

Influence of Gravity on Combustion Synthesis of Advanced Materials

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I. Introduction

COMBUSTION synthesis (CS), also known as self-propagating high-temperature synthesis, discovered in the early 1970s,¹ has generated notable interest because of its potential for producing advanced materials that include powders and near-net shape products of ceramics, intermetallics, composites, and functionally graded materials (see, for example, Refs. 2 and 3). This technology is based on the fundamental 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 (Fig. 1) and yields the final products (powders, materials, alloys) with desired properties. The process possesses low-energy requirements, short reaction times (on the order of seconds), and simple equipment is needed for synthesis. Owing to these specific features, CS is perhaps one of the few methods of materials synthesis that is feasible in space. Indeed, this technology has the potential to prepare advanced materials and net-shape articles rapidly

in one step and with extremely low external energy inputs, critical for use on space platforms.⁴ For this reason, many investigations of CS under microgravity conditions have been reported in the literature.

Further, CS allows one to produce a variety of materials that can find direct aerospace applications. They include different types of intermetallic composites,⁵ which, owing to their unique properties (e.g., low density, high melting point, high corrosion, and oxidation resistance), are good candidates for airframe and turbine applications. Also, high-temperature advanced ceramic matrix composites (e.g., SiC- or Si₃N₄-based), an enabling technology for hypersonic trans-aerospace and missile applications, can be synthesized in the combustion wave.⁶ Finally, Co- and Ni-based alloys, among the best materials for combustors and nozzles,⁷ can be produced by the CS method (see, for example, Ref. 8).

Another motivation for CS studies in microgravity is related to the fundamentals of combustion and structure formation mechanisms in unique conditions of rapid high-temperature reaction waves. It



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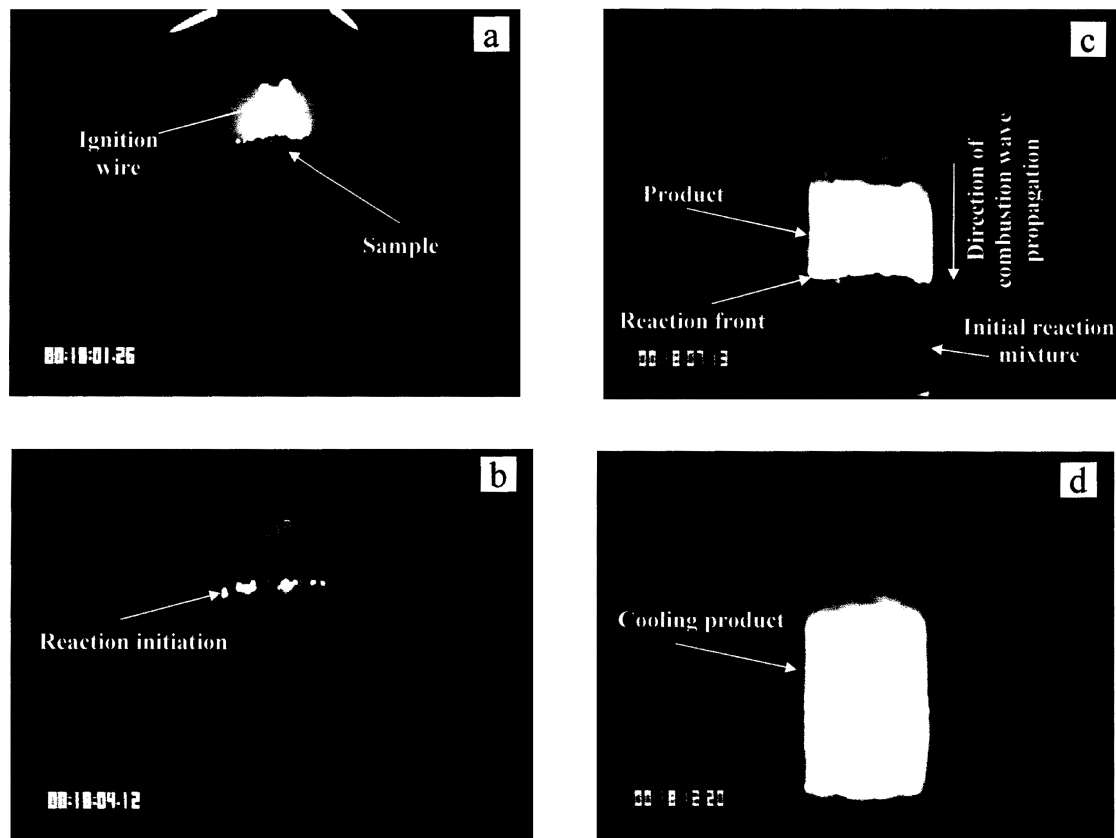


Fig. 1 Wave propagation in combustion synthesis.

is known that combustion of heterogeneous systems, leading to the synthesis of advanced materials, is typically characterized by high temperatures (up to 3500 K) and heating rates (up to 10^6 K/s) at and ahead of the reaction front (see, for example, Ref. 3). These features, although attractive for the synthesis of unique compounds, also make it difficult to study the mechanism of the process, which is essential in order to form materials with tailored microstructures and properties. Indeed a variety of reaction systems has been studied previously under normal gravity conditions, and results have shown that the mechanisms of combustion and structure formation are complex and involve several stages. These include melting of reactants and products, spreading of the melt, droplet coalescence, diffusion and convection in the molten phase, nucleation of solid products, crystal growth, buoyancy of solid particles and bubbles in the melt, and natural convection in the gas phase. Most of these processes are affected by gravity. The removal of such gravitational effects is likely to provide increased control of the reaction front, with a consequent improvement in control of the microstructure of the synthesized products. Thus microgravity experiments can lead to major advances in understanding the fundamental aspects of structure formation that occur under the extreme conditions of the combustion synthesis wave. Finally, the specific features of microgravity environment allow one to produce unique materials, which cannot be obtained under terrestrial conditions.

Prior microgravity research efforts were directed toward various aspects of CS. Different approaches can be used to review this relatively large body of information available in the literature. For example, classification can be based on chemical composition of the products (e.g., carbides, intermetallics, nitrides, etc.). Also, one can sort the data by physical characteristics of the synthesized materials: highly porous, fully dense, or single crystals. Finally, the results can be analyzed from the viewpoint of gravity effects on the parameters of combustion wave propagation (e.g., temperature, velocity, mode, etc.), followed by the corresponding effects on product microstructure and properties.

In this review, we attempt to combine all of the preceding approaches. A general analysis of possible gravity effects on different

processes, which take place during CS, is given in Sec. II. In Sec. III, we analyze the influence of gravity on the combustion parameters (velocity, temperature, and combustion mechanism) of different systems. The results on effects of microgravity on microstructures of the synthesized materials are presented in Sec. IV. Section V is devoted to the specific issue of synthesis of highly porous materials in space. Finally, a brief overview of theoretical works related to gravity influence on CS is given in Sec. VI. Note that we analyze only works related to gravity conditions (i.e., $10^{-5} - 2g$), which can be reached in drop tower experiments or onboard aircraft during parabolic flights and spacecraft. Thus, we do not consider results obtained during large overloads (see, for example, Refs. 9 and 10). Also, in this review we do not analyze materials synthesis by gas-phase combustion techniques, as this information is available in a recent review.¹¹

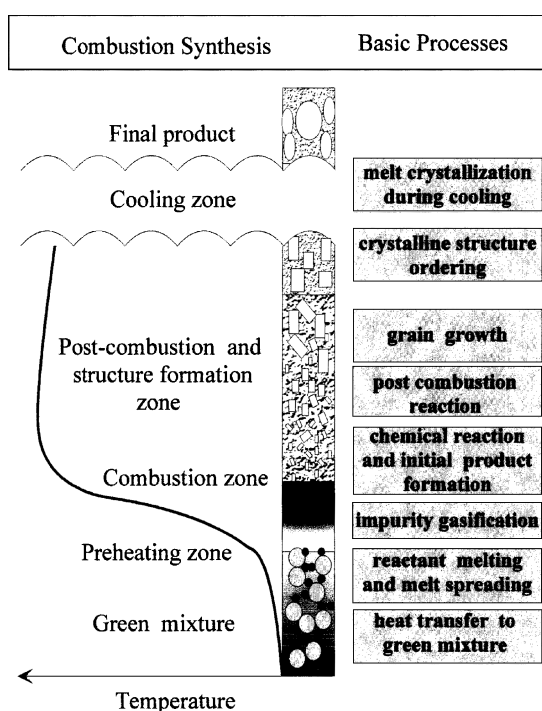
Analysis of the available literature shows that studies involving CS in microgravity have been conducted primarily in the United States, Japan, Russia, and Canada, with recent activity also in Italy and China, and some representative works are shown in Table 1 (Refs. 4 and 12–34). Although the first relevant publication appeared in 1991,⁴ more than 50 papers have since been published in international journals.

II. Gravity-Driven Processes in CS Wave

The typical temperature-time history of the CS process is presented in Fig. 2. This profile can be divided into several characteristic regions. First, the preheating zone is the region in which essentially “inert” heating of the initial reaction mixture occurs. The timescale of this zone varies from 10^{-2} to several seconds, whereas the heating rate is in the range $10^2 - 10^4$ K/s. Second, the combustion zone involves intensive chemical interaction (thus temperature gradients are high, up to 10^5 K/s), which directly influences the mode (e.g., stable, pulsating) and velocity of combustion front propagation. The typical temperature in this zone varies in the range 2000–3500 K, and reaction time is generally less than a second. Third, the post-combustion zone is the region where reaction can still occur; however, it does not influence the velocity of combustion front propagation.

Table 1 Summary of different microgravity research directions in combustion synthesis

System	Conditions, <i>g</i>	Observed effects in microgravity	References
Ti + <i>x</i> C + additives	10 ⁻²	Higher porosity; more uniform pore distribution	Ref. 4 (Russia)
Zr-Al-Fe ₂ O ₃ , ZrO ₂ -Al ₂ O ₃ -Fe	10 ⁻²	Difference in phase composition; finer particles	Refs. 12 and 13 (Japan)
Si(CH ₃) ₄ -H ₂	10 ⁻⁴	Larger particle size and narrower size distribution	Ref. 14 (Japan)
Ti-Al-B	10 ⁻² 10 ⁻⁴	Lower velocity; finer and more uniform microstructure	Refs. 15 and 16 (Japan)
TiO ₂ -C-Al, ZrO ₂ -B ₂ O ₃ -Al B ₂ O ₃ -C-Al	10 ⁻²	Finer and more uniform microstructure; higher porosity	Refs. 17 and 18 (USA)
Zn-S	10 ⁻²	Larger crystals, closer to the ideal wurzite structure	Refs. 19 and 20 (Canada)
Ti-B, TiO ₂ -B ₂ O ₃ -Al	10 ⁻²	Higher combustion temperature	Ref. 21 (USA)
GaO ₂ -P	10 ⁻⁴	Higher conversion; finer products	Ref. 22 (Japan)
(GaO ₂ , In ₂ O ₃)-P		Different light absorption properties	
Ti-C	10 ⁻⁴	Lower gas temperature; higher composition velocity and expansion; finer microstructure	Refs. 23 and 24 (Japan)
Hf-B-Al, Ni-Ti-B	10 ⁻²	Lower combustion temperature and velocity; more uniform phase distribution	Ref. 25 (Canada, USA)
Ni-Al-Ti-B		Smaller particle growth rate; steady wave propagation	Refs. 26–28
Ni-Al, Ti-C	10 ⁻²	Higher expansion velocity	Ref. 29 (USA)
Co ₃ O ₄ -Al; MoO ₃ -Al	10 ⁻⁵	Gravitational sensitivity	Ref. 30 (Russia)
Al clad Ni particles	10 ⁻⁴	Pressed sample: larger and more perfect crystals	
		Loose sample: higher porosity	
Ti-B, B ₂ O ₃ -C-Al	10 ⁻²	Higher porosity and pore size	Ref. 31 (USA)
Ti-C-Fe	10 ⁻²	Lower combustion temperature; finer microstructure	Ref. 32 (Italy)
Cu ₂ O-Al		Finer refractory phase	
Ti-C	10 ⁻²	Finer porosity	Ref. 33 (China)
		Lower temperature	
Ni-Al-Ti-B	10 ⁻²	Smaller particle growth rate; finer and more uniform microstructure	Ref. 34 (USA)

**Fig. 2** Characteristic structure of combustion wave.

This quasi-isothermal zone has a characteristic time up to 10 s. Finally, the cooling zone has temperature gradients up to 10² K/s, and the cooling duration varies from several minutes to hours.

Along with the preceding specific features related to the combustion wave propagation (i.e., temperature, velocity, and heating rate), one can also consider the CS process based on the characteristic microstructural transformations of the reaction media. In general, the initial stage of structure changes is concurrent with the preheating zone, for example, interfacial solid-solid reactions, melting of reactants, etc. However, the major events occur later in the combustion and partly in the postcombustion zones, where the driving force of the process is the reduction of Gibbs free energy resulting from the formation of new chemical bonds, under nonequilibrium conditions (see Fig. 2). In many cases, a so-called initial product forms first, with phase composition and microstructure different as compared to the final product.

During the final stages, which take place mainly in the post-combustion and cooling zones, physical effects are predominant as the free energy decreases further as a result of interfacial surface reduction, ordering of the crystal structure, and other related processes that occur without changes in the chemical composition under quasi-equilibrium conditions. Thus, in general, the initial product structure can be defined as that formed during chemical reaction in the combustion zone, which becomes the starting point of the final structure formation step that later yields the desired product. Note that the characteristics of the reaction front wave (temperature, velocity, degree of conversion) are determined by the processes occurring primarily in the preheating and combustion zones, whereas

microstructure of the synthesized product depends significantly on processes in the postcombustion and cooling zones.

A large variety of physicochemical processes take place during combustion synthesis³: 1) heat transfer from the combustion zone to unreacted particles ahead of the reaction front; 2) formation of eutectic melts and contact melting; 3) spreading of molten phase; 4) coalescence of fused particles; 5) gasification and transport of volatile impurities and reactants; 6) chemical reaction with initial product formation; 7) melting of intermediate products; 8) phase separation of the intermediate products; 9) melt crystallization upon cooling; 10) grain growth; 11) phase transitions in solid products during cooling; and 12) ordering of the crystal structure.

The first eight processes proceed during the rapid increase in temperature to a maximum at the combustion front, whereas the last four occur behind the combustion front with either a constant or gradual lowering of temperature. Because most of the processes are affected by gravity (compare Refs. 11, 35, and 36) it is critical to know if this influence changes the combustion parameters as well as the material properties produced in the unique conditions of CS wave.

Let us make some preliminary estimates of the possible effects of gravity on CS processes. First, these effects can be related to the additional flow that occurs as a result of temperature gradients. This flow can be convection of gases (inert or reactive) present in the reaction chamber or evolved in the reaction front and/or the convection of different molten phases formed in the CS wave. For example, it is known that natural convection in a closed volume becomes significant when³⁷

$$Ra = GrPr = \frac{g\beta\Delta T\delta^3}{\nu\alpha} > 10^3 \quad (1)$$

where Ra , Gr , and Pr are the Rayleigh, Grashof, and Prandtl numbers respectively; β is the thermal expansion coefficient (1/K); α is the thermal diffusivity (m²/s); ν is the kinematic viscosity (m²/s); and δ is the characteristic length (m) over which temperature difference ΔT (K) occurs. For example, evaluation of the preceding relation for liquid metals in a combustion synthesis wave²⁷ shows that this condition is satisfied when $\delta \geq 1$ mm; thus gravity, can play an important role in the mechanism of mass and heat transport in these systems.

Second, combustion of thermite-type systems (e.g., $\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Fe} + \text{Al}_2\text{O}_3$) typically involves formation of two liquids (oxide and metal alloy), followed by their phase separation. The latter process is generally believed to be controlled solely by gravity-driven buoyancy, owing to the difference in product densities (see, for example, Refs. 9, 10, 38, and 39). Indeed, gravity-driven separation of refractory drops in continuous matrix of liquid oxide was the basic physical model underlying all previous theories describing combustion in so-called "liquid" flame (compare Refs. 38–40). Owing to the lack of experimental evidence, which appeared only recently,^{26,29} prior works do not account for other possible mechanisms of phase segregation. For example, the characteristic time of phase separation in stationary (for droplet size) theory³⁸ is

$$t_{\text{ps}} = \frac{L\eta}{(\Delta\rho)d_c^2g} \quad (2)$$

where L is the height of melted layer (m), η is the dynamic viscosity of slag (Pa·s), d_c is the characteristic drop size (m), and $\Delta\rho$ is the difference in density between slag and nonoxide product (kg/m³). Similarly, for the case where self-accelerating process of metal droplets coalescence is important,³⁹ t_{ps} is given by

$$t_{\text{ps}} = \frac{36\eta F}{(\Delta\rho)d_0\alpha g} \quad (3)$$

where F is a tabulated function in the range 0.1–0.5, α is relative volume of reduced metal, and d_0 is the minimum droplet diameter (m) when coalescence process begins. Both these times depend on gravity level g and are in the range 1–10 s. Thus experiments in microgravity conditions, which can be achieved for example during aircraft parabolic flights (10⁻² g for ~20 s), can allow one to verify if buoyancy is the only mechanism for phase separation. These

results can be used to determine whether thermite-type combustion technologies, successfully used in normal gravity conditions, can also be applicable in space.

Finally, let us give a concrete example to show that natural convection can influence the rate of solid particle growth in molten matrix, which is the typical process for CS of composites. Previously obtained experimental results lead to the conclusion that, in general, grain size changes with time according to the following expression (see, for example, Ref. 36):

$$R^n = R_0^n + Kt \quad (4)$$

where R is grain size at time t , R_0 is initial grain size, and n is an exponent that typically varies from two to four for most materials. The rate constant K (m³/s) is given by

$$K = \frac{bD_eC\Omega\tau}{kT} \quad (5)$$

where b is a numerical constant, D_e is the effective diffusivity of the solute in liquid (m²/s), C is the concentration of the solid in liquid, Ω is atomic volume (m³), τ is the interfacial energy (J/m²), k is Boltzmann's constant, and T is the absolute temperature (K).

Note that the effective diffusivity D_e can be affected by gravity in the case of CS processes. The ratio between mass transport by convection and molecular diffusion is characterized by the Sherwood number, defined as

$$Sh = k_c\delta/D_m \quad (6)$$

where k_c is the mass-transfer coefficient (m/s) and D_m is the molecular diffusion coefficient (m²/s). Further, for Ra in the range 10²–10⁴ the relationship between Sh and Ra for the closed volume is¹⁴

$$Sh = 0.55(Ra)^{0.25} \quad (7)$$

Using $Ra = 10^3$, the lower limit in Eq. (1), we obtain $Sh > 3$. Thus convection plays a role in the grain growth process by enhancing D_e . As a result, one can expect a difference in particle growth rates during CS under terrestrial and microgravity conditions, leading to differences in the microstructure and properties of the synthesized materials.

III. Effect of Gravity on Combustion Characteristics

The characteristic feature of CS, as compared to conventional powder metallurgy, is that the process variables, such as combustion wave velocity U_c and temperature-time history $T_c(t)$ are strongly related, that is, a small change in the maximum combustion temperature can result in a large change in the combustion front velocity and hence the characteristic time of synthesis. Such process parameters as green mixture composition, dilution, initial sample density, size, and morphology of reactants influence U_c and $T_c(t)$ and in turn can be used to regulate the synthesis process.³ In this review, we focus on the effects of gravity on the combustion characteristics and provide some general conclusions on using it as an additional parameter for the CS process.

Some representative results on combustion velocity and temperature for different gasless heterogeneous systems investigated under both terrestrial and microgravity conditions are summarized in this section (Tables 2–8). The general conclusion that can be drawn after analysis of the data is that combustion velocity is typically smaller under microgravity conditions, whereas maximum combustion temperature remains essentially constant. However, some exceptions exist as discussed in the following.

A. Combustion Velocity

The parameters of reaction front propagation in the Ti-Al-B system, for different compositions (Ti:B:Al = 1:4:1; 1:2:2 and 1:4:0) and initial relative sample densities in the range 45–75%, were investigated by Odawara et al.^{15,41} Experiments with samples ignited from the top and bottom (Fig. 3) were conducted in both normal gravity and μg conditions (parabolic flight; ~10⁻² g). Table 2 presents

Table 2 Combustion velocity of Ti-B-Al powder mixture compacts^{15,41}

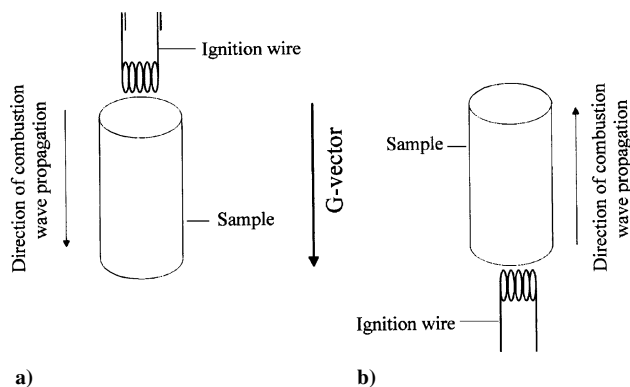
Ti:B:Al	Rel. ρ , %	Combustion velocity, mm/s			
		$10^{-2} g$		1 g	
		U_{down}	U_{up}	U_{down}	U_{up}
1:4:1	50	17 ± 4.5 (27%)	24 ± 5.5 (25%)	18 ± 5 (28%)	26 ± 4 (16%)
	65	18 ± 2 (11%)	18 ± 3 (17%)	20 ± 3 (15%)	21 ± 2 (10%)
1:2:2	65	13 ± 3 (23%)	17 ± 2 (12%)	16 ± 2 (13%)	22 ± 4 (18%)
	70	13 ± 1 (8%)	21 ± 1 (5%)	18 ± 2 (11%)	23 ± 4 (17%)
1:4:0	55	—	58 ± 1 (2%)	44 ± 8 (18%)	70 ± 10 (14%)

Table 3 Characteristic velocity of combustion wave propagation under different gravity conditions²⁶

System	Gravity condition, g	Average velocity, cm/s	RMS deviation, cm/s
(3Ni + Al) + 40 wt.%(Ti + 2B)	1	6.5	1.1
	10^{-2}	4.1	0.6
(3Ni + Al) + (Ti + 2B) + W	1	8.3	1.4
	10^{-5}	7.6	0.8
(Ni + Al) + 5 wt.%(Ti + 2B)	1	15.2	0.4
	10^{-2}	14.3	0.2

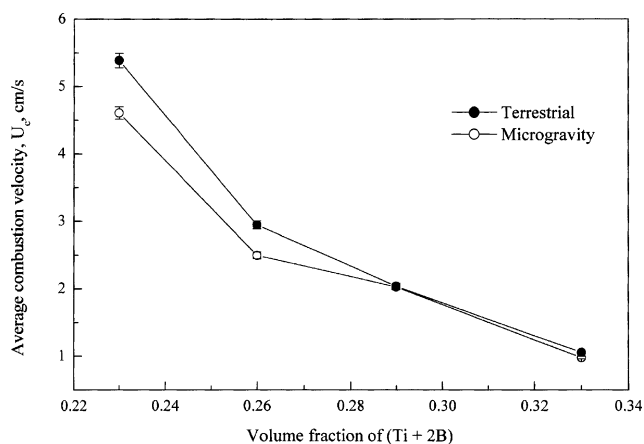
Table 4 Effect of gravity on combustion parameters during CS of Al-HfB₂ and Ni₃Ti-TiB₂ composites²⁵

Volume, %	Microgravity, $10^{-2} g$		Normal gravity, 1g	
	U_c , mm/s	T_c , K	U_c , mm/s	T_c , K
60 (Al)	2.8 ± 0.2	1875 ± 165	3.1 ± 0.2	2055 ± 90
70 (Al)	0.9 ± 0.1	1400 ± 30	1.9 ± 0.1	1765 ± 15
60 (Ni ₃ Ti)	21.5 ± 1.2	1725 ± 135	21 ± 0.5	1745 ± 30
70 (Ni ₃ Ti)	5.5 ± 0.4	1505 ± 10	9.3 ± 1.5	1525 ± 20

**Fig. 3** Direction of combustion wave propagation: from the a) top and b) bottom.

the data for cases where the relative error of velocity measurements was lower than 30%. (For other conditions, the reaction wave propagated in an unstable manner, leading to larger errors and data are difficult to analyze.) The following general trends can be outlined. First, average velocities for ignition from the top U_{down} , where combustion wave propagates parallel to the gravity vector, are generally lower than for samples ignited from the bottom U_{up} , that is, $U_{up} \geq U_{down}$. Second, velocities under normal gravity conditions are slightly higher than for microgravity experiments, that is, $U_{1g} \geq U_{\mu g}$. The later was confirmed by experiments conducted under lower gravity ($10^{-4} g$) during free fall. For example, for Ti + 4B + Al mixture with initial relative density 50%, $U_{up} = 15.5$ mm/s, which is lower than those measured under both normal gravity and parabolic flight environments (see Table 2).

These trends were confirmed by studies of combustion in the complex (Ni-Al)-(Ti-B) system,²⁶ where it was shown that the average

**Fig. 4** Average combustion velocity as a function of volume fraction TiB₂ (Ref. 34) in the (Ni+Al) + (Ti+2B) system.

velocity (ignition from the bottom) is higher in 1 g as compared to microgravity conditions (see Table 3). More important, in all cases, the rms deviations of measured values, characterizing the unsteadiness of front propagation, are about two times larger in 1 g than in μg . It was suggested that convection of gases, both present as inert in the chamber (argon, 1 atm) and released in the reaction front, taking place in terrestrial conditions leads to the observed effects. On one hand, gravity-driven flow of hot gases in the direction of combustion wave propagation preheats surface of unburned part of the sample and thus leads to an increase of U_{up} . On the other hand, the nonuniformity of convection patterns contributes to unsteadiness of combustion front propagation along the sample. These effects can be important not only for fundamentals of structure formation, but also for direct production of net-shape articles by the combustion synthesis method. Indeed, instability of combustion wave propagation usually results in undesired nonuniform properties of the produced materials.⁴² Thus more steady synthesis environment achieved under μg might lead to products with enhanced properties.

The combustion velocities (samples ignited from bottom) obtained during CS of HfB₂-Al and Ni₃Ti-TiB₂ composites under different gravity conditions are shown in Table 4.²⁵ As in previous systems, the combustion velocities are lower under microgravity. In addition, it was found that the effect of gravity on velocity is more pronounced when the amount of liquid phase (Al) in the reaction front increases.

Similar observations were made during the investigations of other intermetallic-ceramic composite systems [i.e., $x(\text{Ni} + \text{Al}) + y(\text{Ti} + 2\text{B})$] (Ref. 34). In these experiments, the compositions (i.e., NiAl:TiB₂ ratio) were varied in such a way that the maximum combustion temperature remained constant ($T_c = 1930$ K) for all mixtures. However, it appears (Fig. 4) that U_{up} increases significantly as the amount of NiAl phase, which melts ($T_{melt} = 1912$ K) in the reaction front, increases. It was also shown that U_{up} is lower in microgravity as compared to terrestrial conditions; however, this difference becomes negligible as the liquid phase (i.e., NiAl) content in the reaction front decreases. Indeed, the compositions with the amount of solid TiB₂ products above 27 vol.% at maximum

Table 5 Combustion temperatures and velocities for the TiC-Al₂O₃-Al and ZrB₂-Al₂O₃-Al reaction system¹⁷

System	Ignition direction	10 ⁻² g		1 g		2 g	
		U _c , mm/s	T _c , K	U _c , mm/s	T _c , K	U _c , mm/s	T _c , K
TiC-Al ₂ O ₃ -Al	Downward	1.84	2153	1.88	2142	2.07	2146
	Horizontal	—	—	2.18	2145	—	—
	Upward	—	—	2.29	2148	—	—
ZrB ₂ - Al ₂ O ₃ - Al	Downward	0.46	≥2273	0.50	2298	0.99	≥2273
	Horizontal	—	—	0.54	2294	—	—
	Upward	—	—	0.59	2302	—	—

Table 6 Combustion velocity for Ti-C system under terrestrial and microgravity conditions²³

Ambient condition	Combustion velocity, mm/s	
	10 ⁻⁴ g	1 g
Air	34.5	29.4
Argon	26.3	18.4

Table 7 Combustion temperature for the B₄C-Al₂O₃-Al system¹⁷

B ₄ C-Al ₂ O ₃ -xAl	T _c , K		
	10 ⁻² g	1 g	2 g
x = 0	2137	2241	2248
x = 3	2141	2144	2149

Table 8 Combustion temperature for the Ti-C-Fe system³²

Sample	T _c , K	
	10 ⁻² g	1 g
Ti/C/10 wt.% Fe	2066	2206
Ti/C/20 wt.% Fe	2078	2139
Ti/C/30 wt.% Fe	2106	2161

combustion temperature exhibit same combustion velocities in both normal and microgravity conditions, whereas U_c in microgravity conditions is smaller for the compositions with less than 27 vol.% TiB₂ (Fig. 4). The preceding results demonstrate the important conclusion that in gasless systems the influence of gravity becomes significant when liquids exist in the reaction front.

Thermite reaction systems (TiO₂-C-Al and ZrO₂-B₂O₃-Al) were also studied under different gravity conditions (10⁻², 1, and 2 g) and ignition orientations (i.e., from the top, bottom, and horizontal).¹⁷ It was again observed that under 1 g the reaction front propagates faster when ignited from the bottom as compared to the top, with the general trend $U_{up} > U_h > U_{down}$ (Table 5). Similarly, the familiar trend of gravity influence on combustion velocity, that is, $U_{μg} < U_{1g} < U_{2g}$, was found in these systems. These features are related to the process of phase separation between cermet (or metal) and slag in thermite systems.⁴³

Although a decrease of combustion velocity is usually observed under microgravity, Tanable et al.²³ reported an increase in U_c during combustion synthesis of titanium carbide foams (Table 6). Microgravity experiments were performed in a drop shaft (10⁻⁴ g for 4.5 s). The reaction was initiated by an electrically heated tungsten filament at the bottom of the pressed compact. It was suggested that the heat loss caused by gas flow decreases because of a lack of convection in microgravity, which increases the temperature in the sample and hence combustion velocity. However, we suspect that the reported combustion velocity values do not account for sample expansion, which occurs in the Ti-C system. In this case, greater expansion in microgravity (see, for example, Ref. 4) can lead to higher observed velocity relative to the reacted part of the pellet (for more details, see Sec. V).

B. Combustion Temperature

The temperature-time characterization of rapid high-temperature process, such as heterogeneous combustion waves, is not easy.⁴⁴

Usually, either thermocouples or pyrometers are used for this purpose.⁴⁵⁻⁴⁸ For the former, several issues should be taken into account for correct temperature measurements, including the relation between characteristic times of the combustion process and thermocouple relaxation (defined by its thickness), interaction of the thermocouple with high-temperature reactants, and its position (e.g., in pore or in contact with powder surface) in the heterogeneous porous medium. With pyrometers, care is required to properly account for the emissivity of the reaction medium as well as relative sizes of the viewing area and reaction front. These lead to problems of measurement accuracy and thus require statistically representative data sets. Unfortunately, most results on T_c available in the literature were reported without an analysis of their accuracy.

Some examples of combustion temperatures T_c recorded using W-Re (type C) thermocouples and two-wavelength infrared pyrometers for various thermite systems¹⁷ are shown in Tables 5 and 7. No significant differences in T_c were found under normal gravity and microgravity. The weak trend [within measurements accuracy, typically not better than 5% (Ref. 49)] of increasing T_c with gravity was explained by the role of gravitation force in densifying the reaction medium. The authors contend that the resulting lower sample porosity decreases heat loss to the pores, increasing combustion temperature.¹⁷

A decrease of T_c under microgravity was observed during CS of composites (Table 4),²⁵ cermets (Table 8),³² and carbides.³³ In the first case, three out of four systems show differences in the range of measurement accuracy. Only for the HfB₂-Al system, with 70 vol.% Al, this difference reached a significant value (~360 K), which was used to explain the corresponding change (~two times) of combustion velocity. However, a similar change in U_c for the Ni₃Ti-TiB₂ system (70 vol.% Ni₃Ti) occurs at essentially constant T_c , with no explanation provided by the authors.²⁵

In the second case (Ti-C-Fe system), a significant decrease of temperature (~200 K) in microgravity experiments was observed only for the composition with the lowest amount of iron (Table 8), whereas for the larger amount of liquid phase (i.e., Fe) in combustion front the differences were negligible. This result contradicts the general conclusion just discussed that gravity influences the combustion process more strongly for systems with a greater amount of liquid phase in the reaction front. Because the statistical accuracy of measurements was not reported, one might expect that the observed discrepancy in T_c is caused by the well-known volume change effect (see, for example, Ref. 26) that occurs during combustion in Ti-C system, which significantly complicates the temperature measurements.

The only opposite result, that is, significant increase in maximum combustion temperature under microgravity (Fig. 5), was reported by Lantz et al.²¹ for the binary Ti + 2B → TiB₂ system. In this case, microgravity conditions were achieved onboard a modified Learjet (10⁻² g for ~20 s), and temperature was measured on the sample surface by using a two-wavelength infrared pyrometer. The large increase in T_c (e.g., 673 K in 1 atm of argon) was explained by a reduction in heat loss because any liquid formed at and ahead of the reaction front is held by capillary forces and is not drawn away by gravity, creating improved reactant contact. It is difficult to comment on these data. The observed trend of increasing T_c with increased inert gas pressure (as shown in Fig. 5) under terrestrial conditions is

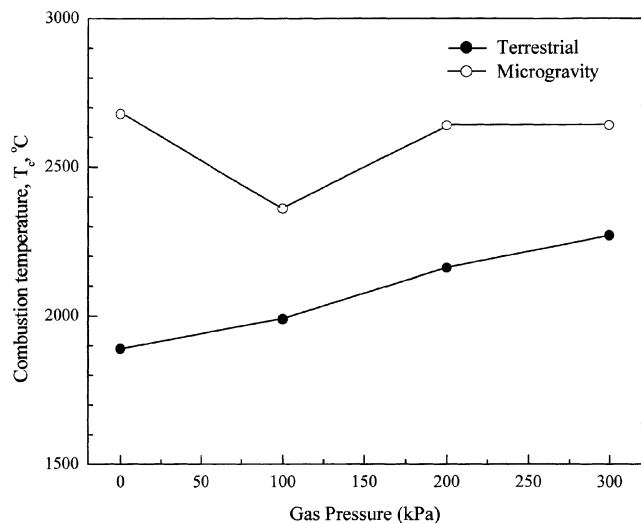


Fig. 5 Effect of gas pressure on T_c for the (Ti+2B) system, under different gravity conditions.²¹

also unusual. Higher pressure generally leads to greater heat losses and thus to lower T_c .

Distributions of gas temperature, as well as sample surface temperature, were investigated during CS in Ti + C system²⁴ under both normal and μg conditions. The gas temperature was measured using three sets of Type K thermocouples installed 12, 13, and 14 cm above the sample bottom (Fig. 6), whereas sample surface temperature was measured in situ with a thermal vision system (Japan Avionics: TVS-8000), which covered temperature range 957–3049 K. It was shown that, as expected, the gas temperature decreases along distance from the sample and maximum values follow the trend: $T_{g, 1g} > T_{g, \mu g}$ (Fig. 6).

The surface-temperature profiles are shown in Fig. 7, where it can be seen that gas convection flow influences temperature. Indeed, owing to the absence of convection in microgravity, the maximum temperature reached at any point along the sample remained essentially constant. However, in normal gravity this temperature increases (decreases) along the sample length when ignited from the bottom (top).

In addition, it was shown that not only the thermal convection of inert gas but also the direct flow gases released in combustion front is important to understand the influence of gravity on combustion characteristics in this system. Thus when the sample is ignited from the bottom, during the early stages of combustion, because directions of both the flow of generated gases and convection of inert gas are the same (i.e., upward), the heat losses are large, and the maximum temperature is relatively low (Fig. 7a). However, T_c increases during the later stages of combustion as heat supplied by the gas flow preheats the unburned part of the sample. On the contrary, when sample is ignited from the top the generated gases flow downward parallel to combustion wave propagation and thus compensate the heat losses caused by upward convective flow. Therefore T_c values near the upper part of the sample are relatively high (Fig. 7c). Later, heat losses caused by the upward gas convection increase, leading to lower combustion temperature.

C. Combustion Mechanisms

The influence of gravity on combustion mechanism has been investigated primarily for the Ni-Al system.^{26–30,34,50} To simplify the task, model experiments were conducted under conditions that allow one to focus on specific features. One such approach is to use instead of powder mixture of two reagents, for example (Ni + Al, Fig. 8a), clad particles (Fig. 8b) consisting of a core of one reagent (Al) encapsulated in a shell of another (Ni), which eliminates complications associated with sharp change of contact area when one reactant melts. Moreover, the mass ratio between reactants in a clad particle is stoichiometric; thus, each particle represents an elemental

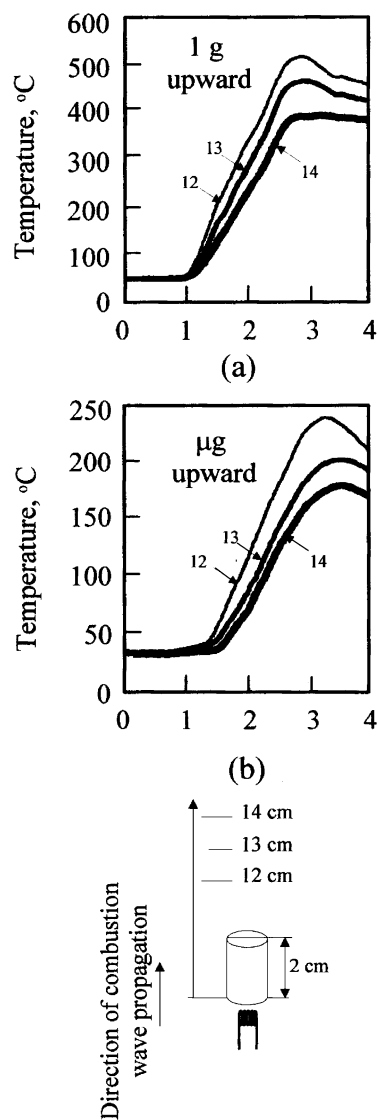


Fig. 6 Gas temperature profiles for the (Ti+C) system, under various conditions; the distance is thermocouple location above the sample bottom.²⁴

reaction cell, used in different theoretical models (see, for example, Ref. 3). For these reasons, one can expect that heat transfer controls propagations of the reaction wave; hence, clad particles are a convenient model to investigate the role of different heat transport mechanisms during combustion wave propagation.

It has been shown that combustion of complex clad particles exhibits novel phenomena. First, it appears that by changing density of the reaction mixture the mechanism of heat transfer, which controls the reaction front propagation, can be varied: radiation for low, gas-phase convection for intermediate, and heat conduction through condensed skeleton for high sample densities.²⁸ Secondly, by experiments conducted in drop tower,²⁷ as well as during parabolic flights onboard DC-9 aircraft²⁶ and confirmed by studies made in MIR space station,³⁰ using these type of particles it is possible to organize so-called “contactless” mode,⁵⁰ where combustion wave propagates through a particle cloud even in vacuum. Let us discuss these issues in detail.

Different trends in changes of combustion velocity U_c have been observed when the initial sample density ρ_0 is varied in gasless system.³ With increasing ρ_0 , U_c either increases monotonically or exhibits a maximum, while the combustion temperature generally remains constant. No typical dependence was obtained for combustion of clad particles (Fig. 9). First, it was shown that within a relatively wide range of initial relative density ρ_r (0.48–0.65)

combustion front velocity U_c increases monotonically as predicted by classical theory. However, when density was changed only 3% more (up to 0.68) U_c increased dramatically (more than five times). Second, and most remarkable, is the increase in combustion front velocity for particle clouds under microgravity (μg) conditions. Moreover, the width of the instantaneous velocity distribution σ , which characterizes the unsteadiness of front propagation, is about three times smaller under microgravity (Fig. 10).^{27,28}

These results were explained by a change in the primary mechanism of heat transfer in the reaction medium. In general, there are three mechanisms of heat transfer during high-temperature reac-

tion wave propagation in porous media: by inert gas in the pore, by contact between solid particles, and radiation. Detailed studies²⁸ show that below a critical density ρ_r^{cr} (in this system, ~ 0.66) heat conduction along the porous medium occurs primarily because of the gas-phase heat convection mechanism, whereas for $\rho_r > \rho_r^{cr}$ the more rapid solid phase heat conduction predominates. This explains the dramatic increase of combustion velocity on the right branch of the curve at $\rho_r = \rho_r^{cr}$ (Fig. 9a).

Further, when the volume of the reaction chamber (i.e., partially filled quartz tube; see Fig. 11a) allows the reaction mixture to expand in microgravity, because of the suspension of reacting particles, the

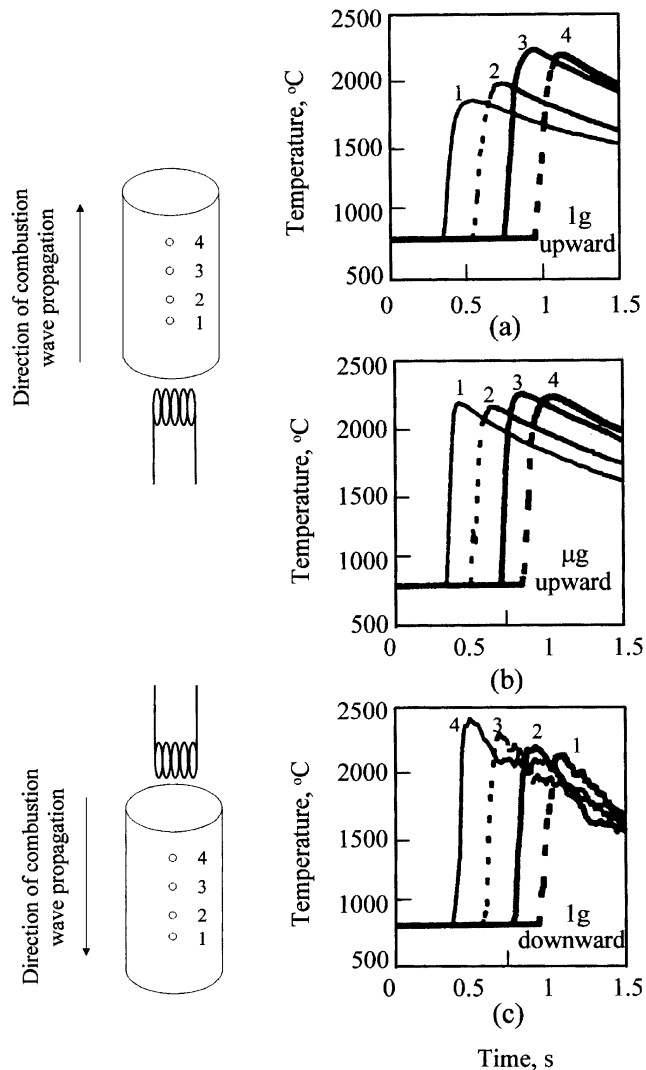


Fig. 7 Sample surface-temperature profiles for the (Ti+C) system, under various conditions.²⁴

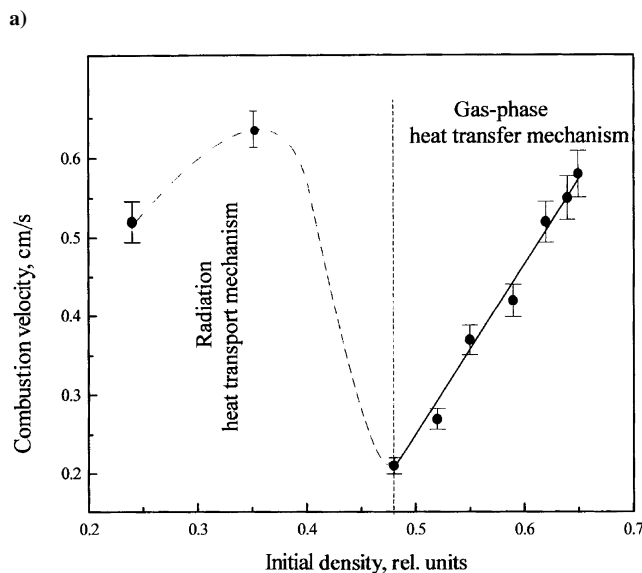
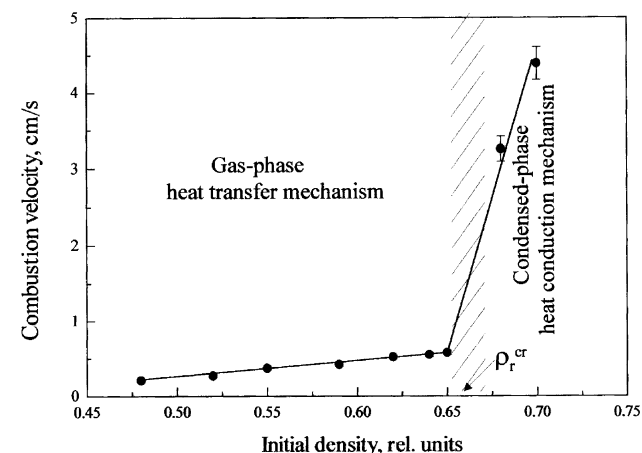


Fig. 9 Combustion velocity as a function of initial sample relative density: a) high-relative-density region and b) low-relative-density region.²⁸

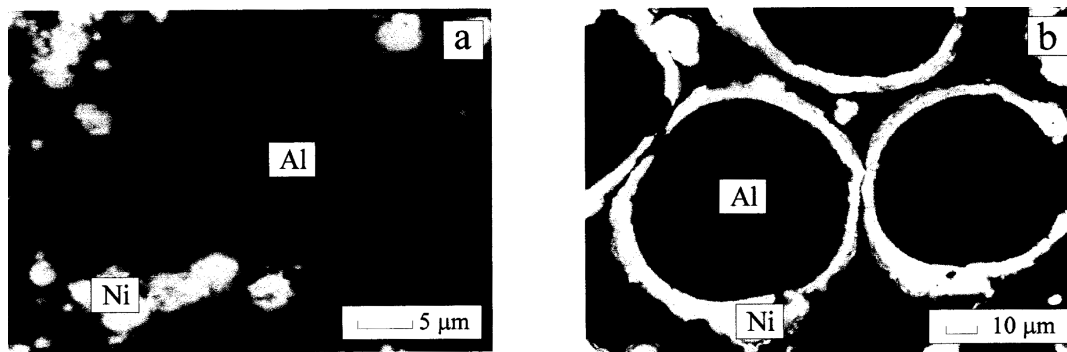


Fig. 8 Microstructure of a) Ni+Al powder and b) Al/Ni clad particles.

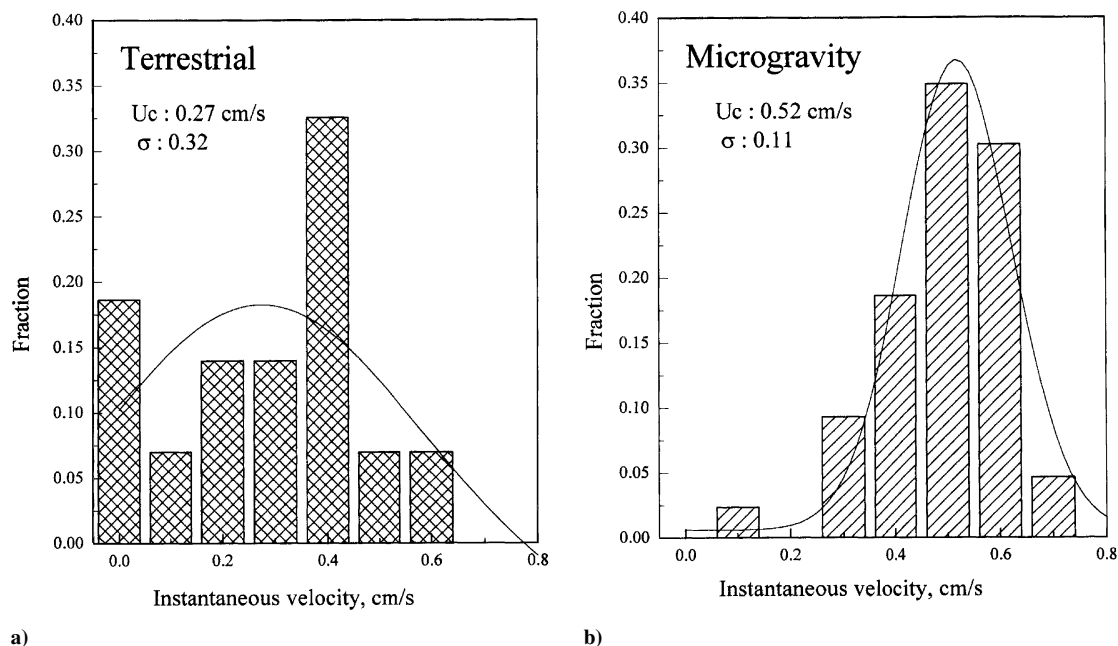


Fig. 10 Distribution of instantaneous combustion velocity under different gravity conditions: a) 1 g and b) 10^{-2} g (Ref. 27).

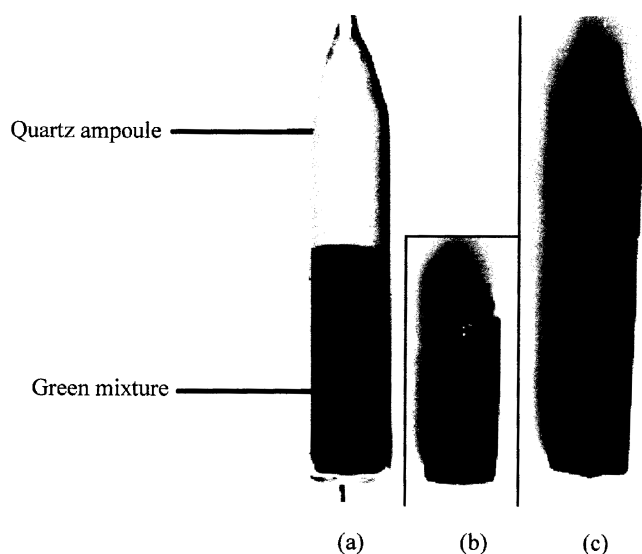


Fig. 11 a) Reactants and samples burnt under b) normal gravity and c) microgravity conditions.³⁰

distance between them increases. The reactant mixture distributes uniformly along the tube volume ($\rho_r \sim 0.2$), and reaction front propagates along this particle cloud in vacuum. In this case, the primary mechanism of heat transfer is radiation, owing to high transparency of low-density heterogeneous media. In the case of cloud combustion, one reacted high-temperature complex particle caused by radiation can ignite several clad particles ahead of the reaction front, instead of fewer for dense media, leading to increased combustion velocity. Finally, because heat transfer is the controlling step of reaction front propagation in such heterogeneous mixtures,⁵¹ it appears that radiation (at ~ 2000 K) in contactless combustion wave provides higher propagation velocity as compared to gas phase convection (Fig. 9b).

Additional results on combustion of clad particle clouds were obtained onboard the MIR Space Station by Merzhanov et al.^{30,52} Both pressed pellets ($\rho_r \sim 0.7$) and loose powder ($\rho_r \sim 0.5$) of Ni-clad Al particles were used for the investigation. For the latter, the powders were placed in evacuated sealed quartz ampoules (Fig. 11a) with the free space (pores + unoccupied ampoule volume) about

70%. Combustion was initiated at the bottom of the quartz ampoule by focused radiation from halogen lamps located around the sample. Gas evolution was insignificant because both Ni and Al were in their condensed state.

The final products from both normal gravity and space experiments are shown in Figs. 11b and 11c, respectively. The space-produced material from initially loose powder has more porous skeleton. Because expansion owing to gas is absent, it was assumed that this product is the result of powder suspension combustion in vacuum. Additional observations and video recordings confirmed that clad particles indeed initially distributed uniformly throughout the ampoule volume, and after ignition combustion front propagated in the gasless cloud. It was also suggested that heat transfer in such clouds can occur by radiation and/or upon particle collisions.

Thus based on the results of microgravity research, a novel phenomenon of combustion in gasless complex particle clouds has been discovered. This process can be used for different applications including synthesis of advanced high-porous materials and intermetallic spherical powders,^{34,52} as well as in propulsion (see, for example, Ref. 53).

IV. Microstructure of Synthesized Materials

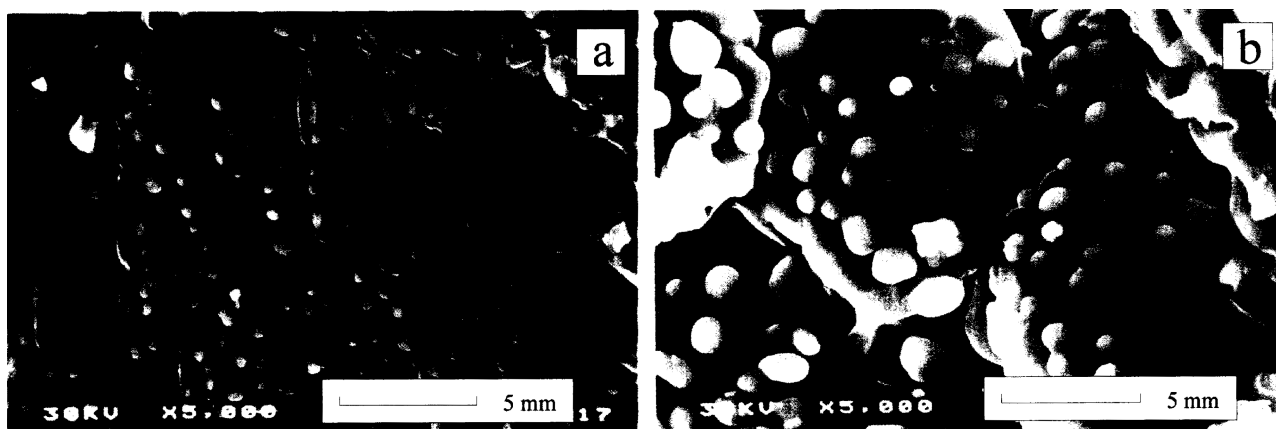
The microstructure of materials defines their properties.⁵⁴ As just discussed in Secs. I and II, combustion synthesis is a novel technique for effectively producing a variety of advanced materials and occurs under unique conditions (e.g., high temperature and its gradients, etc.), where different gravity-driven processes can occur in liquid and gas phases. However, the characteristic length and timescales of CS are relatively small, and thus it is not clear if gravity can significantly influence microstructural transformations in the process. In this context, several important questions have been answered following systematic investigations of CS in microgravity and are addressed in separate subsections.

A. Product Structure: Normal vs Microgravity

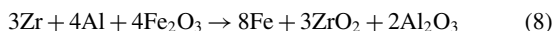
The data on influence of gravity conditions on the process of structure formation during CS are summarized in Table 9. Based on overall analysis, the general conclusion can be made that materials synthesized in microgravity typically have finer and more uniform microstructure than those produced under normal gravity conditions. In the following, we illustrate this statement by several examples.

Table 9 Summary of microgravity research related to product microstructure

System	Conditions, <i>g</i>	Observed effect in microgravity	References
Zr-Al-Fe ₂ O ₃ , ZrO ₂ -Al ₂ O ₃ -Fe	10 ⁻²	Difference in phase composition; finer particles	Refs. 12 and 13 (Japan)
Si(CH ₃) ₄ -H ₂	10 ⁻⁴	Monodispersed particles; larger particle size and narrower size distribution	Ref. 14 (Japan)
Ti-Al-B	10 ⁻² 10 ⁻⁴	Lower propagating velocity; finer and more uniform microstructure	Refs. 15 and 16 (Japan)
TiO ₂ -C-Al, ZrO ₂ -B ₂ O ₃ -Al B ₂ O ₃ -C-Al	10 ⁻²	Finer and more uniform microstructure	Refs. 17 and 18 (USA)
Zn-S	10 ⁻²	Larger crystals, closer to the ideal wurzite structure	Refs. 19 and 20 (Canada)
GaO ₂ -P		Higher conversion; finer products	
In ₂ O ₃ -P	10 ⁻⁴	Finer and more uniform microstructure	Ref. 22 (Japan)
(GaO ₂ , In ₂ O ₃)-P		Different light absorption properties	
Ti-C	10 ⁻⁴	Lower gas temperature; higher combustion velocity; higher expansion; finer microstructure	Refs. 23 and 24 (Japan)
Hf-B-Al, Ni-Ti-B	10 ⁻²	Lower combustion temperature; lower propagating velocity; more uniform phase distribution	Ref. 25 (USA)
Ni-Al-Ti-B	10 ⁻²	Smaller particle growth rate	Refs. 26–28, 43 (USA)
Co ₃ O ₄ -Cr-Mo-Al	10 ⁻⁵	Randomly oriented dendrites	
Co ₃ O ₄ -Al, MoO ₃ -Al		Mechanism of phase separation	
Al-clad Ni particles	10 ⁻⁴	Pressed sample; Larger and more perfect crystals	Ref. 30 (Russia)
Ti-C-Fe	10 ⁻²	Loose sample; Higher porosity	
		Lower combustion temperature; finer and more uniform microstructure	Ref. 32 (Italy)
Cu ₂ O-Al		Finer refractory phase	
Ni-Al-Ti-B	10 ⁻²	Smaller particle growth rate; finer and more uniform microstructure	Ref. 34 (USA)

**Fig. 12** Scanning electron microscope (SEM) micrographs of the products obtained in melting/solidification of the (Zr+Al+Fe₂O₃) system in a) μ g and b) 1-g conditions.¹²

Let us consider the Zr-Al-Fe₂O₃ system, which reacts in self-sustained mode with adiabatic temperature ~ 3130 K following the reaction:



The powder mixtures of initial reactants (Zr-Al-Fe₂O₃) as well as stoichiometric products (Fe-ZrO₂-Al₂O₃) were heat treated in terrestrial and microgravity conditions.¹² In both cases, “chem-

ical ovens” were used, Ti + 4B + Al ($T_{\text{ad}} = 2175$ K) for the former and Ti + C ($T_{\text{ad}} = 3289$ K) for the latter composition. All microgravity experiments were conducted during aircrafts parabolic flights, which achieved $2 \times 10^{-2} g$ for ~ 15 s. Two specific results of gravity influence on microstructure of final products can be outlined here. First, ZrO₂ particles formed in μ g experiments of melting/solidification process in Fe-ZrO₂-Al₂O₃ mixture were much (three to four times) finer as compared to those obtained in terrestrial conditions (Fig. 12). Second, for both systems, the ratio of

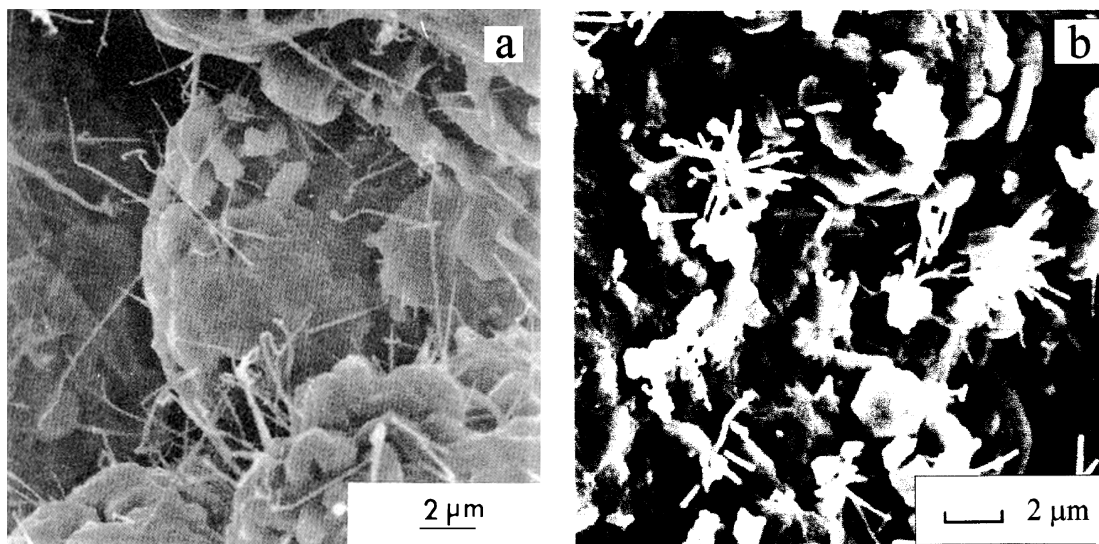
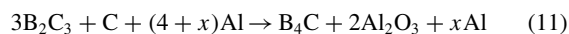
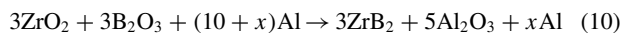
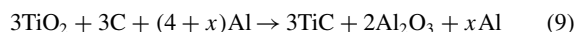


Fig. 13 SEM micrographs of the products synthesized in (B_2O_3+C+Al) system in a) μg and b) 1-g conditions.¹⁷

high-temperature tetragonal to lower-temperature monoclinic ZrO_2 phases was larger in the materials produced under μg than in terrestrial experiments.

Thermite-type reactions were also investigated by Hunter and Moore¹⁷:



The microgravity conditions were attained by flying a Lear jet aircraft through a Keplerian trajectory. Because this maneuver is entered from a slight dive requiring $a \sim 2-g$ pull-up just prior to achieving microgravity, the experiments were carried out in both overload (2-g) and μg ($10^{-2} g$) conditions. It was shown that the product microstructures in all systems are finer for the materials synthesized in microgravity. For example, in the B_2O_3-C-Al system fine (100 nm in diameter) Al_2O_3 -rich whiskers were synthesized in μg conditions, whereas relatively thick ($\sim 1 \mu m$) needle-like structures were obtained at normal gravity (Fig. 13). Gravity influences not only the morphology of Al_2O_3 whiskers, but also the uniformity of pores and Al distribution along the sample volume; more uniform structures were obtained in low-gravity conditions.

Another example relates to CS in oxygen-free ternary Ti-Al-B system, where synthesis was carried out⁴¹ to produce TiB_2-Al metal matrix composite under different gravity conditions, including short-time microgravity environment obtained during free fall ($10^{-4} g$ for 10 s) and parabolic flights ($10^{-2} g$ for 20 s). Again, finer and more uniform composite materials were synthesized under μg conditions. Remarkably, the thickness of Al layer surrounding TiB_2 particles increased progressively with decrease of gravity and correspondingly eliminated regions of Al aggregation, typical for products synthesized under 1-g conditions. This effect was explained by the improvement of wetting between TiB_2 and Al because of the lack of mass migration under low gravity. Further, hardness of samples obtained by hot-pressing the products synthesized under μg conditions was higher as compared to those produced at 1 g (see Table 10).

Combustion synthesis in Ga_2O_3-P , In_2O_3-P , and $(Ga_2O_3, In_2O_3)-P$ systems was investigated in terrestrial and μg environments.²² In this case, microgravity was achieved during free fall of a capsule in the drop ($10^{-4} g$ for ~ 10 s). It was shown in the case of In_2O_3-P system that complete conversion could be achieved in both normal and μg conditions. However, finer and more uniformly distributed InP particles formed in microgravity. For the Ga_2O_3-P system, higher conversion was obtained in μg . Finally, the product synthesized in μg for the complex $(Ga_2O_3, In_2O_3)-P$ mixture followed Vegard's

Table 10 Hardness of the hot pressed products synthesized under normal and microgravity conditions⁴¹

Ti:B:Al (mole ratio)	Vickers hardness, GPa	
	$10^{-2} g$	1 g
1:4:1	9.5 ± 0.4	7.8 ± 0.3
1:2:2	13.1 ± 0.3	9.1 ± 0.6
1:4:0	1.5 ± 0.7	0.6 ± 0.1

rule more precisely than that obtained in terrestrial conditions. All of these effects were attributed to the influence of gas convection on the reaction and structure formation processes.

Microgravity has also been used to produce unique materials that cannot be synthesized in normal conditions. For example, the binary Zn-S system has been investigated to obtain ZnS crystals in the combustion mode.^{19,20} Zinc powder was mixed with melted sulfur to achieve high uniformity of reaction medium, which leads to higher final conversion in the combustion wave. The boiling points of S and Zn are less than the adiabatic combustion temperature (2200 K), and sublimation temperature of ZnS at $P = 1$ atm is lower than its melting point. For these reasons, the experiments were carried out at high argon pressure (> 50 atm). Microgravity conditions were achieved during parabolic flights on KC-135 aircraft (NASA). Combustion synthesis of unconfined samples was carried out in microgravity, which in principle cannot be organized under normal conditions because of gravity-induced flow of melt. The large rectangular crystals (1–2 mm) obtained in μg , about twice as large as in 1 g, were attributed to the uniform cooling of liquid in the absence of convection (Fig. 14). In addition, the lattice parameters of the ZnS crystals synthesized in microgravity were closer to the ideal wurzite structure than those produced in normal gravity.

Further, the La-Zn-S ternary system was investigated to synthesize chalcogenide glasses, which are good candidates for long-wavelength IR materials.⁵⁵ It was shown that μg environment allows direct CS of glass ceramics from elemental powder precursors (La, Zn, and S), and thus permits one to cover a wide range of compositions. However, in normal gravity, to avoid extensive sedimentation of La in liquid phases, one must use fine (1–10- μm) La particles that are not commercially available. Thus, ground-based compositions are limited by using fine La_2S_3 powder. It was found that materials produced under microgravity have higher glass content (e.g., see unreacted Zn particles in Fig. 15a) and microstructural uniformity than those produced in terrestrial conditions (compare Figs. 15a and 15b).

B. Mechanism of Structure Formation

Although the results just discussed are mainly qualitative, they strongly demonstrate that even in the relatively short duration of

combustion synthesis (CS) process (few seconds), and on a relatively small length scale range (0.1–100 μm), gravity force can significantly influence the process of structure formation. Recent investigations have addressed this issue quantitatively. Further, specific mechanisms of structure formation taking place at the extremely high temperatures of combustion wave, which can be influenced by gravity, have also been indentified. The quenching approach (see, for example, Ref. 3), which involves rapid cooling of the combustion front, has been utilized primarily to investigate the mechanisms of microstructural transformation taking place during CS under different gravity conditions.^{27,34} In the most efficient method, the reactant mixture is pressed into a massive wedge-shaped copper block (see Fig. 16). The sample is ignited at the top, and as the combustion wave travels to the apex of the wedge the reaction is quenched progressively as a result of a decreases of the reactant mixture volume, which increases conductive heat losses to walls of the copper block.

For example, in the CS of NiAl-TiB₂ composites,³⁷ used for aircraft turbine applications, it was shown by statistical analysis that the average size of TiB₂ reinforcement grains (<1 μm) in 10⁻² g was smaller than in 1-g conditions (Fig. 17); recall the finer grains yield

superior mechanical properties.⁵⁶ The kinetics of particle growth studied for quenched samples (Fig. 18) showed that grain growth rate is four times smaller under microgravity as compared to 1 g.

Detailed analysis of microstructures and phase compositions in different cross sections of quenched samples revealed that the process of structure formation during CS can in general be divided into four zones (Figs. 19a–19d, under terrestrial conditions), which are characterized as follows³⁴:

1) *Zone 1* is the reaction between Ni and Al with formation of primarily NiAl phase, while Ti and B remain essentially unreacted (Fig. 19a).

2) *Zone 2* is the dissolution of Ti and B in NiAl phase with formation of complex Ni-Al-Ti-B solution (Fig. 19b).

3) *Zone 3* is the crystallization of solid TiB₂ particles from the solution and their growth in NiAl-rich liquid matrix (Fig. 19c).

4) *Zone 4* is the growth and uniform dispersion of TiB₂ particles in NiAl matrix, to yield the final product (Fig. 19d).

All zones just described were qualitatively present in all samples synthesized in both terrestrial and microgravity conditions. Thus, in both cases, the combustion front propagation was controlled by the formation of NiAl, while the TiB₂ particles formed far behind the reaction front. Importantly, overall decrease of transformation rates and hence increase of characteristic zone lengths (L_i) were observed under microgravity conditions (Table 11). Thus, as discussed in Sec. II, the absence of buoyancy-induced motion in the melt phase in the CS wave leads to retardation of mass-transfer processes. This typically results in formation of finer product microstructures, observed under μg conditions by numerous investigators (see Sec. IV.A).

C. Phase Separation in Thermite Systems

The process of phase separation in CS wave is usually associated with thermite or reduction-type systems (e.g., $\text{Me}_1\text{O} + \text{Me}_2 \rightarrow \text{Me}_1 + \text{Me}_2\text{O}$). These systems find wide applications, such as ceramic-lined steel pipes⁹ and production of metal alloys used in orthopedic implants.⁵⁷ Owing to high heat evolution of the reaction, the process results in a significant increase of temperature (up to 3000 K) that is higher than melting points of the products. Further, phase separation, usually observed between the product metal and slag, is believed to occur under the influence of gravitational forces (see Sec. II). Therefore, it might be expected

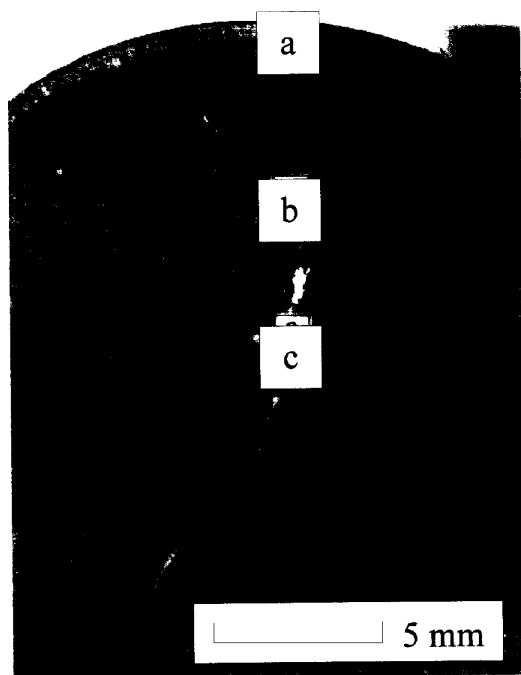


Fig. 14 Typical structure of different parts of the synthesized ZnS sample: a) rectangular crystal zone; b) columnar crystal zone; and c) equiaxial crystal zone.²⁰

Table 11 Length of characteristic microstructural zones formed during CS of TiB₂-NiAl composites³⁴

Zone	Microgravity $L, \mu\text{m}$	Terrestrial $L, \mu\text{m}$
1	400	300
2	5850	4700
3	4250	3250

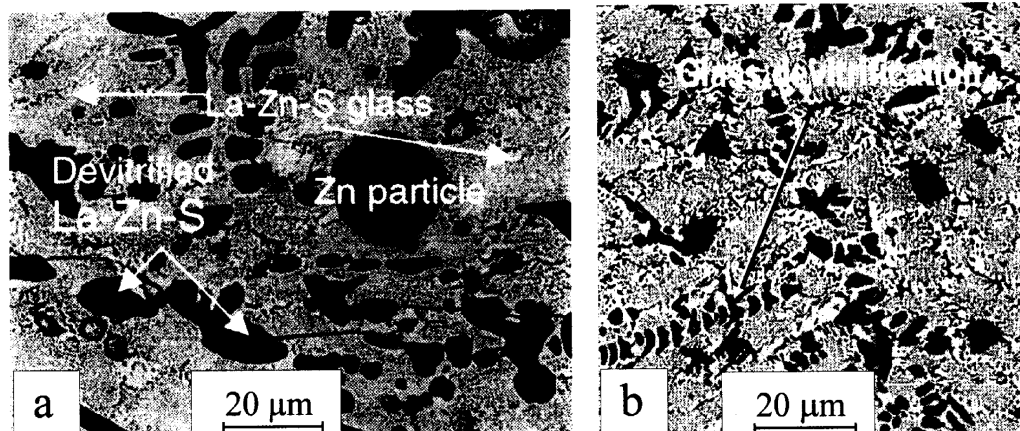


Fig. 15 SEM images of the different parts of the $(\text{La}_{3.2}\text{Zn}_{4.68}\text{S}_{9.4})$ sample synthesized in a) terrestrial and b) microgravity conditions.⁵⁵

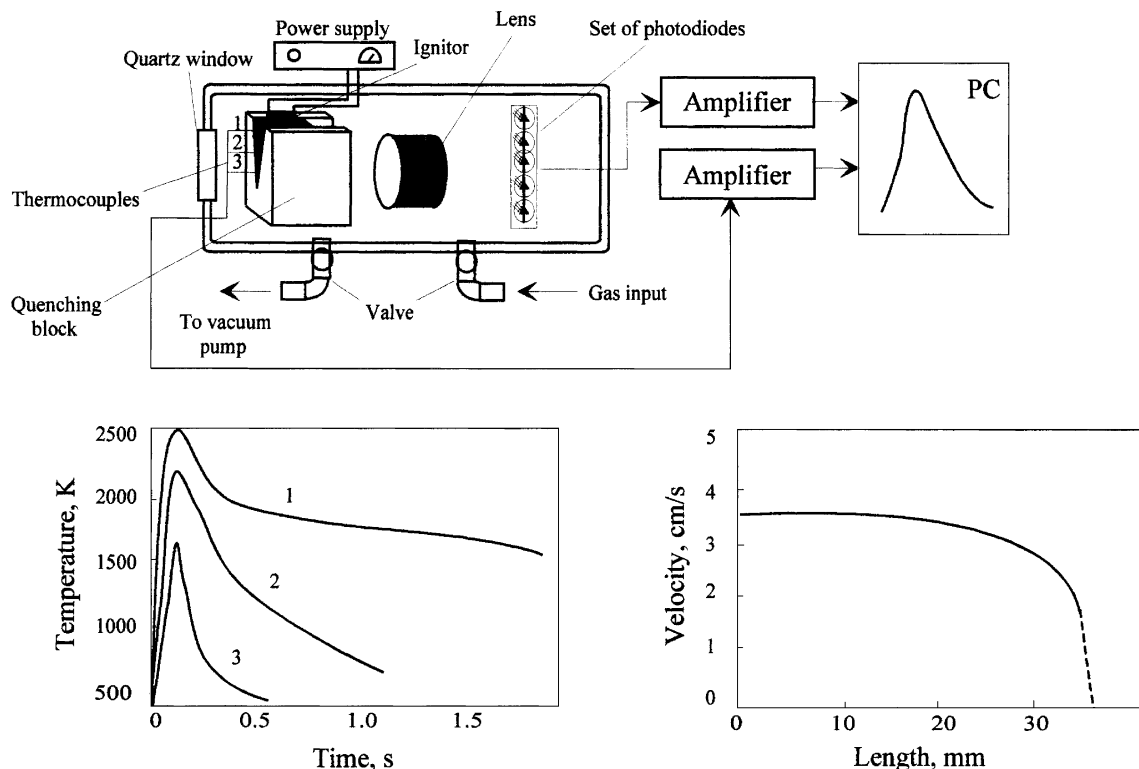


Fig. 16 Schematic diagram of the combustion wave quenching device, along with typical temperature and velocity profiles.

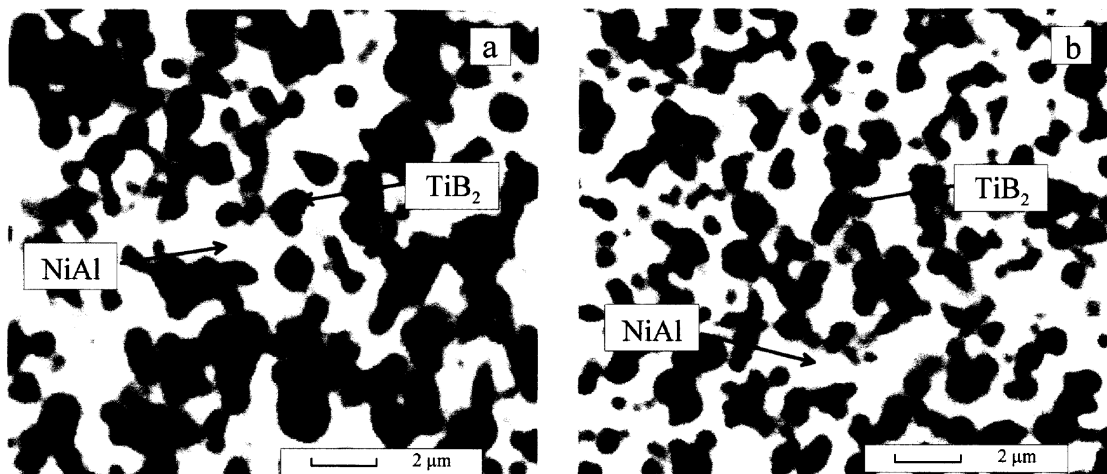


Fig. 17 Typical backscattered electron images of (NiAl-TiB₂) composite microstructures under different gravity conditions: a) terrestrial and b) microgravity.²⁷

that because of the absence of buoyancy in microgravity one should obtain materials with uniform distribution of the oxide phase in metal matrix.

Indeed, for some systems, critical levels of gravity exist above which complete phase separation occurs.^{38,58} However, recent experiments under μg demonstrated that this is not always the case.^{29,43} In this context, three model systems (MoO₃-Al, Co₃O₄-Al, and V₂O₅-Al), in which density differences between the products vary (Table 12), were investigated. The following overall reactions occur in the combustion wave:

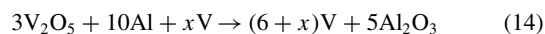
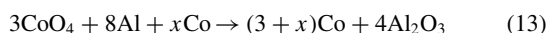
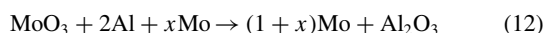


Table 12 Physical properties of reactants and products in model thermite systems⁴³

Property	Co	Mo	V	Co ₃ O ₄	MoO ₃	V ₂ O ₅	Al ₂ O ₃
$T_{m.p.}$, K	1701	2896	2190	2327	1074	963	2123
ρ , g/cm ³	8.92	10.22	6.1	6.07	4.69	3.36	2.8

Experiments with two different compositions (i.e., x) in each system were carried out under identical conditions in different gravity levels (10^{-2} , 1, and 2 g). The parameters of phase separation, primarily ingot relative density ρ and yield ψ , defined as ratio of the metal product mass to the theoretical metal mass formed from reaction, were determined. It was shown that under overload gravity ($\sim 2 g$), achieved as a part of trajectory during parabolic flights KC-135, in Co- and Mo-based systems essentially complete separation occurred with metal yield, $\psi = 99 \pm 1\%$. Further, although ψ values

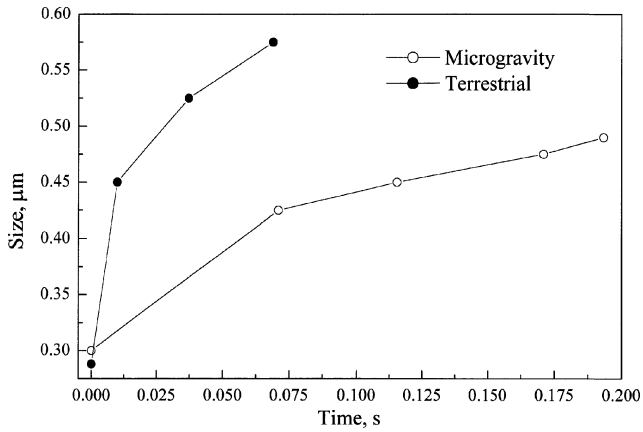


Fig. 18 Average TiB₂ grain size in zone 3 as a function of time under different gravity conditions.²⁷

were lower than in 2-g conditions, they were still relatively high both in 1 g and unexpectedly in 10⁻²-g conditions (Table 13). In addition, ψ was always higher for samples ignited from the bottom, that is, $\psi_{\text{bot}} > \psi_{\text{top}}$. Finally, ψ was larger for compositions with greater amount of metal, that is, $\psi_{\text{Mo}(2.5)} > \psi_{\text{Mo}(2.0)}$ and $\psi_{\text{Co}(12)} > \psi_{\text{Co}(8.5)}$.

Possessing similar trends in yield, Co- and Mo-based systems, however, showed different behavior during the phase separation process itself. For Co-Al₂O₃ in 1-g environment, a thin Al₂O₃ tube with some amount of cobalt droplets formed along the wall of quartz container (Fig. 20a), whereas for the Mo-Al₂O₃ system alumina covered the metal ingot (Fig. 20b). Further, in microgravity the height of the formed Al₂O₃ tube in Co-alumina system was longer; however, more Co droplets were found in slag leading to a decrease in yield. In the same μ g conditions, alumina uniformly covered suspended spherical shaped Mo-ingot. Finally, under 2 g in both cases an alumina cap formed on top of the metals. Note that for V-based system, in all investigated conditions the phases did not separate after reaction: V and Al₂O₃ aggregated in one bulk of material, with nonuniform distribution of metal and slag.

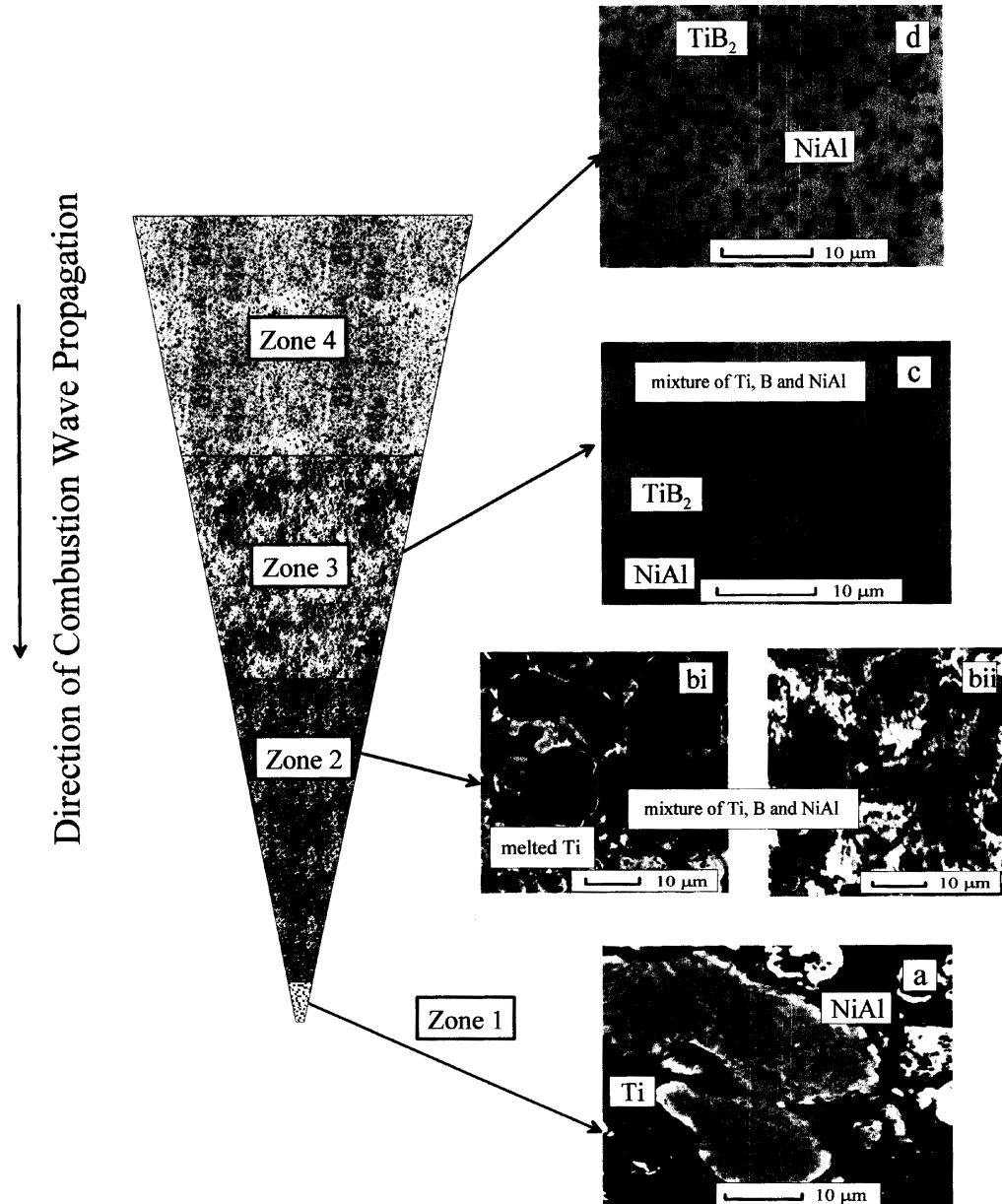


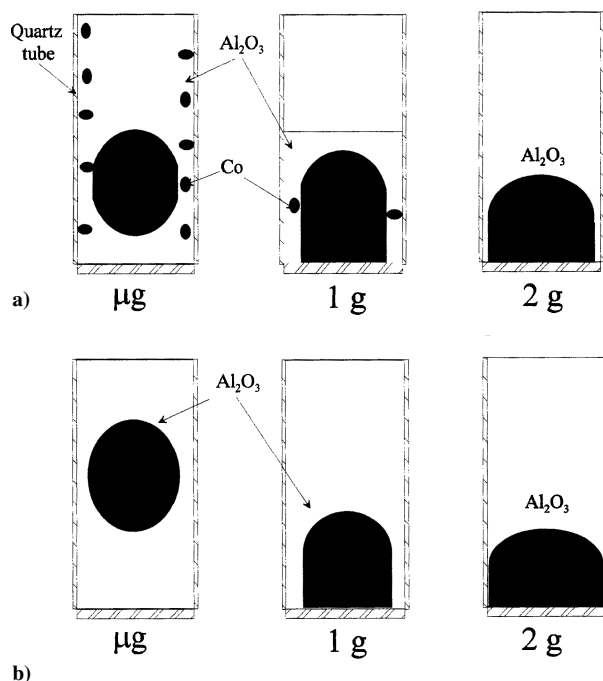
Fig. 19 Characteristics microstructures in different zones of quenched (Ni+Al) + (Ti+2B) sample obtained under terrestrial conditions: a) zone 1; b) zone 2, i) start and ii) end; c) zone 3; and d) zone 4 (Ref. 34).

Table 13 Average yield (%) of the alloy in different experimental conditions⁴³

System	x	T_{ad} , K	Microgravity, 10^{-2} g		Normal gravity, 1 g	
			Top	Bottom	Top	Bottom
MO	2.0	3206	82	89	78	92
MO	2.5	2965	90	93	90	93
Co	8.5	2966	73	86	78	96
Co	12	2690	73	—	90	98

Table 14 Some non-gravity-driven mechanisms of phase separation⁵⁹

No.	Separation mechanism
1	Wettability differences
2	Local nucleation rates differences
3	Surface tension differences
4	Capillary forces
5	Oswald ripening
6	Marangoni convection
7	Momentum owing to directional growth
8	Momentum owing to differences in diffusion rate
9	Solidification-front repulsion

**Fig. 20** Product formation after combustion in Co- and Mo-based thermite systems under different gravity conditions.⁴³

As mentioned in Sec. II (also see Sec. VI.B), all current models of CS in thermite systems suggest that phase separation occurs solely because of buoyancy, owing to the large difference in densities of oxide and product metal. Thus these models predict negligible phase separation effect ($<1\%$) in μg (10^{-2} -g) environments. Indeed, analysis of the literature shows that in various studies of immiscible-alloy solidification under microgravity it was generally assumed that lack of gravitational sedimentation will enable one to obtain a homogeneous droplet distribution of one phase in metal matrix of the other. However, in many cases, space experiments have revealed unexpected macroscopic segregation.^{59–61} The state of the topic can be briefly described by the overview in Table 14,⁵⁹ which lists several nongravity-driven mechanisms that can contribute to immiscible components separation during the CS process.

In the case of Co- and Mo-based compositions, volume content of metals in liquid mixtures with oxide are high ($\sim 45\%$). Thus average distance between metal droplets after reaction should be small, or even percolation limit reached, and thus droplet coalescence occurs in kinetic regime with characteristic time $t_c \sim \sqrt{(\rho R^3/3\sigma)}$ (where σ is surface tension and R is droplet radius⁶²), which for the investi-

gated systems is in the range 10^{-5} – 10^{-4} s. This rapid process, driven by surface tension, might be responsible for the observed effects of separation in microgravity conditions.

Note that surface tension for liquid Mo ($\sigma = 2.2$ N/m) is three-fold higher than for liquid Co ($\sigma = 0.77$ N/m), which allows one to understand why Mo having much smaller life time in liquid state (~ 0.1 s), owing to higher crystallization temperature (Table 12), separates with similar efficiency as Co, which exists in liquid state for much longer time (~ 10 s). This mechanism also explains why phase separation was not observed for the V-based system, where volume content of metal was relatively small ($\sim 35\%$) and also melts existed for short duration (<1 s). In this case, phase separation driven by surface tension takes place in diffusion regime (particles need to move to contact each other), which is slower even under 1-g conditions.

Phase separation in such systems is typically enhanced by use of overload conditions.⁶³ Some experiments have also been conducted to investigate the phase separation effect during CS of Co_3O_4 -Cr-Mo-Al system.²⁶ It was shown that relatively high yield ($\sim 80\%$) can be achieved in μg conditions, whereas microstructures of the alloys are quite different (Fig. 21). Terrestrial samples are characterized by dendrite-type microstructure where the dendrites are aligned in preferential directions (Fig. 21a), as compared to randomly oriented dendrites observed for samples synthesized in microgravity (Fig. 21b). This effect arises as a result of difference in cooling conditions, which are more uniform in μg . Note that this Co-Cr-Mo alloy is a biomaterial used for production of orthopedic implant devices, and the role of Cr and Mo is to impart the desired microstructure and properties.^{57,64}

V. Highly Porous Materials

Highly porous ceramics with relative porosity ϕ in the range 40–70% and cermet (e.g., transition metal carbides and borides) foams with $\phi > 80\%$ make up a class of materials with extremely low densities and unique combination of mechanical, thermal, and acoustic properties. They offer a large potential for lightweight structures, energy absorption, and thermal management applications.^{65,66} In specific conditions of space stations (weightless and vacuum), despite relatively low strength these materials can be widely used as structural and heat insulator elements.

It has been 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.^{4,17,26} Several systems have been studied to understand the mechanism of this influence (Table 15). Although different explanations have been suggested, most are based on the idea that gas formed in the combustion wave interacts with condensed reaction media, leading to a significant increase in product porosity. For this reason, to control the process a variety of gas sources including special additives (e.g., $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$),⁴ reactants (e.g. B_2O_3),¹⁷ and desorption of dissolved gases (e.g., H_2)^{26,67} were investigated.

A. Systems with Special Additives

The first published work concerning the influence of microgravity on CS process was devoted to the synthesis of highly porous materials in weightless conditions.⁴ The initial mixture, containing powders of titanium (Ti), carbon (C), and sodium tetraborate

Table 15 Summary of microgravity research in highly porous materials

System	Condition, g	Observed effect in microgravity	Reference
Ti + xC + additives	10^{-2}	Higher porosity; more uniform pore distribution	Ref. 4 (Russia)
B_2O_3 -C-Al	10^{-2}	Higher porosity and pore size	Ref. 17 (USA)
Ti-B	10^{-5}	Higher expansion velocity and final porosity	Ref. 26 (USA)

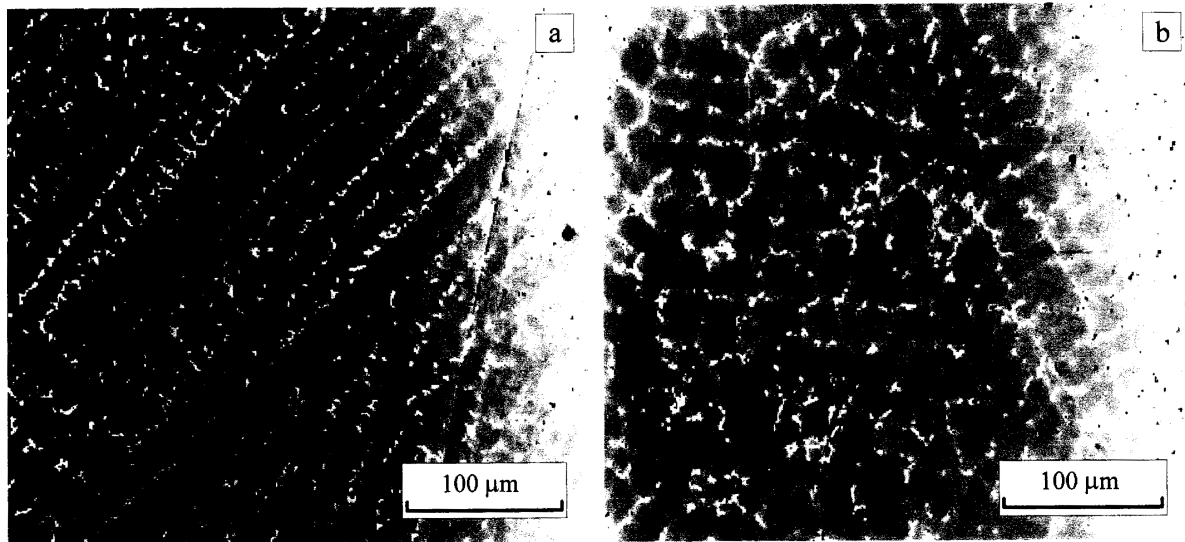


Fig. 21 Characteristic microstructures of the Co-based orthopedic implant alloys produced under a) normal gravity and b) microgravity conditions.²⁶

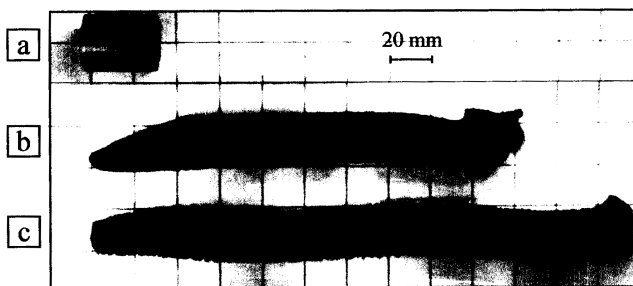


Fig. 22 Photographs of (Ti+C+gasifying additive) samples: a) initial, b) burned in 1 g, and c) burned in μg (Ref. 4).

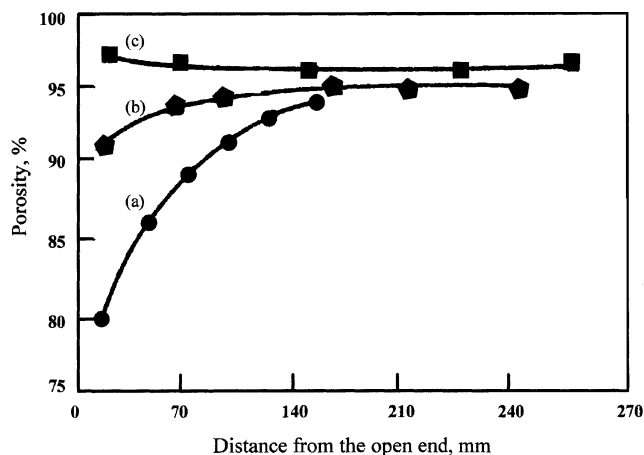


Fig. 23 Porosity distribution along the (Ti+C+gasifying additive) sample after combustion a) in the vertical position in 1 g, b) in the horizontal position in 1 g, and c) in μg (Ref. 4).

($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) as gasifying additive (decomposition temperature ~ 430 K), was pressed into cylindrical pellets, which were inserted into quartz tubes and placed in the reaction chamber. An ambient gas pressure of about 10^{-2} atm was established in the chamber before samples were ignited. The investigations were conducted in both terrestrial and microgravity conditions. In the latter case, the experiments were performed during parabolic flights onboard a II-76K airplane, which allowed weightless (10^{-2} -g) conditions to be maintained for ~ 30 s. It was shown that the materials synthesized in microgravity had higher degrees of expansion (Fig. 22), with

Table 16 Percent elongation for the $\text{B}_4\text{C}-\text{Al}_2\text{O}_3-\text{Al}$ reaction system¹⁷

$\text{B}_4\text{C}-\text{Al}_2\text{O}_3-x\text{Al}$	% expansion		
	10^{-2} g	1 g	2 g
$x = 0$	320	230	200
$x = 3$	195	210	195

larger final porosities (up to 95%), than those produced in normal gravity conditions. More importantly, the porosity distribution was more uniform along the samples produced in microgravity than on Earth (Fig. 23).

The mechanism of sample expansion during CS was also suggested, where two main processes were considered.⁴ The first is the melting of reactants to produce viscous medium in the reaction front. The second is the gas formation from decomposition of additives as a result of high temperature in the combustion wave. The latter increases gas pressure in the pores of the reactant medium with average viscosity η leading to sample expansion and increase of its porosity. It was suggested to estimate the degree of elongation as

$$\Delta l/l = (P_{\text{pore}}^g - P_{\infty}^g)/\eta \cdot \Delta X_r/U_c \quad (15)$$

where P_{pore}^g and P_{∞}^g are the gas pressure (Pa) in the pores of the sample and in the reaction chamber, respectively; ΔX_r is the width of the reaction (m) zone; and U_c is the combustion wave front velocity (m/s).

B. Systems with Gasifying Reactants

The general conclusion that gravity influences sample expansion was confirmed later by Hunter and Moore,¹⁷ during investigation of CS process in $\text{B}_2\text{O}_3-\text{C}-\text{Al}$ system. Importantly, it was shown that the amount of gas generated in the combustion front as a result of initial reactant (i.e., boron oxide) gasification is sufficient to create a highly porous composite, so that special additives are not required in these systems. The extent of expansion increased 1.6 times with decreasing gravity from 2 to 10^{-2} g, and this effect decreased with increasing Al content in the initial mixture (Table 16). To explain these results, it was suggested that increasing gravity increases the inertial force acting against the expanding gases generated at and ahead of the reaction front (sample was ignited from the bottom) and hence decreases the extent of expansion.

Recently, another interesting application of high-porosity materials produced using gasifying reactants was found.^{31,68} It is known that porous materials used for bone replacement applications require 40–60% overall porosity, with pore sizes between 200 and

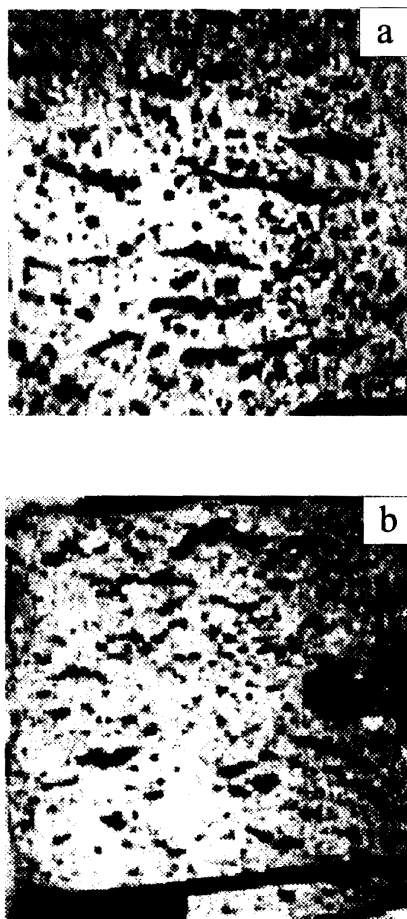


Fig. 24 Photographs of Ti-TiB_x samples synthesized under a) μg and b) 2- g conditions.⁶⁹

500 μm .⁶⁹ In this context, the potential ability of porous materials (e.g., B₄C-Al₂O₃, Ti-TiB_x) synthesized under microgravity was demonstrated. It was shown that the degree of porosity and uniformity of pore size increase in low gravity (Fig. 24) and that the microstructure synthesized is comparable to natural bone (Fig. 25).

C. Desorption of Dissolved Gases

Experiments²⁷ in normal (1- g) conditions showed that for the Ti + C system, even without any additive, unconstrained samples were completely destroyed because of gas desorption (primarily H₂) during reaction. The Ti + 0.8C system was selected for investigation, as no mass loss was observed for this composition. Note that adiabatic combustion temperature of this mixture (2970 K) is higher than the melting point of Ti (1940 K). Thus, the excess titanium (as compared to stoichiometric Ti + C mixture) present in the liquid phase forms a stronger skeleton in the reaction medium, preventing sample destruction.

The characteristic dependences of instantaneous combustion front velocity U_i and relative sample expansion E_i as a function of time for the system are shown in Fig. 26. The sample was ignited in terrestrial conditions, and the combustion front propagated relatively steadily with average velocity $U = 0.95$ 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 in average velocity ($U = 1.2$ cm/s) as well as the sample expansion velocity U_{ex} was detected in μg -conditions. 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). The data on the final relative linear expansion ($E_f = h_f/h_0$, where h_f and h_0 are the final and initial sample heights), final porosity, U and U_{ex} obtained in normal as well in μg conditions are presented in Table 17.

Table 17 Some characteristics of combustion in the Ti-0.8C system²⁷

Condition	$E_f = h_f/h_0$	Final porosity	U_{ex} , cm/s	U , cm/s	$U_r = U - U_{ex}$, cm/s
1 g	3.2	0.85	0.65	0.95 ± 0.05	0.30 ± 0.05
10^{-5} g	4.8	0.90	0.95	1.2 ± 0.01	0.25 ± 0.10

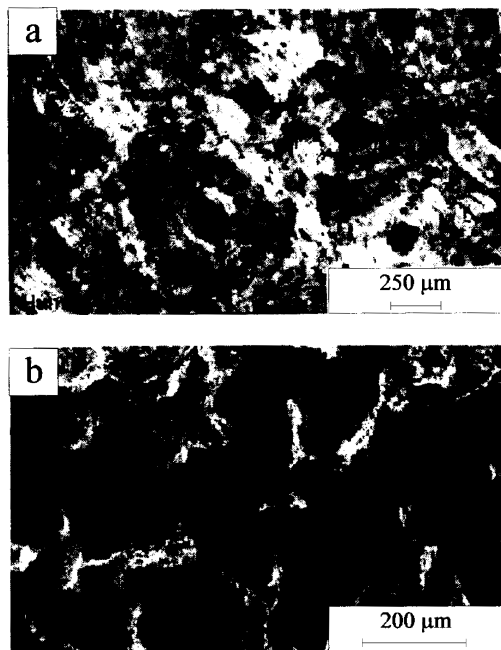


Fig. 25 Porous materials: a) natural bone and b) Ti-TiB_x (Ref. 69).

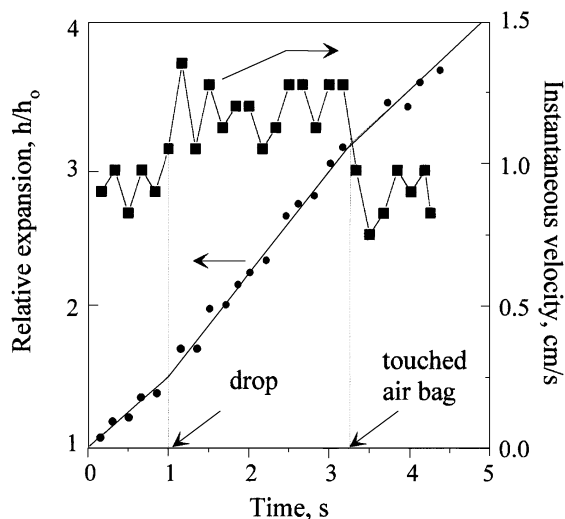


Fig. 26 Instantaneous combustion velocity and sample expansion in (Ti+0.8C) system as a function of time during drop tower experiment.²⁷

The estimated values of relative final linear expansions E_f were 3.2 and 4.8 in normal gravity and drop tower experiments, respectively, so that $E_f^{\mu g}/E_f^{1g} \sim 1.5$. The same result can be obtained based on the analysis of U_{ex} observed at normal conditions and during the drop (Table 17). It is important that gravity does not influence combustion velocity measured relative to the unreacted part of the sample: $U_r = U - U_{ex}$, which defines the real velocity of reaction propagation in the system.

D. Mechanism of Sample Expansion

As just noted, 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, that is, somehow gravity influences the velocity of combustion front propagation, then it also affects the expansion.⁴ However, as just noted, experiments show that at least for some systems (Ti-C), combustion velocity remains essentially constant with changing gravity whereas the rate of expansion and final sample porosity are both higher under lower gravity conditions.²⁷ The second explanation generally proposed is that when ignited from the bottom the weight of the upper (non-reacted) part of the sample affects the reaction zone, decreasing expansion in normal gravity conditions.⁷⁰ However, results shown in Fig. 26 clearly demonstrate that in both μg and terrestrial conditions the rate of sample expansion remains constant during the entire combustion process, while the mass of unreacted part changes continuously.

Because the experimental data could not be explained by the mechanisms proposed previously, a new mechanism was suggested for the effect of gravity on sample expansion.²⁷ The process of porous structure formation is dictated by the competition between the following primary processes: gas evolution (mainly from the powders, either from impurities or from additives), gas motion through the liquid melt formed in the combustion front, and gas escape from the sample. If the permeability of the medium is sufficiently high, then the gas can escape from the sample without expanding the medium. Retarding the rate of gas escape leads to greater interaction between it and the viscous medium, causing larger sample expansion. Owing to elimination of buoyancy and convection processes, microgravity promotes this retardation.

As just discussed, different CS approaches can be followed to yield highly porous materials for a variety of applications including foams and bone replacement. It has been shown clearly that μg conditions favour formation of such materials with uniform pore structures. Although qualitative descriptions of process mechanisms are now available, their quantitative aspects have not been investigated in detail. Some attempts in this direction are briefly described in the next section.

VI. Brief Overview of Relevant Theoretical Works

Theoretical studies related to gravity's (including microgravity) influence on parameters of the CS process have been conducted primarily by research groups from Northwestern University and two institutes from the Russian Academy of Sciences, that is, the Institutes of Structural Macrokinetics and Chemical Physics. These works can be divided in two major parts: 1) gravity effects on CS of highly porous materials (see Sec. V for experimental results) and 2) influence of gravity on CS in liquid flames, that is, systems with combustion temperature higher than melting points of reactants and products (see Sec. IV for details), including phase separation phenomena. As noted in the Introduction, owing to space limitations, the main goal of this work is to overview primarily experimental studies in the field; thus, we only briefly discuss some of the obtained theoretical results next. A previous review of the theoretical efforts can be found elsewhere.⁷¹

A. Combustion Synthesis of Highly Porous Materials

A model describing CS of highly porous materials in gravitational field, taking into account gasification of special additives in the reaction front, was developed in 1996 (Ref. 72) based on prior works of the same researchers on combustion of porous materials with self-deformation (compaction or expansion; see, for example, Refs. 73–75). An equation, which describes sample elongation caused by increase of its porosity caused by gas evolution (as a result of main reaction and/or gasification of additives), was derived. Specifically, medium motion was expressed by the momentum equation as an equilibrium of three forces: pressure (influence on condensed phase by gas in the pores), gravitational field, and resistive force caused by material viscosity. Thus, in general, this one-dimensional model describes viscous flow of porous media in gravitational field, as a result of the difference of gas pressure in pores and ambient environment, under the conditions of combustion wave propagation.

Without going into details, note that the equations which were obtained allow one to introduce a characteristic time of deformation

$$t_{\text{def}} = \eta/[P - (P_0 + W)] \quad (16)$$

where η is the average medium viscosity; P and P_0 are gas pressure in the pores of the sample and in the reaction chamber, respectively; and w is weight (N/m^2) of the upper (unburned) part of the sample per unit area.

Equation (16) is a generalization of the result suggested by Shteinberg et al.⁴ [compare with Eq. (15) in Sec. V], accounting for gravitational effect. However, numerical simulations of the model allow one to predict dependences of sample expansion on parameters such as gravity, reaction medium rheological properties, amount of additives, and sample diameter. It was demonstrated that the model explains a majority of experimental trends known at that time, but recent observations (e.g., that increase of final material porosity under microgravity cannot be explained by the weight factor; see details in Sec. V) require further model development.

The effect of inert additives gasification on the structure of CS wave was investigated,⁷⁶ based on the approach suggested previously for description of the combustion wave propagation with phase transformations⁷⁷ (e.g., melting, boiling, etc.). Two different cases of gasification were considered: 1) during preheating, ahead of the reaction front (where $T_g \ll T_c$); 2) in the reaction zone ($T_g \sim T_c$). Even if $T_g \ll T_c$, the inertia of evaporation (as compared to rapid reaction front velocity) leads to widening of the gasification region, and thus foam is generated mostly in the postcombustion zone. In the other case, when $T_g \sim T_c$, while a pressure peak forms at the beginning of the gas release process, it relaxes at a distance smaller as compared to width of the reaction zone; thus, again the entire expansion occurs under essentially isothermal conditions behind the combustion front.

A mechanism to describe foam formation under isothermal zero-gravity conditions was developed, accounting for nucleation and growth of gas bubbles in supersaturated liquid droplet.⁷⁸ Several stages of foam formation were outlined: 1) induction period of bubble nucleation, when droplet porosity is close to zero; 2) explosive bubble growth, when droplet expansion occurs; and 3) bubble coalescence with constant volume of the two-phase droplet. Note that this approach is applicable to describe foam formation in the combustion wave if induction period is much longer than the characteristic reaction time, so that the process occurs in the postcombustion zone at constant temperature.

To conclude this subsection, it can be noted that the basis for theoretical modeling of the observed complex phenomena leading to formation of highly porous materials during CS has been developed. The next step should involve stronger cooperation between experimentalists and theoreticians to develop accurate quantitative models of the process. We also believe that because the three cases of gas evolution (i.e., special gasifying additives, gas-phase products and impurities desorption) investigated experimentally (see details in Sec. V) have different nature, they should be considered separately.

B. Gravitational Effects in Liquid Flames

The typical initial microstructure of the CS sample is a solid skeleton of powder mixture with relative porosity in the range of 20–70%. However, for many exothermic systems with combustion temperatures higher than melting points of reactants this initial structure is destroyed in the combustion wave, forming a liquid bath. A variety of processes occur in this bath, including chemical reaction, heat and mass transfer, which determine the structure of both combustion wave and final products.

These so-called liquid flames⁷⁹ describe the combustion of most thermite systems.⁴³ In such cases, the liquid bath contains regions with different phase compositions (e.g., metal and oxide), having large difference in their density (see Sec. IV for examples). It is obvious that under these conditions gravity can significantly alter the distribution of phases (both reactants and products) during CS. The question is whether these gravity-driven mechanisms are fast

enough to influence rapid processes that occur in the combustion wave?

A mathematical model that describes gravity-driven phase separation phenomena during CS was formulated by Shkadinsky et al.⁴⁰ Even for the simple case where liquid flame involves only two components (reactant and product), several interesting effects were found. These include 1) multiplicity of stationary combustion regimes caused by the relative motion of components in the gravitational field, resulting in their different stationary distributions and 2) the possibility of extinguishing the combustion wave by gravity.

A more refined model, accounting for the formation of two products with different densities appeared later,⁸⁰ where the Al + Fe₂O₃ system was used as an example for calculations. It was assumed that oxides do not melt and metals (e.g., Al and Fe) are miscible, so that in the product zone the liquid bath is homogeneous. Additionally, the oxide particles retain integrity during the entire process, and only their density changes caused by replacement of some or all initial oxide by the product oxide. Analytical studies show that gravity defines whether one-dimensional uniformly propagating combustion waves exist in the system, and further, whether they might be nonunique.

Both preceding models do not account for the existence of gas phase (in the form of bubbles), which is typically observed experimentally during combustion of high exothermic thermite systems (see, for example, Ref. 57). The problem of gravity-induced gas bubble motion and its influence on the characteristics of liquid flame was examined recently.⁸¹ It was assumed that inert gas bubbles can change their size and position as a result of temperature changes and owing to gas dissolution in melts. However, there are no interactions between the bubbles. Further, the total number of bubbles and gas nucleation centers are considered to be fixed. It was shown that the presence of gas phase affects the thermophysical properties of the reaction medium (e.g., thermal conductivity), which in turn influences the temperature distribution in the combustion wave and hence its velocity. An implicit approximate expression for the combustion velocity was obtained, and calculated trends of velocity dependence on gravity conditions were in good agreement with experimental data obtained under overload conditions in centrifuges.

Some interesting results have also been obtained related to gravity influence on the ignition characteristics of heterogeneous mixtures.⁸² In the model, the initial reaction medium is considered to consist of two reactants, where one (with lower density) melts and the other remains solid during ignition. It is clear that because of gravitational sedimentation the reactants ratio changes in the preheated layer, leading to decreased overall rate. If sedimentation time is significantly larger (smaller) than reaction time, ignition will (will not) occur. Another effect of the gravitational field is that it destroys the symmetry of the ignition conditions (top and bottom), which exists under zero gravity. Finally, ignition criteria accounting for gravitational field were also reported.

It follows from the preceding that several interesting theoretical models have been established to describe gravity influence on liquid flame combustion. However, recent experimental results on phase separation in microgravity conditions (see Sec. IV.C) suggest that new approaches accounting for the observed effects should be developed. For example, in several systems it was shown that final products consist of two melts (metal and oxide), and oxide crystallization takes place first. Further, in many cases the product melts are immiscible. Finally, nongravity-driven mechanisms of phase separation should also be introduced in the models.

VII. Conclusions

As space exploration continues, the issue of materials production in space becomes increasingly important. Along with precursors taken from Earth, the soils of different planets contain a variety of elements, which can be transformed into useful materials by applying special treatments. In this context, combustion synthesis (CS) is one of the few technologies that can be effectively utilized in space. Indeed, extremely low-energy requirements, with the possibility of

using heat generated during the self-sustained reactions for various other space needs, make this approach attractive for applications in nonterrestrial environments, where cost of every joule of energy is high.

The results presented in this review unequivocally demonstrate that a majority of CS technologies developed in normal gravity could be successfully adopted under μg conditions. Remarkably, materials synthesized in space typically possess superior properties as compared to those synthesized on Earth. Further, studies conducted without the disturbing effects of gravity allow one to obtain a deeper understanding of CS phenomena, which in many cases can lead to the development of new technologies. The CS of porous bone replacement materials, as well as pore-free bio alloys and intermetallic-ceramic composites for aerospace applications, are good examples that demonstrate the practical benefits of this approach.

There are some additional processing features of CS, which allow one to synthesize materials and articles that cannot be produced by other methods. The first is extremely high combustion temperature (up to ~ 3500 K), higher than currently achievable in conventional furnaces. An example where this becomes critical involves CS of BN-based ceramics. Owing to its high melting point (~ 3000 K), it is very difficult to sinter pure BN for large-scale articles. However, this temperature can be achieved in a combustion wave, which leads to the one-step production of low-porosity oxygen-free boron nitride materials. The second feature is uniform propagation of the combustion wave (i.e., uniform temperature distribution) along the bulk of the sample, which allows production of large-scale articles with uniform microstructures and properties. Indeed, in conventional furnaces articles of large dimensions suffer from high-temperature gradients along the body, leading to nonuniform sintering conditions and hence nonuniform material properties. In this context, the production of 1-m-diam ceramic-metal mirrors by the CS approach is an excellent example. The third unique feature is extremely high heating rates (up to 10^5 K/s) in the combustion front, which define nonequilibrium condition for the chemical reactions that, in some cases, lead to unique material properties. An attractive illustration is the synthesis of silicon nitride fibers up to several centimeters in diameter at temperature ~ 2200 K, which cannot be reached for this system under equilibrium conditions.

Finally, we believe that materials synthesis in space is an important direction, which should be thoroughly investigated in the near future. Maintaining cutting-edge fundamental and applied studies in the field is necessary for the success of the space exploration program.

Acknowledgment

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