.2, 49.9 and 49.3, respectively. Compared to the decreasing tendency of the relative heat by aging time for $BKNO_3$ (68.51 to 56.44 from the pristine to 16 week aged samples) and ZPP (69.2 to 41.8 from the pristine to 16 week aged samples) [19,20], THPP barely shows a change in the relative heat released. It suggests the explosive power of THPP is maintained against aging unlike $BKNO_3$ and ZPP. Therefore, THPP is the best in long-term stability among three primary explosive charges. In addition, reaction rates of aged THPP samples were calculated to examine the aging kinetically, as shown in Fig. 2(c) and summarized in Table 2. The resulting reaction rates are 1.7, 1.6, 1.3, 2.1 and 2.2×10^{-3} s^{-1} for the pristine and aged samples for 2, 4, 8 and 16 weeks, respectively. Although the error range of calculated reaction rates is approximately 0.5×10^{-3} s^{-1}, it is apparent that the reaction rate for THPP is almost constant (or unchanged) by aging time. Therefore, aging could not load any kinetical change on THPP.

3. Monitoring Oxide Shell Formation by aging Time - TEM-EDS

Since the origin of induced aging is the formation of oxide shell on the surface of metal component, the direct characterization for the oxide shell was performed by TEM-EDS as shown in Fig. 3. In accordance with the results from the analysis of relative heat and reaction rate, any oxide form was hardly detected on TiH_2 even in the 16 week aged THPP sample. Again, it is wholly different compared to the surface oxide formation for the boron of $BKNO_3$ and zirconium of ZPP [19,20]. It is because the presence of hydrogen in TiH_2 prevents the oxygen diffusion into the interior and renders TiH_2 thermally stable. The activation barrier for the oxygen diffusion into the interior of TiH_2 was significant compared to that of boron and zirconium in our DFT (density functional theory)-based computational study (not shown here). Therefore, the hydration of metal component in explosive charges could be a measure of anti-aging treatment.

CONCLUSION

We analyzed the property changes of THPP by aging in terms of the self-generated aging and induced aging. The self-generated aging of THPP was hardly initiated even at a storage temperature of 192 °C according to AKTS simulation with DSC data with varying heating rates (1, 2, 4, and 8 °C/min). It reflected that the self-generated aging for THPP is unthinkable at ambient storage condition. To investigate induced aging by extra oxygen source, relative heats and reaction rates were calculated on THPP samples aged under accelerated aging conditions with 100% RH at 70 °C. Even for the sample aged for 16 weeks, the relative heat and reaction rate were almost unchanged compared to those of the pristine one. It demonstrated that THPP is highly stable to extra oxygen source. It was also confirmed using TEM-EDS characterizations; no oxide evolved even in the 16 week aged sample. The robustness of THPP is probably from the hydration of metal (TiH_2) to prevent oxygen diffusion into the interior, which might be a solution to counter the aging of explosive charges in PMDs.

ACKNOWLEDGEMENTS

This work was supported by the Agency for Defense Development under the Precise Energy Release for the Pyrotechnic Mechanical Device program and the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20174010201460). The authors sincerely thank Professor Taiho Park in the Department of Chemical Engineering in POSTECH for the analytical supports in this manuscript.

REFERENCES

1. L. J. Bement and H. A. Multhaup, *AIAA J.*, **37**, 357 (1999).
2. J. S. Lee, K. L. Lin, C. H. Lin, P. J. Chen, C. W. Huang and S. S. Chang, *Thermochim. Acta*, **173**, 211 (1990).
3. A. Ulas, G. A. Risha and K. K. Kuo, *Propellants Explos. Pyrotech.*, **31**, 311 (2006).
4. N. Yan, B. Bao, F. Zheng and C. Li, *Propellants Explos. Pyrotech.*, **41**, 223 (2016).
5. K. S. Lai, AIAA, ASME, SAE, and ASEE Joint Propulsion Conference and Exhibition (1998).
6. R. P. Olmos, A. Rios, M. P. Martin, R. A. S. Lapa and J. L. F. C. Lima, *Analyst*, **124**, 97 (1999).
7. E. E. Gilbert and G. P. Sollot, *Chem. Eng. News*, **58**, 32 (1980).
8. L. W. Hunter, J. W. White, P. H. Cohen and P. J. Biermann, *Johns Hopkins APL Tech. Dig.*, **21**, 575 (2000).
9. C. S. Gorzynski and J. N. Maycock, *J. Spacecraft Rockets*, **11**, 211 (1974).
10. B. J. Bellott, W. Noh, R. G. Nuzzo and G. S. Girolami, *Chem. Commun.*, **22**, 3214 (2009).
11. V. K. Patel, A. Ganguli, R. Kant and S. Bhattacharya, *RSC Adv.*, **5**, 14967 (2015).
12. D. N. Sorensen, A. P. Quebral, E. E. Broody and W. B. Sanborn, *J. Therm. Anal. Calorim.*, **85**, 151 (2006).
13. J. G. Paik, B. T. Ryu and M. Kwon, *Korean Chem. Eng. Res.*, **52**, 166 (2014).
14. A. Q. Le, L. Z. Sun and T. C. Miller, *J. Propul. Power*, **29**, 299 (2013).
15. S. G. Hosseinia, S. M. Pourmortazavia and S. S. Hajimirsadeghi, *Combust. Flame*, **141**, 322 (2005).
16. S. D. Brown, E. L. Charsley, S. J. Goodall, P. G. Laye, J. J. Rooney and T. T. Griffiths, *Thermochim. Acta*, **401**, 53 (2003).
17. J. Sivan, Y. Haas, D. Grinstein, S. Kochav, G. Yegudayev and L. Kalontarov, *Combust. Flame*, **162**, 516 (2015).
18. D. Ouyang, G. Pan, H. Guan, C. Zhu and X. Chen, *Thermochim. Acta*, **513**, 119 (2011).
19. J. Lee, T. Kim, S. U. Ryu, K. Choi, G. H. Ahn, P. G. Paik, B. Ryu, T. Park and Y. S. Won, *Sci. Rep.*, **8**, 11745 (2018).
20. J. Lee, K. Choi, S. U. Ryu, G. H. Ahn, J. G. Paik, B. Ryu and Y. S. Won, *Nanoscience and Nanotech. Lett.*, **10**, 735 (2018).