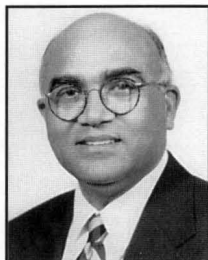


**Chemical Engineering Division of ASEE
Union Carbide Award Lecture
2000**

COMBUSTION SYNTHESIS OF ADVANCED MATERIALS

The Union Carbide ChE Division Lectureship Award is bestowed annually on an exceptional engineering educator and is designed to recognize and encourage outstanding achievements in important fields of fundamental chemical engineering theory or practice.

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Since prehistoric time, mankind has used exothermic reactions for its survival—for example, burning of wood for warmth and preparation of food. The energy from exothermic reactions has also been used to modify properties of materials. Thus it was discovered more than ten thousand years ago that heating a piece of clay in fire converts it into a ceramic with very different and useful properties. Modern technologists sinter net-shape bodies consolidated from powders in furnaces to produce, for example, ceramic shields to protect spacecraft. In both cases, the basic principle is the same: application of external heat to rearrange chemical bonds and shift the material properties in the desired direction. Since rearrangement of chemical bonds may release significant energy itself, however, it is attractive to use this energy *directly* to produce valuable materials. Such a method was discovered some thirty years ago and is called *combustion synthesis* (CS). Comprehensive reviews of this field are available in the literature,^[1-3] with recent achievements summarized in a popular account.^[4]

NATURE OF COMBUSTION SYNTHESIS

Let us introduce this process by considering fine (less than 100 micron, about the thickness of a human hair) powders to two metals: nickel (Ni) and aluminum (Al). Taking these powders in the appropriate ratio (*e.g.*, Ni/Al about 2 by weight), we can mix them thoroughly and create an article with tailored form and shape by using a pressing technique. Next, one spot on the article surface is heated for a few seconds by, for example, a heated tungsten coil or laser beam. The reaction between Ni and Al starts at the hot point and propagates rapidly (about 10 cm/sec) along the volume of the article in the form of a bright glowing (*combustion*)

wave. In the wave, nickel and aluminum melt and react with each other to form (*synthesis*) an intermetallic compound, nickel aluminide (NiAl). Such intermetallics have a number of attractive characteristics, including low density, high corrosion resistance, high strength even at high temperature, and relatively low cost. For these reasons, NiAl-based materials are good candidates for demanding high-temperature applications, such as aircraft turbines and other engine parts.

Some advantages of the CS method over conventional powder metallurgy techniques of advanced materials production include low energy requirements, short synthesis times (on the order of a few seconds), high temperatures (2000-4000 K), and high heating rates (up to 10^6 K/s), which allow one to produce unique (*e.g.*, metastable) compositions. Also, owing to intensive volatilization of impurities at the very high temperatures in the reaction wave, the products of CS are frequently purer than the starting reaction mixture. In addition, there is essentially no limitation on size of the synthesized item, since the heat is generated not by an external heating device but by a chemical reaction that proceeds at every point inside the sample.

These characteristic features make CS different from conventional technologies, which usually take tens of minutes or hours at temperatures that can be achieved in common furnaces (usually less than 2000 K), and possess a non-uniformity of temperature (and hence properties) distribution along large-scale samples. Owing to the fact that CS technology has the potential to prepare advanced materials and net-shape articles in one step, and that it has extremely low external energy requirements, it is also well-suited for use on space platforms.

Efficiency of the method is not the only point of interest regarding this process, however. Even more interesting is the fact that under the unique conditions of CS, reaction kinetics, mechanism of reaction, and product microstructure formation become different from those realized under conventional isothermal or low-heating-rate conditions.

From the viewpoint of chemical nature, three main types of CS processes can be distinguished. First, *gasless combustion synthesis from elements*, where all initial reactants, intermediate, and final products remain in condensed (solid or liquid) state. For this reason, such reactions are sometimes called *solid flame*. The most popular examples are reactions of transition metals with carbon and boron, *e.g.*,



The second type, called *gas-solid combustion synthesis*, involves at least one gaseous reagent in the main combustion reaction. Nitridation of titanium and silicon are common examples:



The third main type of CS is *reduction (thermite) combustion synthesis*, where metal or nonmetal oxides (*e.g.*, Fe_2O_3 , B_2O_3 , TiO_2) react with a reducing metal (*e.g.*, Al, Mg, Zr, Ti), resulting in the appearance of another, more stable oxide, and reduced metal. This reaction may be followed by the interaction of the formed reduced metal with other elemental reactants to produce desired products. An example of this type of CS is



where TiB_2 is the desired product and Al_2O_3 can be removed (*e.g.*, by centrifugal separation) and used separately, or a ceramic composite material ($\text{Al}_2\text{O}_3 + \text{TiB}_2$) can be produced.

In addition to the three main types of CS processes, there are two more recently developed types where the initial reactants are all in either gas^[5,6] or liquid phase,^[7] while

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the final products are in solid state and are formed by a fast propagating reaction wave.

In physical terms, there are two modes by which combustion synthesis can occur: *self-propagating high-temperature synthesis* (SHS) and *volume combustion synthesis* (VCS). In both cases, reactant powders are pressed into a pellet, typically cylindrical or parallelepiped in shape. The samples are then heated by an external source (e.g., tungsten coil, laser) either locally (SHS) or uniformly (VCS) to initiate an exothermic reaction. The characteristic feature of the more prevalent SHS mode is, after initiation locally, the self-sustained propagation of a high-temperature reaction wave through the heterogeneous mixture of reactants. Thus, the SHS mode of reaction can be considered as a well-organized wave-like propagation of the exothermic chemical reaction through a heterogeneous medium, followed by the synthesis of desired condensed products. During VCS, the second mode of CS, the entire sample is heated uniformly in a controlled manner until the reaction occurs essentially simultaneously throughout the volume. This mode of synthesis is more appropriate for weakly exothermic reactions that require preheating prior to ignition. A sequence of video frames of reaction wave propagation during CS of nickel aluminide by the SHS mode is shown in Figure 1.

TYPES OF MATERIALS SYNTHESIZED

Since the initial discovery of the process, the number of products synthesized by CS has increased rapidly and currently exceeds 500 different compounds. Specifically, these include advanced materials such as carbides, borides, silicides, nitrides, oxides, intermetallics, and their composites. Examples of

these, along with their applications, are given in Table 1. Most of these compounds possess high heats of formation—this is the main reason why they can be produced by CS without external heating.

In general, methods for the large-scale production of advanced materials by combustion synthesis consist of three main steps:

- *Preparation of the green mixture*
- *High-temperature synthesis*
- *Post-synthesis treatment*

A schematic diagram of these steps is presented in Figure 2. The first step is similar to the procedures commonly employed in powder metallurgy, where the reactant powders are dried (e.g., under vacuum at 80-100°C), weighed into the appropriate amounts, and mixed (e.g., by ball mixing). For some applications, cold pressing of the green mixture is

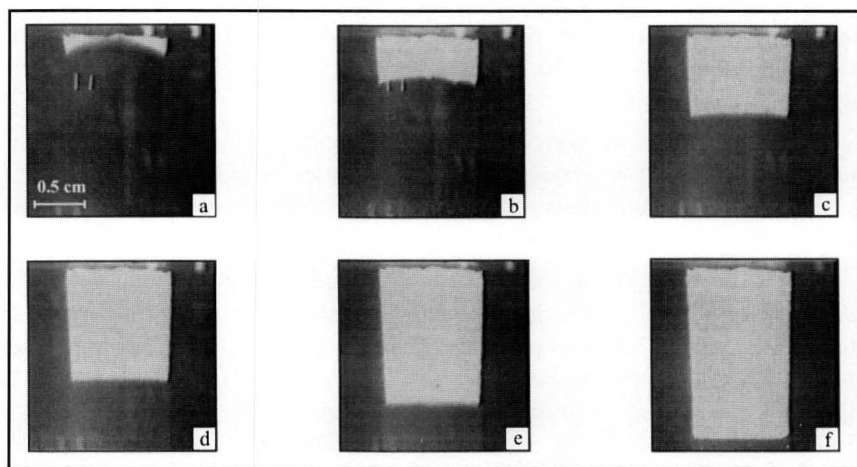


Figure 1. Sequence of video frames of reaction wave propagation during combustion synthesis of nickel aluminide by the SHS mode: (a) ignition, $t=0$; (b) 0.1s; (c) 0.2s; (d) 0.4s; (e) 0.6s; (f) complete reaction, 0.8s.

TABLE 1
Types of Materials Synthesized

<u>Composition</u>	<u>Chemical Formula</u>	<u>Examples of Applications</u>
Carbides	TiC, ZrC, HfC, TaC, NbC, SiC, TiC-Cr ₂ C ₃	Abrasives, cutting tools, ceramic reinforcements
Borides	ZrB, TiB ₂ , HfB ₂ , MoB, TaB ₂ , LaB ₆ , NbB ₂	Abrasives, cutting tools, cathode
Silicides	Ti ₃ Si, TiSi, MoSi ₂ , Zr ₂ Si, ZrSi	Heating elements, electrical connectors, Schottky barriers for electronics
Intermetallics	Aluminides of Ni, Zr, Ti, Cr, Co, Mo, Cu, etc. Titanites: Ti-Ni, Ti-Co; Ti-Fe	Aerospace and turbine materials, shape memory alloys
Nitrides	TiN, ZrN, NbN, HfN, TaN, VN, AlN, Si ₃ N ₄ , BN	Ceramic engine parts, ball bearings, nuclear safety shields
Hydrides	TiH; ZrH; ZrNiH ₃ ; Ti ₂ CoH ₃ Zr _{0.9} ; Nb _{0.1} C _x N _{1-x} H _{0.19}	Hydrogen storage, catalytic materials
Oxides	YBa ₂ Cu ₃ O _{7-x} ; Bi ₄ V ₂ O ₁₁ ; LaSrCrO ₃ ; Na _{0.5} Bi _{4.5} Ti ₄ O ₁₅ ; BaBi ₂ Ni ₂ O ₉	High-temperature superconductors, gas sensors, fuel cells
Chalcogenides Phosphides	Sulfides of Mg, Ti, Zr, Mo, W; GaAs; Phosphides of Al, Ga, and In	High-temperature lubricants, semiconductors

necessary, especially for the production of low-porosity or poreless materials. The final step in sample preparation determines the type of product synthesized; a powder product results from uncompacted powder reactants, while sintered products from cold-pressed compacts. Pressing the green

mixture into special molds or machining pressed initial compacts yields complex-shaped articles.

The main production technologies of combustion synthesis are presented in the second block of Figure 2. They may be classified into several major types: powder production and sintering, and densification, by techniques including hydraulic, isostatic, or shock-wave pressing, extrusion, and hot-rolling. For highly exothermic reactions, where the products are in molten state, centrifugal casting is used to produce, for example, ceramic-lined pipes.

The third main step of CS technologies is post-synthesis treatment. Powder milling and sieving are used to yield powders with a desired particle size distribution. The synthesized materials and articles may also be machined into specified shapes and surface finish. Examples of combustion-synthesized articles, including ceramic engine parts, electric heating elements, high-temperature dielectrics, and cutting tools, are shown in Figure 3.

Owing to the characteristic features of CS, including high temperatures and short reaction times, unique materials can be made that cannot be synthesized by alternative techniques. Thus, CS combined with pressing has been used to obtain ceramic and intermetallic matrix-diamond *composites* with up to 20 wt% synthetic diamond, for advanced cutting tools.^[8] The graphitization during high-temperature treatment of diamond makes it impossible to produce such composites using conventional furnace techniques, while in the rapid combustion wave, diamond particles retain their shape, surface quality, and mechanical properties. The characteristic microstructure of the diamond-containing portion of a NiAl/diamond composite synthesized by CS is shown in Figure 4a (next page).

Another unique example is synthesis of silicon nitride *whiskers* with aspect ratio (ratio of length to diameter) of more than 10^4 and length up to several centimeters^[9] (see Figure 4b). Such whiskers are widely used to reinforce different types of brittle ceramics to enhance their mechanical properties.

Finally, CS has been applied successfully in the production of so-called *functionally graded materials* (FGM). The concept of FGMs is to tailor nonuniform spatial distribution of components and phases in materi-

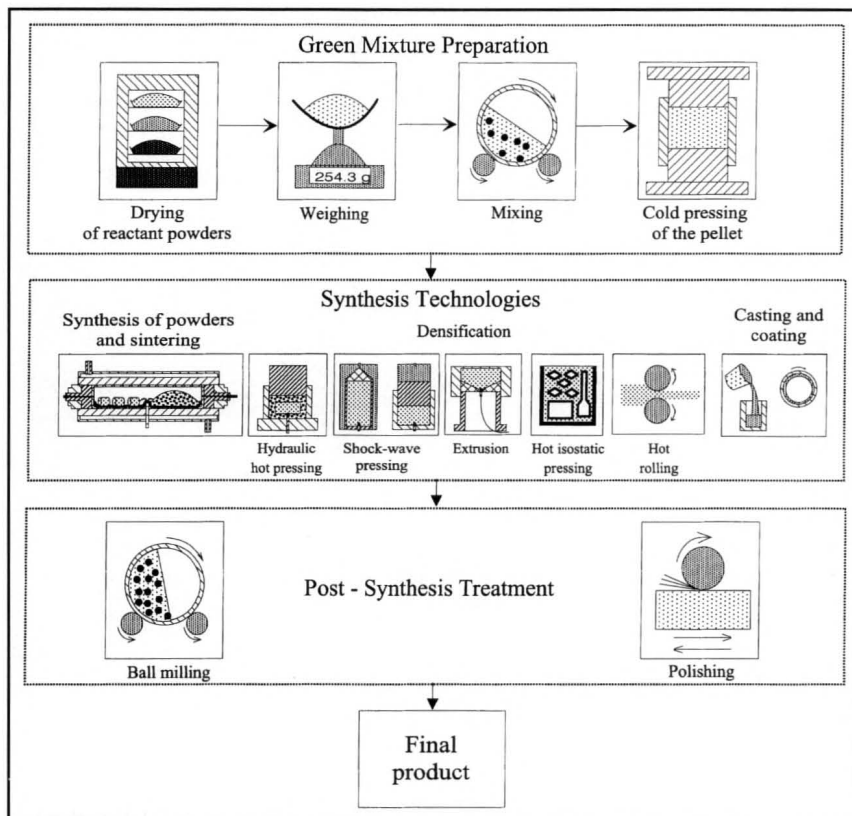


Figure 2. The main steps of combustion synthesis.

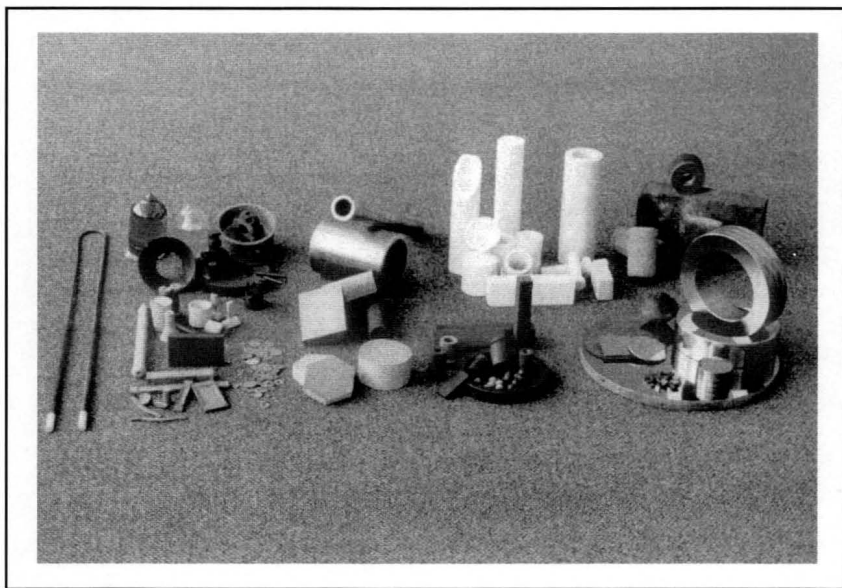


Figure 3. Examples of articles produced by combustion synthesis (photograph courtesy of Academician Alexander G. Merzhanov, Chernogolovka, Russia).

als, and hence combine mechanical, thermal, electrical, chemical, and other properties that cannot be realized in uniform materials. For example, the material structure may have a smooth transition from a metal phase with good mechanical strength on one side to a ceramic phase with thermal resistance on the other side (see Figure 5a). With a gradual variation in composition, FGMs do not have intermaterial boundaries found in multilayer materials, and hence they exhibit better resistance to thermal stress.^[10] The microstructure of a $\text{Cr}_3\text{C}_2/\text{Ni}$ FGM, consolidated from a green compact consisting of powder layers with different Cr-C-Ni compositions by the CS+hot pressing method^[11] is shown in Figure 5b.

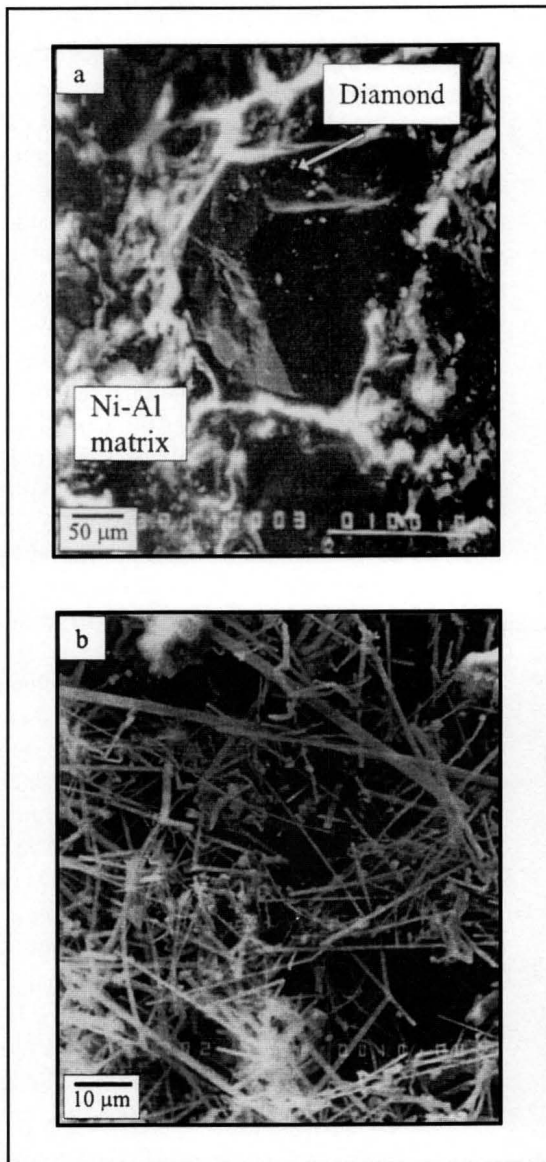


Figure 4. Examples of unique materials produced by combustion synthesis: (a) NiAl matrix/diamond composite, (b) silicon nitride whiskers.

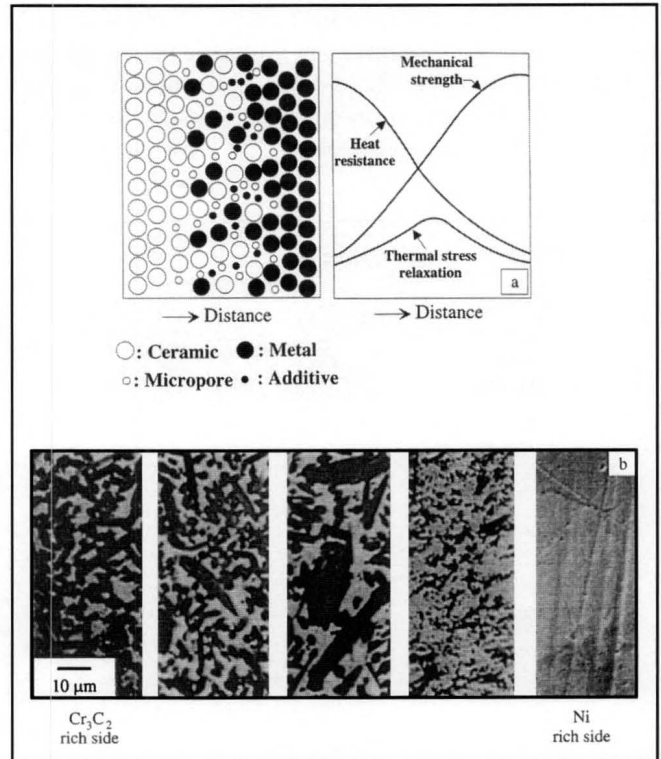


Figure 5. Functionally graded materials (FGMs): (a) the concept of FGM; (b) $\text{Cr}_3\text{C}_2/\text{Ni}$ FGM

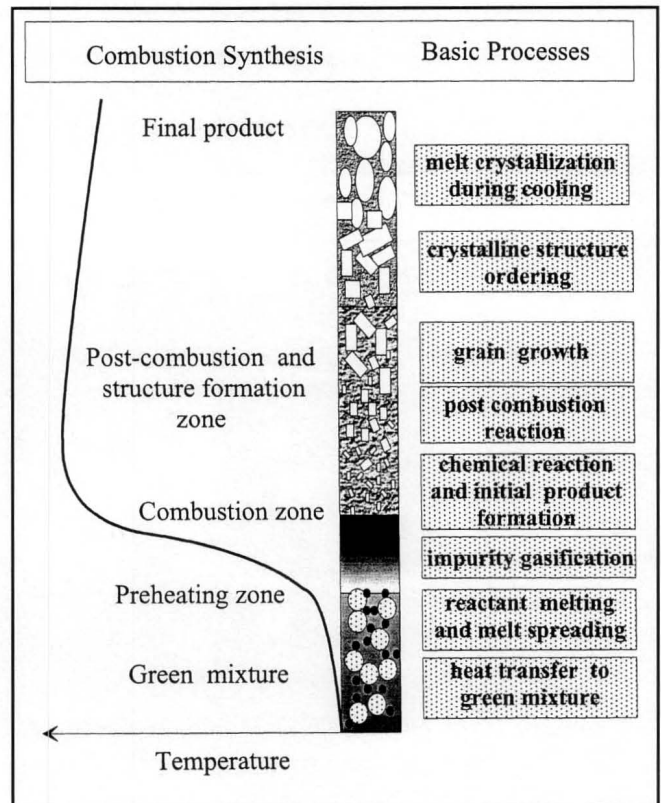


Figure 6. Characteristic structure of the reaction wave during combustion synthesis.

MECHANISMS OF COMBUSTION SYNTHESIS

The features of high heating rates, high temperatures, and short times of reaction completion discussed above, although attractive for the synthesis of unique compounds, also make it difficult to study the mechanism of reaction wave propagation, which is essential in order to form materials with tailored microstructures and properties. Based on the results obtained in CS, a new field of fundamental research that incorporates concepts and principles from various branches of science and engineering, which investigates initial stages of chemical reactions in the combustion front and materials structure formation in the heterogeneous medium after passage of the front, is being developed.

In general, characteristics of the combustion wave are determined by the processes occurring in the heating, reaction, and post-combustion zones (see Figure 6). The length

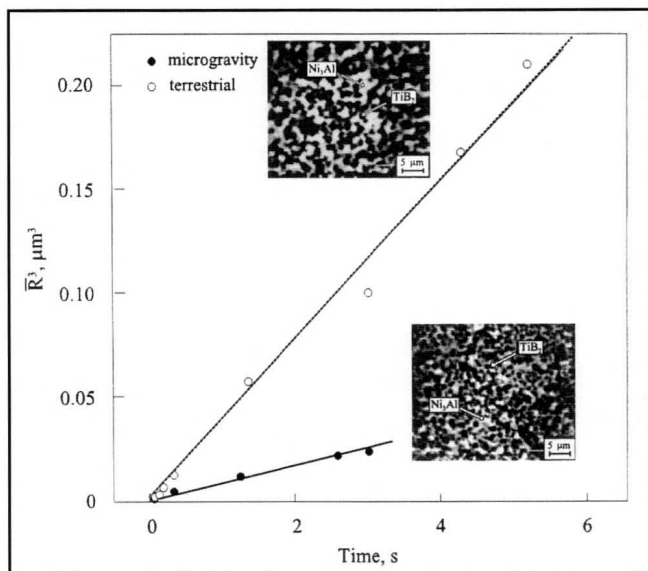


Figure 7. Evolution of TiB_2 (dark phase) grain size in Ni_3Al (light phase) matrix during combustion synthesis in the $(Ti+2B) - (3Ni+Al)$ system, in microgravity and normal gravity conditions.

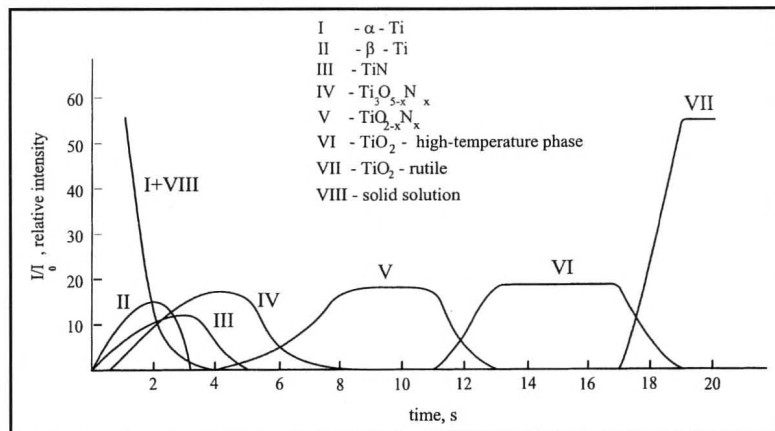


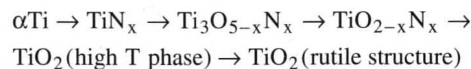
Figure 8. Dynamics of phase formation during combustion of titanium in air.

of the preheating zone varies from 0.05 to 0.3 mm, while the total wave is generally 1 to 2 mm and may be as wide as 20 to 30 mm for multistage reactions. A variety of physico-chemical processes occur in different portions of the CS wave. The initial stage of structure formation is concurrent with the chemical reaction, where the driving force of the process is a reduction of Gibbs free energy resulting from formation of new chemical bonds under non-equilibrium conditions. In the final structure-formation process, physical effects are predominant where the free energy reduces further due to interfacial surface reduction, ordering of the crystal structure, and other related processes that occur without changes in the chemical composition under quasi-equilibrium conditions.

To study the variety of structural transformation processes, it is necessary to use a wide range of methods. For example, the evolution and morphological features of the microstructure during CS can be identified using a layer-by-layer microscopic and composition analysis of quenched samples.^[12] The dynamics of phase composition and crystal structure ordering can be monitored continuously by time-resolved X-ray diffraction (TRXRD).^[13] Also, microstructural analysis of the combustion front, using a digital high-speed microscopic video recording (DHSMVR)^[14] provides important information about the local conditions, which affect the synthesis process.

An illustration of the quenching technique involves comparison of the dynamics of structure formation in terrestrial and microgravity conditions. It has been shown that the microstructure of CS products is *finer* and more *uniform* in microgravity. For example, the growth rate of TiB_2 grains in molten Ni_3Al matrix during CS was four times smaller in microgravity ($10^{-5}g$) as compared to normal ($1g$) conditions (see Figure 7), thus yielding a final cermet product with finer grains that provide superior mechanical properties.^[15]

The application of the TRXRD method, which allows one to obtain X-ray patterns of several non-overlapping lines of each phase in complex systems every 0.1 seconds of observation, can be demonstrated on the combustion of titanium in air.^[16] In this system, a complicated mechanism was observed involving four *intermediate phases* that preceded the formation of the final *equilibrium* TiO_2 product:



The kinetics of the appearance and disappearance of each phase are shown in Figure 8.

Finally, by using the DHSMVR method of *in-situ* observation of rapid processes, with a rate of recording up to 12,000 frames/second occurring at the microscopic level (spatial resolution of approximately 1.5 microns), significantly new information

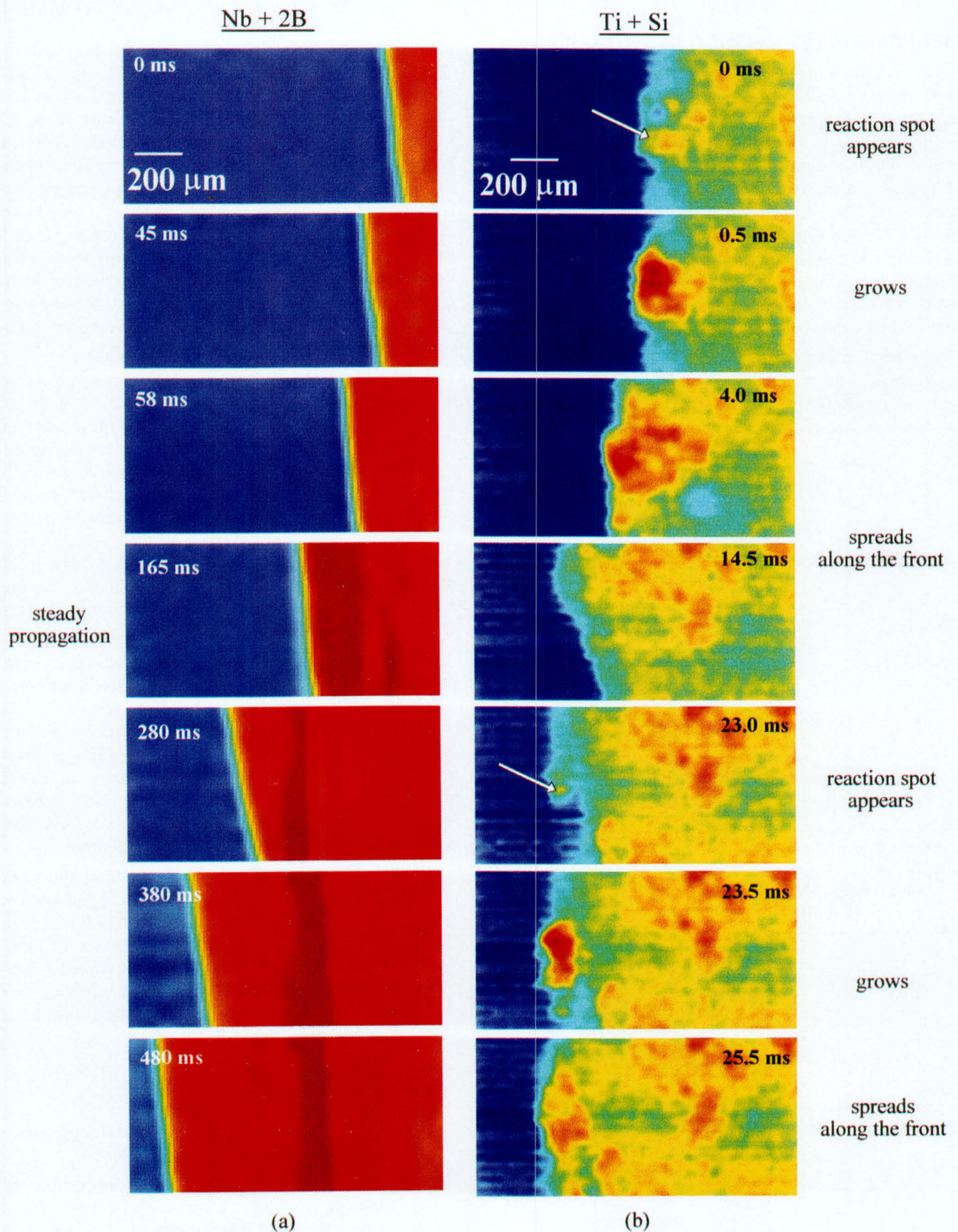


Figure 9. Microstructures of reaction wave during combustion synthesis: (a) quasihomogeneous reaction wave; (b) scintillating reaction wave.

about the microstructure of gasless heterogeneous combustion waves was recently obtained. It was shown^[17] that while on the *macroscopic* length and time scales, the reaction appears to move in a steady mode, on the *microscopic* level it may have a complex unsteady character that is related to the reaction mechanism. In general, we may classify these waves into two types, according to their microstructures: *quasihomogeneous* reaction waves and *scintillating reaction* waves. In the former case, the wave moves steadily and there is relatively little variation of temperature along the surface of the front (see Figure 9a). In the latter case, however, a hot-spot initiates the reaction ahead of the front and the wave moves forward only as a consequence of the appearance of the hot-spots (see Figure 9b). Thus, an essential temperature nonuniformity exists in the reaction front that leads to nonuniformity of the product microstructure formation. In this case, the extent of nonuniformity can be controlled, *i.e.*, the number and frequency of scintillations decrease by using finer reactant powders or samples with higher initial density.^[4]

THE CHALLENGES AHEAD

There are some successful commercial applications of the combustion-synthesis technique for production of advanced materials. They include nitride ceramics, high-temperature heating elements, shape-memory alloys, ceramic-lined pipes, and high-performance composites. In my own laboratory at Notre Dame, we are currently working on two major applications with industrial partners. The first involves enhancement of cobalt-based alloys, where we are working with Zimmer, Inc., a world leader in production of orthopedic implants, to develop stronger alloys as well as new CS-based technology that will eliminate several manufacturing steps. The second project relates to improving production of emergency oxygen by combustion of low-exothermic condensed reactants, where we are collaborating with B/E Aerospace, Inc., the leading manufacturer of chemical oxygen generators for passenger aircraft applications.

While combustion synthesis offers a number of potential advantages over conventional techniques, some hurdles need to be overcome before it can enjoy widespread use. The foremost among these is a mechanistic understanding of reaction and structure-formation processes, which are indeed complex owing to the heterogeneous nature of the reaction media. This understanding is critical in order to produce materials with tailored microstructures and properties. As discussed above, excellent analytical tools are now becoming available that facilitate this understanding. Based on such insights, combustion synthesis is expected to become an important technique in the 21st century for the production of a variety of advanced materials.

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