# Combustion Reactions of Some “Metal-Oxide” Systems under Conditions of Zero and Applied Magnetic Fields: Thermal Imaging Experiments

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## Abstract

The effect of an external magnetic field of 0.2 T on the self-propagating high temperature syntheses (SHS) of a mixture of first row transition metals and their oxides was studied by using a very sensitive thermal imaging method involving an IR-camera and software developed by MIKRON Instrument Co., Inc. (M9100 Pyrovision Series – Imaging Pyrometer). For the basic conversion of first row transition metals to their corresponding oxide, there was no observable difference in propagation behavior between applied and zero field reactions. However the average wave velocity for the iron system showed a significantly greater value when the SHS was conducted under conditions of an applied field. This enabled accurate monitoring of the combustion process in particular propagation velocity, maximum temperature, cooling rates, synthesis wave width and pathway. Several interesting phenomena, such as hole formation in the pellet and combustion wave segmentation were detected in some systems.

## Introduction

In physical inorganic chemistry there are number of synthesis techniques. One of the most common and traditional method for high-temperature materials synthesis is termed as the “Heat and Beat synthesis”. This process involves a solvent-free technique. The major deficiency with this technique is that it is difficult to overcome the solid-state diffusion barrier [1]. This barrier is resolved by processing the starting material through repeated grinding, heating, and cooling stages. There is a current search for faster and more economical methods for solid state synthesis [2, 3]. In 1967 Russian scientists (*Merzhanov and his co-workers*) performed the first characterization and identification of “*solid flame*” phenomenon [4]. This characterization was completed in a gas-less solid-state reaction in which both the reactantand product remain in the solid state even at elevated reaction temperatures and has come to be known as Self-propagating High-temperature Synthesis (SHS) [5, 6].

One of the main task of any combustion experiment is to collect and explain the combustion wave characteristics. To date a number of experimental techniques were developed for that purpose. Two bichromatic IMPAC pyrometers (Infratherm IS5) were used simultaneously to record thermal data between 300 and 1000°C and between 1000 and 3000°C for intermetallic SHS reactions of Al-Ni-Ti [7]. Data were collected with a precision of +/- 5°C for SHS reactions of binary, ternary, and quaternary for pelletized systems under conditions of zero fields. An optical pyrometer was used to examine a variety of systems during SHS. A point on the sample surface with a size of 1.5 mm was used to acquire data at 50 ms intervals. These thermal data were plotted as a function of time. Propagation and wave velocity modes were

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*corresponding author. Email: maxim1968@mail.ru studied by using SensiCam camera (Cook Corporation). This camera is a high speed CCD camera which acquires a large number of images, with a frequency close up to 40 Hz. SHS experiments were conducted in air or, in some cases, under an argon flux The majority of experiments were ignited using tungsten wire heated by a DC current (18 A, 8 V). Average combustion temperature for Al-Ni (Al-Ti and Ni-Ti) binary systems was calculated to be 1550°C and the propagation mode was thought to be spinning with several centres. A Ti-C combustion system had an average reaction temperature of 2670°C and a stable mode of propagation. Work was also done on ternary systems such as Al-Ni-Ti and Al-Ti-C, with the average combustion temperature and mode of propagation of 1580°C spinning and 2000°C pulsating, respectively. One quaternary system, Al-Ni-Ti-C, was investigated and showed an average combustion temperature of 1830°C, with the process showing spinning modes with several centres [8].

A ThermoCAM SC2000 IR-camera was also used to investigate the formation of $Mg_{0.5}Zn_{0.5}Fe_2O_4$ by SHS in powder form, by measuring the heat transfer and thermal characteristic of zero field SHS reactions, this reached a maximum temperature of about 1290°C. The combustion wave propagated in a steady manor, as the complete sample was analyzed and displayed propagation from one side of the powder sample to the other. This data showed details on the micron scale and the form of wave propagation was determined with great accuracy [9].

Mechanically activated self-propagating high-temperature synthesis (MASHS) studies were made on an Fe-Al system [10]. The investigators simultaneously acquired TRXRD and thermal data from these experiments. MASHS involves two main steps. The first step involved mechanical activation of pure elemental powdered sample by co-milling inside a planetary mill for a short time at given frequency and energy shock. The second step is the SHS reaction which proceeds to completion on ignition to form the product. Temperature was recorded using AGEMA Thermovision 470 at 200 ms intervals, with a field of view of 13 cm x 13 cm with each pixel in the infrared picture corresponded to an area of 1 mm x 1 mm. The results showed that mechanical activation introduced during the MASHS milling step significantly decreased the ignition temperature by more than 100°C, but significantly increased the wave front velocity by 2.5-12 $mms^{-1}$ when compared to the traditional SHS preparation techniques.

Work using the AVIO TVS 2000ST infrared camera was done at LURE to study SHS waves for the production of Ti-C [11]. Samples were ignited using a hot graphite rod and images were recorded between 50 and 1650°C. Results show that after 15 seconds the steady propagation wave stopped and the heat was transferred to the end of sample without reaction. The wake then propagated again after a pause of 5 seconds and temperatures in excess of 1600°C were observed.

The Mikron 9104 camera was used for the first time to attribute combustion parameters for the formation of complex oxides by SHS [12]. The combustion parameters for pure and substituted lanthanum manganites $La_{1-x}A_xMnO_3$ (A~Ca, Sr) were established from the thermal images analysis: $T_{max}$~1850°C and $U_{comb}$~3.87 $mms^{-1}$ for non-doped material $LaMnO_3$; $T_{max}$~$1650^0$C, $U_{comb}$~3.52 $mms^{-1}$ for Ca-substituted compound using an oxide dilutant, CaO (x~0.4), and $T_{max}$~1900°C and $U_{comb}$~3.92 $mms^{-1}$ for Sr-substituted material with a double internal oxygen source, ($SrO_2$+$NaClO_4$) (x~0.4).

Mikron 9104 optical pyrometer has also been used to obtain high resolution thermal images of an SHS reaction of ferrite systems. The camera recorded surface temperature ranges 866-2222°C, allowing for the thermal characterization of the SHS wave. Real-time observation of energetic process was achieved as the camera collected 30 frames per second; each frame consisting of 776 x 484 pixels with an accuracy of +/- 1%. Investigation of SHS reaction to form $ZnFe_2O_4$ in applied and zero fields showed that reaction temperature did not exceed 866°C. Reactions was carried out with $Mg_{0.5}Zn_{0.5}Fe_2O_4$ showed that on average, applied field reaction had an observed temperature of 1070°C and zero field experimental temperature was 1060°C. Reactions carried out on $MgFe_2O_4$ showed that applied field reactions to have approximately 49°C higher reaction temperatures. The same system had a faster wave velocity for applied field reaction by 0.78 $mms^{-1}$. High resolution of this system allowed for the acquisition of propagation and temperature modes [13].

In this paper we report on the combustion reactions of some selected first row transition metals with their corresponding oxides. In particular we follow the thermal changes in the reaction and use this to show that an applied external magnetic field directly influences the combustion process.

## Experimental

All reagents were obtained from the Aldrich Chemical Company (UK) and used as supplied. The particle size of all the initial reagents was in the range of 10-50 μm. The affinity for the metal powders to oxidize in air was sufficiently low in comparison to the time it took to mix, compress, and initiate the reactions. In accordance with that, all the experiments were carried out in air. The pellets were prepared for the simple elemental conversion of metal to its metal oxide. All the systems (except the Ti-system) used sodium perchlorate ($NaClO_4$) as an internal oxidizing agent. Addition of sodium perchlorate is necessary, because the SHS reaction proceeds rapidly and simple diffusion of air is not a practical way of supplying oxygen inside of the sample. Oxidation of metals is extremely exothermic and as such, this is the driving force of the reactions. Ratios of the metal, metal oxide, and sodium perchlorate were ascertained after many pre-tests. In general, all the pellets were made to a weight of 0.75 g. Metals and metal oxides were crushed in a mortar and pestle separately from the sodium perchlorate to prevent pre-ignition. Crushed metal and metal oxide mixture was added to the crushed sodium perchlorate in a gentle manner, to produce a homogeneous mixture. Pellets were pressed under one-ton pressure and were 16 mm in diameter and used within 20 min of preparation, as there is evidence from previous work that the mixture once prepared could degrade over time. After SHS all the pellets were ground and washed with distilled water to remove traces of co-produced NaCl. The mixture was ignited on a ceramic mat in air by use of a Rekrow RK-2060 Micro torch. This induced a solid flame that moved through the pellet.

Details of the preparation procedure as well as ratio of the initial reagents for the each particular chemical composition were as follows:

*$Fe/Fe_3O_4/NaClO_4$ pellets.* ($4Fe+Fe_3O_4+NaClO_4$) (1)

*$Ti/TiO_2/NaClO_4$ pellets.* ($Ti+TiO_2+NaClO_4$) (2)

*$Mn/MnO/NaClO_4$ pellets.* ($5Mn+MnO+NaClO_4$) (3)

*$Co/Co_3O_4/NaClO_4$ pellets.* ($6Co+Co_3O_4+NaClO_4$) (4)

For the IR thermal imaging work pellets of the green mixture were placed vertically in front of the surface of an IR-camera lens using a sample holder that allowed two permanent magnets of 0.2 T to be added and taken away according to the experimental requirements. Distance between the two surfaces was fixed at 12 cm. IR-camera output signals were pre-calibrated by using steel, tungsten or silver incandescent wires. Computer software ranges provided an opportunity to measure signals in four different temperature ranges: 800-1200, 1200-1650, 1650-2400 and 2400-3000°C. IR-camera scanning process was carried out from the fixed surface of the pellet with a focused size of 263 mm and a scan rate of 30 images per second. Standard size of each individual point on the surface was 16 $mm^2$. Equipment and software provided an opportunity to measure the combustion parameters of temperature and velocity by using four different reference points. These four points may be chosen arbitrarily inside the limits of the surface (2 x 3 mm) in accordance with the direction and velocity of combustion wave propagation. The whole IR collection time for each SHS process was ~35 s. Powder X-ray diffraction measurements were performed in the reflection mode on a BRUKER ASA-S System spectrometer with PSD-50 m using unfiltered CuKα radiation.

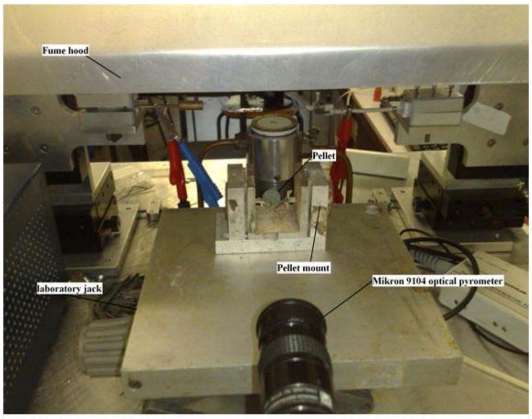

Fig. 1. Photograph of the pellet mount used for zero plus applied field SHS reactions.

The pellet mount was placed on a lab jack and its position imprinted on the laboratory jack so that the mount would always be placed in the same position after changing pellets and other experimental manipulations. The laboratory jack was used to adjust the mount and bring it into line with the thermal camera as shown in Fig. 1. The camera was focused by making a loop from a nichrome wire and placing it at the position where the pellet would normally be placed. A small current was passed through the nichrome wire using a power pack. The image appeared on the computer screen where it enabled the lens to be adjusted to get a sharper image. The camera was focused so that it observed a 2-3 mm window just below the nickel frame. This step was necessary to prevent in-folding of the pellet during the reaction obscuring the view of the SHS wave as it progressed through the pellet. Experimental setup is shown below in Fig. 2.

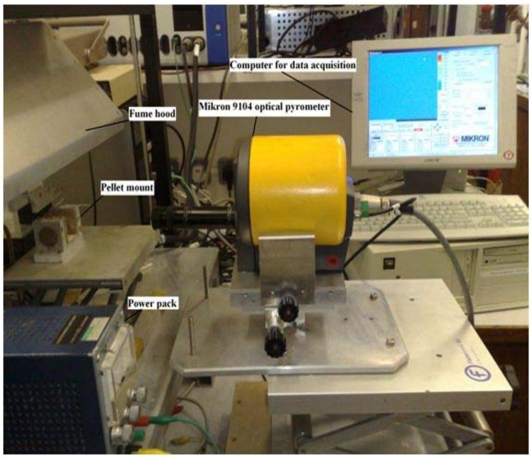

Fig. 2. Experimental setup for thermal analysis

The optimum temperature region chosen to investigate each of the first row transition metal oxides is listed below in Table 1.

**Table 1**

The Mikron 9104 optical pyrometer temperature range chosen to be investigated for each system.

| First Row Transition Metal Oxides. | Temperature Region (°C) |
|---|---|
| $Fe_2O_3$ | 1067 – 1645 |
| $Co_3O_4$ | 1067 – 1645 |
| MnO | 1067 – 1645 |
| $TiO_2$ | 1303 – 2222 |

Description of the method used to measure wave-velocity, so that a comparison could be made between the different experiments, are as follows: a temperature contour was picked and depended on the exothermicity of the reaction; a standard of 5 frames was chosen to monitor the propagation of the wave (temperature contour moves with the wave); a 2 cm portion of the frame to the right or left of the frame was chosen; three points at 0, 1 and 2 cm from either the right or left of the frame were chosen to monitor the motion of the advancing wave; difference is calculated and a factor is determined to account for the real distance travelled, according to the 2-3 mm window measured; average of these three points, together with the fact that camera takes 30 frames per second, were used to calculate speed of the wave through the frames.

The Mikron 9104 camera used to carry out this thermal analysis was capable of taking images in real-time because it has two detectors; one detector captures one frames’ worth of information, while simultaneously transferring the previous frames data using the other detector. Coupled with the fact that the camera is able to take 30 frames per second, data were collected in real time and were not stroboscopic in nature.

The Mikron camera software produced images and data in its own format. Data from this software package was expressed in a qualitative fashion and hence made quantitative comparisons between the different experiments difficult. Additionally, a limiting factor of the software is that large file sizes are generated when increasing the number of frames taken at any one time. The computer was unable to process data if the number of frames taken was in excess of a 500 frame sequence. In the experiments described, this computer failure did not occur, however, in future experiments, system may not be capable of handling experiments where wave velocity is sufficiently slow or oscillates for a significant length of time, and it may not be possible to acquire a full set to analysis.

## Results and Discussion

### *$Fe/Fe_2O_3/NaClO_4$ system*

Some of the post-SHS pellets from the reaction of Fe, $Fe_2O_3$ and $NaC1O_4$ had holes in them. These holes indicated that the camera may have been focused directly on that region of the pellet and thus the experiment had to be voided. The Mikron camera was set to a temperature range of 1067-1645°C, allowing the maximum temperature reached to be noted. The same setup was used for the reactions in an applied 0.2 T magnetic field and zero field.

Table 2 below gives the average maximum temperature for applied and zero field reactions.

Average wave velocity for zero and applied magnetic field are given together with the associated standard deviations and the propagation mode was also stated. Fig. 3 gives an example of an oscillating wave moving through an applied field for the $Fe/Fe_2O_3/NaClO_4$ system. An interesting point is that a majority of the post-SHS pellets had several randomly arranged holes in them, regardless of whether the reaction was conducted in or out of a magnetic field. The pre-SHS pellets were reddish in colour and post-SHS pellets were black in colour.

Results showed an average maximum observed combustion temperature for the iron system in an applied field of 0.2 T to be 1464°C and in zero field – 1412°C. The highest temperature that was reached in this system coincides with the maximum wave velocity. The higher reaction temperature could indicate that reaction was cleaner or greater final product was formed in the oxidation of metallic iron to its oxide.

**Table 2**

Average maximum temperature reached during SHS reaction, average wave velocity for thermal analysis and enthalpy of SHS reaction $\Delta H_r$ (kJ) calculated for all the systems containing Metal/Metal oxide/$NaClO_4$.

| Metal/ Metal Oxide/ $NaClO_4$ ($\Delta H_r$ (kJ)) | Zero field | | | Applied 0.2 T magnetic field | | |
|---|---|---|---|---|---|---|
| | Av. of Max Temp (°C) | Av. Wave Velocity $mms^{-1}$ | Av. Wave Propagation | Av. of Max Temp (°C) | Av. Wave Velocity $mms^{-1}$ | Av. Wave Propagation |
| Mn/MnO (-388.47) | 1291 (18) | 3.59 (0.95) | Steady | 1326 (55) | 2.98 (0.46) | Steady |
| $Co/Co_3O_4$ (-674.50) | 1235 (27) | 3.57 (0.44) | Spinning | 1271 (17) | 3.04 (0.78) | Spinning |
| $Ti/TiO_2$ (-946.60) | 1633 (4) | 1.67 (0.28) | Steady | 1622 (7) | 1.40 (0.31) | Steady |
| $Fe/Fe_2O_3$ (-1400.35) | 1412 (20) | 1.42 (0.4) | Steady | 1464 (19) | 2.5 (0.8) | Oscillating |

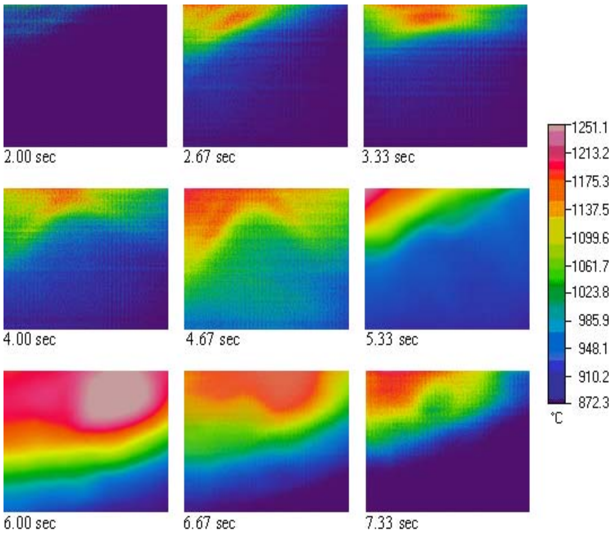

Fig. 3. Oscillating mode of propagation seen for SHS reaction in applied field for the $Fe/Fe_2O_3/NaClO_4$ system. The camera caption area is 2 x 3 mm.

In order to calculate adiabatic temperature for the reaction to form products, calculations were done and are given below. Calculations for all the investigated systems were made using the same schemes and results are listed in Table 2.

$$4Fe + Fe_2O_3 + NaClO_4 + 0.5\ O_2 \rightarrow Fe_2O_3 + Fe_3O_4 + FeO + NaCl$$

$$\Delta H_r = \Delta H_f\,(Product) - \Delta H_f\,(Reagents) = \Delta H_f\,(Fe_3O_4 + Fe_2O_3 + FeO + NaCl) - \Delta H_f\,(Fe_2O_3 + NaClO_4) = (-1108.8 - 263 - 411.3 - 823.4)-(-823.4 - 382.75) = (-2606.5) - (-1206.15) = -1400\ kJ$$

Hot spots (heat islands) were often seen in all modes of propagation in the experiments described. These patches of heat are described when a hot spot occurs before the actual surface wave front reaches that part of the sample. The present data contains to our knowledge the first report of `hot-spots` for any SHS system studied. These heat islands are formed because the SHS wave moved through the bulk of reactant ahead of the SHS wave surface. Hot spot can therefore pre-ignite green mixture at the surface ahead of SHS wave surface and may have caused the surface wave to jump forward. This erratic wave movement makes it harder to define clearly the path of the wave front. It is believed that hot spots occur due to in-homogeneity of the green mixture and passage of the synthesis wave more quickly through the bulk than the surface. Often the region where hot spots occurred existed where there is more percentage of fuel in comparison to moderator.

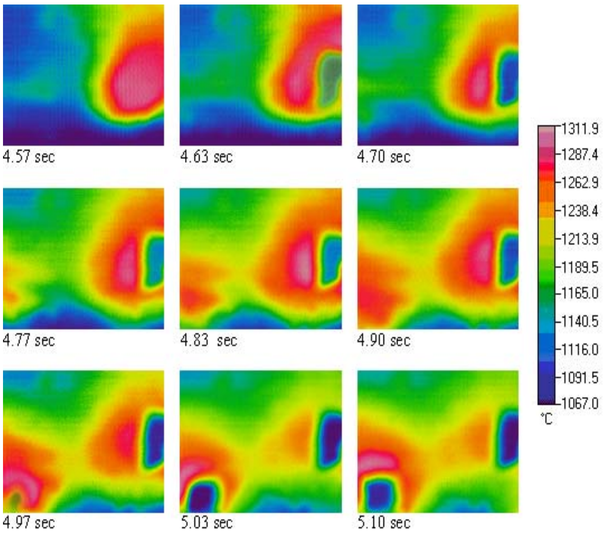

Fig. 4. Time-lapse thermal images showing the formation of two holes on the $Fe/Fe_2O_3/NaClO_4$ pellet. The camera caption area is 2 x 3 mm.

Figure 5 shows the formation of hot spot at 3.4 seconds that reaches a maximum exothermicity after 3.50 seconds. Additional heat islands are formed at 3.63 seconds. At 3.8 seconds, it is possible to see that several more heat islands appeared such that a new region of reaction wave occurred and that the SHS wave jumped forward.

Holes were observed in post-SHS pellets for the $Fe/Fe_2O_3/NaClO_4$ system as seen in Fig. 4. At 4.63 seconds into the duration of reaction, a hole was observed in the pellet and an additional hole was observed in the pellet at 4.97 seconds. Sequential holes suggested that as the wave propagated through the pellet, holes appeared just behind the wave front. Prior to appearance of the hole the reaction temperature in the region was highest in the 2 mm x 3 mm window. This observation could be attributed to the presence of unreacted sodium perchlorate and sodium chloride being ejected from the reaction.

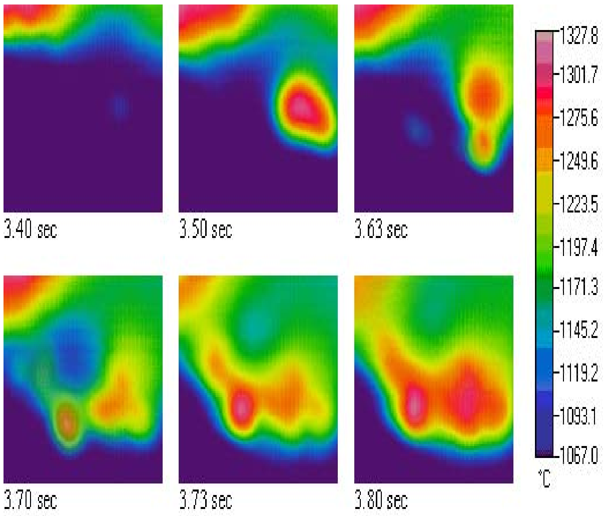

Fig. 5. Time-lapse thermal images that show heat islands forming during SHS reaction in zero field for the $Fe/Fe_2O_3$ /$NaClO_4$ system**.** The camera caption area - 2 x 3 mm.

An alternate explanation for the holes and fragmentation of pellets could be found from the heterogeneity in the pellet. A high local heat source could result in higher temperatures in certain locations and thus the region of the pellet could become very hot allowing metal and metal oxide to become partly melted and fused together. On the cooling stage species could become detached from the bulk of pellet and ejected from the pellet, as it was initially seen in Fig. 4 at 4.57 seconds and 4.90 seconds. These times coordinated with the region where holes appeared and were the hottest, which could provide a localized energy spike and result in an ejection of the pellet fragment.

### *$Ti/TiO_2/NaClO_4$ system*

One observation from the titanium system was that the highest setting of the camera was needed (1303 to 2222°C). Average maximum temperature and wave velocity results of four separate reactions of both applied and zero magnetic field reactions together with observed modes of propagation for the systems are given in Table 2. Below is an example of a steady state wave propagating through the $Ti/TiO_2$ system. The wave moves quite smoothly through the sample and the distance traveled is clearly defined. Both applied and zero field reactions showed a steady mode of propagation and Fig.6 below gives an example of the applied field reaction.

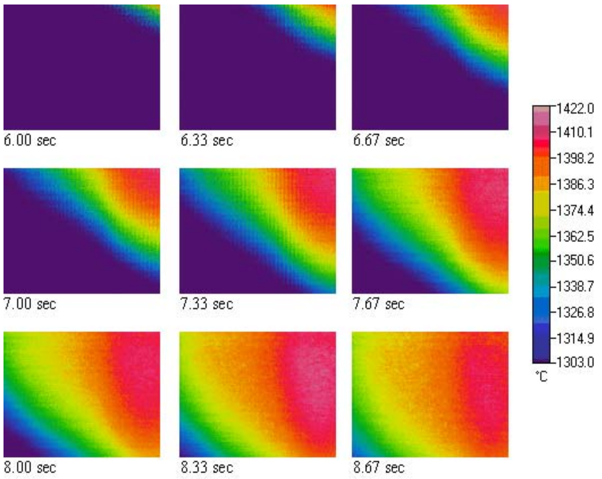

Fig. 6. A steady state wave propagation through the $Ti/TiO_2$ pellet for an applied field SHS reaction. The camera caption area - 2 x 3 mm.

The preparation procedure for the titanium-containing system was different from the other systems due to highly exothermic nature of this reaction. There was no need to add sodium perchlorate and thus the reaction proceeds rapidly on ignition. Reactions were very vigorous and for both applied and zero field reactions and the steady mode of propagation was observed.

The wave propagated faster for the titanium system when no external field was applied and this coincided with a higher maximum reaction temperature. Average maximum temperature reached in the applied field was 1622°C, whereas in a zero field it was 1632°C, indicating that zero field reactions have a 10°C higher reaction temperature than applied magnetic field reactions. This difference in reaction temperature falls within one standard deviation, so it is possible that applying a magnetic field did not affect the observed maximum temperature. Results indicated that the wave propagated slightly faster through the pellet when no external field was applied. Previous thermal imaging data showed that the reaction temperature was higher when an external field was applied. These findings seem to coincide well with the fact that the wave also moves faster when there is no external field, however the results do fall within error.

The $Ti/TiO_2$ system is diamagnetic, and as such, the external field should not have an effect on the initial reagents, in contrast to the other systems such as iron or cobalt-containing. The fact that results fall within error can be rationalized by this observation. The magnetic field may have an effect on the transient ions produced during the intermediate stages of reaction. Perhaps not adding the internal oxidant, such as sodium perchlorate, could have resulted in an incomplete reaction due to the lack of oxygen and resulted in incomplete conversion for SHS. Additionally, for the $Ti/TiO_2$ and $Ti/TiO_2/NaClO_4$ systems deformed pellets had holes present, which could be an indication that NaCl was ejected from the post-SHS pellet. It can be suggested that when sodium perchlorate was absent from the green mixture, there wasn’t substantial variation in the intermediate or final composition of the reaction, in comparison to the initial data when sodium perchlorate was added. In the titanium system without sodium perchlorate, there was a marked increase in the percentage conversion of titanium by applying a magnetic field to an SHS reaction.

## *Mn/ MnO/NaClO$_4$ system*

Results obtained for the maximum measured temperature for the Mn/ MnO/ $NaClO_4$ system are given in Table 2 together with the propagation mode. A steady propagation mode is seen for applied and zero field reactions. Fig. 7 is an example of a steady state wave propagating through a zero field manganese system. The wave moves quite smoothly through the sample and the distance travelled is clearly defined. Applied field reactions occur with an average maximum temperature 35°C greater than reactions in zero fields. Zero field reactions were slower, but both of these results do fall within error, which makes it difficult to determine if this difference is significant. The Manganese system followed in the trend of other systems that the applied field SHS reactions occurred at slightly higher temperatures, as was seen in for iron system. It is therefore difficult to truly justify this difference; however the trend can be acknowledged that in general, the average temperature of applied reaction was higher. In this case, manganese is diamagnetic whereas the manganese oxide is paramagnetic, since oxide only plays the part of moderator and thus has no significant role in the reaction other than to control exothermicity.

## *Co/Co$_3$O$_4$/NaClO$_4$ system*

Average results for the maximum temperature reached of the cobalt system are listed in Table 2. A spinning mode of propagation was noted this is an unstable combustion mode that travels in an erratic manner through the sample. In contrast to steady and oscillating modes of propagation, for spinning modes the wave velocity can be measured in two directions – horizontally (Vx) and vertically (Vy). The values for wave velocity calculated for spinning modes correspond to the vertical measurement (Vy) in Table 2. An example of the spinning mode is given in Fig. 8.

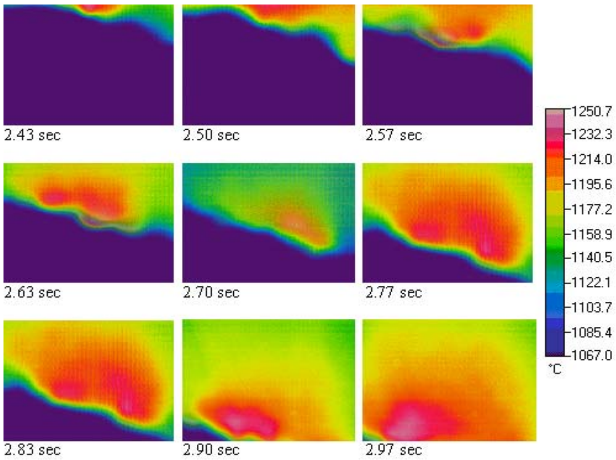

Fig. 7. Steady mode of propagation observed for the Mn/MnO/NaClO$_4$ system as an SHS wave propagates through the pellet. The camera caption area - 2 x 3 mm.

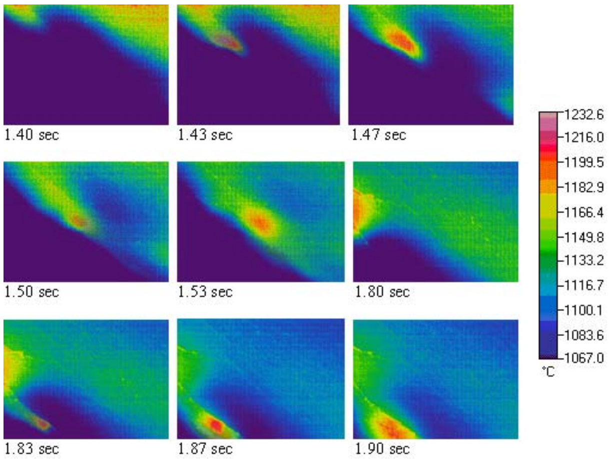

Fig. 8. Thermal images of SHS wave propagates through a pellet by spinning mode for applied field reaction of a Co/Co$_3$O$_4$/NaClO$_4$ system. The camera caption area - 2 x 3 mm.

The wave front observed in the series of thermal images above is in the form of spot that travels through the pellet. The spinning mode is an erratic propagation mode with at least one centre. Both applied and zero field reactions show spinning modes of propagation. Wave propagation was not fully recorded in all Co/Co$_3$O$_4$/NaClO$_4$ experiments due to experiment difficulty. Cobalt pellets was segmented during many experimental trials and this segmentation would caused the pellet to fall out of the view of thermal imaging camera.

In the cobalt system the average maximum temperature was higher for applied field experiments. The recorded temperature was about 36°C higher, however this value was again just above error and significance cannot be definitively determined. This trend was also seen in the iron and manganese systems. Zero field reaction had a faster wave velocity compared to applied field experiments, however this result also falls within the experimental error. In applied and zero field experiments, the reaction proceeded in a spinning fashion. The most obvious difference in the cobalt reaction was that there was segmentation in the post-SHS product.

Segmentation appeared in the direction of propagation wave and was evident in applied and zero fields. On some thermal images it is possible to see the segmentation due to the glow emitted by the hot regions; it is also shown in the thermal image series shown in Fig. 9**.** The regions that have segmented in Fig. 9 between 4.33 and 5 seconds can be clearly seen. Purple regions in the middle of SHS wave were the void space created by segmentation and were below the range of the pyrometer measurements. Purple regions in these diagrams could be caused by any temperature below the minimum threshold of the camera measurements. Segmentation seen is most likely due to the spinning mode of propagation, as this propagates in X and Y directions at different speeds and could potentially cause a shear force on the pellet causing segmentation.

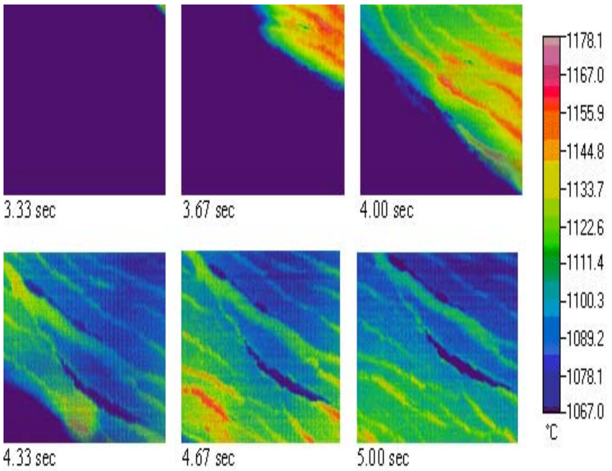

Fig. 9. Time lapse diagrams of segmentation occurring on a pellet of the Co/Co$_3$O$_4$ /NaClO$_4$ system. The camera caption area - 2 x 3 mm.

It is necessary to note that segmentation seen for the cobalt system and reported in present paper has previously seen by *Curfs* [8], for 1:1 Ni-Ti binary system. *Curfs* showed that pellet was segmented and propagation mode was spinning [8]. In all the other systems studied segmentation was not observed. Unstable mode of reaction could be the cause of this segmentation effect in the particular system.

## Conclusion

It was shown that an applied magnetic field affected SHS process in a binary and ternary systems, containing transition metals and its oxides, when the maximum exothermicity is achieved. In addition, it is also shown that applied magnetic fields have an effect on velocity and propagation mode in some of the systems investigated. For the wave velocity it was shown that all, except ferromagnetic iron system, reactions displayed waves that propagated faster in zero field experiments than applied field experiments. All the other systems showed a faster reaction rate when a magnetic field was applied. In all the systems, except diamagnetic titanium, it was also determined that there were higher reaction temperatures for zero magnetic fields. The pellet form of samples limiting the level of pre-organization of magnetic powers along the magnetic field lines, thus it is possible to say that any influence of the field took place in the post-ignition phase, and so it is likely that the magnetic field has an influence on the intermediate ionic phase, where the mass transport of ions during the SHS reaction in zero field is random, but after an application of magnetic field a directionality is achieved.

It is known that SHS reactions proceed via ionic intermediates. The propagation wave has a directional nature, hence an ionic pulse or slow movement of charge occurs. The movement of charge is effected by the external magnetic field which can result in a more complete reaction and preferential phase composition. Charged species are generated during the SHS process and moves in the direction of the SHS wave front and the charged species interacting with the externally applied magnetic field. Its alignment with the external field causes a uniform mixture at the reaction site, that results in a more exothermic reaction and greater product due to increased permeability of oxygen to the reaction site. This would also indicate why in nearly all cases the repeat results of applied reaction were similar in value when compared to the same reaction in zero fields where the repeats were not as close together. Also this could explain why the applied field reaction were seen to be more complete, as the field helps in the organization of ions at the site of chemical reaction and thus cause a more complete reaction in an applied magnetic field. Thus, externally applied magnetic field could have a profound effect due to its ability to fine tune the reaction as it occurs at the wave front.

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