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# Tantalum-Tungsten Oxide Thermite Composites Prepared by Sol-Gel Synthesis and Spark Plasma Sintering

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## Abstract

Energetic composite powders consisting of sol-gel derived nanostructured tungsten oxide were produced with various amounts of micrometer-scale tantalum fuel metal. Such energetic composite powders were ignition tested and results show that the powders are not sensitive to friction, spark and/or impact ignition. Initial consolidation experiments, using the High Pressure Spark Plasma Sintering (HPSPS) technique, on the sol-gel derived nanostructured tungsten oxide produced samples with higher relative density than can be achieved with commercially available tungsten oxide. The sol-gel derived nanostructured tungsten oxide with immobilized tantalum fuel metal (Ta - $WO_3$) energetic composite was consolidated to a density of 9.17 g.cm$^{-3}$ or 93% relative density. In addition those parts were consolidated without significant pre-reaction of the constituents, thus the sample retained its stored chemical energy.

## Introduction

The search for new energetic materials continues to be motivated by the desire to optimize performance and sensitivity. Energetic materials, containing both oxidizers and fuels can be divided into two main types, monomolecular energetics, where oxidizer and fuel moieties are contained within a single molecule such as TNT, and energetic composites of separate oxidizer and fuel phases such as black powder. Energetic composites are of significant interest due to the wide range of material properties that can be tailored by controlling the chemical composition and the particle size of the fuel metal and oxidizer, independently. One of the main subsets of energetic composites consists of thermite materials where the fuel is a metal and the oxidizer is metal oxide. Thermites composites have been studied intensively due to the wide variety of potential applications such as demolition of concrete [1], self-destructive electrical components [2], primers [3],

stab detonators [4], and reactive fragments [5]. A more thorough review of thermite reactions and applications is covered by Wang et al. [6]

Due to its relatively high enthalpy of formation of its oxide (-1675.7 kJ.mol$^{-1}$ at 25°C) and its low melting point (660°C), aluminum has been widely used as a fuel metal. Nanometric sized aluminum has been studied with a variety of oxidizers such as $Fe_2O_3$, $Bi_2O_3$, CuO, $MoO_3$, $WO_3$, and polytretafluoroethelyne (PTFE). Nanometric aluminum – metal oxide thermite reactions have been shown to be highly energetic and proceed at relatively high rates. Although aluminum – metal oxide energetic composites have been widely studied, most studies have focused on reactions of loose powders, partially confined systems, or resin-bonded energetic composite materials [7,8,9,10]. There have been comparatively few studies with alternative fuel metals such as Ta, Zr, Hf, or Si mixed with oxidizers [11]. And those studies have focused on loose powders or consolidated parts with relatively low percentage (<50%) of theoretical maximum density (TMD).

One of the exciting potential applications of energetic composites is as multifunctional energetic material (MFEM). Simply defined MFEM's are energetic materials that in addition to providing stored chemical energy perform at least one other important physical attribute that can be utilized in an engineered system [12]. Rates and mechanisms in fully dense self-propagating high temperature synthesis (SHS) thermite reactions have only been available for study in limited materials [13,14]. In the present study we have investigated the system where Ta is the fuel metal and $WO_3$ is the oxidizer. Ta - $WO_3$ is a particularly interesting system because of its high theoretical density (9.85 g.cm$^{-3}$) and its potential as a structural material. The stoichiometric thermite reaction for the Ta - $WO_3$ energetic composite can be described by the following equation:

$$6 \, Ta + 5 \, WO_3 \rightarrow 3 \, Ta_2O_5 + 5 \, W \tag{1}$$

The energy release from the stoichiometric reaction, producing $Ta_2O_5$ and W, is 320.6 kJ.mol$^{-1}$ Ta with an adiabatic combustion temperature of 2190°C.

We have developed sol-gel processes that enable the production of a wide range of metal oxides and their precursors [14]. The process takes advantage of recent progress in the use of organic proton scavenging agents to produce metal oxide precursors. The precursors can then be processed into aerogels, xerogels, or nanopowders of the desired materials. . The method is especially versatile as it enables the facile incorporation of additional phases into the composite [15]. This approach has been used successfully to prepare energetic nanocomposite materials [8,14,16]. Using these techniques allows for the tailoring of the product morphology, crystallinity, and even the production of nanocomposite powders [16,17,18]. The sol-gel technique makes it possible to tailor the particle size of the fuel metal and oxidizer independently and therefore the energy delivery rate (finer composites leads to higher power generation) [19].

The goals for this study were to synthesize nanostructured – amorphous $WO_3$ with immobilized Ta metal particles using sol-gel techniques and to consolidate the Ta -$WO_3$ energetic composite to near theoretical density without significant reaction to ensure complete retention of the chemical energy. To achieve densification without reaction, it is necessary to use accelerated consolidation techniques. One such technique is spark plasma sintering (SPS). The process combines the application of pulsed DC current with uniaxial pressure. Its advantages stem from a combination of factors including high heating rate (up to about 2000°C.min$^{-1}$, high pressure (up to about 1 GPa), and electromigration [20]. The high pressure is obtained in a modification of die design, as has been reported previously [21]. We utilized this modified SPS technique in our study, which we will refer to as High Pressure Spark Plasma Sintering (HPSPS).

**Experimental**

*A. Synthesis of WO$_3$ sol-gel and formulation of Ta - WO$_3$ composites*.

The tungsten salt used in this study was WOCl$_4$ (F.W. = 339 g.mol$^{-1}$; 98% from Aldrich). The epoxide used as a gelation agent was 3,3,-dimethyloxetane (DMO) obtained from Aldrich and reported to be 98% pure. The solvents utilized were 200 proof ethanol from Aaper, cyclohexane (HPLC grade; from Aldrich) and de-ionized and distilled water.

A typical gel synthesis experiment involves the following steps: 14.76 g (43.5 mmol) of WOCl$_4$ was dissolved in 125 mL of an ethanol/H$_2$O solution with a 95/5 vol % composition. Dissolution of the tungsten salt results in a solution that was slightly turbid. This solution was subsequently filtered through a Buchner funnel lined with filter paper to give a clear colorless solution. Then 20 g (235 mmol) of DMO was added (epoxide/metal ion ratio of 5.4) to the WOCl$_4$ solution while stirring. With the use of epoxides for this gelation in some cases significant heat generation is realized, which in some cases may lead to a flash boil of the synthesis solution. The cautious addition of the epoxide to the metal salt solution is recommended in a well-ventilated space [22]. In all cases, a rigid white gel formed within 5 min after addition of the DMO. Formulation of the Ta - WO$_3$ composites followed a procedure identical to that described above with the exception that 9.2 g (52.2 mmol) of capacitor grade Ta metal (H.C. Starck; particle size 5 μm) was added. For the composite the mixture was stirred rapidly, with a Teflon-coated stir bar on a magnetic stir plate, to ensure uniform distribution of the Ta fuel metal throughout the matrix, until gelation occurred.

***B. Processing of metal oxide gels.***

The wet gels and composite gels were covered and allowed to age for at least 24 h under ambient conditions. After that they were immersed in a bath of absolute ethanol where they were washed for ~3 days. The solvent was changed in the bath 1-2 times a day during this wash process. This process was necessary to wash out the organic byproducts of the DMO used in the synthesis. The wet gels were subsequently washed with cyclohexane for ~2 days, changing the solvent bath 1-2 times per day. The cyclohexane was decanted off and the wet gel dried at ambient temperature in a fume hood. After air drying the resulting $WO_3$ gel and composite gels were dried at 110°C under dynamic vacuum for 24 h. This preparation led to the synthesis of 10 g of $WO_3$ sol-gel material. Figure 1 shows a TEM image of the as-synthesized sol-gel $WO_3$. It can be observed that the particle size is approximately 10 nm. The surface area of the sol-gel derived $WO_3$ was measured to be 141 $m^2$/g by the BET method [23].
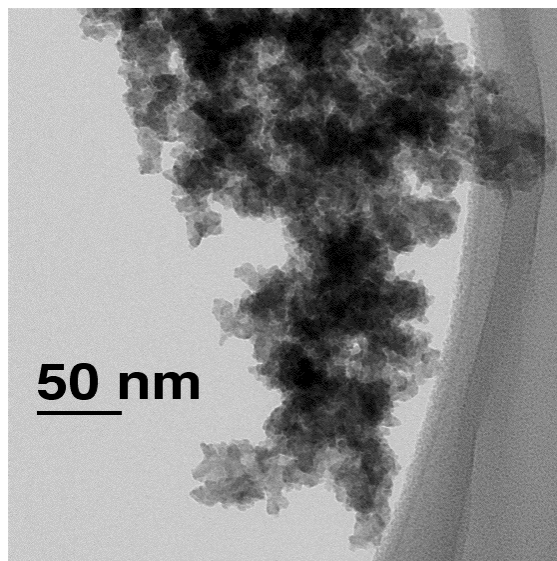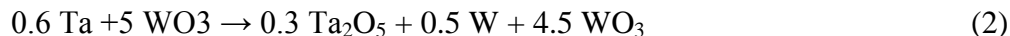


Figure 1. A TEM image of the as-dried $WO_3$.

### C. Initial Ta - WO₃ powder formulations

Due to safety concerns, initial energetic composite powders were made highly fuel deficient, i.e., sub-stoichiometric with respect to Ta. An example of sub-stoichiometric reaction containing 10 mol % of the stoichiometric quantity of Ta is

$$0.6 \text{ Ta} + 5 \text{ WO3} \rightarrow 0.3 \text{ Ta}_2\text{O}_5 + 0.5 \text{ W} + 4.5 \text{ WO}_3 \qquad (2)$$

where the excess $WO_3$ acts as a diluent leading to lower adiabatic reaction temperature. As stated above, the adiabatic combustion temperature for Eq (1) is 2190°C and with this dilution, the adiabatic temperature for Eq (2) is 447°C. Using the computer program HSC, we calculated the adiabatic reaction temperatures while varying the stoichiometric Ta content, as can be seen in Table 1.

Table 1. Adiabatic reaction temperature of the Ta - WO₃ thermite reaction with varying Ta content.

| Ta [ % Stoich. ] | $T_{ad}$ [ °C ] |
|---|---|
| 100 | 2190 |
| 50 | 1472 |
| 40 | 1394 |
| 30 | 1106 |
| 20 | 788 |
| 10 | 447 |

### Characterization of WO₃ and Ta – WO₃ powders

Morphology and composition of the energetic composites were examined on a Hitachi S4500 field emission scanning electron microscope (SEM) operated at 10 kV in backscattered-electron mode. The $Ta - WO_3$ energetic composite was embedded in epoxy and polished using traditional polishing techniques for cross-section examination. The phase composition was determined for each sample by X-ray diffraction (XRD). The XRD was performed on a Scintag PAD V powder diffractometer operated at 45 kV and

35mA using Cu $K_{\alpha 1}$ radiation ($\lambda$ = 1.54056 Å). A JEOL transmission electron microscope (TEM) was used to determine the morphology and particle size of the $WO_3$.

### D. Consolidation by Spark Plasma Sintering.

In this study the HPSPS method was used to consolidate the Ta - $WO_3$ energetic composite. The method is described in detail elsewhere [21], but essentially consists of a compound graphite die assembly with certain internal components, see Figure 2 below. This die design allows for pressures as high as 1 GPa although in this study the pressure did not exceed 300 MPa. Heating rates were varied from 100 to 500°C.min$^{-1}$ and hold temperatures ranged from 300 to 600°C.
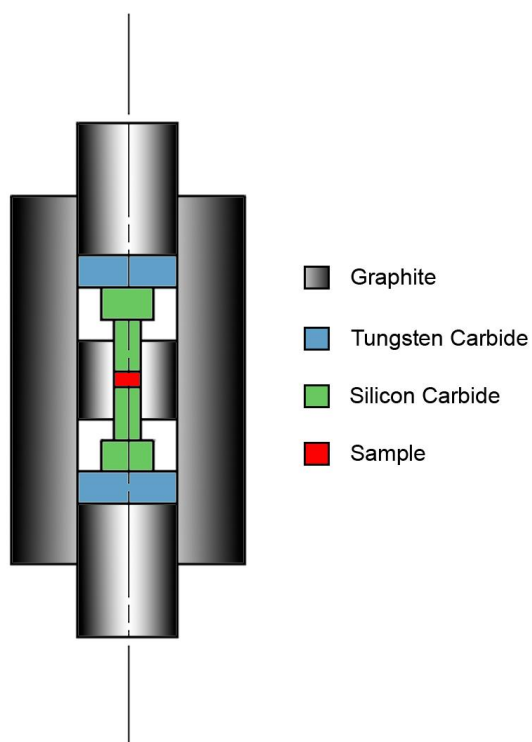
Figure 2. Schematic representation of high-pressure spark plasma sintering (HPSPS) die assembly.

**Results and Discussion**

*A. WO₃ and Ta – WO₃ Powders*

We have reported extensively on the use of organic epoxides as gelation agents for the sol-gel synthesis of a number of transition metal oxides from inorganic salt precursors [14]. A mechanistic study revealed that the epoxide acts as an irreversible proton scavenger that induces hydrolysis and condensation of metal ion species to form a sol [24]. These processes result in a slow and uniform pH increase throughout solution, which affords the uniform gel that is critical to the formation of a well dispersed composite. The structure and substitution on the epoxide dictates its reactivity and thus affords some control over the rate of pH. In the case of tungsten (VI) the 1,2-epoxides, such as propylene oxide, react rapidly and result in precipitates instead of monolithic gels. By comparison, when 1,3-epoxides are used, the pH rise is slower presumably due to the lower reactivity, and in the case of tungsten (VI) salts leads to the formation of rigid monolithic gels.

We have utilized this synthetic approach to formulate nanostructured energetic materials [16,17]. The energetic ingredients and composites formulated using this methodology have unique reaction (combustion) characteristics that have been detailed elsewhere [7,8]. To briefly summarize the nanostructural evolution, the sol particles of $WO_3$ phase grow around and eventually encapsulate the solid suspended Ta particles to form a nanostructured energetic nanocomposite as the sol transforms to a gel. This process takes advantage of the viscosity increase of the sol-gel solution as it approaches its gel point. Once the gel forms the matrix is rigid and has effectively "frozen" Ta into place with in the gel network. This process creates an energetic composite that consists of an intimate mixture of micron-sized crystalline Ta dispersed throughout a nano-network of amorphous tungsten (VI) oxide. Figure 3 is a backscattered-electron SEM image of as-dried Ta - WO3 composite particles embedded in epoxy (dark grey). The lightest regions are Ta and the medium grey is amorphous tungsten (VI) oxide. Note that the tantalum particles are encapsulated by the tungsten oxide phase.
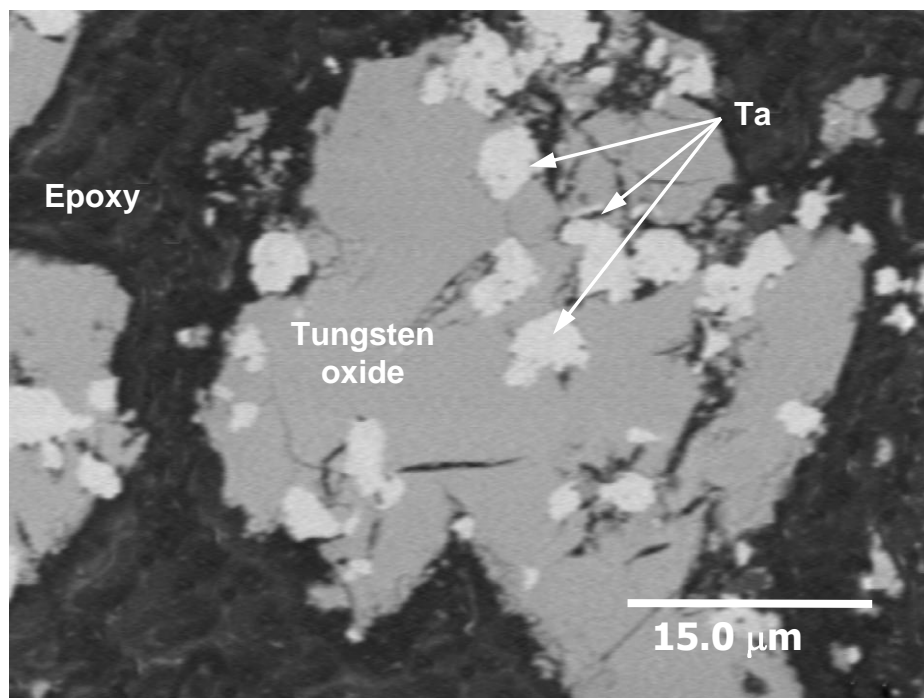
Figure 3. Backscattered-electron SEM image of as-dried Ta - WO$_3$ composite particles embedded in epoxy (dark grey). The lightest regions are Ta and the medium grey is amorphous tungsten (VI) oxide.

XRD analysis on the sol-gel prepared $WO_3$ shows two broad peaks which indicate that the powder has an amorphous structure. In addition, XRD analysis on the Ta - $WO_3$ energetic composite shows that the composite maintains the amorphous structure of the $WO_3$ while incorporating crystalline peaks from the Ta particles. Figure 4 shows the XRD patterns for both the $WO_3$ powder and the Ta – $WO_3$ energetic composite.
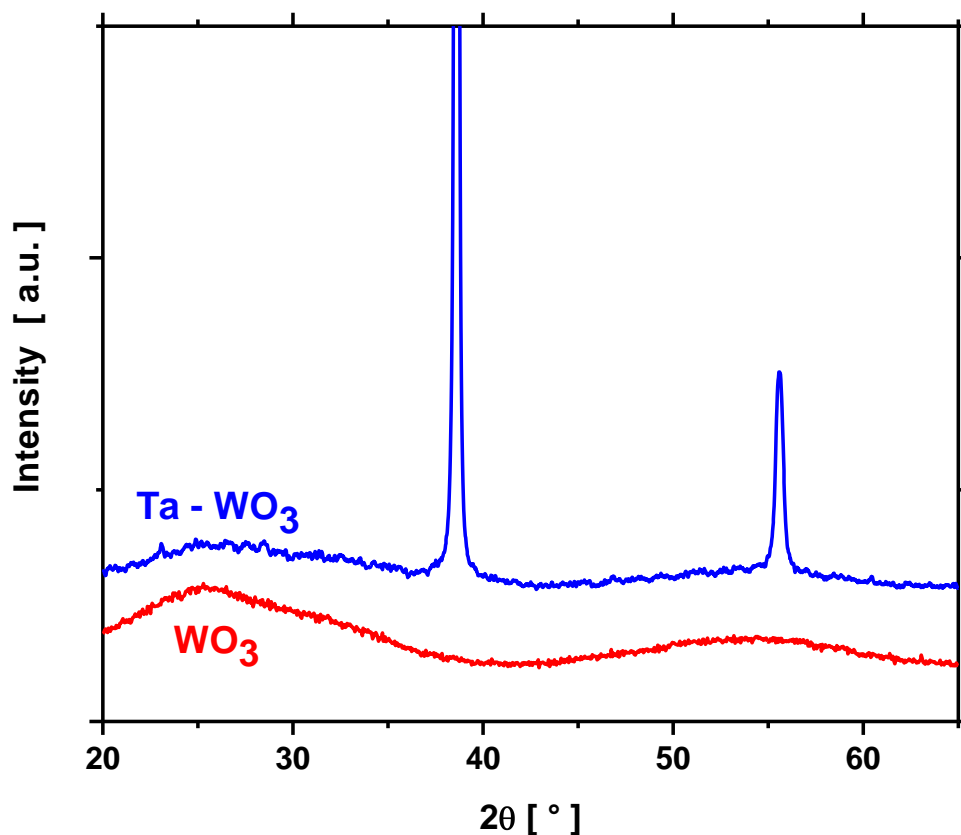


Figure 4. X-ray diffraction patterns from amorphous tungsten (VI) oxide (red) and energetic composite Ta - $WO_3$ powder (blue).

*B. Sensitivity of Ta - WO₃ powder mixtures.*

Since the Ta - WO$_3$ composite mixture has a large exothermic enthalpy of reaction and has an adiabatic reaction temperature sufficiently high to self-sustain the reaction, we investigated the sensitivity of the composite by prescribed tests. These tests are designed to determine the sensitivity of the composite to friction, spark, and impact stimuli.

The response of composite formulations to friction was evaluated using a Bundesanstalt für Materialprufüngen (BAM) friction-testing machine manufactured by Julius Peters Company in Berlin, Germany [25]. This test provides critical information for safe material handling and processing. The tester utilizes a fixed porcelain pin and a movable porcelain plate that performs a reciprocating motion. Weights from 0.5 to 36 kg were attached to a torsion arm which allows for the applied force to be varied. The measure of frictional sensitivity of a material is based upon the largest pin load at which one ignition occurs in ten trials. The Ta - WO$_3$ composite was found to have zero events out of ten trials with the 36 kg weight on the torsion arm.

The sensitivity of energetic composites toward electrostatic discharge was measured using a modified Electrical Instrument Services electrostatic discharge tester [26]. The instrument consists of three parts: the capacitor bank, a charging system and the discharging system. The capacitor bank has a range of capacitance from 50 to 20,000 pF. The voltage range is up to 10,000 V and energy output up to 2 J. To perform the electrostatic measurement, a 35 mg portion of energetic composite powder was loaded into a metal stub with Teflon washer seated on top. The metal stub with the Teflon washer is then covered with 1 mm thick Mylar tape to keep the energetic composite powder from dispersing out of the metal stub. A spark discharge of variable energy is sent from an electrode tip to the sample. The sensitivity is defined as the highest energy setting at which no ignition occurs in ten consecutive trials. The lowest energy setting for this instrument is 0.04 J and the highest 1 J [26]. None of the ten powdered samples of Ta - WO$_3$ reacted at the highest energy input setting of 1 J.

The impact sensitivity of energetic composites was evaluated with a drop hammer machine [27]. The drop hammer test is a quick and safe single way of determining the overall safety without using much sample. This is the best known way to evaluate impact sensitivity. To briefly discuss the process, a 2.5 kg weight is dropped from a present height on a tower towards a small amount (35 mg) of energetic composite material. Test results are reported as $DH_{50}$, a value that represents the height in centimeters at which the probability of reaction is 50% [27]. Samples of energetic composite were placed on a piece of carborundum paper sitting on a steel anvil. The weight is then dropped on the energetic composite. Visual events that constitute a reaction are any evidence of spark, flame, or report on impact. The operator made visual evaluations for ignition events. The Ta - $WO_3$ composite powder had zero ignitions out of fifteen trials at the highest drop height setting of 177 cm. Thus, the impact sensitivity of the composite was off scale for the instrument and therefore is quite insensitive to that stimulus.

The sensitivity testing indicates that the composite material is insensitive to spark, friction, and impact stimulus. These results led us to conclude that the composite would be a good candidate for consolidation at elevated temperatures.

### C. Consolidation of $WO_3$ powders

Initial consolidation studies were performed on sol-gel prepared tungsten oxide instead of the Ta - $WO_3$ energetic composite powders. This allows exploration of consolidation parameters necessary for the matrix material without concern for a thermite reaction occurring. The tungsten oxide was consolidated by HPSPS using a range of consolidation temperatures from 300 to 600°C and pressures from 150 to 300 MPa. Hold time was constant at 5 min. The displacement profile from an HPSPS experiment performed at 300 MPa and 600°C can be seen in Figure 5. Note that densification begins as low as 150°C and ends abruptly at ~375°C, such an abrupt halt is possibly indicative of crystallization. XRD of powder heat-treated at 400°C shows full crystallization. This sample resulted in a density of 6.75 g.cm$^{-3}$, or 94.3% of the theoretical density of $WO_3$. For comparison, commercial $WO_3$ powder, sintered at 600°C and 300 MPa, only reached 5.32 g.cm$^{-3}$ (74.3 %TD). In contrast to the sol-gel prepared $WO_3$, the corresponding

displacement and displacement rate data for the commercial $WO_3$ powder showed only negligible densification. This is indicative of an alternative densification method occurring in sol-gel prepared powders compared to crystalline commercial powder. We propose that this mechanism is likely viscous flow due the abrupt halt to displacement at 375°C which corresponds with XRD confirmed crystallization of the powder after heat treatment to 400°C. It appears that the amorphous nature of the $WO_3$ can allow densification of this composite by viscous flow at relatively mild consolidation conditions which enable densification of energetic composites without significant pre-reaction. The low temperature consolidation of sol-gel prepared $WO_3$ leads to the possibility of consolidation of composite Ta-$WO_3$ powders to near full density without significant pre-reaction.
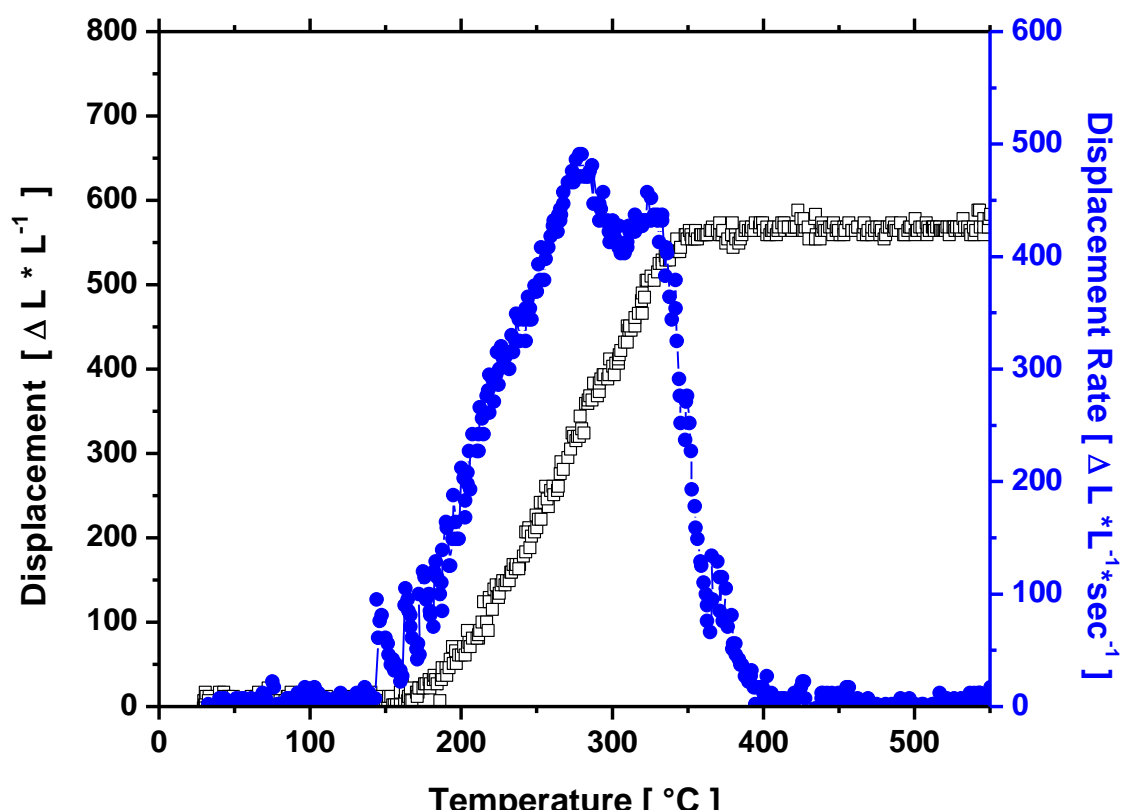


Figure 5. Displacement and displacement rate data for an HPSPS consolidation run at 300 MPa and 600°C.

*D. Consolidation of Ta – WO₃ powders*

After initial consolidation runs were achieved without ignition of the Ta – $WO_3$ energetic composite with sub-stoichiometric compositions, experiments continued with increasing Ta content until fully stoichiometric Ta - $WO_3$ thermites were made. Figure 6 below shows the density as a function of Ta content for samples consolidated at 500°C and 300 MPa. The highest achieved density of as-processed powders was 8.56 g.cm$^{-3}$ (87 %TD), but when powders were dried overnight 150°C to remove adsorbed water and consolidated under the same conditions, the maximum density increased to 9.17 g.cm$^{-3}$ (93.3 %TD) as depicted by the red triangle in Figure 6.
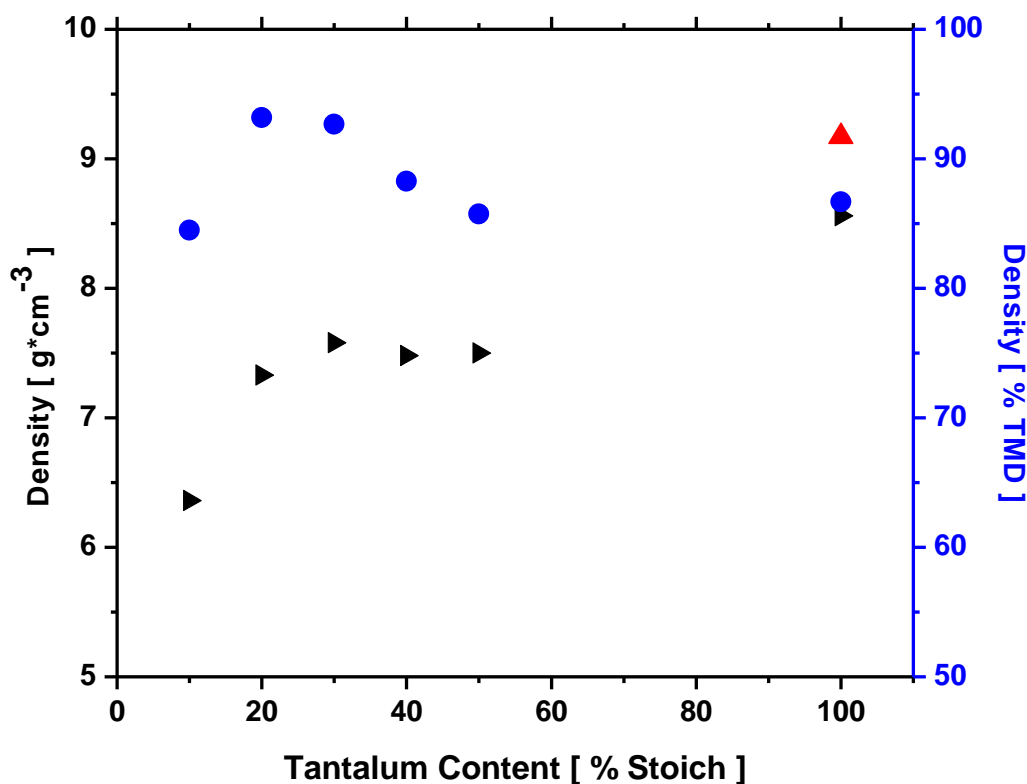


Figure 6. Density of Ta - $WO_3$ samples as a function of Ta content. All sample consolidated at 500°C and 300 MPa for 5 minutes.

### E. Energy Release of Consolidated Ta – WO₃ pellet

In addition to consolidating the Ta - WO₃ energetic composite powder to high theoretical maximum densities, the ability for the consolidated samples to retain a large fraction of its stored energy is imperative. Figure 7 shows a thermogram of a fully stoichiometric Ta - WO₃ sample consolidated to 85% TD by HPSPS. The thermogram was obtained by securing the sample directly to a thermocouple and inserting the assembly into a preheated furnace at 1000°C. This enables the high heating rates ($\sim$600°.min$^{-1}$) necessary to initiate the thermite reaction. DTA traces to 1500°C at 20°C.min$^{-1}$ do not initiate the reaction. It can be observed that the there is a sharp temperature increase starting around 650°C which is indicative of the ignition temperature of the sample at this heating rate. Following the ignition temperature, we observe a peak temperature of approximately 1100°C. Since reactions characteristics depend on heating rate [28], these values represent only the reaction under the stated conditions. However, the thermogram shows that the sample has stored energy after consolidation. The inset image in Figure 7 shows a similar sample that has been initiated by a small torch. Detailed experiments are in progress to accurately determine the ignition and peak temperatures along with energy output of consolidated samples as a function of density and degree of pre-reaction.
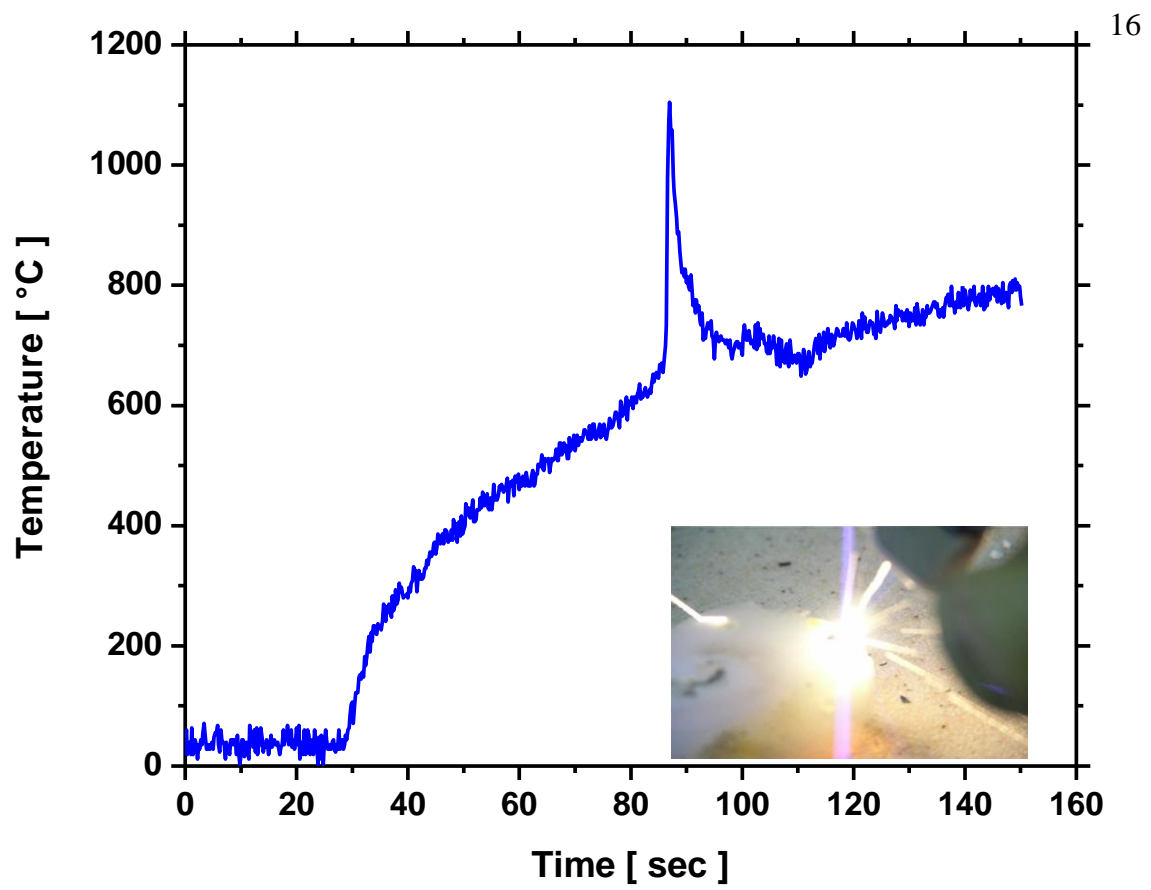
Figure 7. Plot of temperature versus time of a consolidated specimen during thermal initiation. Inset photo shows a sample initiated by open torch.

**Conclusions**

Ta - WO$_3$ energetic composite powders have been prepared by sol-gel synthesis with various amounts of Ta fuel and consolidated using the High Pressure Spark Plasma Sintering (HPSPS) technique. The uniqueness of the sol-gel synthesis is that instead of having separate loose powders of each constituent, we have a nanostructured WO$_3$ oxidizer in a gel form with the immobilized micron-size Ta fuel embedded in the gel. Such powder configuration permits for the constituents to be in intimate contact with one another. In addition, the amorphous nature of the WO$_3$ oxidizer prior to consolidation allows for the densification of the energetic composite by viscous flow at relatively mild consolidation conditions. Furthermore, we have successfully consolidated the energetic composite powders to densities ranging from 84 - 93% of their theoretical values. In addition, we have briefly shown that the consolidated samples retain stored energy, but have not quantified the energy output as a function of density. Future studies will focus on the laser, thermal and shock initiation of the consolidated samples as a function of density to establish their energetic parameters.

## Acknowledgements

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