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Effects of Gravity on Combustion Synthesis in Heterogeneous Gasless Systems

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The first systematic experimental investigation of combustion synthesis from elements conducted under low (10^{-4} m/s^2) gravity conditions is reported. Several classes of gasless heterogeneous reaction systems were studied, e.g., Ni-Al, Ti-C, and Ni-Al-Ti-B. A variety of gravity-related effects were observed. It was shown that the convection of inert gas, occurring in the reaction chamber during the combustion process in terrestrial conditions, leads to instability of combustion front propagation along the sample. Also, composite materials (Ni_3Al-TiB_2) produced in microgravity have finer size of refractory phase (TiB_2) that is more uniformly distributed in the Ni_3Al intermetallic matrix. The grains formed in terrestrial conditions were approximately 50% larger. The results obtained with quenched samples showed that this difference is related to the buoyancy enhanced coalescence process. For the Ti-C system, dynamics of sample expansion have been determined, and materials with final porosity up to 90% have been synthesized in microgravity conditions without the use of any gasifying additives. Finally, it was observed that the combustion velocity for loose Ni-Al mixtures in microgravity is about three times larger than in terrestrial conditions. This effect may be explained by a change in the primary mechanism of heat transfer through the reaction medium.

Introduction

COMBUSTION synthesis (CS) is an attractive technique to synthesize a variety of advanced materials.[1–4] It is based on the concept that, once initiated locally by means of a thermal source of short-time service, a highly exothermic wave of chemical interactions self-propagates through the heterogeneous reaction medium and yields the final products (powders, materials, and net-shape articles) with tailored physical and mechanical properties. Some advantages of this method over alternative techniques of advanced materials production include low-energy requirements, short synthesis times (on the order of a few seconds), high temperatures (2000–3000 K), and heating rates (up to 10^6 K/s), which allow one to produce unique, e.g., metastable, compositions.

From the viewpoint of chemical nature, three main types of CS can be distinguished. The infiltration type involves reaction between gas and solid reactants. In thermite type synthesis, the reaction includes at least one oxide and a reducing metal. In gasless combustion synthesis from elements, the focus of this paper, the reaction occurs typically between two initially solid elements, e.g., Ti + C and Ni + Al.

A key requirement in the synthesis of advanced materials is a control of the product properties. This requires an understanding of the mechanism of product synthesis. Hence, it is essential to develop a fundamental understanding of the physicochemical processes that occur under the extreme conditions of the combustion wave. A variety of reaction systems have previously been studied under normal gravity conditions, and results have shown that combustion and structure formation mechanisms involve several stages. These include melting of reagents and products, spreading of the melt, droplet coalescence, diffusion and convection in the liquid metals and nonmetals, nucleation of solid products, crystal growth, buoyancy of solid particles and bubbles in the melt, and natural convection of gas. Most of these processes are affected by gravity. Hence, microgravity experiments provide information about separate stages and permit the general mechanisms of combustion and structure formation to be revealed without the disturbing effects of gravity. Additionally, the specific features of the microgravity environment allow the production of unique materials that cannot be obtained under terrestrial conditions.

Results of Previous Relevant Works

A summary of the relevant microgravity research by other investigators in combustion synthesis is given in Table 1. The prior work can be classified into two main groups: synthesis of high porous materials and influence of gravity on microstructure of CS products.

CS of High Porous Materials

The first published work concerning the influence of microgravity on CS process involved the synthesis of high porous materials.[5] The system containing titanium, carbon, and gasifying additives ($Ti + xC +$ additives) was investigated. It was shown that, in microgravity, materials with ~5% of theoretical density could be synthesized, which was somewhat lower than for horizontally positioned samples obtained during CS in terrestrial condition (7% density). More importantly, the porosity distribution was more uniform along the samples produced in microgravity conditions than on Earth. The mechanism of sample expansion during CS in general has been discussed.[5] Two main processes were suggested to understand the growth of reacting samples. The first is the melting of reactants to produce an elastic medium. The second is the decomposition of additives due to high temperature in the combustion wave. The increase of gas pressure in the pores of the viscous medium leads to sample expansion and to increase of its porosity. However, the role of gravity in the mechanism was not discussed.

The general conclusion that gravity influences sample expansion was confirmed later by Moore et al.[6] during investigation of CS process in B_2O_3-C-Al system, where the adiabatic temperature is high enough to transfer one reactant (B_2O_3) to the gas phase. It was shown that the gas generated in the combustion front owing to reactant evaporation is sufficient to create a highly porous composite. The extent of expansion increased 1.6 times with decreasing gravity from 2 to 10^{-2} g. It was suggested that increasing gravity leads to increasing the inertial force acting against the expanding gases generated at and ahead of the reaction front (the sample was ignited from the bottom) and, hence, decreases the extent of expansion.

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Table 1 Summary of relevant microgravity research by other investigators in combustion synthesis

System	Conditions, g	Observed effects in microgravity	Reference
$Ti + xC +$ additives	10^{-2}	Higher porosity; more uniform pore distribution	Shteinberg et al.,[5] 1991 (Russia)
B_2O_3-C-Al	10^{-2}	Higher porosity	Moore et al.,[6] 1992 (United States)
Ti-Al-B	10^{-2} 10^{-5}	Finer and more uniform microstructure	Odawara et al.,[7] 1993 (Japan)
Zr-Al-Fe_2O_3	10^{-2}	Difference in phase composition; finer particles	Odawara et al.,[7] 1993 (Japan)
TiO_2-C-Al, ZrO_2-B_2O_3-Al B_2O_3-C-Al	10^{-2}	Finer and more uniform microstructure	Hunter and Moore,[8] 1994 (United States)
Zn-S	10^{-2}	Larger crystals, closer to the ideal wurzite structure	Goroshin et al.,[9] 1994 (Canada)
Ti-B	10^{-2}	Higher combustion temperature	Lantz et al.,[10] 1995 (United States)

Thus, two different gas sources (gasifying additives and reactant gasification) that affect sample elongation have been investigated. In both cases, it was shown that gravity influences the formation of porous structures during combustion synthesis, and materials with higher porosity and more uniform pore distribution can be produced in microgravity as compared with normal conditions.

Microstructure of CS Materials

The thermite type system Zr-Al-Fe_2O_3, which can react in self-sustained mode with adiabatic temperature 3129 K (calculated with initial temperature of $T_0 = 300$ K) according to the reaction

$$Zr + Al + Fe_2O_3 \rightarrow Fe + ZrO_2 + Al_2O_3 \tag{1}$$

and powder mixture Fe-ZrO_2-Al_2O_3 with the same composition as obtained by reaction (1) were heat treated in terrestrial and microgravity conditions to clarify the effect of gravity on properties of the product.[7] It was observed that, for both systems, the ratio of high-temperature tetragonal to the lower temperature monoclinic ZrO_2 phase was larger for the materials produced under microgravity. Also, ZrO_2 particles formed in microgravity by melting/solidification of Fe-ZrO_2-Al_2O_3 mixture were much finer as compared to those obtained in the terrestrial condition.

Several thermite type reactions were also investigated in microgravity by Hunter and Moore[8]:

$$3TiO_2 + 3C + (4 + x)Al \rightarrow 3TiC + 2Al_2O_3 + xAl \tag{2}$$

$$3ZrO_2 + 3B_2O_3 + (10 + x)Al \rightarrow 3ZrB_2 + 5Al_2O_3 + xAl \tag{3}$$

$$3B_2O_3 + C + (4 + x)Al \rightarrow B_4C + 2Al_2O_3 + xAl \tag{4}$$

The product microstructures in TiO_2-C-Al and ZrO_2-B_2O_3-Al systems were found to have more uniform and finer porosity for the materials synthesized in microgravity. For the B_2O_3-C-Al reaction, as just discussed, one reactant (B_2O_3) transfers to the gas phase. In this case, fine (100-nm-diam) Al_2O_3 whiskers were synthesized in the microgravity condition, whereas relatively thick (~1-μm), needlelike structures were obtained at normal gravity.

The binary Zn-S system has been investigated to produce ZnS crystals in the combustion mode.[9] Combustion synthesis of unconfined samples was realized in microgravity, which in principle cannot be organized in gravity condition due to gravity-induced flow of melt. The larger rectangular crystals obtained in microgravity were attributed to more uniform cooling of the liquid in the absence of convection. In addition, the lattice parameters of the crystals synthesized in microgravity were closer to the ideal wurzite structure than those of typical ZnS powders.

The results of gravity influence in combustion of TiO_2-B_2O_3-Al and Ti-B systems were reported by Lantz et al.[10] It was shown that, for the binary system, maximum combustion temperature T_c in microgravity was ~400°C higher than in ground experiments. However, a decrease of T_c (~60°C) for the thermite type system was observed. Interestingly, in spite of the higher temperature, TiB_2 synthesized in microgravity by direct reaction between Ti and B had finer microstructure than that produced in normal gravity conditions.

On the basis of these microgravity research, one can conclude that gravity influences the product microstructure formed during combustion synthesis. Materials with generally finer and uniform microstructures are produced in microgravity, as compared to normal gravity conditions.

Goals and Approaches of the Present Work

Although all prior results have a qualitative character, they strongly demonstrate that even in the relatively short duration of combustion synthesis (a few seconds), gravity force may significantly influence the process of structure formation. Further investigations should answer the questions at the next level: What is the nature of obtained effects, and what are the specific mechanisms of structure formation taking place at the high temperatures of combustion wave that can be influenced by gravity? The answers to these questions are of great importance for developing accurate models of the fundamental processes, as well as for controlling the microstructure and properties of the synthesized materials. For these reasons, a quantitative study of the processes discussed, i.e., grain growth and sample expansion, is necessary to be conducted under different gravity conditions.

Thus, the main goal of the present work was to study the influence of gravity on the combustion and structure formation processes that occur during gasless CS from elements, taking into account the tasks and questions noted earlier. The following four directions for experimental investigation have been explored.

1) Examine the effect of gravity on dynamics of sample expansion during CS.

2) Study the effects of gravity on the structure formation mechanisms during CS of dense composite materials.

3) Investigate the combustion of highly porous mixtures (with porosity greater than that for loose powders), which cannot be obtained in normal gravity.

4) Determine the influence of gravity force on the characteristic features of combustion front propagation in heterogeneous media.

Experimental Setup

Our experiments were conducted in the 2.2-s Drop Tower (NASA Lewis Research Center, Cleveland, Ohio) providing a microgravity environment (~10^{-4} m/s^2) during 2.2 s of drop time. The restrictions of weight and dimensions of the experimental setup for the Drop Tower facilities dictated its design (Fig. 1). The reaction chamber, battery, power distribution box, specially constructed ignition module and video camera (SONY CCD-IRIS) were fitted into a standard NASA rig (96 × 84 × 40 cm). A microcomputer (Tattletale) controlled ignition and drop processes.

Three different interchangeable sample holders were used in the experiments (Figs. 2a–2c). The first was made from two boron nitride (a thermal shock resistant high-temperature ceramic) plates, with cylindrical holes for three samples and ignition electrodes (Fig. 2a). The outer part had three slits to observe wave front propagation. The entire assembly was mounted in an aluminum cup holder and installed in such a way that one of the samples could be ignited from the bottom, the second from the side, and the third from the top. Ignition occurred when electric current was applied to a 0.5-mm tungsten filament imbedded inside an intermediate ignition mixture (typically Ni + Al). This system provides relatively fast and reliable ignition, which is important in the limited time (2.2 s) experiments. Also, use of the ignition mixture does not influence sample purity

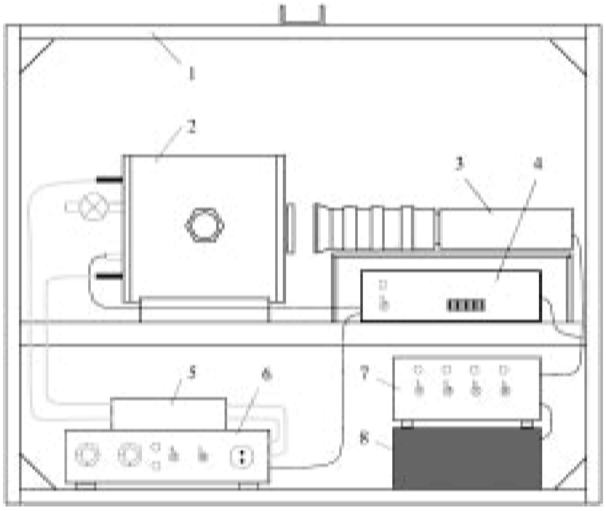


Fig. 1 Schematic diagram of the experimental setup; 1, NASA rig; 2, reaction chamber; 3, video camera; 4, microcomputer; 5, fuse box; 6, ignition module; 7, power distribution box; and 8, battery pack.

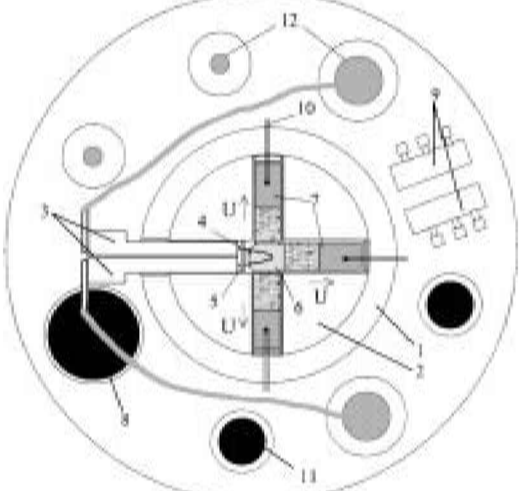
or reaction mechanism. This setup was used to study the influence of gravity on the combustion behavior and microstructure of the final product. For this, experiments were conducted in both terrestrial and microgravity conditions, with the samples located under three different angles between the combustion velocity front and gravity force vectors.

Another sample holder was a vertical quartz tube (9 cm long) placed on a boron nitride support (Fig. 2b). Ignition could be initiated from either the top or the bottom of the sample. This holder was designed for studies in which the sample expands greatly during the synthesis, to yield highly porous or foamlike materials. In addition, the effect of gravity on combustion of loose reactant mixtures was investigated using this assembly.

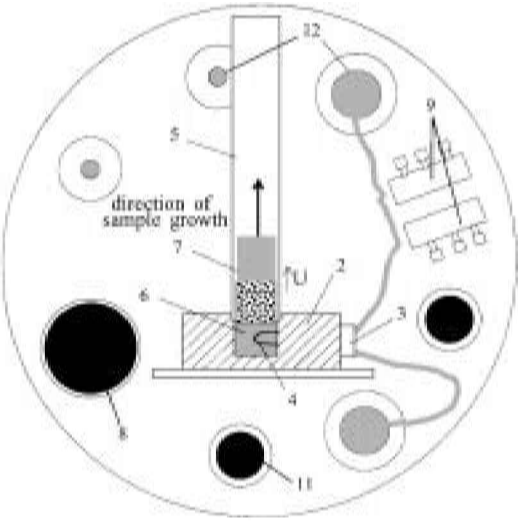
Finally, the wedged brass block (Fig. 2c) was used to perform quenching experiments to investigate the microstructure formation in microgravity conditions. The use of a massive block to rapidly remove heat was originally demonstrated during the combustion of heterogeneous solid fuels.[11] This technique was later applied to quench reacting pellets during combustion synthesis.[12] In this method, a reactant mixture is pressed into a wedge-shaped cut in a brass block (item 13 in Fig. 2c). The sample is ignited from the top, and the reaction is progressively quenched due to a decrease of the reactant mixture volume as the combustion wave travels to the apex of the wedge. A set of thermocouples was used to measure the temperature at several locations of the reacting pellet. The quenched sample was examined layer by layer, from its tip (initial mixture) to the top (final product), to elucidate the evolution of material structure formation during combustion synthesis.

The sample fixed in the appropriate holder was placed in the reaction chamber, which was first evacuated to about 10^{-2} atm and then filled with high-purity argon to 1 atm pressure. The rig with the experimental setup was enclosed in a drag shield and suspended on a steel wire at the top of the Drop Tower. At the operator's signal, the wire was cut and the apparatus fell freely for a distance of 27 m, followed by deceleration at the end when reaching an air bag. A video camera was connected by optic cable with the tower video system center, which allowed us to record the combustion process during the drop. The location of the combustion front $F(t)$ at each moment of time (every $\frac{1}{30}$ s) was evaluated using image analysis techniques (for details, see Ref. 13). The combustion wave propagation was characterized quantitatively, and several parameters were used for this purpose, including the instantaneous, $U(y, t)$, and average, $\bar{U}$, velocities of the combustion wave, as well as the dispersion of the instantaneous velocities σ_U (Table 2).

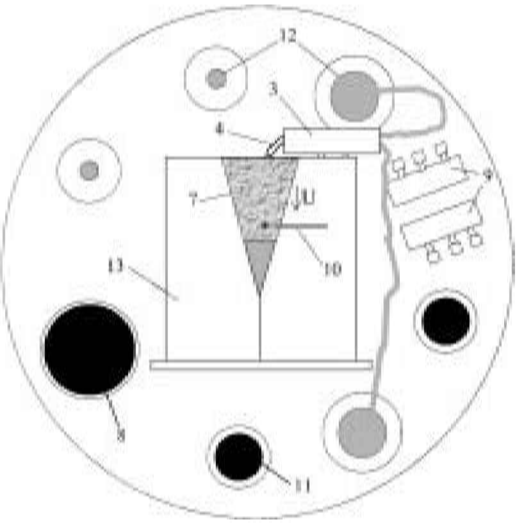
After reaction, the phase composition of the product was identified by x-ray diffraction (XRD) and the microstructure was analyzed using scanning electron microscopy (SEM) along with energy dispersive x-ray spectrometry (EDX).



a) Sample combustion in three different directions



b) Investigations of sample expansion during combustion synthesis



c) Quenching of the combustion front

Fig. 2 Sample holders used in the experiments; 1, aluminum cup; 2, boron nitride plate; 3, ignition electrode; 4, tungsten filament; 5, quartz tube; 6, ignition mixture; 7, sample; 8, vacuum/argon port; 9, thermocouple connector; 10, thermocouple; 11, spare port; 12, electrode; and 13, wedged brass block.

Table 2 Characteristics of combustion front propagation

Characteristic	Parameter
Average position of combustion front at time t	$\bar{F}(t) = \frac{\int_0^{y_0} F(y,t)\,\mathrm{d}y}{y_0}$
Instantaneous combustion front velocity $(t_i - t_{i-1}) = \frac{1}{30}$ s	$U(y,t) = \frac{\partial F(y,t)}{\partial t} \approx \frac{F(y,t_i) - F(y,t_{i-1})}{t_i - t_{i-1}}$
Average combustion front velocity for duration of experiment	$\bar{\bar{U}} = \frac{\int_{t_i}^{t_f}\int_0^{y_0} U(y,t)\,\mathrm{d}y\,\mathrm{d}t}{y_0(t_f - t_i)}$
Dispersion of combustion velocities for duration of experiment	$\sigma_U = \sqrt{\frac{\int_{t_i}^{t_0}\int_0^{y_0} [\bar{U}(t) - U(y,t)]^2\,\mathrm{d}y\,\mathrm{d}t}{y_0(t_f - t_i)}}$

Table 3 Systems under investigation

Experimental conditions	System	Comments
Three-samples setup; initial sample porosity = 0.4	S1: 60 wt% (3Ni + Al)+ 40 wt% (Ti + 2B) 90 wt% S1 + 10 wt% W (Ni + Al) + x wt% (Ti + 2B)	$U_c = U_c$(angle); grain size and phase distribution in product; synthesis of poreless materials
Quartz tube; initial sample porosity = 0.4–0.5	S2: Ti + 0.8C Ti + C + xNi Ti + C + 20 wt% Ni-Mo	Sample expansion; synthesis of foam materials
Quartz tube; loose powders	S3: Ni + Al Cladded Ni-Al particles	Instantaneous velocity distribution; heat conduction mechanism
Wedged brass block; initial sample porosity = 0.3–0.4	S1; 90 wt% S1 + 10 wt% W S3; Cladded Ni-Al particles	Quenched front; mechanistic study

Systems Under Investigation

The systems under study (Table 3), were chosen to investigate different aspects of the influence of gravity on the combustion synthesis process. They all have the common feature that at least one liquid phase exists in the reaction front. Because of this feature, gravity can be expected to play a role in the mechanism of combustion and structure formation through buoyancy and convection. For example, it is known[14] that natural convection in a closed volume becomes significant when

$$Ra = Gr\,Pr = \frac{g\beta\Delta T\delta^3}{\nu\alpha} > Ra_{\mathrm{cr}} \tag{5}$$

where Ra, Gr, and Pr are the Rayleigh, Grashof, and Prandtl numbers, respectively; the subscript cr refers to critical value; β is thermal expansion coefficient (1/Kelvin); α is thermal diffusivity (square meter per second); ν is kinematic viscosity (square meter per second); and δ is characteristic length (meter) over which temperature difference ΔT occurs. Evaluation of Eq. (5) for liquid metals in a combustion synthesis wave for typical values of parameters ($\beta \sim 10^{-4}$ K^{-1}, $\alpha \sim 10^{-7}$ m^2/s, $\Delta T \sim 10^3$ K, and $\nu \sim 10^{-6}$ m^2/s; for the cylindrical geometry of interest, $Ra_{\mathrm{cr}} \sim 10^3$) shows that this condition is satisfied when $\delta > 1$ mm. Hence, for samples where molten zones longer than 1 mm occur in the vicinity of the combustion wave front, we can expect natural convection to play a meaningful role. Such length dimensions are readily available during CS of a variety of systems.

The first system selected (S1) is the (3Ni + Al) + (Ti + 2B) mixture, where a ceramic–intermetallic composite can be produced by the reaction[15]

$$3\mathrm{Ni} + \mathrm{Al} + x(\mathrm{Ti} + 2\mathrm{B}) \rightarrow \mathrm{Ni_3Al} + x\mathrm{TiB_2} \tag{6}$$

This system has a relatively high-combustion velocity (~5 cm/s); hence, the characteristic time of combustion front propagation along the sample (length ~2.5 cm) is only 0.5 s, which is less than the drop time (2.2 s). Thus, the combustion front propagation is fully completed in microgravity conditions. Also, the combustion temperature of the investigated mixture ($x = 1.95$; $T_c = 1933$°C; Ref. 15) exceeds the melting point of $\mathrm{Ni_3Al}$(1395°C) but is lower than the melting point of $\mathrm{TiB_2}$ (2300°C). For this reason, it is possible to investigate the role of buoyancy in the processes of nucleation and growth of $\mathrm{TiB_2}$ grains in the $\mathrm{Ni_3Al}$ melt. Also note that intermetallic matrix composites of this type exhibit superior mechanical and heat resistance properties, which make them excellent candidates for high-temperature applications.[16]

Several systems have been studied (see Table 3) to understand the mechanism of sample expansion in the combustion wave. As already discussed, two sources of gas formation in the combustion wave (gasifying additives[5] and reactant gasification[6]) have previously been considered in the context of gravity influence on sample expansion. However, another common source of gas formation should also be taken into account. It is known that reactant powders typically used in CS have relatively high specific surface areas and contain a variety of absorbed gases.[17] For example, commercial Ti powder used in our experiments contains ~0.4 mg $\mathrm{H_2}$/g Ti (data from vendor). Because of the high temperature in the combustion wave, these gases are released, generating additional gas pressure in the pores of the medium. In fact, sample expansion by this mechanism of gas formation is frequently observed and special sample constraining is needed to prevent it in many systems.[18] It is not easy to separate the effects of special gasifying additives[5] and of desorbed gases on the expansion process. Additionally, no data are available on the dynamics of sample elongation, which can shed some light on the expansion mechanism. For example, if inertial forces, i.e., weight of upper unburned part of sample, affect the expansion,[7] then the expansion rate should increase as the combustion wave propagates upward along the sample in normal gravity conditions, but remain constant in the absence of gravity.

In this work, as an example, we present the results of gravity influence on CS in Ti + xC reactant mixture. Experiments in normal ($g = 10$ m/s^2) conditions show that for the Ti + C ($x = 1$) system, unconstrained samples were completely destroyed, because of gas evolution (primarily $\mathrm{H_2}$, from gas chromatography measurements)

Table 4 Characteristics of the reactant powders

Powder	Size, μm	Purity, wt%	Vendor
Ni	5	99.9	Cerac
Al	<44	99.5	Aesar
Ti	<44	99.5	Cerac
Ni/Al cladded	70	99.8	Sherritt
B (amorphous)	0.1	98.0	Russia

Table 5 Characteristic velocity of combustion wave propagation under different gravity conditions

Sample ignition location	Velocity, cm/s			
	Terrestrial conditions		Microgravity conditions	
	Average value, $\bar{U}$	Dispersion, σ_U	Average value, $\bar{U}$	Dispersion, σ_U
Bottom	5.5	1.1	4.8	0.7
Side	5.4	0.7	4.8	0.5
Top	5.3	0.7	4.8	0.5

during reaction. For this reason, we selected the Ti + 0.8C system (S2) for investigation, since no mass loss was observed for this mixture. The adiabatic combustion temperature of S2 mixture (2700°C), calculated using a thermodynamic computer program,[19] is higher than the melting point of Ti (1670°C). Thus, the excess amount of titanium (as compared to the stoichiometric Ti + C mixture) present in the liquid phase forms a stronger skeleton in the reaction medium, preventing sample destruction.

The influence of gravity on the mechanism of combustion wave propagation in highly porous (loose powders) media was studied. We expected to find a change in the behavior of reaction front propagation due to the decrease of contact between particles in microgravity conditions. The results on combustion of Ni + Al system (S3) are shown here as an example. In this system, nickel aluminide is formed during the reaction in the combustion wave:

$$\mathrm{Ni + Al \rightarrow NiAl} \qquad (7)$$

and this reaction is well studied in terrestrial conditions.[20,21]

As shown in Table 3, various systems have also been studied using the quenching technique to elucidate the structure formation mechanisms. The results for S1 are presented here to illustrate the influence of gravity on these processes.

The characteristics of reactant powders used are listed in Table 4. The samples were prepared by ball-mixing the elemental reactant powders in the required stoichiometry, followed by uniaxial cold pressing. The pellets were cylindrical in shape, with a diameter of 10 mm and typical length of 20–30 mm.

Results and Discussion

All experiments were conducted under otherwise identical conditions in both normal gravity ($g = 10$ m/s^2) and microgravity ($g = 10^{-4}$ m/s^2) to make a direct comparison and to establish the effects of gravity on combustion and structure formation in the investigated systems.

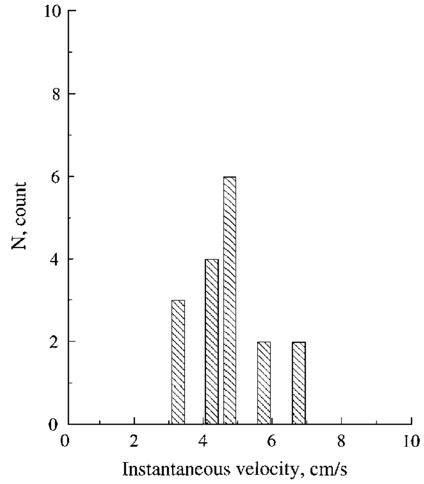
Influence of Gravity on Combustion Velocity

Several systems were studied (see Table 3) to determine the influence of gravity on combustion front propagation. They can be divided into two main groups: dense samples and loose powders.

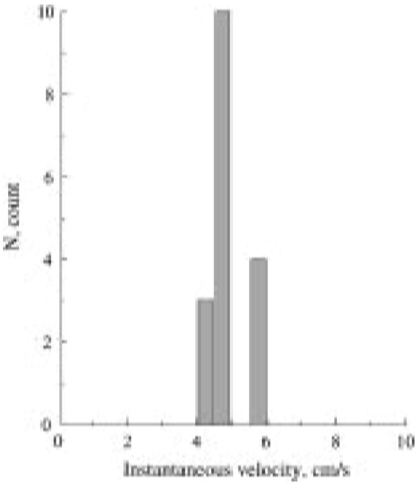
Dense Samples

Initial pellet densities were in the range 55–60% of theoretical. In these systems, the sample sizes remain constant during the CS process. Also, as already noted, the relatively high combustion velocity (~5 cm/s) allows the combustion process to be completed during the short drop time (~2 s).

The values of calculated average combustion front velocity $\bar{U}$ and dispersion σ_U of instantaneous combustion velocities, for different directions of reaction front propagation in system S1 are presented in Table 5. The data show that $\bar{U}$ is larger in terrestrial conditions.



a) Normal conditions



b) Microgravity

Fig. 3 Distribution of instantaneous combustion velocity during reaction in (3Ni + Al)-(Ti + 2B) system.

Further, in all cases, the dispersion σ_U, characterizing the steadiness of front propagation, is also greater in terrestrial conditions than in microgravity. The distributions of instantaneous velocity shown in Fig. 3 illustrate this point, where a wider distribution is observed for normal gravity as compared to microgravity. Also, for pellets ignited from the bottom, at $g = 10$ m/s^2, the velocity generally increases while approaching the end of the sample, whereas at $g = 10^{-4}$ m/s^2 it remains relatively constant. All of the features just noted were also observed during combustion synthesis of S1 + 10 wt%W and (Ni + Al)-(Ti + 2B) systems.

We believe that convection of inert gas, taking place in the reaction chamber during the combustion process in terrestrial conditions, leads to instability of combustion front propagation along the sample. Also, due to preheating of the upper part of the sample by convective gas flow, the combustion wave accelerates while propagating from the bottom to the top of the sample. These effects can be important in the case of direct production of net-shape articles by the CS method. Indeed, instability of combustion wave propagation may result in undesired nonuniform properties along the surface of the produced material.[22]

Loose Powders

To investigate the role of gravity on the mechanism of heat transfer in loosely packed powders during combustion, Ni + Al mixture (S3) and Ni/Al cladded particle powders[23] were studied (Table 3). The quartz tube was partially filled with reactant mixture, which was ignited from the bottom (Fig. 2b). The data obtained during combustion of the loose (20% of theoretical density) S3 mixture are shown in Fig. 4. In terrestrial conditions, the combustion front

Table 6 Some characteristics of combustion in Ti-0.8C system

Condition	$E = h_f/h_0$	Final porosity	$\bar{\bar{U}}_{\mathrm{ex}}$, cm/s	$\bar{\bar{U}}$, cm/s	$\bar{\bar{U}}_r = \bar{\bar{U}} - \bar{\bar{U}}_{\mathrm{ex}}$, cm/s
Normal conditions	3.2	0.85	0.65	0.95 ± 0.05	0.30 ± 0.05
Microgravity	4.8	0.90[a]	0.95	1.2 ± 0.1	0.25 ± 0.10

[a] Final porosity of the sample synthesized during Drop Tower experiment including normal and microgravity conditions.

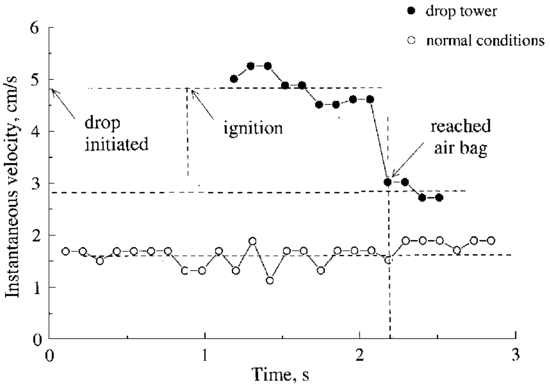


Fig. 4 Instantaneous combustion velocity in (Ni + Al) system as a function of time in microgravity and normal conditions.

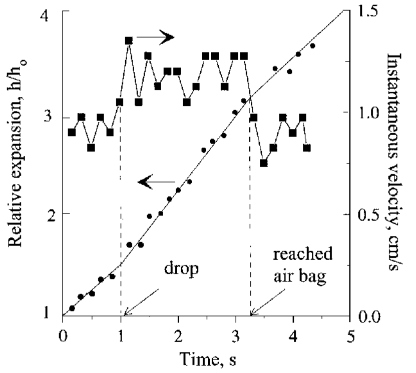


Fig. 5 Instantaneous combustion velocity and sample expansion in (Ti + 0.8C) system as a function of time during drop experiment.

propagates relatively steadily, with an average velocity ~1.6 cm/s. To describe the results obtained in microgravity, we note that only a part of the sample was reacted at $g = 10^{-4}$ m/s^2, and ignition was done about 1 s after the drop initiated. The average front velocity in microgravity was about 5 cm/s, which is much higher than in normal conditions. However, the effect of increasing velocity in microgravity conditions was not observed when the quartz tube was completely filled with the reaction mixture.

These results may be explained by a change in the primary mechanism of heat transfer in the reaction medium. Three main mechanisms of heat transfer during high-temperature reaction wave propagation in porous media include conduction by inert gas in the pore, conduction by contact between solid particles, and radiation. The results of previous works show that the first two dominate during the combustion of loose powder mixtures in terrestrial conditions.[13,24] When the volume of the reaction chamber, i.e., quartz tube, allows the reaction mixture to expand in microgravity, due to the suspension of reacting particles, the distance between them increases. Thus, the effect of heat conduction decreases, while the role of radiation increases.[25] Inasmuch as heat transfer is the controlling step of combustion front propagation in highly porous mixtures, and very high temperatures occur in the reaction front, we may expect that heat transfer by radiation provides higher propagation velocity as compared to heat conduction.

Even after impact, in the case of a partially filled tube (Fig. 4), the front velocity was larger than in experiments conducted fully under normal gravity. This effect can be explained by consolidation of the unreacted part of the mixture due to deceleration when reaching the air bag.

Influence of Gravity on Sample Expansion

The characteristic dependencies of the instantaneous combustion front velocity U and sample expansion as functions of time for the S2 system are shown in Fig. 5. The sample was ignited in terrestrial conditions, and the combustion front propagated rather steadily with $\bar{\bar{U}} = 0.95$ cm/s for about 1 s. The reaction chamber was then dropped, and during 2.2 s the process occurred in microgravity. A noticeable increase of average velocity ($\bar{\bar{U}} = 1.2$ cm/s), as well as the sample expansion velocity U_{ex}, was detected in microgravity conditions. Note that both U and U_{ex} were measured, using frame by frame video analysis, relative to the reacted part of the pellet (ignition from the bottom, see Fig. 2b). The data on the final relative linear expansion ($E = h_f/h_0$, where h_f and h_0 are the final and initial sample heights), final porosity, average expansion ($\bar{\bar{U}}_{\mathrm{ex}}$) and average combustion front ($\bar{\bar{U}}$) velocities obtained in normal as well in microgravity conditions are presented in Table 6.

Relative final linear expansions E equal to 3.2 and 4 were achieved in normal and drop tower experiments, respectively. As shown in Fig. 5, only about half of the sample reacted in microgravity. Taking this into account, we estimated relative expansion in microgravity conditions to be $E = 4.8$. The same result can be obtained based on the analysis of $\bar{\bar{U}}_{\mathrm{ex}}$ observed at normal conditions and during the drop. From Table 6, the ratio of these velocities $\bar{\bar{U}}^{\mu g}_{\mathrm{ex}}/\bar{\bar{U}}^{\mathrm{norm}}_{\mathrm{ex}} \approx 1.5$ is approximately the same as the ratio between the linear expansion values, $E^{\mu g}/E^{\mathrm{norm}} = 1.5$. It is also interesting that gravity does not influence combustion velocity measured relative to the unreacted part of the sample, $\bar{\bar{U}}_r = \bar{\bar{U}} - \bar{\bar{U}}_{\mathrm{ex}}$, which defines the real velocity of reaction propagation in the system (see Table 6). Finally, qualitatively similar results for gravity influence on combustion and expansion processes were obtained for other investigated systems as well (see Table 3).

As already discussed in the context of previous relevant works, two different mechanisms of the influence of gravity on sample expansion have been suggested. The first is based on the assumption that sample expansion depends on the relative combustion velocity, i.e., if somehow gravity influences the velocity of combustion front propagation, then it also affects the expansion.[5] However, our experiments show that, at least for the systems investigated, combustion velocity $\bar{\bar{U}}_r$ remains essentially constant with changing gravity, whereas the rate of expansion and final sample porosity are both higher for lower gravity conditions. The second explanation generally proposed is that when ignited from the bottom, the weight of the upper (nonreacted) part of the sample affects the reaction zone, decreasing expansion in normal gravity conditions.[6] Our results shown in Fig. 5 clearly indicate that in each of the microgravity and terrestrial conditions, the rate of sample expansion remains constant during the entire combustion process, whereas the mass of unreacted part changes continuously.

Because our results cannot be explained by the mechanisms proposed previously, we suggest a new hypothesis for the effect of gravity on sample expansion. The process of porous structure formation is dictated by the competition between the following primary processes taking place behind the combustion front, where relatively large volume of liquid phase exists: gas evolution (mainly from the powders, either from impurities or from additives), gas motion through the liquid, and its eventual escape from the sample. If the permeability of the medium is high enough, then the gas can escape from the sample without expanding the medium. Retarding the rate of gas escape leads to greater sample expansion. Buoyancy and convection processes are decreased in microgravity, increasing the residence time of gas in liquid, resulting in increase of sample expansion.

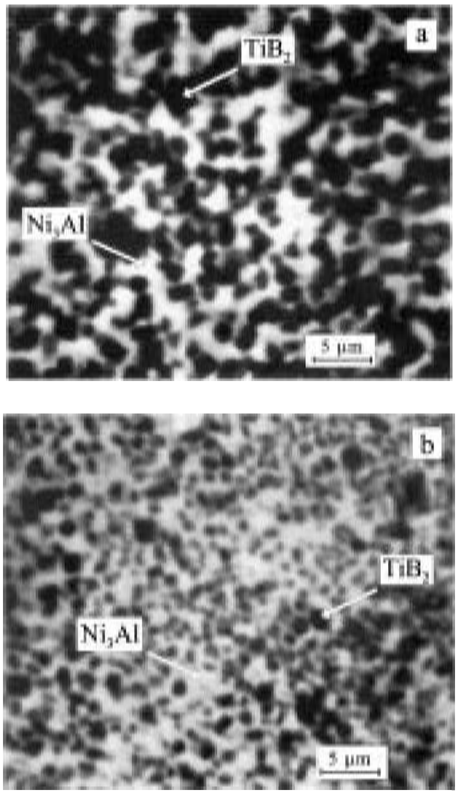


Fig. 6 Characteristic microstructures of Ni_3Al-TiB_2 composite synthesized in a) normal and b) microgravity conditions.

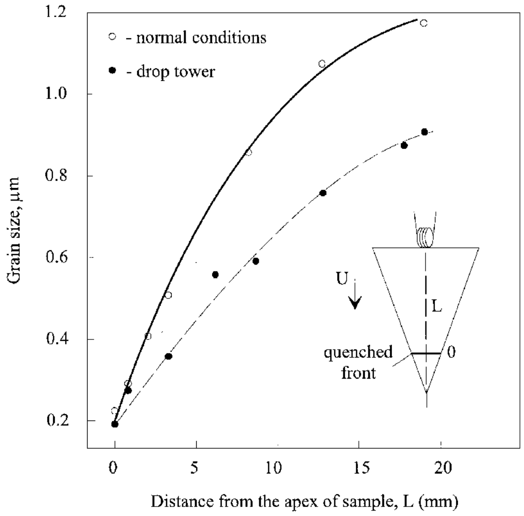


Fig. 7 Evolution of TiB_2 grain size in (3Ni + Al)-(Ti + 2B) quenched sample.

Influence of Gravity on Microstructure of Composites

It was observed that gravity influences not only propagation of the combustion wave but also microstructure of the final product. In Fig. 6, characteristic microstructures of materials synthesized in terrestrial (Fig. 6a) and microgravity (Fig. 6b) conditions are presented. Both show grains of TiB_2 (dark phase) dispersed in the Ni_3Al matrix (light phase). Statistical analysis showed that the average size of TiB_2 grains in the material produced in normal gravity was 1.4 ± 0.2 μm, whereas in microgravity it was 0.9 ± 0.2 μm. The results obtained for samples quenched in the wedged block showed that this difference is related to the process of grain growth during CS. The characteristic dependencies of average TiB_2 particle size as a function of the distance from the quenched front are shown in Fig. 7, for normal and microgravity conditions. In both cases, very fine particles ($\sim$0.1 μm) of TiB_2 formed immediately in the reaction front. However, the rate of particle growth in the microgravity condition is lower than at $g = 10$ m/s^2. Measurements of characteristic cooling time from the maximum combustion temperature (1933°C) to the melting point of Ni_3Al (1395°C) in different sample cross sections showed that at least $L = 15$ mm of sample becomes completely solid in 2.2 s, i.e., before the experimental setup reaches the air bag. Thus, the results presented in Fig. 7 truly indicate the difference in grain growth under the two conditions.

It is known that when solid and liquid phases coexist for some period, microstructural changes can occur (cf. Ref. 26) such that larger particles grow at the expense of smaller ones so as to lower the free energy of the system (Ostwald ripening). The grain growth mechanism can also be controlled by the process of solid particle coalescence. Buoyancy due to the difference in density of liquid (Ni_3Al) and solid (TiB_2) products may promote both mechanisms.[27]

The terminal velocity of a spherical particle in a liquid medium is described by Stokes' equation

$$V_t = \frac{2}{9}\frac{g|\rho_s - \rho_l|}{\mu}R^2 \tag{8}$$

where ρ_s is the density of the solid particle, e.g., 4310 kg m^{-3} for TiB_2; ρ_l is the density of the liquid, e.g., 6500 kg m^{-3} for Ni_3Al; and μ is the dynamic viscosity, $\sim 4 \times 10^{-3}$ Pa s for Ni_3Al. The last property was estimated assuming ideal mixing of the elemental constituents (Ni and Al). In this case, taking the average size of initial TiB_2 particles as $R = 0.2$ μm, we have $V_t = 0.05$ μm/s. The corresponding value of Peclet number ($Pe = RV_t/D$, where D is diffusivity, typical value 10^{-9} m^2/s) equals 10^{-5}, and so buoyancy influences mass diffusion only slightly. On the other hand, within the characteristic time of about 2 s, the particles move about 0.1 μm, which is comparable with the distance between the TiB_2 particles in the Ni_3Al melt. Thus, buoyancy is likely to increase the number of collisions between the solid particles, accelerating the particle coarsening by coalescence. Hence, we believe that the observed effect of gravity on particle growth (Figs. 6 and 7) is due to buoyancy enhanced coalescence.

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