Investigation of aging induced processes on thermo-kinetic and combustion characteristics of tungsten pyrotechnic delay composition

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A B S T R A C T
A degradation in performance parameters related to thermal decomposition and combustion behaviour of tungsten based pyrotechnic delay composition can occur when subjected to accelerated aging conditions in a controlled environment. The present study utilizes various methods to quantify the extent of degradation in thermo-kinetic and burning characteristics as well as to postulate a fundamental aging mechanism for traditional tungsten (W) pyrotechnic delay material, which has not been attempted in the past. The delay composition based on metallic fuel (W) and perchlorate oxidizer is subjected to aging at constant temperature of 71 °C and 95% relative humidity, for 2 and 12 weeks, respectively. Experiments including thermal analysis, combustion temperature profile and burning rate measurements are conducted together with numerical simulation of an actual pyrotechnic delay device. Moreover, the reaction mechanism, chemical kinetics, and combustion behaviour between pristine and aged cases are examined. Results illustrate that there exist two aging induced processes, which increases the presence of large agglomerated particles, high metal oxide content by thickening the outer oxide layer of metallic fuel, and more unreacted oxygen to instigate incomplete combustion in aged samples. This alters the reaction pathway of combustion process, lowers average thermal conductivity, and reduces diffusion of reactants in aged samples, thus causing significant decrement in the heat of reaction (31%), combustion zone temperature (10%), reactivity (12%), and burning rates (10%), such that the overall pyrotechnic delay device experiences misfiring during operation or a failure in accomplishing its actual intended task.

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1. Introduction

Energetic devices often utilize pyrotechnic delay compositions to generate a precise time delay between two ignition events with high repeatability and reliability [1,2]. Combustion characteristics of such mixtures are especially significant in controlling this precise time delay. However, fundamental reaction/combustion mechanisms involved with pyrotechnic compositions are not yet completely understood, even to the present time. This is mainly due to their complex physical and chemical processes, multiple overlapping reactions, condensed phase heat release, etc. [3,4]. Typically, reaction mechanism in such mixtures include solid-solid reactions and solid-liquid reactions involving one molten component, and some solid-gas reactions [5,6].

Most extensively used pyrotechnic composition in various fields has been traditional tungsten delay, which consists of W, potassium perchlorate (KClO₄), barium chromate (BaCrO₄) and diatomaceous earth (SiO₂). Past studies have reported about burning characteristics, combustion velocities and reaction mechanisms of this delay composition [3,7–10]. Shachar and Gany [3] have studied the effect of tungsten particle size and its content on the burning rate and effective activation energy of different delay mixtures. Similarly, Nakamura et al. [7,8] showed that the linear burning rate of W/KClO₄/BaCrO₄ delay composition increased with pressure and high metal content in the mixture resulted in large burning rates. Further, it was mentioned that the external pressure had significant outcome on heat of reaction and maximum combustion temperature of this delay composition. Lu et al. [9] have reported that the thermal conductivity of the mixture was significant in causing an increase in burning rates for high metal content composition. In another thermal behaviour study [10], the reaction characteristics of various formulations of W delay mixtures were investigated.

Typically, pyrotechnic delay materials are expected to have long shelf-life since they are stored for long time before actual usage. When subjected to such prolonged storage, these materials
experience different loads and severe conditions caused by temperature, gravity, vibration, humidity, stress, etc. Due to this aging process, a gradual degradation in performance characteristics and sometimes different failure modes were observed commonly in most solid fuels [11,12]. This include various problems such as decrease in heat release, inconsistent burning rates, lower combustion zone temperature, reduced ignition characteristics and sensitivity, increase in oscillatory burning behaviour, and reduction of reaction rate, etc. Various degradation mechanisms that triggered above outcomes include chemical reaction between oxidant and binder [11], slow decomposition of oxidants [12], prior oxidation of metallic fuels, etc. In order to investigate their long term effects within a realistic time frame, pyrotechnic samples were aged for short duration at constant elevated temperatures. Subsequently, Arrhenius or Berthelot equation [13] was utilized to determine the long term storage duration at ambient-like temperature by extrapolating the short duration storage data at elevated temperature.

Many investigations have studied the aging process of various pyrotechnic materials as well as composite solid propellants that were subjected to accelerated aging of temperature and humidity to improve upon their shelf-life [4,11-17]. From thermal analysis of these aged samples, it has been generally reported that prolonged storage causes a decrease in overall heat of reaction and an increase in activation energy [15,16]. In addition, aging studies on zirconium (Zr) based pyrotechnic materials have stated that pre-oxidation of metallic fuel was an important factor in affecting their performance characteristics as well as flame temperature [4,15], which was significantly enhanced in the presence of moisture.

It is well recognized that pyrotechnic delay materials undergo degradation in their performance characteristics due to the aging phenomenon. However, the extent to which these parameters are influenced need to be quantified from different aspects to ensure their safe intended usage when stored over longer time. Though, a plethora of literature are available on various pyrotechnic delay mixtures, a complete understanding of their combustion/reaction mechanisms is still limited. In addition, previous studies have focused mainly on the thermal characterization in order to obtain thermodynamic and chemical kinetic parameters of aged materials [14-16]. However, studies on the influence of aging on the combustion behaviour (specifically on temperature profiles, maximum combustion temperatures, burning rate vs. pressure plots) of these materials have not been reported in the past. Moreover, a fundamental understanding of aging mechanism that causes such reduced performance in pyrotechnic delay is lacking from the combustion aspect. The present study emphasizes on these facets of aging and also on improving the current knowledge on reaction characteristics and governing combustion mechanisms that would allow pyrotechnic delay materials to be further effective in the respective field.

In this study, W based pyrotechnic delay composition was considered to investigate the impact of accelerated hygrothermal aging on its thermal decomposition behaviour, reaction kinetics, and combustion behaviour, and postulate a fundamental aging mechanism for this mixture. This delay mixture in the form of powder and pressed pellets were aged under constant temperature and relative humidity (RH) over specified time. Thermo-kinetic analysis, combustion temperature experiments and combustion photography were implemented in this study. The influence of aging induced processes on different characteristics of aged W delay samples were discussed with respect to the unaged/pristine case. In addition, numerical simulation of an actual pyrotechnic delay device containing W delay has been performed, in order to show the role of W as well as its aging effect on the overall performance of this device and support the experimental efforts in understanding the aging mechanism with W delay mixtures.

2. Experimental approach

2.1. Pyrotechnic material

All pyrotechnic delay samples considered in the present study were delivered by Hanwha Corporation Ltd. It consisted of tungsten as metallic fuel, KClO4 as oxidant, BaCrO4 as modifier, and SiO2 as diluent, along with some binder. The compositional ratio for W/KClO4/BaCrO4/SiO2/binder was 48/10/36/5/1, by mass. Average particle sizes for all these solid ingredients were maintained to be ~45 μm, except for BaCrO4 (~10 μm). For better readability, this pyrotechnic mixture will be referred to as W delay further in this article. This specific formulation was designed to provide desired overall burn times and burning rates, as per requirements of a particular energetic delay device utilized for defence applications.

The mechanical mixture of these ingredients (powder form) were utilized for thermal analysis, morphological and spectroscopic analysis, and combustion temperature measurements. In addition, this mixture was pressed into pellet form in hydraulic press for utilizing in burning rate experiments. The pressed pellet, of diameter 20 mm and length 20 mm, was used to measure its actual bulk density. Theoretical maximum density (TMD) was calculated using mass fraction and density of each ingredient in the mixture. The actual measured density and TMD of this mixture were 3.24 gm/cm³ and 6.12 gm/cm³, respectively. Porosity of pressed pellets was then calculated as a ratio of actual density to TMD (47%). Both mechanical mixtures and pressed pellets were categorized into three groups, namely pristine, 2 weeks and 12 weeks hygrothermally aged, based on their aging duration. Accelerated aging was performed in a closed chamber at constant temperature and relative humidity (RH) of 71 °C and 95% respectively, for 2 and 12 weeks, which were selected based on [16,17] and often common in most aging studies. The variation in actual density of these pressed pellets due to aging was marginal (< 1%). Typically, in most aging studies, samples were subjected to accelerated aging under elevated temperature and high RH conditions for short duration in order to simulate/imitate natural aging, which occurs over a longer time under ambient storage conditions in reality [12,14]. Further, van’t Hoff equation was utilized to predict the equivalent storage period for which these samples would have aged under room temperature [15]. Based on this, the natural aging period at temperature of 25 °C and acceleration factor of 3.5 for 2 weeks and 12 weeks aged samples were calculated as 12.2 years and 73.2 years, respectively.

2.2. Methodology

Thermal behaviour of this W delay was investigated by using differential scanning calorimetry and thermogravimetry (Mettler Toledo, DSC 3+ and TGA 2) facilities. A mechanical mixture of 2–3 mg was placed inside 40 μl aluminium crucible sealed with a lid having 0.5 mm perforation for DSC tests, which were performed under 40 ml/min of nitrogen flow inside the furnace in the temperature range of 30–630 °C. On the other hand, TGA experiments were performed with a standard 70 μl alumina open pan with sample weight of ~4 mg in the temperature range of 30–900 °C under 40 ml/min of nitrogen flow. The heating rate was varied as 1, 2, 4, 8, and 10°C/min for both these experiments. All experimental conditions and procedures followed the International Confederation for Thermal Analysis and Calorimetry Kinetics Committee’s recommendations [18]. Further, the heat release from each thermal reaction can be calculated by utilizing Eq. (1). In the present study, it was determined by integrating the area under the peak in DSC curves using tangential baseline type method in Advanced Thermo
Kinetic Analysis Software (AKTS) [19-20].

\[ Q = \int_{t_0}^{t_{\text{end}}} S(t) - B(t) \, dt \]  

where \( S(t) \) and \( B(t) \) indicate the measured DSC data as a function of time and the baseline signal. Further, \( Q, t_0 \) and \( t_{\text{end}} \) represent the heat of reaction (J/g), start time and end time in a reaction peak, respectively.

Friedman isothermal method was employed to extract the chemical kinetic parameters, namely the effective activation energy \( (E_a) \) and pre-exponential factor \( (A_0) \), from DSC curves obtained at various heating rates [21]. Under non-isothermal conditions, the product of the heating rate \( (\beta = \frac{dT}{dt}) \) and reaction rate can be determined using a relationship expressed in the form of Arrhenius equation as in the following Eq. (2).

\[ \beta \frac{d\alpha}{dT} = \frac{A_0 f(\alpha)}{R} \exp \left( \frac{-E_a}{RT} \right) \]  

Taking logarithm on both sides of Eq. (2) yields

\[ \ln \left( \beta \frac{d\alpha}{dT} \right) = \ln(f(\alpha)A_0) - \frac{E_a}{RT} \]  

where \( R, T, \alpha \) and \( f(\alpha) \) correspond to the universal gas constant, temperature, reaction progress/product mass fraction and a function reflecting on the dependence of the reaction rate on the reaction progress, respectively. Further, \( -E_a/R \) and \( \ln(f(\alpha)A_0) \) represent the slope of the linear equation \( (y = ax + b) \) and its intercept with vertical axis, respectively. Here, \( x \) is \( 1/T \) and \( y = \ln(\text{d}\alpha/\text{d}t) \). In this study, AKTS program was utilized to obtain the chemical kinetic parameters as well for various cases.

Surface morphology of different pyrotechnic samples was examined using a field-emission scanning electron microscope (FE-SEM) (Model JSM-7800F Prime, JEOL Ltd, Japan), equipped with in-lens Schottky plus field emission electron gun and secondary detectors. Elemental mapping was performed using energy dispersive spectroscopy (EDS), coupled with FE-SEM to identify the sample elemental composition. The resolution for SEM imaging was 1.00 nm (15 kV). X-ray diffraction (XRD) analysis was performed using a powder x-ray diffractometer (Rigaku, SmartLab model), equipped with Ultra250 detector and Cu target with tube voltage of 3 kV. The diffraction peak intensities obtained in the 2θ range of 10° to 90° were analyzed in PDFX V2.8 software using Crystallography Open Database [22]. Approximately 4 mg of mechanical mixtures were used for these techniques. The actual W delay samples before combustion and their corresponding product residues from strand burner tests were analysed in both SEM-EDS and XRD.

Combustion temperature profile was obtained using a boat type configuration setup shown in Fig. 1a, similar to that reported in previous studies [23,24]. About 100–130 mg of mechanical mixture was packed inside this cylindrical configuration (8 mm diameter and 3.5 mm length), which was kept open on the top side. A K-type thermocouple (0.6 mm bead size) was inserted ~2.0 mm into the sample from the bottom through a small port at the center of this configuration. Ignition was achieved by blowing a butane gas torch onto the top surface of the sample for a few seconds. Temperature data were collected using NI DAQ 9123 module at the sampling rate of 100 Hz and LabVIEW software. Experiments have been repeated more than twice for all samples considered in this study and an average temperature profile was presented for discussion.

A windowed strand burner developed previously at our lab was utilized for determining the burning rate of pressed pellets as a function of pressure, in the range of 1–40 bar under nitrogen ambience, through combustion photography (Fig. 1b). Pressed cylindrical pellets were cut into samples with rectangular cross section of 6 mm × 4 mm and length of 10 mm. The experimental test procedure and further details of the setup were reported elsewhere [25]. Combustion process was captured using a high-speed camera (Phantom V711, with resolution of 800 × 600 pixels2) fitted with a 105 mm Nikon macro lens, at a framing rate of 100 fps and exposure time of 10 or 50 μs, depending upon experimental conditions. Ignition was achieved using red hot nichrome wire connected to a regulated DC power supply. High-speed camera and ignition source were triggered externally with 5 V pulse to ensure synchronization between the image acquisition and wire heating. A custom MATLAB code was utilized to locate the leading reaction zone locations in subsequent burning images, which were then plotted against the framing time intervals. The slope of
Table 1: Elemental composition (weight %) of different W delay samples obtained using SEM-EDS.

<table>
<thead>
<tr>
<th>Sample/Element</th>
<th>O</th>
<th>W</th>
<th>K</th>
<th>Cl</th>
<th>Ba</th>
<th>Cr</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical concentration (pristine)</td>
<td>18.5</td>
<td>42.2</td>
<td>2.3</td>
<td>2.0</td>
<td>23.9</td>
<td>10.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Pristine</td>
<td>31.2</td>
<td>7.5</td>
<td>2.0</td>
<td>2.4</td>
<td>40.7</td>
<td>14.2</td>
<td>2.0</td>
</tr>
<tr>
<td>2 weeks hygrothermally aged</td>
<td>29.3</td>
<td>11.3</td>
<td>0.2</td>
<td>0.4</td>
<td>39.7</td>
<td>13.6</td>
<td>5.4</td>
</tr>
<tr>
<td>12 weeks hygrothermally aged</td>
<td>36.6</td>
<td>6.7</td>
<td>1.1</td>
<td>1.5</td>
<td>36.1</td>
<td>12.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

a straight line in the above plot provided the burning rate. Most burning rate data at each pressure were repeated at least once and the error involved in this measurement was calculated to be ±3% for each data point.

3. Results and discussion

3.1. Sample morphology and composition

Surface morphology of different W delay samples were observed in SEM and their elemental composition and mapping were obtained using EDS analysis. All ingredients were evenly distributed in the mixture for pristine case (Fig. 2), with their particle sizes less than 45 μm, except for BaCrO₄ (< 10 μm). Relatively large scale aggregates of BaCrO₄ particles were noticed in SEM images of hygrothermally aged samples (Fig. S1 of the supplementary material). The level of this agglomeration caused by moisture was noticed to be gradually increasing with the aging period of these samples, which will have an impact on the combustion behaviour (see later in Section 3.4).

The elemental composition obtained from EDS for these mixtures is presented in Table 1, which indicates that the oxygen content was more with hygrothermally aged samples when compared to pristine ones. This implies that the oxidation process of metallic fuel was affected in aged samples. However, with 2 week aged sample, the oxygen content is less because the region selected for this analysis comprised of more W particles, which was not an ideal case to represent the entire mixture. Therefore, the disparity noticed with this sample is more of an experimental error, rather than the actual behaviour of the sample itself. Furthermore, it also causes less content for K and Cl. More importantly, significant cracks on the surface of oxidant particles (KClO₄) as well as diluents (SiO₂) are clearly evident for aged samples, as shown in Fig. 3. This feature is in addition to micro-cracks and uneven surfaces typically noticed on metal fuel particles of aged mixtures [16,17].

XRD analysis was performed to identify actual ingredients in these mixtures and shown in Fig. 4, wherein the data for aged
cases were translated vertically for clarity. The presence of additive was not recognized with these samples. However, considerable amount of reduced oxidant (K$_{0.97}$Cl$_{0.04}$O$_2$) was observed with 2 weeks aged case, indicating that decomposition of oxidant has occurred during the aging process. The presence of moisture influences the splitting of vulnerable C-O bond in the oxidant and enhances the decomposition of KClO$_4$ [26]. These results affirm that there exists excess elemental oxygen content causing pre-oxidation of the metal fuel due to prior decomposition of the oxidant in hygrothermally aged W delay samples, similar to previous study on Zr based pyrotechnic delay composition [15,16].

### 3.2. Thermal analysis

DSC and TGA curves were obtained at four different heating rates for various W delay mixtures, under nitrogen flow. These curves for pristine or unaged W delay sample are shown in Fig. 5, at the heating rate of 8 °C/min and temperature range of 30–600 °C. The pristine case will be considered first before looking into the influence of hygrothermal aging on thermal behaviour of this mixture. In actual DSC curve, the pristine delay exhibited one endothermic and two exothermic peaks in the tested temperature range. Subsequently, mass loss in TGA curve was also observed in two distinct steps, each one associated to exothermic peaks in the former. The endothermic peak noticed at temperature of ~304 °C corresponds to the crystalline transition of KClO$_4$ from rhombic to cubic structure, as reported by previous studies [3,27]. In addition, there was no discernable mass loss associated with this particular reaction.

The first exothermic peak (~390 °C) was caused by the pre-oxidation reaction of metallic fuel, since it involved a minor heat release. TGA curve shows ~1% decrement in the total mass due to this reaction, referred to as first stage mass loss. However, the second exothermic peak seen at ~487 °C was significant and started at an onset temperature of ~465 °C. This exotherm was composed of overlapping sub-reactions that include decomposition of KClO$_4$, major combustion reaction of tungsten with oxygen, and also possibly further decomposition of unreacted oxidant [10]. The heat of reaction obtained from this exothermic peak was ~615 J/g, which was considerable higher than that of first exothermic peak. This implies that majority of the fuel was oxidized apparently in the second exothermic reaction. Furthermore, second stage mass loss corresponding to this reaction was determined to be ~2.4%. Overall mass loss of the sample was less than 5% during these reactions.

Since, most pyrotechnic delay compositions typically undergo condensed phase combustion (solid–solid or solid–liquid reactions), the mass loss associated with the second exothermic reaction was due to the dissipation of unreacted oxygen. This reaction mechanism and thermal decomposition behaviour were similar to that reported by previous studies on traditional tungsten delay compositions [3,7,9], though the metal content of the delay mixture was relatively high in the present study. This caused a noticeably higher heat of reaction in the present study than that was reported previously.

Reaction mechanism of typical W delay composition involves decomposition or melting of KClO$_4$ oxidant, followed by primary oxidation reaction of fuel and oxygen from the former, and secondary oxidation reaction with BaCrO$_4$. Generally, the oxidant decomposition process initiates the entire reaction system of this delay mixture. The oxidation reaction results in WO$_3$, BaWO$_4$ and KCl as major products along with certain heat release. These products will be confirmed later when looking at XRD analysis of reaction products in Section 3.4. Note that the presence of small quantity of SiO$_2$ does not significantly influence the metal oxidation reaction and decomposition of KClO$_4$ with this delay mixture.

DSC and TGA curves of samples subjected to hygrothermal aging of 2 and 12 weeks are shown in Fig. 6, in comparison to pristine ones. At the outset, it can be clearly seen that there was a significant influence of aging on exothermic reactions as well as mass loss of these samples, observed at specific temperatures. However, the peak temperature of these reactions remain almost the same, except for the first peak in 12 weeks aged case. Note that the endothermic peak was unaffected by aging process. On the other hand, the area under both exothermic peaks were considerably reduced in aged samples, which is translated into decrease in their heat of reaction. The first exothermic peak (~390 °C) caused by the pre-oxidation reaction was hardly noticed with both aged samples. However, significant reduction of ~31.2% in heat of reaction was observed with the second exothermic peak (~380 J/g) in 12 weeks aged sample (Fig. 6a).

In correlation with DSC, the mass loss associated with each exothermic reaction was reduced as well in TGA curves. The first stage mass loss was not significant with both aged samples. However, the second stage mass loss was observed to gradually decrease over a wide temperature range and the oxidation reaction completed earlier (Fig. 6b). Mass loss of 2 weeks and 12 weeks aged samples was 1.5% and 1.6%, respectively. This is in contrast to pristine samples, where the mass loss occurred rather sharply and the reaction took place over slightly longer period. The above observation suggests that the rate of reaction progress between W and oxygen was slowed down and the reaction could be incomplete to certain extent with aged samples. Such aspects will be noticed when looking at actual burning behaviour of pellet type samples later in Section 3.4.

The heat of reaction and mass loss determined from two exothermic reactions are presented in Table 2, for all three cases. There is a gradual decrement in the heat release and corresponding mass loss of these samples for an increase in the aging time, which is predominant with the second peak. This trend of reduction in heat of reaction with aged samples has been reported commonly in past studies [2,15–17]. The heat of reaction and mass loss obtained at various heating rates for different samples considered in the present study are listed in Table S1 (supplementary material). The overall trend in the thermal behaviour of these delay mixtures does not vary significantly over various heating rates (Fig. S2). A consistent decrement in heat of reaction and mass loss for hygrothermally aged samples relative to pristine ones implies that aging causes reduction in reaction progress of W delay composition.
3.3. Reaction kinetics

The effective activation energy as a function of reaction progress was determined by employing the Friedman isoconversional analysis [21] on DSC curves. The AKTS thermo-kinetics software was utilized for performing this analysis to evaluate the reaction rate and reaction progress, from which pre-exponential factor and effective activation energy were further calculated. These parameters were obtained for the second exotherm in DSC curves, the main oxidation reaction contributing to major heat release (Table 2), and occurred in the temperature range of 420–540°C. Reaction rate variations with temperature obtained at various heating rates for three different cases are shown in Fig. 7. Here, a typical increase in reaction rate was noticed when the heating rate was increased, implying that the sample must reach high temperatures to achieve the same reaction progress. Further, the peak reaction temperature also shows the tendency to increase with heating rates. With hygrothermally aged samples, the range of this oxidation reaction (between reaction initiation and end temperature) was reduced when compared to pristine samples. In addition, the peak reaction temperature and reaction rate for major second exotherm decreased when samples were hygrothermally aged (Table 2). Note
that, since the actual content of fuel and oxidizer in aged samples was reduced, the oxidation reaction gets completed in short time, which was observed as higher peak and narrow width for 2 weeks aged samples. Thus, these samples appear to have high reactivity, although it is because of less content of reactants. Further, the shoulder seen with 12 weeks aged samples was caused by thicker oxide cap (Fig. 7c). More importantly, aged samples indicate consistent decrease in their heat of reaction with increase in aging period, regardless of slight discrepancies in reaction rate curves. For brevity, plots for the extent of reaction progress ($\alpha$) and logarithm of reaction rate ($\ln((d\alpha/dt))$) at various heating rates are presented in Fig. S3 and their reaction parameters in Table S1 of the supplementary material, for all three cases.

In reaction rate plots, the slope and intercept of a straight line connecting a constant reaction progress in all heating rate curves represent the effective activation energy and pre-exponential factor, respectively for that particular value. Similarly, these parameters were obtained for various reaction progress values from 0 to 1. Figure 8 shows the effective activation energy ($E_a$) and pre-exponential factor ($\ln((f(\alpha) \times A))$) variation with reaction progress for pristine and aged samples, in the range of $0.1 < \alpha < 0.9$. $E_a$ was observed to broadly vary from 160 to 360 kJ/mol due to overlapping of multiple reactions in that temperature range. For pristine samples, $E_a$ attained a peak (325 kJ/mol) at $\alpha = 0.12$, which tended to decrease gradually until $\alpha = 0.40$ and remained almost constant further in $0.4 < \alpha < 0.9$ range. The average $E_a$ for pristine sample was calculated to be $246 \pm 30$ kJ/mol. This is comparable to the value reported by Shachar and Gany [3], for traditional W delay mixture (6–8 μm metal particles), although with slightly different pyrotechnic formulation.

A trend similar to pristine samples was noticed for 2 weeks hygrothermally aged ones with peak $E_a$ of 365 kJ/mol at $\alpha = 0.11$, followed by the plateau regime in $0.45 < \alpha < 0.9$. However, for 12 weeks hygrothermally aged ones, this peak (304 kJ/mol) was noticed at $\alpha = 0.65$, with only minimal variation of $E_a$ in the range of $0.1 < \alpha < 0.7$ and rapid decrement for $\alpha > 0.7$. The average effective activation energy along with the standard deviation was determined as $277 \pm 39$ and $274 \pm 26$ kJ/mol for 2 weeks and 12 weeks hygrothermally aged samples (Fig. 8a), respectively. Note that, the disparity in $E_a$ as a function of extent of reaction progress between 2 weeks and 12 weeks aged samples could be due to the result of samples from different batch processing of materials, which might have had some slight compositional variations. On the whole, high $E_a$ was observed for aged samples relative to pristine ones. This is attributed to pre-oxidation of metallic fuel in the mixture caused by the presence of reactive oxidant decomposition products formed during the aging process. Conversely, such reactive decomposition products increase the reactivity of the mixture resulting in low $E_a$ for some pyrotechnic materials, as reported in previously [17]. Note that, the variations of $E_a$ are often compensated by the pre-exponential factor (Fig. 8b). Since, the peak reaction temperatures of aged samples were shifted to lower values

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**Fig. 7.** Reaction rates of different W delay samples obtained at various heating rates. (a) Pristine, (b) 2 weeks hygrothermally aged, and (c) 12 weeks hygrothermally aged.
3.4. Combustion behaviour

The reaction zone temperature profiles of different W delay samples were obtained experimentally and shown in Fig. 9, for comparison. These temperature profiles follow similar trend for all three cases. The theoretical adiabatic temperature for pristine W delay composition is predicted as 2700 °C. Since, this experiment involves high heat losses due to its small scale, adiabatic conditions cannot be considered. Pristine W delay sample indicated a maximum combustion temperature of 718 °C, as expected, at 1.85 s after the start of a steep temperature rise in the profile. This is similar to that of reported by Nakamura et al. [8] for W/KClO₄/BaCrO₄/SiO₂ (64/36/30/5) composition at ambient pressure conditions, despite the slight variation in their formulation with the present study. It has been illustrated that the metal content in typical delay composition influences the maximum temperature attained during its combustion. In addition, the temperature rise time (\(T_r\)), which is the time needed to reach the maximum temperature from the onset of temperature rise, is significantly dependent on the thermal diffusivity of the delay mixture. Therefore, a large temperature rise time implies slow heat conduction into the delay material. From the combustion profile in the present study, it can be affirmed that the mixture thermal conductivity is important in transporting the heat from the reaction zone to unreacted layers of the material.

When subjected to hygrothermal aging, W delay samples showed a decrement in the maximum combustion temperature and a slight increase in the temperature rise time. The maximum combustion temperature and \(T_r\) for 12 weeks aged sample were determined as 640 °C and 1.95 s, respectively. There is a considerable decrease in the maximum temperature attained in this aged sample, due to the reduced metallic fuel content available for combustion. This corroborates with the EDS elemental composition results (Table 1). In other words, the actual composition of the aged delay mixture itself was altered to have less content of metallic fuel. Since maximum combustion temperature is related to sensible enthalpy of the reaction products, the final composition of the residue gets modified depending upon the former, as will be seen later. In addition, the temperature rise time was increased, which suggests that the average thermal conductivity of aged delay mixture was less compared to the pristine case. As expected, Table 3 shows that this disparity in above parameters have an increased effect for longer aging period.

Pellet delay samples were utilized to determine their burning rate as a function of pressure in a windowed strand burner. Based on realistic conditions experienced by this pyrotechnic delay composition, pressure range was considered from 1 to 40 bar. Hot nichrome wire was placed at the top surface of pellet samples, which provided the ignition. Instantaneous burning snapshots of different W delay pellets show qualitative features of their combustion behaviour under pressurized conditions, as shown in the supplementary material (Fig. S4). The actual burning rates were deduced from these images, and the effect of pressure and hygrothermal aging on the combustion mechanism of different W delay pellets are discussed.

Burning images of W delay pellets exhibited typical features of combustion dominated by condensed phase reactions (Fig. S4), for both pristine and hygrothermally aged samples, at pressure of 40 bar. Highly luminous regions were observed in the condensed phase that separate the unburnt region from the reaction/combustion zone with these samples. Reaction product gases emanated from the sample regressing surface in normal directions only at the location of reaction zone. A steady state propagation in the reaction zone was attained with minimal heat loss effect in the lateral direction [28]. In addition, the shape of product residues was retained the same as their unburnt pellets after the reaction. These observations suggest that the reaction between metallic fuel (W) and perchlorate oxidant (KClO₄) occurred in predominantly solid-liquid phase with minimal gas phase reactions,
A linear increase in burning rate with pressure was observed with pristine W delay pellets. However, this increment was not as significant as in the case of composite solid propellants, which undergoes predominantly gas phase combustion. An increment in burning rates of 29% was noticed in the pressure range of 1 to 5 bar, which then reduces to 17% further in the range of 5 to 40 bar. The burning rate vs. pressure plot follows Vielle’s burn rate equation, $r = aP^n$. A power law fit to these data points result in the pressure exponent $n$ of 0.13 for pristine W delay pellets. Such low $n$ value is typical of W delay compositions [9]. Further, the burning rates were not observed to undergo transition from conductive to convective burning regimes. These features are mainly attributed to the dominant condensed phase reactions associated with conductive heat transfer mechanism of W delay composition.

The burning rate range, pressure exponent and temperature coefficient for pristine and hygrothermally aged cases are presented in Table 3. When subjected to hygrothermally aging, the pressure exponent varied only slightly with W delay pellets (Fig. 10). However, a considerable reduction in burning rates with both aged samples was clearly evident compared to pristine ones, over the entire pressure range. A decrement of 5–10% in burning rate was observed with W delay pellets, at each pressure level. Typically, such reduction in burning rates due to aging is common among composite solid propellants [31–33]. However, the quantitative extent of reduction in burning rates due to the effect of hygrothermal aging on W pyrotechnic delay compositions is evident only from the results of the present study.

Combustion product analysis was performed using XRD and SEM-EDS for all three cases considered in this study, with residues obtained from strand burner tests at 20 bar. The main diffraction peaks detected from XRD analysis include BaWO$_4$, Cr$_2$O$_3$ and KCl, along with some unreacted W in the product residue of pristine sample (Fig. 11). Though, decomposition products of KClO$_4$ and W initiated the reaction mechanism for this delay, BaCrO$_4$ has been involved in the reaction at a later stage (secondary). This is corroborated through the presence of BaWO$_4$ and Cr$_2$O$_3$ as dominant compounds in this analysis. The presence of some unreacted W in the residue is due to fuel-rich nature (excess W) of the delay composition utilized in the present study. The stoichiometric mixture for W/KClO$_4$/BaCrO$_4$ composition was reported to be 37/38/25, by weight [9]. Except for some undetected intermediate species, this XRD pattern is similar to that reported for traditional W delay as in previous studies [8,23].

For hygrothermally aged samples, the presence of KCl and unreacted W was noticed to a larger extent compared to pristine case. Further, the diffraction peak intensity of the dominant product (BaWO$_4$) was considerably reduced as well in aged samples, especially at 26° and 54°. These features imply that the level of incomplete combustion with aged samples was more than that of pristine case. In addition, the reaction involving BaWO$_4$ formation was also affected due to aging, which in turn reduced the overall heat release associated with this delay sample (Table 2), as described before in Section 3.2. Note that since pellets of product residues were grounded for these analyses, the surface morphology of different W delay samples remain mostly the same.
(Fig. S5 in the supplementary information). However, EDS of these samples showed a large amount of elemental W, with reduced amount of elemental K and Cl for aged cases (Table S2). This means that some of decomposition products (KCl) of oxidant and unreacted oxygen escaped during combustion, which was noticed as large amount of gases in high-speed burning images of aged samples (Fig. S4). This convective flow of unreacted species caused a heat loss from the propagating combustion/reaction zone, and therefore also mildly contributed to the reduction in burning rates.

3.5. Aging mechanism of W delay

Reaction characteristics of unaged W delay involves the chemical reactions as shown in Fig. 12 during its oxidation process (without the participation of SiO$_2$) [3,7,10]. Here, the tungsten oxidation reaction was initiated primarily by the decomposition process of oxidant. This increased the temperature of the overall system to allow for further reaction with BaCrO$_4$, which now acts a secondary oxidizer in the mixture. However, its presence in the delay mixture reduces the reactivity and the reaction propagation rate through increased diffusion time between the fuel and oxidizer. Recall that the maximum combustion temperature attained for unaged delay composition was 718 °C (Table 3), which is considerably less than the decomposition temperature of BaCrO$_4$ (1400 °C) [23]. This further affirms that the secondary reaction between BaCrO$_4$ and W predominantly occurred in the condensed phase as well (solid-liquid reaction), similar to the primary oxidation reaction. The final products from these reactions were observed in the XRD analysis of combustion residues (Fig. 11).

For hygrothermally aged samples, it is mentioned before that two significant processes occur during prolonged storage, which are (1) prior decomposition of the oxidant and (2) pre-oxidation of the metallic fuel [15-17]. Due to these processes, the overall reaction mechanism of the system encounters additional reactions as presented in Fig. 12, along with the ones that occurred in unaged samples. In this scheme, a large level of unreacted oxygen can be noticed after the completion of reaction process, thus leaving more tungsten un-oxidized. This further causes incomplete oxidation of aged W delay sample, which was originally fuel-rich in nature before the aging period. Consequently, the heat release caused by the oxidation reaction is reduced significantly (Table 2). This decrement in heat release increases with increase in aging time, since the aging induced processes tend to become severe over longer storage time. In addition, the reactivity of the overall mixture decreased as well (Fig. 8), implying that the pre-oxidation process dominates the prior decomposition process of oxidant, for this type of W delay mixture. Furthermore, it was observed that aged powder samples fail to ignite under atmospheric conditions causing duds, from a different set of experiments performed to study their ignition behaviour. Similar behaviour for zirconium based pyrotechnic materials that exhibit ignition duds when subjected to aging has been reported in our previous study [29].

Many significant physical and chemical parameters impact the overall combustion characteristics of multi-component pyrotechnic delay mixtures. These include composition of the delay, particle sizes of fuel and oxidizer, actual mixture density, bulk thermal conductance of the mixture, progress in chemical reaction rate, heat transfer processes, heat release from the reaction, final combustion zone temperature, and ambient temperature and pressure [3,7,8]. When subjected to hygrothermal aging, most of these parameters are altered considerably, thus affecting the burning behaviour of pyrotechnic delay mixtures in many ways. Due to the pre-oxidation reaction of the fuel, metal oxide (WO$_4$) content in the aged mixture is increased, thus modifying its actual composition. The presence of metal oxide in this mixture reduces the maximum reaction zone temperature attained as well during combustion, which is incomplete as a result of unreacted gaseous oxygen, eluding into the ambient, caused by the prior decomposition reaction of oxidant. Moreover, ingredients present in the form of large agglomerated particles in aged mixtures (Fig. S1) imply that the available surface area of fuel and oxidizer particles was decreased, thus not allowing for large number of contact points between them for complete combustion to occur.

Bulk thermal conductance of the mixture and conductive heat transfer processes are significant in determining the reaction propagation rate of pyrotechnic delay pellets, since the effect of lateral heat loss and convective heat transfer are marginal. Note that the thermal conductivity of metallic oxide (WO$_4$) is lower than the corresponding metal (W), therefore a large content of metal oxide in aged pellet implies that its average thermal conductivity is less compared to unaged one. In addition, a thick metal oxide layer attributes to slow diffusion of oxidizer into metal particles in aged samples, which is one of the rate determining step in the chemical reaction. Both these aspects suggest that the reaction rate of the
mixture is reduced, thus slowing down the heat release rate, which in turn further decreases the rate of heat conduction from the reaction zone into the unreacted part of the pellet. Thus, the slow conductive heat transfer mechanism caused by alternate reaction pathway results in the reduction of burning rates with aged samples. The present study ascertains that the aging induced processes alter the fundamental mechanism of chemical reactions at molecular level, which is translated into reduction of bulk characteristics such as heat of reaction, maximum combustion zone temperature, rate of conductive heat transfer, and burning rates of aged pyrotechnic delay samples. These processes are presumed to occur in most pyrotechnic materials regardless of their composition, provided condensed phase reactions are dominant in such materials, which is the significant aspect emphasized in this study.

4. Numerical simulation

A two dimensional simulation of an actual pyrotechnic time-delay device was performed, in order to predict the burn time and examine the reaction propagation structure of the W delay material inside the delay tube, for pristine and hygrothermally aged cases. The heat of reaction and chemical kinetic parameters extracted experimentally from DSC curves using Arrhenius type reaction rate model for different samples were utilized in the simulation code. The governing conservation equations and calculation were similar to that reported by our previous studies [34-36]. The level set and ghost fluid method were utilized to track the structural response of the outer casing [37]. The Mie-Gruneisen equation of state (EOS) was used for the unreacted BKN03 and the JWL EOS was used for the reactive material. These equations were solved using third-order Runge-Kutta method and third-order non-oscillatory method for the temporal and spatial discretization, respectively. Note that chemical kinetics were extracted at temperatures lower than actual conditions experienced by delay material during the operation of pyrotechnic device. However, it has been reported before that these parameters considerably reflect global chemical reactions associated to high temperature conditions [35].

The computational domain utilized for the present study is shown in Fig. 13, wherein the outer casing is made up of aluminium. The delay material inside the case was ignited by the flame from BKN03, which gets ignited by the igniter. Initial ignition temperature of 1000 K for 20 ms was applied to the top part of the computational domain (igniter portion). The pre-exponential factor and £ corresponding to BKN03 were 9.16 x 10^5 1/sec and 1.8 x 10^4 kJ/kmol, respectively [38]. For boundary conditions, the left side of x-axis was considered to be axisymmetric and the bottom side of y-axis was assigned with zero-gradient for transport properties.

The results obtained for temperature evolution and reaction progress inside the delay tube during the reaction propagation of pristine samples are shown in Figs. 14 and 15, respectively. The
igniter reacted for short time (0.1 s) and initiated the reaction in the pyrotechnic delay. The reaction propagation of the delay occurred similar to that of the instantaneous combustion images from strand burner experiments (Fig. S4), and dominated by conductive heat mechanism. It can be observed that there was stable and continuous reaction propagation of the delay material because of its sufficient heat release and reaction rate. Due to considerable heat transfer to the outer casing of the delay tube and its high thermal conductivity, the heat conduction to the unreacted region of the delay material happened relatively faster near the wall compared to the central region. This caused marginally high reaction propagation rate near the wall and therefore the protruded shape in the middle section of the delay material (at 1.97 s). The delay section burned for 1.90 s after its ignition at the burning rate of 2.00 mm/s. This rate of propagation is slightly less than the experimental data obtained at atmospheric pressure due to the heat loss from the reaction zone to wall of the delay tube and then to the surrounding outer ambience.

For hygrothermally aged samples, the ignition temperature was maintained the same but the heat of reaction and chemical kinetics from their corresponding experimental DSC curves were utilized for the simulation. The temperature and reaction progress plots for 2 weeks and 12 weeks aged cases are presented in Figs. 16 and 17, respectively. By comparing these results with pristine case, it affirms that the overall reaction temperature of the propagation zone lowered and the burning time of the delay section increased significantly. This is mainly due to their low heat of reaction and reaction rate, and increased activation energy caused by the aging process. The burning time and burning rate for 12 weeks aged case were determined as 2.45 s and 1.55 mm/s, respectively. The reduction in reaction zone temperature and burning/reaction rate of aged cases increased gradually with increase in aging time (Table 4), and this trend agrees quite well with the experimental results presented in previous subsections. Typically, in aging studies of solid propellants, the reduction in their burning rates is observed in the range of 10–20% relative to un-aged samples [32,33]. In the present study, the decrease in burning rate and increase in burning time for aged samples were 20% and 25%, respectively, which are comparable to variations observed with previous studies on solid propellants. Moreover, this study is the first attempt to quantify the degradation in burning rate of pyrotechnic delay compositions subjected to accelerated aging.
conditions. Therefore, comparison with standards or previous studies cannot be made with respect to the combustion behaviour. Although, the reaction propagation of the delay section completed and achieved the heat transfer to the bottom igniter of the delay tube, the reduction in burning rate and increase in delay time would eventually cause failure or misfiring during operation of the overall pyrotechnic delay device.

5. Conclusion

In this study, a tungsten (W) based pyrotechnic delay composition was considered to investigate the aging mechanism and its influence on the thermal decomposition and combustion characteristics of the mixture. This delay mixture was composed of W, KClO₄, BaCrO₄, and SiO₂. The delay composition was subjected to accelerated aging conditions at constant temperature of 71 °C and 95% RH for 2 weeks and 12 weeks, respectively. Experimental studies were conducted to quantify the extent of degradation or deterioration in different performance parameters of aged delay mixtures such as heat of reaction, activation energy and reaction progress, combustion zone temperature and burning rates, with respect to the pristine case. Numerical simulation of the reaction propagation of an actual pyrotechnic delay device containing W delay was performed to predict its combustion characteristics and compare with the experimental data.

Reaction characteristics of W delay mixture consisted of pre-oxidation reaction, oxidant decomposition and major oxidation of W, which caused mass loss in two stages. Combustion temperature profile and burning rates indicated that reaction propagation was governed by predominantly conductive heat transfer mechanism. When subjected to hygrothermal aging, there existed two aging induced processes that influenced the thermo-kinetic and combustion behaviour in various ways. Pre-oxidation reaction caused an increase in metal oxide content of aged delay mixtures, which reduced the bulk thermal conductivity and the rate of diffusion of reactants into each other. Prior oxidant decomposition reaction produced more unreacted oxygen that eluded into outer ambience and resulted in increased incomplete combustion of aged mixtures, which was further enhanced by the presence of large agglomerated particles. All these aspects combined together to degrade the performance characteristics namely heat release, reactivity, combustion zone temperature and burning propagation rate, through changes in chemical reaction pathways. Further, the results obtained from numerical simulation concurred well with experimental observations on the degradation in combustion behaviour of aged samples. The present study has provided some valuable insights into the influence of aging on the fundamental reaction
mechanism of W delay that altered its bulk reaction and combustion characteristics.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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References