

Combustion Synthesis of Advanced Materials: Fundamentals and Applications

Arvind Varma[†] and Alexander S. Mukasyan

Department of Chemical and Biomolecular Engineering, and Center for Molecularly Engineered Materials,
University of Notre Dame, Notre Dame, IN, 46556, USA

(Received 20 October 2003 • accepted 9 March 2004)

Abstract—The combustion synthesis (CS) of materials is an advanced approach in powder metallurgy. The number of products synthesized by CS has increased rapidly during recent years and currently exceeds 1,000 different compounds. The same features, such as high temperatures and rates, self-sustained manner of microstructure formation in non-equilibrium conditions, that make CS an attractive technology also define difficulties to study the nature and mechanisms of this process, which in turn are essential to control the properties of the synthesized materials. In this survey paper, we present results of our recent work both in fundamental studies of mechanisms for rapid reaction wave propagation in heterogeneous media and in using the CS approach to synthesize different types of advanced materials, including bio-alloys and nano-sized powders.

Key words: Combustion Synthesis, Advanced Materials, Mechanisms and Kinetics, Wave Propagation, Gravity

INTRODUCTION

The **combustion synthesis** (CS) of materials is an advanced approach in powder metallurgy [Varma, 2000; Varma and Mukasyan, 1998]. The process is characterized by unique conditions involving extremely fast heating rates (up to 10^6 K/s), high temperatures (up to 3,500 K), and short reaction times (on the order of seconds). As a result, combustion methods offer several attractive advantages over conventional technologies. The foremost is that solely the heat of chemical reaction (instead of an external source) supplies the energy for the synthesis. Also, simple equipment, rather than energy-intensive high-temperature furnaces, is sufficient. Further, an attractive aspect of combustion process is its ability to produce materials of **high-purity**, since the high temperatures purge the powders of any volatile impurities adsorbed or present in the reactants. Remarkably, the high temperature gradients, combined with rapid cooling rates in the combustion wave, may form **unique microstructures**, which are not possible to achieve by conventional methods of powder metallurgy.

There are two modes by which combustion synthesis can occur (Fig. 1): **self-propagating high-temperature synthesis** (SHS) and **volume combustion synthesis** (VCS). In both cases, reactants may be pressed into a pellet, typically cylindrical or parallelepiped-shaped. 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 SHS mode is, after initiation locally, the self-sustained propagation of a reaction wave through the heterogeneous mixture of reactants, followed by the synthesis of desired condensed products. During VCS, the entire sample is heated uniformly in a controlled manner until the reaction occurs essentially simultaneously throughout the volume, which

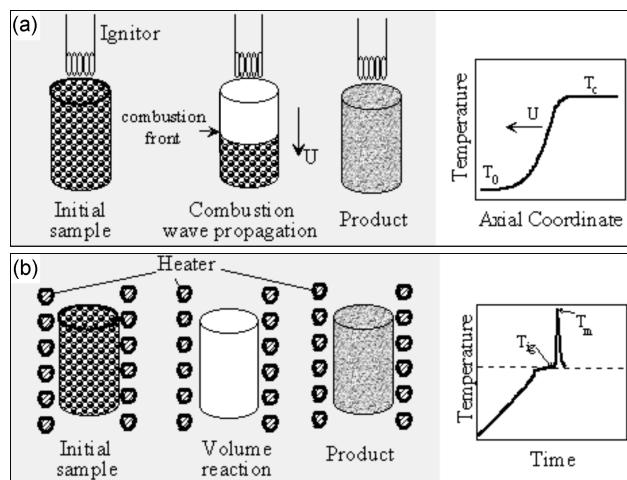


Fig. 1. The modes of combustion synthesis: (a) SHS; (b) VCS.

leads to uniform microstructure and phase composition of the synthesized material. This mode of synthesis is more widely used for weakly exothermic reactions that require preheating prior to ignition, and is sometimes referred to as the **thermal explosion** mode.

The number of products synthesized by CS has increased rapidly during recent years and currently exceeds 1,000 different compounds. Specifically, these materials include carbides (TiC, ZrC, SiC, B₄C, etc.), borides (TiB₂, ZrB₂, MoB₂, etc.), silicides (Ti₅Si₃, TiSi₂, MoSi₂, etc.), nitrides (TiN, ZrN, Si₃N₄, BN, AlN), oxides (ferrites, perovskites, zirconia, etc.), intermetallics (NiAl, Ni₃Al, TiNi, TiAl, CoAl, etc.) as well as their composites. The principles and prospects of CS as a technique for advanced materials production are presented in various reviews [Munir and Anselmi-Tamburini, 1989; Merzhanov, 1990; Moore and Feng, 1995; Varma et al., 1998a].

In this survey paper, we present results of our recent work both in fundamental studies of rapid reaction wave propagation in heterogeneous media and in using the CS approach to synthesize different types of advanced materials, including bio-alloys and nano-

[†]To whom correspondence should be addressed.

E-mail: avarma@nd.edu

[‡]This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

sized powders.

MECHANISTIC STUDIES

The same features, such as high temperatures and rates, self-sustained manner of microstructure formation in non-equilibrium conditions, that make CS an attractive technology also define difficulties to study the nature and mechanisms of this process, which in turn are essential to control the properties of the synthesized materials. Despite extensive investigations, the mechanism of reaction wave propagation in heterogeneous media, which determines synthesis conditions, is not well understood. However, it is well recognized that knowledge of *heat transfer* in porous reaction media, as well as *kinetics* of both the chemical reaction and structure formation are essential for understanding CS mechanisms.

We have developed several novel methods for investigating propagation of rapid chemical reactions in heterogeneous media. These include a *digital high-speed microscopic video recording* (DHSMVR) technique [Hwang et al., 1998], which allows *in-situ* observation of rapid ($\sim 10^4$ frame/s) processes occurring at the microscopic level ($\sim 1 \mu\text{m}$) and *computer-assisted electrothermography* (CAE) method [Pelekh et al., 2000] for measuring kinetics of heat evolution during high-temperature (1,000–3,000 K) rapid ($t_r \sim 10^{-3}$ s) chemical reactions. By using these techniques, we have investigated characteristic features of kinetics and combustion wave microstructure for a variety of systems with different interaction mechanisms: solid-solid (e.g. Ta-C), solid-liquid (e.g. Ti-C), liquid-liquid (e.g. Ni-Al) and gas-solid (e.g. Ti-N₂). It was shown that the classical approach, based on the quasi-homogeneous concept, in many cases could not be applied to describe the behavior of CS systems. Thus a new sub-field of combustion science, i.e. *Microstructural Mechanisms of Combustion Wave Propagation* in Heterogeneous Media, has been established. Based on the obtained results, a new physical understanding of phenomena was created, which is different as compared to the classical models. These findings allow us to establish new methods to control the combustion process, microstructure and properties of the synthesized materials. Below we present selected results, which illustrate our recent progress in this research direction.

1. Microstructural Aspects of Reaction Wave Propagation in Porous Media

By using the DHSMVR method, our previous experimental investigations [Rogachev et al., 1994; Mukasyan et al., 1996, 1999a; Hwang et al., 1997] have shown that macroscopically steady reaction fronts in heterogeneous mixtures exhibit random microscopic fluctuations in shape and instantaneous velocity, which are directly related to the microstructure of the reaction mixture. A new *relay-race* mechanism of combustion wave propagation in heterogeneous media was suggested. In this case, combustion proceeds by two sequential steps: rapid reaction of a single reaction cell, followed by an ignition delay during which preheating of the neighboring cells occurs.

We have also developed a theoretical model, which accounts for heterogeneity of the reaction medium (e.g. random distribution of particles, thermal resistance between them) and explains the observed data [Mukasyan et al., 1996; Varma et al., 2001]. In addition, based on the local conditions during reaction (i.e., microstructure of the combustion wave), we have developed and evaluated

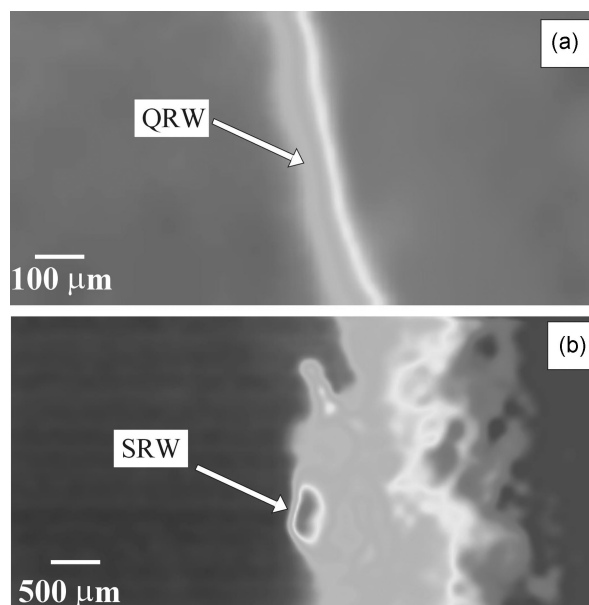


Fig. 2. Two regimes of SHS mode: (a) Quasihomogeneous; (b) Scintillating Reaction Wave [Varma et al., 1998b].

several new criteria for determining the specific mechanisms of combustion wave propagation [Hwang et al., 1998].

Further, it was shown that at smaller time scales (10^{-3} – 10^{-4} s) in all investigated systems, the characteristics of self-propagating high-temperature reaction waves in heterogeneous mixtures are even more complex [Varma et al., 1998; Mukasyan et al., 1999b]. However, these waves follow two modes, classified according to their microstructures (see Fig. 2): *quasihomogeneous reaction wave (QRW)* and *scintillating reaction wave (SRW)*. It was also found that in different systems, the reaction wave may propagate by either a single or a combination of the two modes.

In recent work, the characteristic features of SRW propagation were *quantitatively* analyzed [Mukasyan et al., 2000]. As a result, a number of parameters, which fully describe the process of reaction front propagation, were introduced and their dependences on

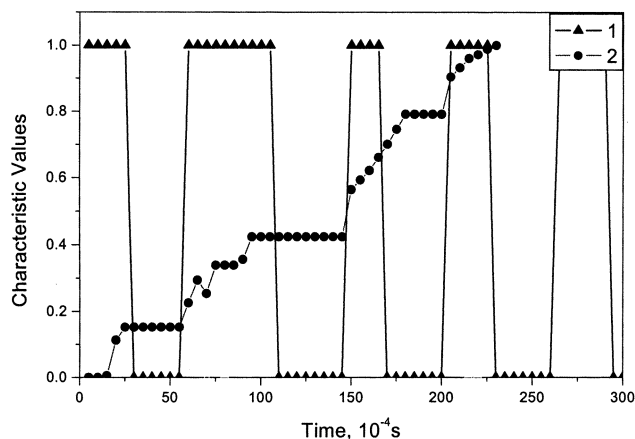


Fig. 3. Characteristic values of active and passive stages (curve 1) and location of the reaction front (curve 2) [Mukasyan et al., 2000a].

the reaction medium microstructure (e.g. porosity, characteristic length scales, etc.) were established. For example, for Ti+Si system, statistical analysis of experiments revealed the following general picture of the combustion process. The chemical reaction propagates as a consistent repetition of “active” and “passive” stages with characteristic values 1 and 0, respectively (see Fig. 3, curve 1). The active stage is characterized by existence of regions (super-adiabatic hot spots) with temperature, T_s , higher than average reaction temperature, T_c , while in passive stage the temperature of the entire area is equal to or less than T_c . It was also shown that the existence of hot spots correlates with movement of the reaction front. During the active stage, the combustion front propagates rapidly, while it hesitates when hot spots are absent (Fig. 3, curve 2). Also, the following conclusions were made about the influence of reaction medium density (ρ) on the above picture of reaction front propagation: (i) number of cycles per length decreases with increasing ρ ; (ii) the average duration of active stage increases with increasing ρ , while average hesitation time remains essentially constant. These and other obtained results for the intrinsic mechanism of combustion wave propagation are explained by taking into account microstructural characteristics of the reaction medium (e.g. scale of het-

erogeneity, contact surface area, distance between reacted particles, etc.).

Our next step was devoted to establishing dependence of the above-discussed parameters on the scale of heterogeneity (e.g. reactant particle size) of the reaction medium [Mukasyan et al., 2004a]. Experiments were conducted using 1 : 1 atomic mixture of silicon and titanium powders. The mean particle size of silicon powder was 5 μm , while four size ranges of Ti powders were used: <26 μm , 26–45 μm , 45–75 μm , and 75–106 μm . The relative sample density was also held constant at a value of 0.60. It was shown that such parameters of SRW wave as number and size of hot spots, as well as average distance between their appearance, correlated strongly with the number, size and location of the titanium particles (Fig. 4). These data again confirmed our SRW model of combustion wave propagation in heterogeneous powder mixtures.

2. Kinetics of Rapid High-Temperature Reactions

As noted above, we have developed a computer-assisted electrothermography (CAE) method to determine the intrinsic *kinetics* of reactions under conditions similar to those realized during com-

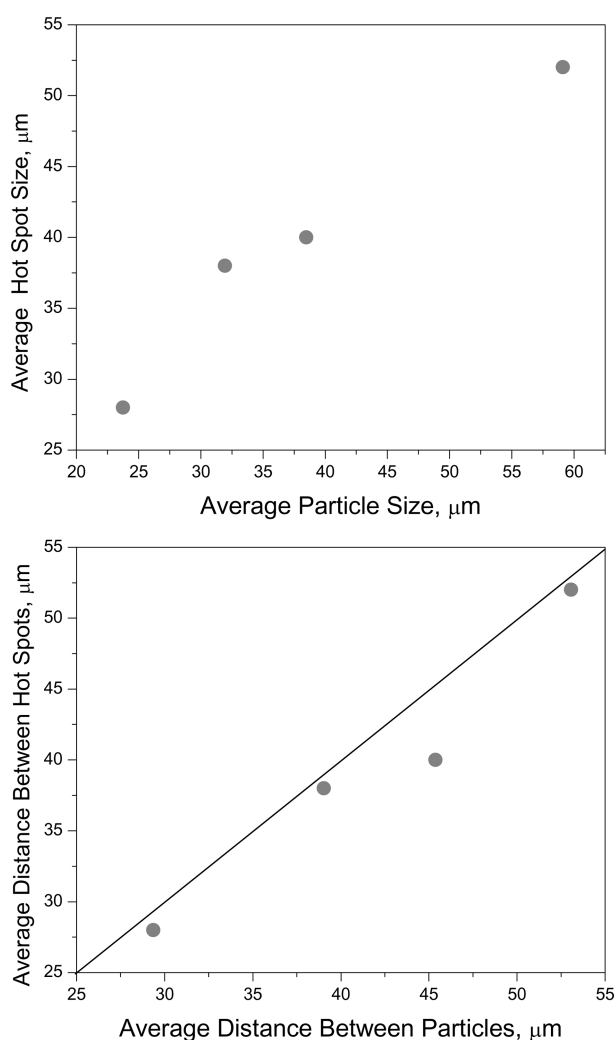


Fig. 4. Correlations between microstructures of the reaction medium and the combustion wave [Mukasyan et al., 2004a].

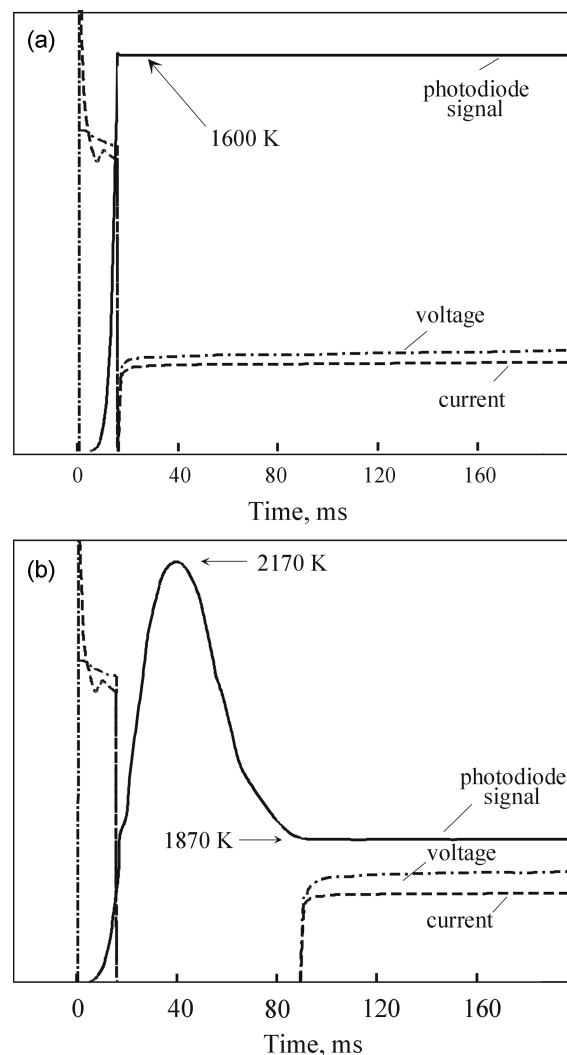


Fig. 5. Characteristic experimental curves for heating titanium wire in nitrogen to different set-points: (a) $T=1,600$ K; (b) $T=1,870$ K [Pelekh et al., 1999].

bustion synthesis of materials [Pelekh et al., 2000]. To illustrate the technique, it was applied to investigate the kinetics and other features associated with the reaction of titanium with nitrogen at 1 atm pressure. The temperature range 1,400–2,300 K, and heating rates 10^4 – 10^5 K/s, were studied. For example, experimental curves for voltage, current and photodiode signal, obtained upon heating a 50 μm radius Ti wire in nitrogen up to 1,600 K are presented in Fig. 5. Analysis of these data shows that at temperatures below the melting point of titanium (1,940 K), the reaction follows parabolic rate law, corresponding to a sharp-interface model with nitrogen diffusion through the developing titanium nitride layer as the rate controlling step [Pelekh et al., 1999]. The obtained activation energy value (210 kJ/mol) is in good agreement with this model.

The influence of preheating rate on kinetics of high-temperature reactions in gas-solid systems was also investigated by the CAE technique [Thiers et al., 2000]. Two systems were studied: Nb–N₂ and Ti–N₂, in the temperature ranges 2,100–2,500 K and 1,350–1,600 K, respectively. The results show that reaction kinetics of both systems is enhanced by increasing the rate of preheating to the desired reaction temperature. Analysis of the experimental data, in the context of the sharp-interface model, shows that the activation energy of diffusion does not depend on heating rate, while the pre-exponential factor is affected. Additional experiments suggest that fast nonisothermal preheating, even though of short duration ca. 10 ms, influences chemical activity of the solid reactant.

It was also found [Thiers et al., 2001] that at higher temperatures (e.g. 1,600–1,800 K for the Ti–N₂ system) and high preheating rates, the process of metal nitridation occurs in the so-called **overshoot-mode**, where one cannot control the temperature of the reacted system. It was shown that this phenomenon could be considered as **self-ignition** of the metal in nitrogen and its characteristics (rate, amount of heat released, maximum temperature, etc.) depend strongly on heating rate. This effect was explained by changes in the surface area of the solid reactant during the preheating period: lower preheating rates to the set-point temperature cause significant changes in the metal reactant microstructure (primarily reduction of specific surface area), which decreases rate of the subsequent chemical interaction. It was found that activation energy, E_a , measured under nonisothermal conditions ($E_a=330$ kJ/mol), was different from that obtained in isothermal experiments ($E_a=210$ kJ/mol). An important conclusion was made that, in general, isothermal kinetics may not be applicable for nonisothermal cases.

Finally, in recent work [Kharatyan et al., 2004], we studied the influence of preheating rate on the kinetics of **gasless** Mo–Si reactions at high temperatures (above Si melting point, 1,683 K). It was shown that an increase of heating rate, V_h , in the range 10 – 10^5 K/s, leads to a substantial increase in the rate of chemical reaction. At high heating rates ($>10^3$ K/s), the first stage of interaction involves rapid reaction due to direct Mo dissolution in Si melt. Further, the formation of MoSi₂ phase, owing to crystallization from eutectic (MoSi₂–Si) melt, is primarily responsible for the observed intensive heat release under these conditions. At lower V_h , a thin layer of Mo₅Si₃ phase formed at earlier stages (solid-solid interaction) significantly retards reaction at higher temperatures and changes the mechanism of interaction.

3. Mechanisms of Thermal Explosion in Heterogeneous Systems

March, 2004

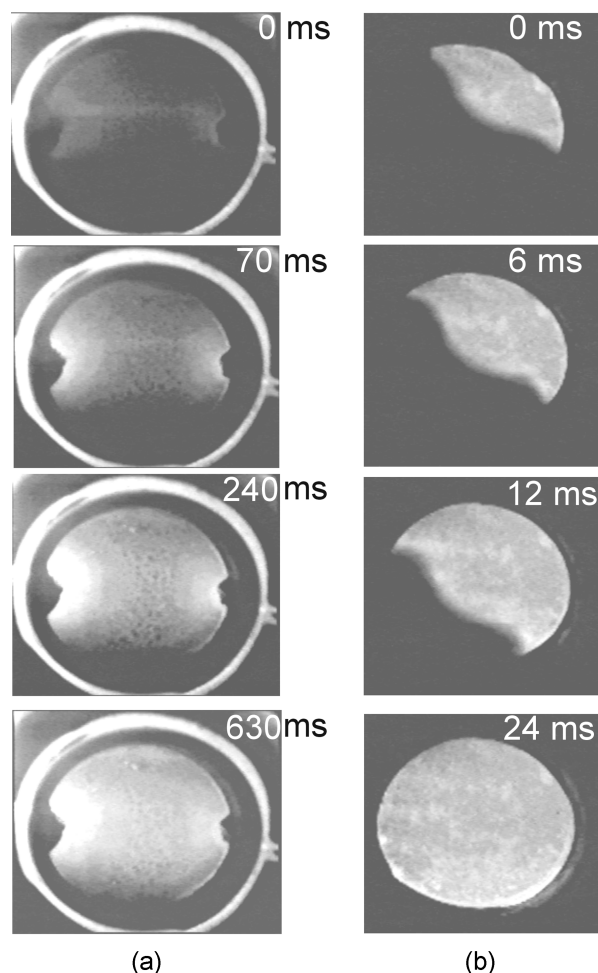


Fig. 6. Typical sequences of frames obtained by DHSMVR during TE in systems: (a) 2Cu+Al and (b) 3Ni+Al [Rogachev et al., 2002].

Thermal explosion (TE) phenomena were investigated in different **intermetallic** systems, including binary powder mixtures Cu–Al and Ni–Al [Rogachev et al., 2002]. A sequence of video frames, shown in Fig. 6, reveals that samples maintain their size and shape during TE in both cases. However, a qualitative difference in the processes was found. All Ni–Al samples self-ignite locally and then a high temperature front propagates along the sample similarly to a combustion wave. This feature was not seen for the Cu–Al system, where instead we observed only relatively uniform changes of sample brightness (temperature) with time. Further, the temperature-time histories of sample surfaces using an infra-red thermal video system are shown in Fig. 7. It is clear that during all stages of the TE process, temperature changes essentially uniformly along the sample surface for the Cu–Al system (Fig. 7a). However, for the Ni–Al system, uniform temperature distribution is observed only during the inert preheating, while during thermal explosion, zones with relatively large temperature gradients form (Fig. 7b). In the latter case, note that the observed essentially linear and wide temperature profile is not similar to typical profiles of a conventional combustion wave. These results suggest that, in this case, we have propagation of a **virtual thermal wave** (VTW). For an observer, such spreading of high temperature regions appears similar to the propa-

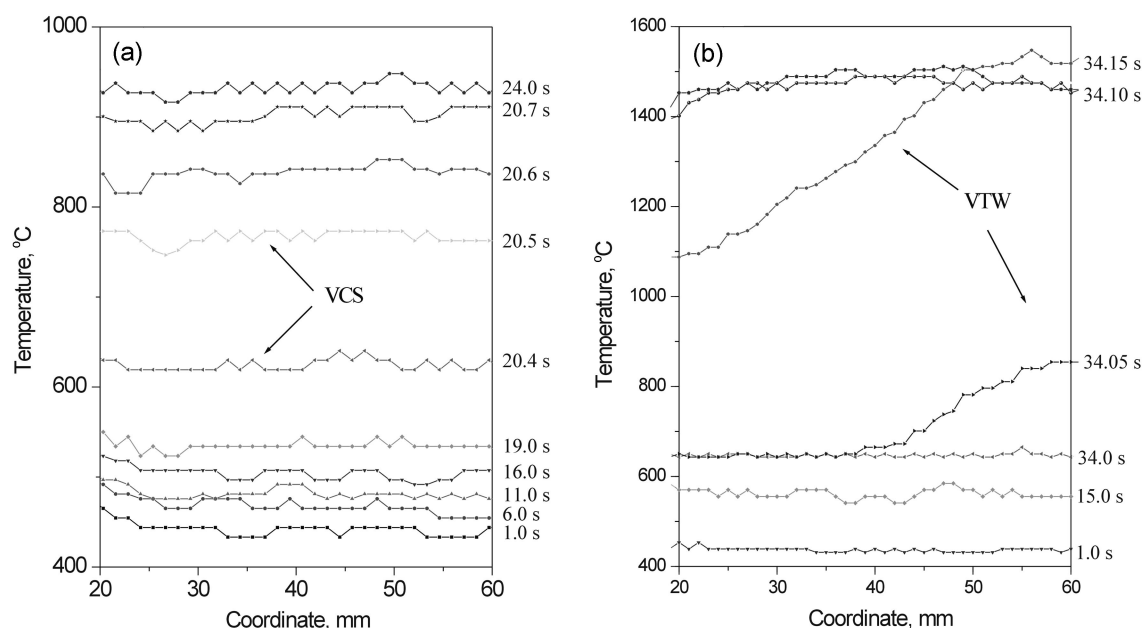


Fig. 7. Characteristic temperature distributions along the sample surface at different times during TE in systems (a) 2Cu+Al; (b) 3Ni+Al [Rogachev et al., 2002].

gation of a combustion wave. However, the important difference is that in the former case, the reactions at each point of the reaction medium proceed essentially independently of heat release in other parts of the sample. Thus VTW is a process of sequential *local self-ignition*, which “propagates” through the sample without significant heat exchange between neighbor areas. Thus, for the first time, two qualitatively different modes of thermal explosion (i.e. uniform VCS and VTW) were observed experimentally [Rogachev et al., 2002].

The same approach was used to investigate thermal explosion in *clad particle* systems [Thiers et al., 2002]. In this case, each particle consists of an Al core and a Ni shell, with outer diameter $\sim 100\ \mu\text{m}$ and Ni surface layer thickness $\sim 7\ \mu\text{m}$, which corresponds to a composition of Ni (67.6 wt%) and Al (32.4 wt%) close to 1 : 1 mole ratio (the latter can be changed easily by varying thickness of the

Ni layer). It was shown that, in contrast to a mixture of Ni and Al powders, the TE process typically occurs in the uniform VCS mode. Also, the ignition temperature in the mixture of Ni and Al powders is near the Al melting point (933 K) and does not depend on heating rate, while for clad particles is higher by $\sim 100\ \text{K}$ and decreases with increasing rate of preheating. This feature is related to crack formation in the outer solid shell. Finally, it was also shown that dynamics of phase transformation during the pre-ignition stage involved formation of non-equilibrium Al rich (such as Al_3Ni) phases.

4. Combustion Mechanisms in Different Heterogeneous Systems

Different aspects of combustion mechanisms in gasless clad particle, gas-solid and liquid-type systems were studied. Investigation of the combustion wave propagation (SHS mode) in a powder sample consisting of *Ni clad Al particles*, was conducted using the quench-

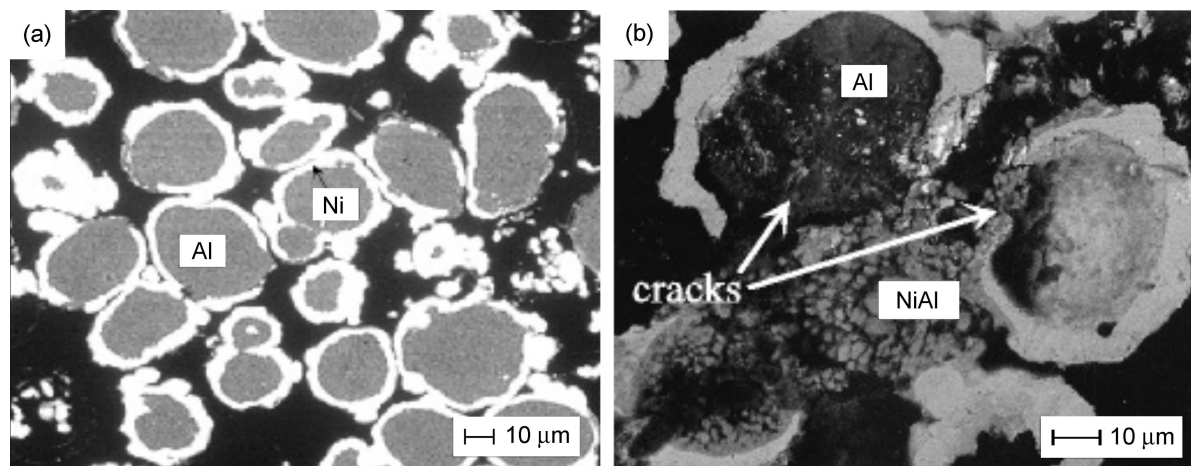


Fig. 8. Typical microstructures of Ni clad Al particles at different stages of interaction [Mukasyan et al., 2001a].

ing technique and layer-by-layer SEM/EDX analysis [Mukasyan et al., 2001a]. It was confirmed that essentially no reaction occurs until Al melts (see Fig. 8a). Upon reaching the Al melting point (933 K), reaction between liquid Al and solid Ni shell starts, the shell cracks, liquid aluminum flows out and wets surrounding particles (see Fig. 8b), triggering fast propagation of the combustion wave in the mixture. The cracking of Ni shell occurs by mechanical stress owing to the vast difference of thermal expansion coefficients of solid Al and Ni, and due to the sharp change of aluminum density upon melting. Further, when temperature reaches the melting point of Ni (1,728 K), coalescence of particles takes place, leading to a rapid change in microstructure with formation of agglomerates involving many particles. The coalescence proceeds slower in the case of clad Al/Ni particles as compared to a mixture of Al and Ni powders. We also showed that by changing sample density for the clad particle system, the primary mechanism of heat transfer in the reaction front can be varied: thermal conduction through condensed skeleton for high, thermal conduction of gas for intermediate, and radiation for low densities. Finally, by experiments conducted under low gravity (see section 6), it was demonstrated that combustion of *clouds* of such complex particles could be achieved even in inert atmosphere.

It was shown experimentally that in Ta-N and Ti-N systems, gas infiltration plays a key role in the mechanism of *spin combustion*. The influences of two main parameters of infiltration combustion, initial sample density (ρ) and reactant gas pressure (P), were investigated. Based on the results, pressure-density (P - ρ) diagrams were constructed, which present regions of different wave propagation behavior. For example, it was shown that for both reaction systems, a range of nitrogen pressure exists where increasing initial sample density results in transition from spin to steady planar mode with the simultaneous decrease in combustion velocity. Further, for some range of ρ , decrease of P leads to termination of combustion without observation of spin or oscillation modes. Finally, it was also shown that the phase composition of products depends on the combustion mode [see Mukasyan et al., 2000b for details].

5. The Effects of Gravity on CS in Heterogeneous Systems

The main goal of our research was to study the influence of gravity on the combustion characteristics of heterogeneous systems [Mu-

kasyan et al., 1997a, b; Lau et al., 2001, 2002, 2003]. Two main directions for experimental investigation were explored: (i) the influence of gravity force on the characteristic features of heterogeneous combustion wave propagation (average velocity, instantaneous velocities, shape of combustion front); (ii) the effects of gravity on the structure formation mechanism during the CS of intermetallic-ceramic *composite materials*. We next present some results obtained by us focusing on the materials science issues, while a comprehensive review of the effects of gravity on CS appears elsewhere [Mukasyan et al., 2004b].

Experiments were conducted in both the Drop Tower (NASA Glenn Research Center) providing microgravity environment ($\sim 10^{-5}$ g) for 2.2 s, and during the parabolic flights of DC-9 and KC-135 aircrafts, yielding $\sim 10^{-2}$ g condition for about 20 s. The reaction chamber, battery, power distribution box, specially constructed ignition module and video camera (SONY CCD-IRIS) were fit into a standard NASA rig (96×84×40 cm). A microcomputer (Tattletale) controlled and synchronized ignition, temperature measurements and gravity conditions. Three different easily interchangeable sample holders were used in the experiments. The first was used to study the influence of gravity on the *combustion behavior and microstructure* of the final product. For this, experiments were conducted in both 1-g and mg conditions, with the samples located at three different angles between the combustion front velocity (U_c) and gravity force vectors. The second sample holder was a vertical quartz tube, placed on a boron nitride support. Ignition could be initiated from either the top or the bottom of the sample. This holder was designed for studies in which the sample expands greatly during the synthesis, to yield *highly porous or foam-like materials*. In addition, the effect of gravity on combustion of loose reactant mixtures was investigated using this assembly. Third, a wedged brass block was used to perform quenching experiments to investigate the microstructure formation in μ g conditions. Initiated from the top, the combustion wave propagates in the direction of increasing heat losses and finally stops at some critical section of the wedge. The quenched samples were examined layer-by-layer, from the tip (initial mixture) to the top (final product), to elucidate the *evolution of material structure formation* during combustion synthesis. Details of the experimental setup and techniques are available elsewhere

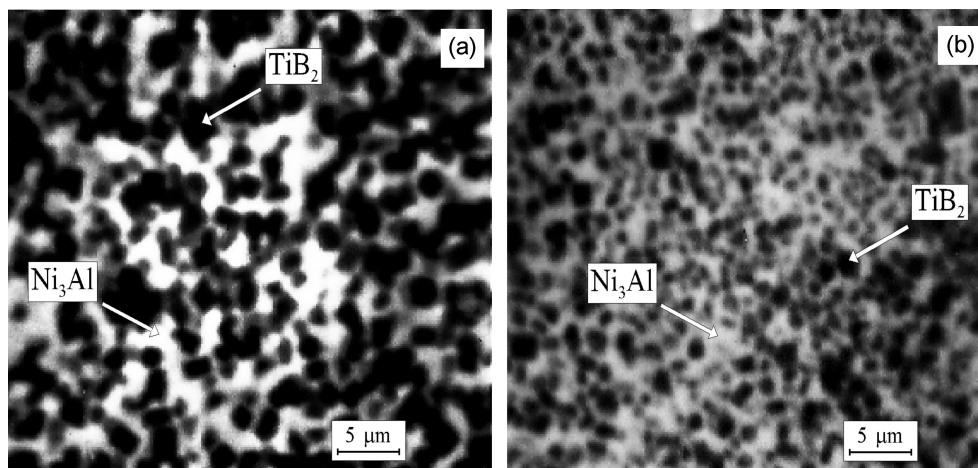


Fig. 9. Characteristic microstructures of $\text{Ni}_3\text{Al-TiB}_2$ composites synthesized in (a) 1-g; (b) μ g conditions [Mukasyan et al., 1997b].

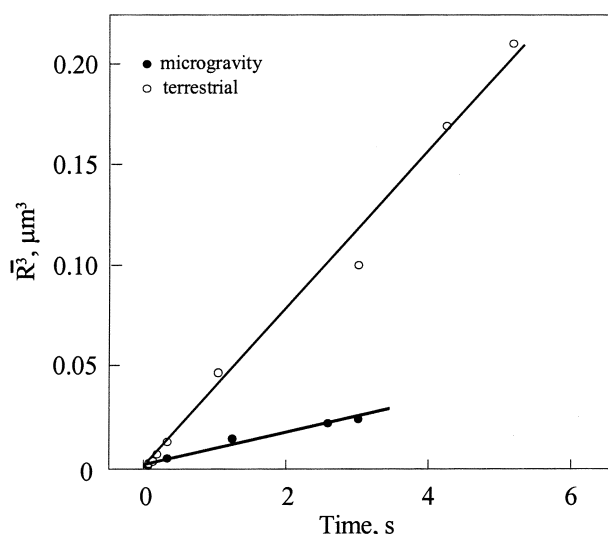


Fig. 10. Evolution of TiB_2 grain size (\bar{R}^3) during CS of $(\text{Ti}+2\text{B})-(3\text{Ni}+\text{Al})$ system in different gravity conditions [Mukasyan et al., 1997a].

[see Mukasyan et al., 1997a for details].

All experiments were conducted under identical conditions in both normal (1 g) and microgravity, to make a *direct comparison* and to establish the effects of gravity on combustion and structure formation in the investigated reaction systems. For example, it was observed that gravity influences not only propagation of the combustion wave in $\text{TiB}_2\text{-Ni}_3\text{Al}$ system, but also *microstructure* of the final product [Mukasyan et al., 1997b]. In Fig. 9, characteristic microstructures of materials synthesized in (a) terrestrial and (b) μg conditions are presented. Both show grains of TiB_2 (dark phase) dispersed in the Ni_3Al matrix (light phase). Statistical analysis showed that the average size of TiB_2 grains in mg environment was **50% smaller** than in 1-g condition; recall that finer grains yield superior mechanical properties.

The results obtained for samples *quenched* in the wedged block showed that this difference is related to the process of *grain growth* during CS. The characteristic dependencies of average TiB_2 particle size as a function of reaction time are shown in Fig. 10, for both 1-g and mg conditions. In both cases, very fine particles ($\sim 0.1 \mu\text{m}$) of TiB_2 formed immediately in the reaction front. However, the rate of particle growth in mg was **~ 4 times smaller** than in 1g conditions, thus leading to finer grains.

Additional, experiments were conducted under both terrestrial and mg conditions using more exothermic initial mixtures with different ratios between solid (TiB_2 or TiC) and liquid (NiAl) phases in the $\text{TiB}_2\text{-NiAl}$ and TiC-NiAl systems [Lau et al., 2001]. Based on detailed analysis of synthesized samples, we reached the following *general conclusions*:

- Even over a short duration of time (\sim seconds), gravity enhances mass transfer process in chemically active liquids and hence leads to an increase in microstructural transformation rates.
- Combustion synthesis in mg conditions favors the formation of materials with a *finer microstructure*.
- Smaller volume fraction of liquid phases in the reaction front results in less pronounced gravity effect on combustion and prod-

uct microstructure during CS.

Further, EDX analysis on quenched samples permitted us to determine the detailed mechanism of microstructure formation during CS in the complex Ni-Al-Ti-B system. It was shown that this process could be divided into the following characteristics zones:

1. Zone 1: reaction between Ni and Al with formation of NiAl_x phases, while Ti and B remain essentially unreacted;
2. Zone 2: Ti and B dissolve in NiAl phase, forming separate regions of complex solutions;
3. Zone 3: intensive coalescence of separate regions of melted solutions, with formation of uniform melted matrix;
4. Zone 4: crystallization of solid TiB_2 particles from the solution and their growth in NiAl -rich liquid matrix.

Finally, it was established that gravity conditions do not influence the qualitative picture of microstructural transformations in the CS wave, i.e. all the above mentioned characteristic zones exist in samples reacted under both normal and microgravity ($\sim 10^{-2}$ g). However, overall *decrease of transformation rates* and hence increase of characteristic zone lengths (L_z) were observed consistently under mg conditions [Lau et al., 2001].

SYNTHESIS OF ADVANCED MATERIALS

Based on the fundamental studies discussed above, we have synthesized various advanced materials with tailored microstructures and properties for different applications. Two such directions are described below.

1. CS of Bio-Alloys

The first example involves a novel efficient and flexible technique, *Low-Pressure Combustion Synthesis* (LPCS), to produce pore-free *orthopaedic implant materials* in a single step. In this research, special attention was paid to phase separation mechanism during combustion of thermite systems, as well as to characterization of LPCS-alloys, including analysis of chemical composition, microstructure, hardness, friction and tensile properties [Varma et al., 2002; Li et al., 2003].

The developed method possesses several advantages over conventional processes, such as low energy requirements, short processing times and simple equipment. In addition, it was shown that microstructure of CS-material is finer and more uniform as compared to the conventional standard (Fig. 11). Further, it was found that among the various additives, at identical loading, Cr_3C_2 is the most effective one for increasing material hardness (Fig. 12). Remarkably, with increasing carbon added as Cr_3C_2 , the hardness of LPCS Co-alloys increases (Fig. 12b) to values that are significantly higher than with graphite or carbon black (Fig. 12c) and even the commercially produced wrought Co-alloy.

Finally, comprehensive analysis of various material properties led to the conclusion that for hardness, the as-synthesized LPCS-alloy is the best candidate. However, if ductility is the optimized parameter, then LPCS+HIP treatment should be considered. Finally, if tensile strength is important, then LPCS+Cast alloy is the preferred choice.

2. Nano-scale Oxide Powders by Aqueous CS

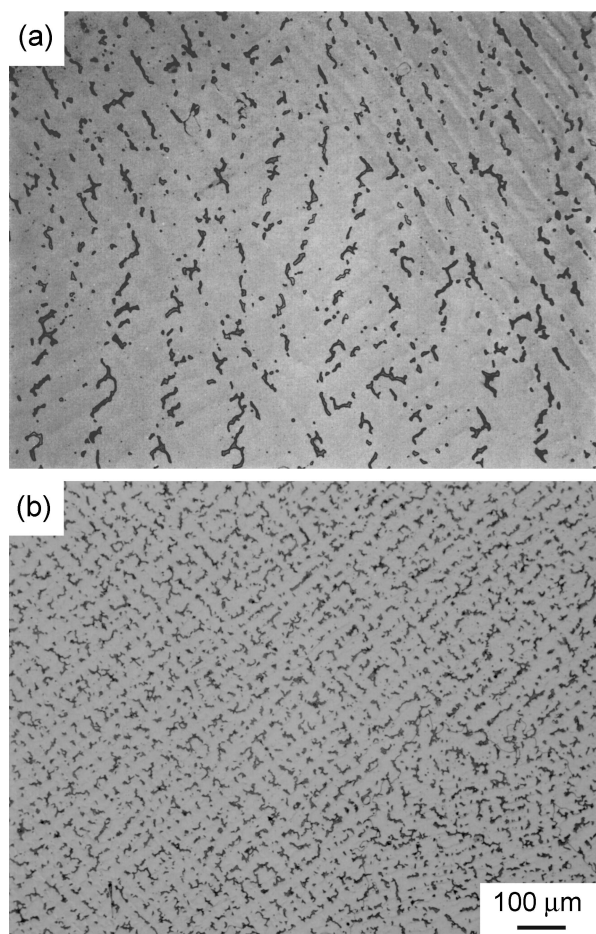


Fig. 11. Typical microstructures of pore-free Co-alloys with 0.33 wt% C: (a) LPCS-synthesized, (b) Conventional sample [Varma et al., 2002].

Another example relates to the direct synthesis of oxide nanopowders by using the combustion approach. The aqueous (or solution) combustion synthesis is an attractive technique for the formation of different oxides including ferrites, perovskites and zirconia. It involves a self-sustained reaction between an oxidizer (e.g. metal nitrate) and a fuel (e.g. glycine, hydrazine) [Patil et al., 2002; Mukasyan et al., 2001b]. The reactants are first dissolved in water in the desired ratio and the obtained solution thoroughly mixed, to reach molecular level homogenization of the reaction medium. After pre-heating to water boiling point and its evaporation, the mixture can be ignited or self-ignites and temperature rises rapidly (up to 10^4 °C/s) to values as high as 1,000 °C. Simultaneously, this self-sustained reaction converts the initial mixture to fine well-crystalline powders of desired compositions.

As an illustration of the method, two classes of perovskites (i.e. LaGaO_3 and LaCrO_3), doped with Sr and Mg, were synthesized. In these cases, an aqueous solution was made of desired metal nitrates and glycine [Deshpande et al., 2003]. The ratio between nitrates was maintained constant corresponding to the desired product composition, while ratio between fuel and oxidizer, ϕ , was changed. It was shown that depending on ϕ , the reaction could proceed in three different modes: smoldering combustion synthesis (SCS), $\phi < 0.7$, with maximum temperature, $T_m < 73$ K; volume combustion synthe-

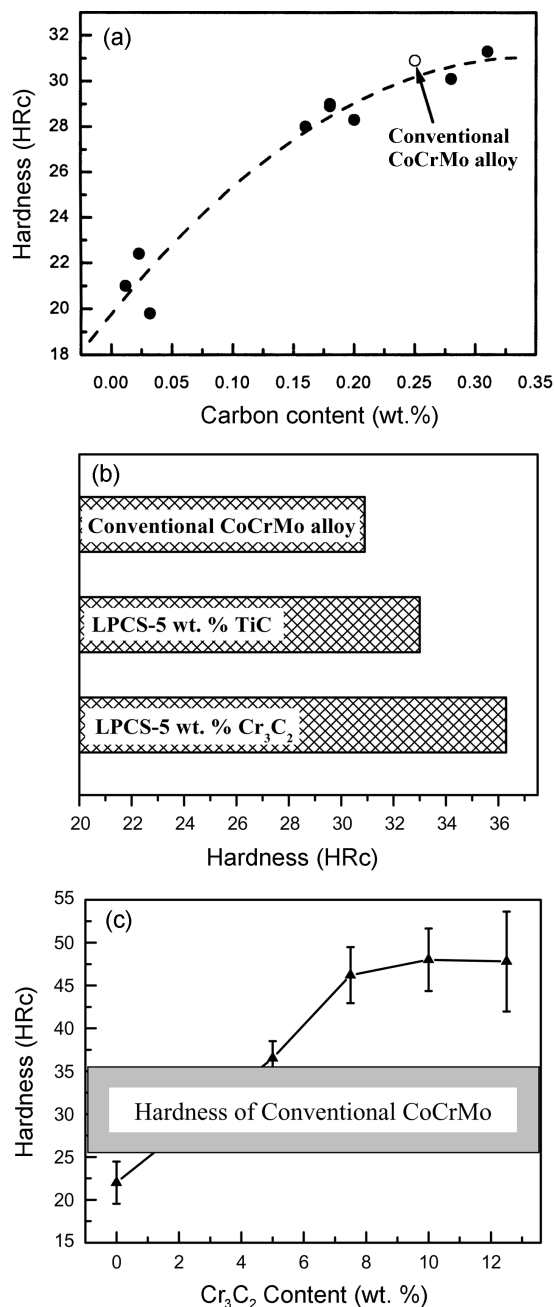


Fig. 12. Influence of different additives on hardness of Co-Based alloys: (a) Hardness increases with increasing addition of graphite or carbon black. (b) For the same extent of carbide/nitride additives, Cr_3C_2 exhibits the most hardness enhancement. (c) Dependence of alloy hardness on Cr_3C_2 content (bars, standard deviation) [Varma et al., 2002].

sis (VCS), $0.7 < \phi < 1.2$, $1,423 \text{ K} < T_m < 1,623 \text{ K}$; and self-propagating high-temperature synthesis (SHS), $1.2 < \phi < 1.6$, $1,073 \text{ K} < T_m < 1,373 \text{ K}$. Detailed studies allowed us to conclude that the optimum mode for synthesis is SHS, which, as compared to other modes, leads to formation of powders with highest surface area and desired phase composition directly in the combustion wave (Fig. 13).

In another work [Deshpande et al., 2004], synthesis of three major iron oxide phases, i.e. α - and γ - Fe_2O_3 and Fe_3O_4 , by combustion approach was studied, using a simple iron nitrate precursor along

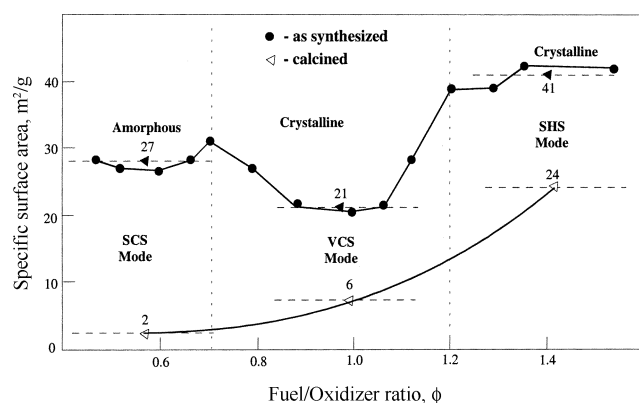
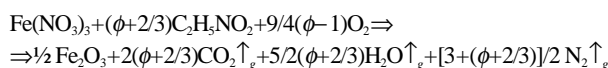


Fig. 13. Characteristics of synthesized powders, combustion mides and BET surface areas as a function of the fuel/oxidizer ratio; open symbols as-synthesized, filled symbols-calcined [Mukasyan et al., 2001b].

Table 1. Phase compositions and surface areas of iron oxide powders synthesized by combustion approach [Deshpande et al., 2004]

Phase composition	Specific surface area, m ² /g
Fe ₃ O ₄	50
α-Fe ₂ O ₃	65
γ-Fe ₂ O ₃	125
α+γ-Fe ₂ O ₃	200

with different fuels: glycine, hydrazine and citric acid. An example of the chemical reaction between iron nitrate and glycine is shown below:



Note that in the above equations, $\phi=1$ means that the initial mixture does not require atmospheric oxygen for complete oxidation of fuel. In addition, **complex fuels**, i.e. mixtures of glycine and hydrazine, were also used to enrich desired product composition and properties.

To our knowledge, for the first time in the literature, different iron oxide powders with well-crystalline structures and surface area in the range 50-200 m²/g were produced by a single approach (Table 1). It was illustrated that aqueous CS is a flexible technique where precursors are mixed on the molecular level and, under the unique conditions of rapid high-temperature reactions, nanoscale powders of desired compositions can be synthesized in one step, avoiding additional calcination procedures. Thus the method is promising for the synthesis of a variety of powders with fine microstructures and tailored properties.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (grants CTS0202765 and CTS-99073211) and NASA (grant NAG3-2213). We are also grateful to Prof. A. Rogachev, Dr. S. Hwang, Dr. A. Pelek, Dr. L. Thiers, Dr. C. Lau and Ms. K. Deshpande for their participation in the research described here.

REFERENCES

- Deshpande, K., Mukasyan, A. S. and Varma, A., "Aqueous Combustion Synthesis of Strontium-Doped Lanthanum Chromate Ceramics," *J. Am. Ceram. Soc.*, **86**, 1149 (2003).
- Deshpande, K., Mukasyan, A. S. and Varma, A., "Synthesis of Iron Oxide Nanopowders by Combustion Approach: Reaction Mechanism and Properties," *Chem. Mater.* (2004, in review).
- Hwang, S., Mukasyan, A. S. and Varma, A., "Mechanisms of Combustion Wave Propagation in Heterogeneous Reaction Systems," *Combust. Flame*, **115**, 354 (1998).
- Hwang, S., Mukasyan, A. S., Rogachev, A. S. and Varma, A., "Combustion Wave Microstructure in Gas-Solid Systems: Experiments and Theory," *Combust. Sci. Tech.*, **123**, 165 (1997).
- Kharatyan, S. L., Chatilyan, H. A., Mukasyan, A. S., Simonetti, D. A. and Varma, A., "Influence of Heating Rate on Kinetics of Rapid High-Temperature Reactions in Condensed Heterogeneous Media: Mo-Si System," *AIChE J.* (2004, in press).
- Lau, C., Mukasyan, A. S. and Varma, A., "Materials Synthesis by Reduction-Type Combustion Reaction: Influence of Gravity," *Proc. Combust. Inst.*, **29**, 1101 (2002).
- Lau, C., Mukasyan, A. S. and Varma, A., "Reaction and Phase Separation Mechanisms during Synthesis of Alloys by Thermite Type Combustion Reactions," *J. Mat. Res.*, **18**, 121 (2003).
- Lau, C., Mukasyan, A. S., Pelek, A. and Varma, A., "Mechanistic Studies in Combustion Synthesis of NiAl-TiB₂ Composites: Effects of Gravity," *J. Mater. Res.*, **16**, 1614 (2001).
- Li, B., Mukasyan, A. S. and Varma, A., "Combustion Synthesis of CoCr Mo (F-75) Implant Alloys: Microstructure and Properties," *Mater. Res. Innov.*, **7**, 245 (2003).
- Merzhanov, A. G., "Self-Propagating High-Temperature Synthesis: Twenty Years of Search and Findings," In *Combustion and Plasma Synthesis of High-Temperature Materials*, edited by Z. A. Munir and J. B. Holt, New York, VCH Publishers, 1 (1990).
- Moore, J. J. and Feng, H. J., "Combustion Synthesis of Advanced Materials," *Prog. Mater. Sci.*, **39**, 243 (1995).
- Mukasyan, A. S., Costello, C., Sherlock, K. P., Lafarga, D. and Varma, A., "Perovskite Membranes by Aqueous Combustion Synthesis: Synthesis and Properties," *Sep. & Purif. Tech.*, **25**, 117 (2001b).
- Mukasyan, A. S., Hwang, S., Rogachev, A. S., Sytchev, A. E., Merzhanov, A. G. and Varma, A., "Combustion Wave Microstructure in Heterogeneous Gasless Systems," *Combust. Sci. Tech.*, **115**, 335 (1996).
- Mukasyan, A. S., Lau, C. and Varma, A., Review: "Influence of Gravity on Combustion Synthesis of Advanced Materials," *AIAA J.* (2004, in press).
- Mukasyan, A. S., Lau, C. and Varma, A., "Gasless Combustion of Aluminum Particles Clad by Nickel," *Combust. Sci. Tech.*, **170**, 67 (2001a).
- Mukasyan, A. S., Marasia, J. A., Filimonov, I. A. and Varma, A., "The Role of Infiltration on Spin Combustion in Gas-Solid Systems," *Combust. Flame*, **122**, 368 (2000b).
- Mukasyan, A. S., Pelek, A. and Varma, A., "Combustion Synthesis in Gasless Systems under Microgravity Conditions," *J. Mater. Synth. Proc.*, **5**, 391 (1997a).
- Mukasyan, A. S., Pelek, A., Varma, A., Rogachev, A. S. and Jenkins, A., "The Effects of Gravity on Combustion Synthesis in Heterogeneous Gasless Systems," *AIAA J.*, **35**, 1821 (1997b).

- Mukasyan, A. S., Rogachev, A. S. and Varma, A., "Mechanism of Reaction Wave Propagation during Combustion Synthesis of Advanced Materials," *Chem. Eng. Sci.*, **54**, 3357 (1999a).
- Mukasyan, A. S., Rogachev, A. S. and Varma, A., "Microscopic Mechanisms of Pulsating Combustion in Gasless Systems," *AIChE J.*, **45**, 2580 (1999b).
- Mukasyan, A. S., Rogachev, A. S., Mercedes, M. and Varma, A., "Microstructural Correlations between Reaction Medium and Combustion Wave Propagation in Heterogeneous Systems," *Chem. Eng. Sci.* (2004, in review).
- Mukasyan, A. S., Rogachev, A. S. and Varma, A., "Microstructural Mechanism of Combustion in Heterogeneous Reaction Media," *Proc. Combust. Inst.*, **28**, 1413 (2000a).
- Munir, Z. A. and Anselmi-Tamburini, U., "Self-Propagating Exothermic Reactions: The Synthesis of High-Temperature Materials by Combustion," *Mater. Sci. Reports*, **3**, 277 (1989).
- Patil, K. C., Aruna, S. T. and Mimani, T., "Combustion Synthesis: An Update," *Curr. Opin. Solid State & Mater. Sci.*, **6**, 507 (2002).
- Pelekh, A., Mukasyan, A. S. and Varma, A., "Electrothermography Apparatus for Kinetics of Rapid High-Temperature Reactions," *Rev. Sci. Instrum.*, **71**, 220 (2000).
- Pelekh, A., Mukasyan, A. S. and Varma, A., "Kinetics of Rapid High-Temperature Reactions: Titanium-Nitrogen System," *Ind. Eng. Chem. Res.*, **38**, 793 (1999).
- Rogachev, A. S., Mukasyan, A. S. and Varma, A., "Thermal Explosion Modes in Gasless Heterogeneous Systems," *J. Mater. Synth. Proc.*, **10**, 29 (2002).
- Rogachev, A. S., Shugaev, V. A., Kachelmayer, C. R. and Varma, A., "Mechanisms of Structure Formation During Combustion Synthesis of Materials," *Chem. Eng. Sci.*, **49**, 4949 (1994).
- Thiers, L., Leitenberger, B., Mukasyan, A. S. and Varma, A., "Influence of Preheating Rate on Kinetics of High-Temperature Gas-Solid Reactions," *AIChE J.*, **46**, 2518 (2000).
- Thiers, L., Mukasyan, A. S. and Varma, A., "Thermal Explosion in Ni-Al System: Influence of Reaction Medium Microstructure," *Combust. Flame*, **131**, 198 (2002).
- Thiers, L., Mukasyan, A. S., Pelekh, A. and Varma, A., "Kinetics of High-Temperature Reaction in Titanium-Nitrogen System: Nonisothermal Conditions," *Chem. Eng. J.*, **82**, 303 (2001).
- Varma, A. and Mukasyan, A. S., "Combustion Synthesis of Advanced Materials", in ASM Handbook," *Powder Metal Technologies and Applications*, **7**, 523 (1998).
- Varma, A., "Form from Fire," *Scientific American*, **283**(2), 58 (2000).
- Varma, A., Li, B. and Mukasyan, A., "Novel Synthesis of Orthopaedic Implant Materials," *Adv. Eng. Mater.*, **4**, 482 (2002).
- Varma, A., Mukasyan, A. S. and Hwang, S., "Dynamics of Self-Propagating Reactions in Heterogeneous Media: Experiments and Model," *Chem. Eng. Sci.*, **56**, 1459 (2001).
- Varma, A., Rogachev, A. S., Mukasyan, A. S. and Hwang, S., "Complex Behavior of Self-Propagating Reaction Waves in Heterogeneous Media," *Proc. Natl. Acad. Sci. USA*, **95**, 11053 (1998b).
- Varma, A., Rogachev, A. S., Mukasyan, A. S. and Hwang, S., Review: "Combustion Synthesis of Advanced Materials: Principles and Applications," *Advances in Chemical Engineering*, **24**, 79 (1998a).