

The Asia-Pacific Conference on Combustion (ASPACC) is a biennial meeting sponsored by the Combustion Institute and organized by members of the Asia-Pacific regional sections. Its goal is to promote exchange of information and to elevate combustion science and technology through regional and global scientific partnership. The 12th ASPACC will be hosted by the Japan Section of the Combustion Institute, and will be held on July 1 to 5, 2019 in Fukuoka, Japan. The conferences will provide a forum for mutual exchange of information in the Asia-Pacific combustion community involved in both fundamental and application oriented research and development works.

PLENARY SPEAKERS :

Professor Evatt Hawkes, University of New South Wales Unravelling engine combustion using large-scale computations

Professor Naian Liu, University of Science and Technology of China Combustion of Fire Whirl : How much do we know?

Professor Kang Y. Huh, Pohang University of Science and Technology Combustion Modeling and Simulation in Era of the Fourth Industrial Revolution

Professor Min Suk Cha, King Abdullah University of Science and Technology Recent understanding with flames under external electric fields

Professor Yei-Chin Chao, National Cheng Kung University Hydrogen Peroxide Revisited : the Role as an Energy-Saving Combusiton Enhancer and a Non-Toxic Green Propellant for Satellites and Hybrid Rockets

Speakers from Japan and India Sections are to be determined.

CONFERENCE VENUE :

Fukuoka International Congress Center 2-1 Sekijo-machi, Hakata-ku, Fukuoka 812-0032, JAPAN

IMPORTANT DATES :

Submission of full paper: Notification of paper acceptance: Conference dates: 25th January 2019 1st April 2019 1st - 5th July 2019

PAPER SUBMISSION :

Full length papers should follow the format given on the conference web site. The Program Committee will select papers for presentation on the basis of peer reviews of each paper. All selected papers should be presented by one of the authors. Technical papers are solicited in all areas of combustion science and technology including the following areas.

- Gas-Phase Reaction Kinetics
- Soot, Nanomaterials, and Large Molecules

- Diagnostics

- Laminar Flames

- Turbulent Flames
- Spray, Droplet, and Supercritical Combustion
- Detonations, Explosions, and Supersonic Combustion
- Solid Fuel Combustion Fire Research
- Stationary Combustion System and Control of Greenhouse Gas Emissions
- Internal Combustion Engines Gas Turbine and Rocket Engine Combustion
- New Concepts

YOUNG INVESTIGATOR AWARDS :

Young Investigator Awards will be awarded to the best performing young author-presenter from research students or postdoctoral researchers (or equivalent).

BEST PAPER AWARDS :

Best paper awards will be awareded to the best papers presented at ASPACC2019.

WOMEN IN COMBUSTION MEETING :

All women conference participants are invited to join together for a time to network and share their experiences. The interactive meeting will convene during the conference.

ORGANIZING COMMITTEE :

Chair: Toshiaki Kitagawa, Kyushu University Co-chair: Fumiteru Akamatsu, Osaka University Co-chair: Kenji Yamamoto, Mitsubishi Heavy Industries, Ltd. In 2019, the Organizing Committee is spread in the community of the Asia-Pacific regional sections of the Combustion Institute, mainly the Japan Section.

PROGRAM COMMITTEE :

Chair: Masato Mikami, Yamaguchi University Co-chair: Shuhei Takahashi, Gifu University

CONTACT:

For additional information please contact Contact address: aspacc19@combustionsociety.jp Website: http://www.combustionsociety.jp/aspacc19/

Full length paper submission will be available in early December on the conference web.

R	toom 5 (411/412)	
	OS8-13. Solid Fuel Co	ambustion
	Fri., 5 Jul., 09:30 - 1	1050, Room 5 (411/412)
	Chair: Jian Gi	ao (Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, China)
	ASPACC2019-1243	Short-Wave Emission Spectrum Features During Fast High-Temperature Reactions of Condensed Systems
		Alexander Vanovich Kirdyashkin (ar Eastern Federal University, Russian Federation), Ramil Mahmutovich Gabbasov (Tomsk Scientific Center SB RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics and Materials Science RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics and Materials Science RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics and Materials Science RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics and Materials Science RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics and Materials Science RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics and Materials Science RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics and Materials Science RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics and Materials Science RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics and Materials Science RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics and Materials Science RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics and RAS), Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics), Russian Federation), Ramil Materials Science RAS, Russian Federation), Vitaly Georgievich Salamatov (Merzhanov Institute of Structural Macrokinetics), Russian Federation), Russian Federatin (Russian Federation), Russian Fe
		Federation), Aleksey Nikolaevich Panchenko (Institute of High Current Electronics SB RAS, Russian Federation), Sergey Sergeevich Minaiv (Far Eastern Federal University, Russian Federation)
	ASPACC2019-1248	The adverse effects of moisture on the natural aging of zirconium-based energetic material
		Byungheon Han (Seoul National University, Korea), Korea), Kanagaraj Gnanaprakash (Seoul National University, Korea), Jack J Yoh (Seoul National University, Korea, Korea)
	ASPACC2019-1340	Slow and fast thermal decomposition characteristics of metalized explosives in fuel-rich and oxygen-rich conditions

Yoonsik Park, Yoocheon Kim, Jack J Yoh (Seoul National University, Korea)

The adverse effects of moisture on the natural aging of zirconium-based energetic material

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Abstract

This study investigates the adverse effects of moisture to the energetic materials using Zirconium (Zr) and Iron (III) oxide (Fe₂O₃) as energy sources. The moisture thermally decreased the heat of reaction and made the reaction difficult by increasing the activation energy. By using the X-ray photoelectron spectroscopy (XPS), decomposition of oxidizer, Fe₂O₃, and formation of ZrO₂ process was investigated. Finally, Transmission Electron Microscopy-Energy-Dispersive X-ray Spectroscopy (TEM-EDS) and Fast Fourier Transform (FFT) image analysis were used to analyze the Zr surface in depth, which is the main energy source. Moisture acted on the surface of Zr to directly form oxide layer and ZrO2, as well as generating cracks on the surface, allowing penetration of oxygen to the deep inside. As a result, moisture was the critical factor of natural aging and has adversely affected both the oxidizing agent, Fe₂O₃, and the energy source, Zr.

1 Introduction

A high energy material is a composite material composed of a solid fuel and an oxidizer. These materials are the substances which chemical enthalpy and thermal enthalpy change abruptly by the external impact. Therefore, high-energy materials are used extensively in various practical fields such as energetic materials, propellants, airbags, and the like, which require a momentarily large force.

The high energy materials are highly reactive thus their performance easily deteriorates by exposure to heat, vibration or moisture during long term storage. These external conditions can lead to malfunction or misfire of energy materials, resulting in lower reliability and greater risk.

Therefore, the analysis of the aging effects and the prediction of the performance is the one of major research topic that has emerged recently, and many studies have been conducted to study the causes of these aggressions and the changes in their performance. As a representative example, a lot of experiments tried to simulate the actual aging environment through temperature accelerated aging method, moisture accelerated aging method and cycling accelerated aging method [1]. However, such efforts have not been practically researched for samples aged under normal storage conditions.

Thus, in this paper, the Zr/Fe_2O_3 composite which widely used as an ignition agent was prepared in the three conditions: 8 years natural aged condition, 8 weeks accelerated aged

Corresponding author. Fax: +82-02-880-1507 E-mail address: jjyoh@snu.ac.kr condition except moisture and non-aging condition. Finally, the effect of moisture on practical storage conditions was determined thermally/chemically/structurally by using DSC, XPS and TEM-EDS.

2 Experiment and Results

2.1 Sample preparation

As shown in table 1, samples were divided into three groups according to aging types: pristine sample (#1), 8 years natural aged sample under the normal storage conditions (#2), and 8 weeks temperature accelerated aged sample in the condition of 91 °C and RH 0% (#3). The 8 weeks accelerated aging sample (#3) correspond to those stored at room temperature (25 °C) for about 150 years by the van't Hoff equations (1) as below [2].

$$t_u = t_A \cdot F^{\frac{(T_A - T_u)}{\Delta T_F}} / 365.25 \quad (1)$$

where t_u is the period of natural aged, T_u is the temperature of natural aging (i.e., 25 °C), t_A is the period of accelerated aging, and T_A is the temperature of accelerated aging condition. F means the reaction rate change per 10 °C of change.

The comparison of the 8 weeks temperature aged sample (#5) with the 8 years natural aged sample (#4) provides good results in confirming natural aging conditions except the temperature factors.

Sample · No.	Aging condition				Activation
	Temperature	Relative	Aging	type	energy
		Humidity	Duration		(kJ/mol)
#1	-	-	-	No aged	114.9
#2	Seasonal	Seasonal	8 years	Natural	133.3
#3	91℃	0%	8 weeks	Thermal	118.9

Table 1: Three kind of samples according to aging type. pristine sample (#1), 8 years natural aged sample (#2), and 8 weeks temperature accelerated aged (#3)

2.2 High-speed images of Zr ignition

Instantaneous snapshots of ignition process of Zr powder, which is a primary source of this energetic material, are shown in Fig. 1, at time intervals of 40μ s. The images are recorded at a framing rate of 50,000 fps and with a spatial resolution of 400×250 pixels². Nd:Yag laser (1064 nm) with a pulse width of 10 ns and pulse frequency of 10 Hz is used to ignite the sample. A small quantity of Zr powder pressed into a paraffin pellet of diameter 40mm is the sample used for this experiment. A region of high intensity near the sample surface is noticed in these images (Fig. 1b), which represents the formation of plasma of Zr powder, and followed by the breakdown into finer particles subsequently, right above the irradiated sample surface area. This is phenomenon of plasma formation is mainly due to the laser ignition source, which has high energy density per pulse. Similar studies would be performed on the energetic samples that are subjected to various aging conditions to study their ignition characteristics.



Figure 1: High-speed images of Zr ignition process

2.3 DSC and TGA result for the reaction kinetics

The reaction between Zr and Fe_2O_3 is known to form the end product of Fe as the reduction form of oxidant, Fe_2O_3 , and ZrO_2 as the oxidation form of energy source, Zr as below chemical formula (2) [3].

$$2Fe_2O_3 + 3Zr \rightarrow 3ZrO_2 + 4Fe$$
 (2)

Fig. 2 shows the DSC and TGA curve at the same time for the un-aged Zr/Fe₂O₃ (#1). Experiments were performed at a heating rate of 10 °C/min and an initial mass of about 2.1 g was used. Other experimental conditions were controlled according to ASTM-E698-11. The reaction starts at about 390 °C, and TGA also begins to increase in mass at this temperature range meaning ZrO₂ formation as a result of reaction. Therefore, it can be inferred that the heat of reaction of Zr/Fe₂O₃ is greatly influenced by the initial amount of both Zr and Fe₂O₃.



Figure 2: DSC and TGA curve for pristine Zr/Fe₂O₃ (#1).

2.4 Calorimetry and Activation energy

The calorimetry results for the entire sample $(\#1 \sim \#3)$ are shown in Fig. 3 and the activation energy were calculated by ASEM-E698-11 and shown in Table 1. In the Fig. 3, each point represents the individual experiments performed and the solid line represents the Lorentz distribution. The square box shows the average heat of enthalpy distribution of each sample.

As shown in Fig. 3, the heat of enthalpy value was the lowest in the natural aging sample (#2), and the heat of enthalpy decrease in accelerated aging sample (#3) was marginal. As shown in Table 1, the activation energy was increased by about 16 % in the natural aging sample (#2) compared to the pristine sample (#1), but only by about 3 % increase was observed in the accelerated aging sample (#3).

The decrease in the heat of enthalpy in the natural aging sample means that the amount of Zr than the initial energy source decreased or the amount of Fe₂O₃ decreased. Also, the formation of oxide film by aging increases the activation energy [4]. In the accelerated aging samples (#3), the heat of enthalpy reduction and activation energy increase were not obvious, thus it can be reasonably concluded that moisture has a great influence on these changes.



Figure 3: The calorimetry results for the entire sample (#1~#3)

2.5 XPS analysis: chemical state of Zr-bond and Febond

The XPS experiment was performed to confirm the chemical bonding state of Zr and Fe, and the results are shown in Fig. 4. As shown in Fig. 4(a), the amount of ZrO_2 , the final product of reaction in Zr, showed the greatest intensity in the naturally aged sample. This indicates that moisture is a important factor in ZrO_2 formation. F.C. Lglesias et al [5] already showed that ZrO_2 could be formed by the reaction of water and Zr under normal room temperature conditions. Therefore, natural aging of Zr by the moisture proceeds as the following equation (3). The oxidation of Zr was not caused by the oxidant, Fe₂O₃, but a moisture.

$$Zr+xH_2O \rightarrow ZrO_x+xH_2 (0 \le x \le 2)$$
 (3)

Decrease of Fe₂O₃ was also present in the accelerated aging sample, but the reduction of oxidant was the severe in the

natural aged sample. The (0001) crystal plane of Fe₂O₃ easily accepts moisture and changes to Fe₃O₄ [6]. At that time, hydrogen and Fe₃O₄ react with each other to form Fe. However, since Fe is excellent in reactivity, it readily bonds with oxygen in the air and presents in FeO or Fe₃O₄ state. This process could occur at room temperature and be expressed as below chemical equation.

 $\begin{array}{lll} Fe_2O_3 \left(0001 \ surface \right) + H_2O & \rightarrow & Fe_3O_4 + H_2 \\ Fe_3O_4 + 4H_2 & \rightarrow & 3Fe + 4H_2O \\ Fe+O_{2, \ atmosphere} \ or \ Fe+H_2O_{atmosphere} & \rightarrow & FeO \ or \ Fe_3O_4 \end{array}$

In conclusion, Zr/Fe_2O_3 reacts with moisture to form a reaction product, which has a great influence on the performance degradation and this process can explain the result of heat of enthalpy reduction.



Figure 4: XPS results for confirming the chemical bonding state of Zr (a) and Fe (b) in the samples #1 to #3

2.6 TEM-EDS and FFT image of Zirconium surface

The TEM and FFT images of the Zr surface, main energy source, are shown in Fig. 6 and Table 2, respectively. The Zr and α -Zr layers were present in the non-aged samples (#1), but the monoclinic-ZrO₂ layer was formed and oxygen layer was formed outermost in the case of the natural aged sample (#2). However, in the accelerated aging sample (#3), only the Zr layer, the α -Zr layer and the oxygen layer were found. The depth of oxygen penetration was also deepest at about 40 nm in natural aging samples. On the other hand, the oxygen penetration depth of the accelerated aging sample was about 20 nm.

The monoclinic-ZrO₂ found in the natural aging sample is the most thermally stable form of ZrO₂ phase. In general, ZrO₂ is known to form monoclinic-ZrO₂ via tetragonal-ZrO₂ [7], however it is known that transition from tetragonal-ZrO₂ to monoclinic-ZrO₂ occurs rapidly in the presence of moisture. The cracks can occur during this process and oxygen can penetrate deeply due to these cracks. The laminated structure

shown in the natural aging sample, that is, 'Zr - α -Zr - monoclinic-ZrO₂ - oxygen layer', is the most stable layered structure that Zr could form.

Therefore, moisture acts in the direction of decreasing the reactivity most on the Zr.

3 Conclusion

The effect of moisture on the aging of Zr/Fe_2O_3 was analyzed thermally/chemically/structurally and the aging process of Zr and Fe by the moisture was suggested. This led to a decrease in heat of enthalpy and an increase in activation energy, which ultimately led to a drastic decrease in the performance of energy materials. The performance degradation process of Zr and Fe₂O₃ by moisture is shown in Fig. 5.

The (0001) plane of Fe_2O_3 is excellent in reactivity with moisture, and forms a Fe_3O_4 structure by bonding with the OHgroup of water. Fe_3O_4 reacts with formed H₂ to reduce to Fe, and Fe binds immediately with ambient oxygen to form FeO or Fe₃O₄. As a result of aging, oxygen is reduced and the role of the oxidizing agent is critically decreased.

Since Zr is highly reactive, it binds with ambient oxygen to form a-Zr. In the presence of water, water directly acts to promote the formation of oxide layer and tetragonal ZrO_2 , which is formed initial form of ZrO_2 . However, the water promotes the conversion of the tetragonal phase to monoclinic, forming a thermally stable form of monoclinic ZrO_2 thus, reducing the reactivity.

As a result, Zr decreases its role as an energy source by stable structure, and Fe_2O_3 loses oxygen and decreases its role as an oxidant, reducing the enthalpy of the entire Zr/Fe₂O₃ system.



Figure 5: Reduction of oxidant role of Fe_2O_3 (a) by the aging progress and reduction of reactivity of Zr (b) by the aging progress.

4 Acknowledgment

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References

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Figure 6: TEM-EDS results (a)-(c) for all samples (#1-#3) and FFT images (d~f) for the natural aged sample surface (#2). FFT image analysis is shown in Table 2.

Layer	d-spacing (nm)	(h, k, l)	Phase
٨	0.1677	(1, 1, 0)	7.
A	0.2556	(0, 0, 2)	Ζľ
	0.1704	(1, 2, 1)	
В	0.1398	(2, 2, 0)	Zr ₃ O
	0.2561	(0, 0, 2)	
	0.3888	(0, 1, 1)	
С	0.5079	(1, 0, 0)	ZrO_2
	0.3313	(1, 1, 1)	

Table 2: Miller indices (h, k, l) and d-spacing confirming the phase and the crystal structure of Fig. 6 (d)~(f).