

MICROWAVE INDUCED COMBUSTION SYNTHESIS OF CERAMIC AND CERAMIC-METAL COMPOSITES

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ABSTRACT

We have used microwaves to induce self-propagating high temperature synthesis (SHS) in the reaction $3\text{TiO}_2 + 3\text{C} + (4+x)\text{Al} + 3\text{TiC} + 2\text{Al}_2\text{O}_3 + x\text{Al}$. The SHS process was studied for $x = 0$ and 4, using slow and fast heating rates and with and without the application of uniaxial pressure. Less than 50 watts was required to internally ignite the samples using a TE₁₀₂ microwave cavity mode. Uniaxial stresses in the range of 200 - 1400 psi were continuously applied along the vertical axis of some of the processed samples as the SHS reactions were initiated. SEM photomicrographs clearly indicate differences in the formation of whiskers and other microstructural features in the products obtained from microwave and conventional hot wire techniques. The $x = 0$ samples processed with fast and slow microwave heating rates reached higher densities than the conventionally processed samples.

INTRODUCTION

In recent years, there has been a renewed interest in combustion synthesis reactions, commonly called self-propagating high-temperature synthesis (SHS).¹ These SHS reactions are an attractive, energy efficient approach to the synthesis of high temperature composite materials and metastable phases.¹⁻³ Generally, the SHS process is ignited at the surface of the material by thermal radiation. This thermal energy can come from a laser beam⁴ or a heating coil situated close to the sample surface.⁵ Alternatively, the entire sample can be heated to the ignition temperature in a isothermal furnace.⁶ In these types of combustion synthesis methods, a temperature gradient is produced in the material with the surface always hotter than the center.

A completely different approach for igniting the SHS process occurs when microwaves are used as the heating source. Microwaves will volumetrically heat non-conducting materials leading to an inverted temperature gradient where the center of the material is hotter than the surface. In this approach, a combustion wavefront propagates radically outward from the center of the sample. This

process can produce a completely different product morphology and lead to a more complete conversion of reactants.⁷

In this study, conventional and microwave induced combustion synthesis of ceramic and ceramic-metal composites were investigated. The model reaction system used in this research was: $3\text{TiO}_2 + 3\text{C} + (4+x)\text{Al} \rightarrow 3\text{TiC} + 2\text{Al}_2\text{O}_3 + x\text{Al}$ where $x = 0$ and $x = 4$. For $x = 0$, the combustion synthesis reaction product, TiC-Al₂O₃, does not contain any excess liquid aluminum. However, for the case $x = 4$, an excess amount of liquid aluminum created by the combustion synthesis reaction will infiltrate into the porous SHS ceramic composite leading to a denser product. The incorporation of a ductile metal into a brittle ceramic composite matrix has considerable potential for substantial improvement in fracture toughness for both low and high temperature applications.³

EXPERIMENTAL PROCEDURE

Reactant powders for this study were supplied by Alfa Inc., Cerac Inc. and Fisher Scientific Inc. These powders were used as ingredients for the reaction mixture without further particle separation, purification or other processing. The reactant powders were proportionally weighed and thoroughly mixed using porcelain ball milling. The reactant mix was then uniaxially cold pressed to ~ 50% green density and dried in an oven at 150°C for 30 minutes prior to ignition.

A magnetron source was used to excite a rectangular waveguide cavity in the TE₁₀₂ mode at 2.45 GHz as shown in Fig. 1. This mode has electric field maxima along the lines defined by $z/L_z = 0.25$ and 0.75 and $x/L_x = 0.5$. There is no field dependence along the y axis. A cold-pressed cylindrical sample, 0.13 cm in diameter and 0.13 cm high was placed on a quartz holder for one atmosphere isotropic ignition or inside a quartz tube with a piston on top to provide a vertical force for uniaxial pressure ignition. Samples were placed approximately half way down the y axis ($y/L_y = 0.5$) along one of the maximum E field lines ($z/L_z = 0.75$

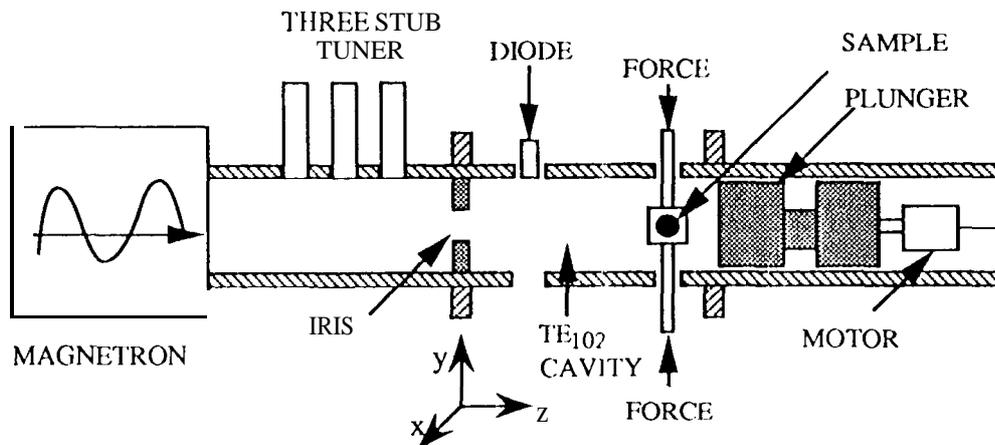


Fig. 1. Schematic of magnetron system.

and $X/L_x = 0.5$).

The surface temperature of the sample was measured using a non-contact Everest Interscience IR thermometer (range -30- 11 00°C) and/or an Accufiber non-contact pyrometer (range 500 - 3000°C). Densities of conventional and microwave processed samples were measured using Archemedi's principle. The microstructure of the synthesized product was then examined using a scanning electron microscope interfaced with an X-ray diffraction facility (JEOL JXA-849 SEM).

RESULTS AND DISCUSSION

Cold-pressed green samples, weighting ≈ 3 grams with 50% theoretical density, were studied using both microwave and conventional processing methods. The microwave power was controlled to ignite the samples with $x = 0$ using both a fast and slow heating profile. The time-temperature profiles for the fast and slow cases are shown in Fig. 2a and Fig. 2b. The sample temperature was measured using both Everest Interscience IR thermometer and an Accufiber non-contact pyrometer from the side holes of the cavity. Data from these two instruments were linked together to obtain a smooth curve. A higher starting power of 75 watts was required to ignite the sample for the fast heating rate case, Fig. 2(a), as compared to 50 watts starting power needed for the slow heating rate case, Fig. 2(b). The ignition temperature, as measured at the side of the sample surface, is lower ($T_i = 300^\circ\text{C}$) for fast heating compared to slower heating ($T_i = 650^\circ\text{C}$). The ignition temperature, T_i , for $x = 0$ samples measured by the conventional technique was $\approx 1200^\circ\text{C}$.³ Thus, very high thermal gradients are produced during the microwave processing.

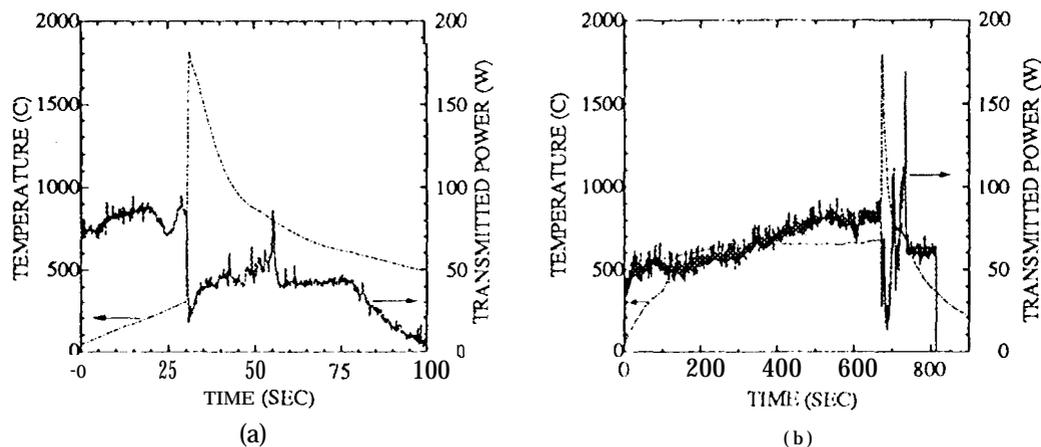
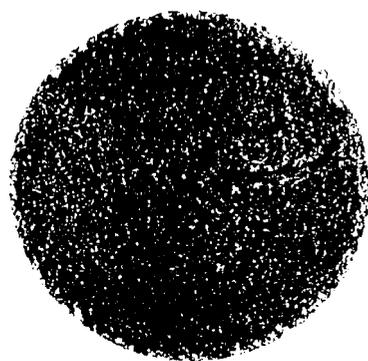


Fig. 2: (a) Temperature and transmitted power for fast heating rate ($x = 0$)

(b) Temperature and transmitted power for slow heating rate ($x = 0$)

Figures 3a and 3b show photographs of a sample cross section cut through the center of the ignited product. The fast heating case was ignited near the center and produced equally distributed porosity except for a crack line from the center to the surface. This crack line is probably due to the high thermal gradient between the center and surface of the sample when it was ignited. The slower heating case, Fig. 3b, has a milky outside surface and two different circular layers separated by a crack rim. These two layers are probably due to the initially melted aluminum ($T_m = 660^\circ\text{C}$) being pushed toward the sample surface leading to a non-uniform distribution of the powders. When this sample was ignited, two different phases are formed and a crack rim develops due to the thermal expansion mismatch between the two adjacent circular layers. Also the aluminum extruded toward the sample surface becomes a barrier for microwave penetration and thus inhibits the further ignition of powders. These results suggest that a fast microwave heating rate can insure a more complete chemical reaction of the mixed powders leading to a more uniform microstructure. A thorough understanding of the thermal gradient problem is needed to validate this conjecture.



1 mm

Fig. 3: (a) Sample cross-section (fast heating, $x = 0$).



1 mm

(b) Sample cross-section (slow heating, $x = 0$).



1 mm

Fig. 4. Sample cross-section (fast heating, $x = 4$).

For the $x = 4$ case, slow microwave ignition was difficult due to arcing initiated by the excess aluminum at the sample surface. On the other hand, ignition using a fast microwave heating rate was successful and a uniform microstructure was observed as shown in Fig. 4.

A comparison of the densities of the processed samples is shown in Table I. For $x = 0$ microwave processed samples without using uniaxial stress, the fast heating rate led to a higher density as compared to slow microwave heating and conventional hot-wire techniques. For the $x = 4$ case, conventional and fast microwave processed SHS samples had the same density. When a uniaxial force of 1000 psi was applied during fast microwave ignition ($x = 0$, and 4), SHS samples with a density - 85% were obtained which are similar to the conventional SHS product. From these experiments, the only difference between microwave and conventional SHS ignition occurs for $x = 0$. When $x = 4$, the excess amount of aluminum uniformly infiltrated the pores for both cases.

Table I. Densities of processed samples.

Excess aluminum	Uniaxial force	Microwave ignition (%) theoretical density		Conventional ignition (%) theoretical density
		fast	slow	hot-wire technique
x	psi			
0	0	75	60	50
4	0	75	—	75
0	1000	85	60	85
4	1000	85	—	85

For the microstructure study, we considered the $x = 0$ and $x = 4$ cases and compared the conventional hot-wire SHS samples to the samples ignited by fast microwave heating. For the $x = 0$ case, microwave SHS samples that had a higher density also had a more uniform microstructure as compared to the conventional case. The morphology of the microwave samples looked similar and contained the same complete chemical reaction composition ($TiC + Al_2O_3$) as the conventional SHS samples. For all the $x = 4$ cases, whiskers were observed in SEM photomicrographs for microwave and conventional processed samples. Figure 5a and 5b shown strikingly different whisker morphology between the two techniques. In the conventional case, Fig. 5a, the excess amount of liquid Al and gases produced during SHS reaction resulted in the formation of Al₂O₃-Al hollow whiskers with a bulbous head at the top of each whisker. This behavior suggests a vapor-liquid-solid (VLS) mechanism of whisker formation.³ The microwave ignited sample possessed whiskers with completely different features shown in Fig. 5b. These whiskers are solid, much smaller in size, and do not have the bulbous head feature. Further research is needed to accurately define the mechanism responsible for these different whisker formations. One possible explanation is that microwaves ignite the SHS sample internally and the process

quickly reaches a much higher combustion temperature. The aluminum metal and even alumina may vaporize due to this higher temperature combustion synthesis process. Such a vapor-vapor-solid (VVS) reaction may result in the formation of solid Al_2O_3 whiskers, possibly related to the crystal orientation preference of Al_2O_3 . The formation of these whiskers in ceramic-metal composites using microwave SHS could lead to improve mechanical properties in the combustion synthesis products.

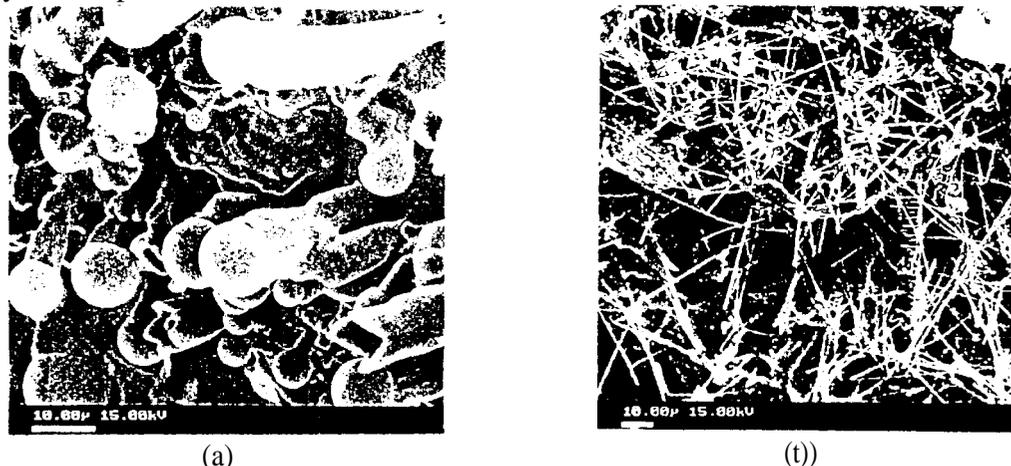


Fig. 5. SEM micrograph of $x = 4$ (a) conventional uniaxial pressed SHS sample, (b) microwave uniaxial pressed SHS sample.

CONCLUSION

This study has demonstrated the ability to ignite the combustion synthesis process $3\text{TiO}_2 + 3\text{C} + (4+x)\text{Al} \rightarrow 3\text{TiC} + 2\text{Al}_2\text{O}_3 + x\text{Al}$ with microwave energy using slow and fast heating rates. All the slow heating rate cases produced an uncompleted reaction. A uniform microstructure with 75% theoretical density was achieved for $x = 0$ with a fast heating rate. For $x = 4$, solid Al_2O_3 whiskers were observed in the microwave SHS product as compared to the hollow whiskers with bulbous heads for the conventional SHS product. The application of a uniaxial force during the SHS process produced high density, homogeneous products for both the microwave (fast heating) and conventional techniques. This investigation suggests that further studies should emphasize SHS reactions using uniaxial or isostatic pressure.

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