TECHNOLOGICAL FUNDAMENTALS OF SHS COMPACTING

G. A. Adadurov,* I. P. Borovinskaya, Yu. A. Gordopolov,
and A. G. Merzhanov

UDC 621.7.044.2

Different versions of the shock-wave treatment of SHS systems are considered. It is shown that a combination of SHS with explosive compaction is the most promising method as regards development of new materials. This method was used to produce high-density materials with diverse properties such as refractory hard alloys, high-temperature superconductors, etc. The method allows the structure formation to be controlled during the material synthesis, and this is demonstrated by producing fine-grained ceramics.

Self-propagating high-temperature synthesis (SHS) is an effective method for producing a wide class of materials. SHS is a highly exothermic interaction of chemical reactants in burning condensed phase [1, 2]. The thermal wave which is formed in a mixture of powdered reactants propagates spontaneously within the initial material and brings about chemical conversions that result in useful reaction products. The velocity of the synthesis wave is 10^{-3}-10^{-2} m/sec. High temperatures ($\sim10^3$ K) in the reaction zone facilitate the diffusion processes and yield products free of impurities.

In most of the SHS processes the reaction products appear as powders or porous blocks (cakes) subjected to subsequent milling and sintering by ordinary powder metallurgy methods. Fine porous (compact) materials are produced under high pressures, using presses or well-known shock-wave compacting [3, 4]. The latter treatment of SHS products has certain advantages. It does not require complicated equipment, which is replaced by explosives, it provides the highest pressures ever attained ($\sim10^5$ bar) in the powders, and equivalent loading conditions in porous blanks of a complex shape; the last factor is of special importance. This version of explosive treatment of SHS systems (final products) is the simplest. It was efficiently used, in particular, for commercial production of high-temperature superconductors (HTSC) from SHS powders [5-7]. With this method, the explosive compaction schemes tested with ordinary (non-SHS) powders, the experience gained in solving the problems associated with explosive compaction and long-time practice of implementation of this type of process can be used without any limitations. Specificity which may arise in using SHS powders is only attributed to the properties of the SHS products themselves.

Studies of the effect of high dynamic pressures generated by detonation on the initial SHS compositions and SHS processes are also very promising. These variants of shock-wave treatment of SHS systems seem more attractive since they allow high pressure to be applied to the materials at the structure formation stage during their synthesizing. It should be noted, however, that the former version has no direct relation with the SHS problem since the chemical reactions involved are not layer-by-layer self-sustained combustion. They occur either in the compaction shock wave (shock-wave synthesis) or embrace the whole material simultaneously as an aftereffect (shock-wave initiation). Shock-wave initiation and shock-wave synthesis are independent and rather extensive research fields, with their own history, and they are mentioned only for more thorough analysis of possible shock-wave consequences for exothermic compositions ordinarily used in SHS. This can be illustrated by the titanium diboride production in the exothermic titanium–boron powder system under shock wave [8].

---

*Deceased.

Institute for Structural Macrokinetics, Russian Academy of Sciences, Chernogolovka. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 63, No. 5, pp. 538-546, November, 1992. Original article submitted January 9, 1992.

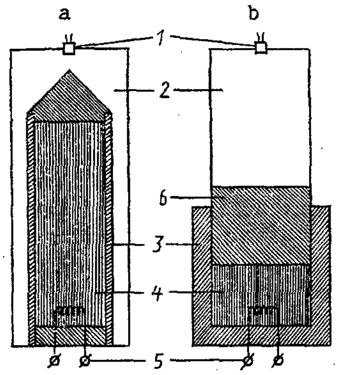

Fig. 1. Experimental schemes with explosive loading of the reaction products: 1) electric fuse; 2) explosive; 3) metal container; 4) initial mixture; 5) electric igniter; 6) massive piston.

Of special interest is a combination of SHS processes with explosive compaction. Application of high pressure to the heated reaction products can change (improve) the final product properties, since the simultaneous effect of high temperature and pressure behind the combustion wave front has a great impact on the material structure formation. Moreover, it eliminates the intermediate milling stage in producing blanks and articles which appear more compact since, due to high temperatures, the material remains plastic during compaction. The shock wave velocity is $\sim 10^3$ m/sec, which is several orders of magnitude higher than the combustion wave velocity. Therefore, the dynamic pressure acts on the material for a very short time, which allows a selective action of high pressure on any synthesis stage. If the characteristic width of the aftereffect region in the combustion wave exceeds the size of the initial charge, they occur in it as successive SHS stages. Then, varying the detonation initiation time, it is possible from the same initial SHS composition to produce relatively homogeneous final specimens with different structures and, consequently, different properties. When the width of the aftereffect region is comparable or smaller than the charge size, the shock-wave loading may give final specimens with a gradient of the structure and physicomechanical properties.

The idea of combining SHS with explosive compaction of the heated chemical reaction products appeared as early as the 1970s [2], but its development started quite recently [9-20]. By the early 1970s there had already existed different designs of ampoules for storing condensed materials in single- or multistage shock-wave loading and in dynamic isoentropic compaction, and various kinds of physicochemical conversions were implemented, including diamond and diamondlike boron nitride materials, described later in the reviews [21, 22]. The ampoule designs should have been modified by adding electric devices for igniting the reaction mixture, solving the problem of discharge of the gaseous reaction products from the ampoule and providing heat insulation of explosives from the burning synthesis products. At that time the main ideas of and the most promising trends in combining SHS with shock-wave loading were developed, high-acid carbides and borides of some metals from groups 4 to 6 of the periodic system were produced. In later studies [9-13] the authors investigated the shock-wave effect on SHS in the complex Ti–C–Ni–Cr system. In [14] the effect was studied for the hybrid Ti–N–O system, and the binary Ti–C and Ti–B systems were considered in [15-19]. In [20] dynamic compaction of heated SHS products was used to produce $TiC-Al_2O_3$ composites.

The simplest schemes of explosive loading experiments are shown in Fig. 1. In one case (Fig. 1a) the explosion products behind the sliding detonation wave front are compacted by a thin-walled cylindrical container. In the other (Fig. 1b) a normal falling detonation wave is used for acceleration of the metal piston that compacts the reaction products in a massive metal container. In both cases the reaction mixture is initiated by an incandescent coil in the bottom part of the container. In the top part of the container transducers are mounted which record the combustion wave passing. Detonation is initiated in the upper part of the charge at a definite moment of time after the transducers are operated. In experiments it is sometimes necessary to provide thermal insulation of explosives since the temperature of the reaction product behind the combustion front substantially exceeds the ignition temperature of most explosives. As was shown by the studies, the problems are not fundamental and can be solved by perfecting the container design. The combustion gas discharge problem can also be solved. All the schemes of shock-wave loading of the heated SHS products are the same as shown in Fig. 1 with slight modifications.

When SHS is combined with dynamic loading, the reaction mixture of a solid combustible and a solid oxidizer appears most convenient since it burns nearly without gas release. Even in the early studies some researchers tried to use shock-wave

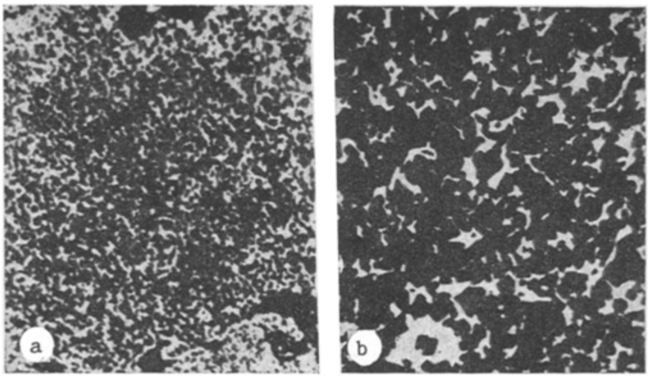

Fig. 2. The specimen structure produced from burning titanium and black powders with nickel and chromium additives under the action of high pressures on the reaction products: a) dynamic pressures; b) static pressures (COMPO specimen section), ×2000.

loading of different titanium carbide and boride SHS stages. The reaction mixture was placed into a cylindrical ampoule, 10 cm in length, with an inner diameter of 1 cm. The shock-wave compression was performed at the moment when the heating zone reached the opposite end of the cylindrical specimen. Thus, shock-wave loading acted on all the SHS stages. In some experiments pressure was as high as 70-500 kbar. The products were tested mainly by x-ray methods. The studies showed that in the heating and reaction regions there were products of a complex composition, and the x-ray patterns had lines which could not be identified. The products in the after-burning and structure formation regions were densely packed titanium carbide or boride rods. No new phases were found.

The results can be interpreted as follows. The heat released from SHS is combined with material heat induced by shock-wave compaction. After the pressure removal the specimen can be heated to 2000 K and above. It is cooled by heat conduction at atmospheric pressure. This results in annealing of new phases or high-pressure phases (if they were produced before). Therefore, the main emphasis was placed on application of dynamic pressures to the final SHS stages in order to produce dense specimens. Experiments with shock-wave compaction of carbides and borides of some metals from groups 4 to 6 of the periodic system, heated to 1500-3000 K after the synthesis, were conducted. The products were shaped as rods, tubes, and disks with a 97% density of the theoretical one. The articles have a homogeneous and fine-grained structure with 1-3 μm grain size. Similar results were obtained for THM-50 and THM-20. The microstructural analysis showed that titanium carbide grains were rounded and enveloped in a homogeneous nickel–molybdenum binding.

The differences in the action of dynamic and static pressures on the material structure formation in SHS compaction may be clearly demonstrated in a system of titanium and carbon (block) powders with nickel and chromium admixtures [9-13], since the system is well studied and widely used, in particular, for production of SHIM-3B materials. Both variants of shock-wave loading schemes shown in Fig. 1 were used. Apart from the initial mixture composition, the detonation delay time, geometrical size of the charge, and explosive type were varied in the experiments. The microstructure and phase composition of the materials produced were investigated with x-ray microanalyzers.

A comparative analysis showed that the material structure and properties of the materials produced depended essentially on the factors just enumerated and differed markedly from those of the materials obtained from the same initial substances under the action of static pressure. Figure 2a is a typical microphotograph of a specimen produced under dynamic pressure. For comparison (Fig. 2b) a microphotograph of the specimen is given which was produced from the same initial mixture under static pressure (a press). The structural studies showed that the structure of the materials produced with the explosive method consisted of finer, more homogeneous titanium–chromium carbide grains (the dark region). The microphotographs illustrate the range of a possible grain size variation with different explosive loads and detonation delay times, since the static pressures can be considered as a limiting case of a shock wave with a small amplitude and long duration. The material density amounted to 97-99% (of the theoretical one), and the hardness was 90-92 HRA. In [12] it was shown for the same system (Ti–C–Ni–Cr) that the production of fine-grained ceramics with 0.2-0.3 μm grain size was feasible, that opens the prospects of manufacturing ceramic materials which become plastic at relatively low temperatures.

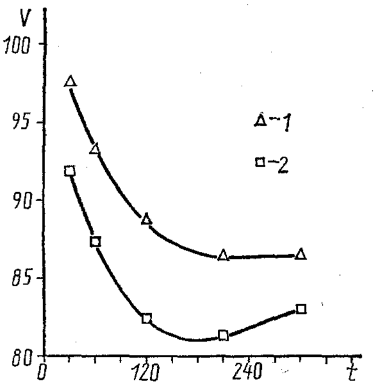

Fig. 3

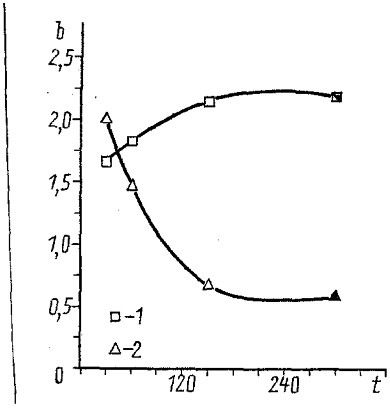

Fig. 4

Fig. 3. Plot of titanium carbide density V, % of theoretical value, versus the detonation delay time t, sec: 1) with annealing; 2) without annealing.

Fig. 4. Volume fraction of interfaces in titanium carbide b, μm^{-1}, versus detonation delay time t, sec: 1) phase interfaces; 2) inner interfaces.

The formation of fine-grained structures is a specific and practically important result of the shock-wave action on the heated SHS products. The effect may be ascribed to crystallization suppression (limitation of the grain growth) by the shock wave and the following rarefaction wave or by dynamic recrystallization. In [15] the feasibility of producing high-density fine-grained ceramics (with this method) was studied in the Ti–C system. The shock-wave procedure shown in Fig. 1a was used. The initial reactants (titanium and black powders) were thoroughly mixed in a ball mill. A stoichiometric composition of the powder mixture was used with a C/Ti ratio of 1.0. A charge cylinder, 1.6 cm in diameter and 15 cm in length, was obtained from the powder mixture by compaction. The compacted charge was inserted into the reactor, which consisted of a steel container (a cylindrical ampoule), 2-cm outer diameter, 0.2 cm wall thickness, and 15-cm length, located coaxially inside a cylindrical liner (a striker) with a certain clearance. The liner was a section of a circular tube made of soft steel with a diameter of 3 cm, wall thickness of 0.2 cm, and length of 15 cm surrounded by an explosive layer. The air space between the liner and container walls was provided because of the necessity of thermal insulation of the explosive. The clearance was also used for the released gas discharge. The explosive used in the experiments was a powder mixture of trinitrotoluene, ammonia, and barium saltpeter in a ratio of 14/36/50 with density of 1.1 g/cm^3 and detonation speed of 2.5 cm/sec. An explosive charge with a 2-cm layer thickness was used in all the experiments. Combustion of the initial exothermic composition (a compacted charge) was induced by a heat pulse (electric ignitor) in the bottom part of the ampoule; then the wave was recorded by a thermocouple mounted at the upper end of the ampoule for the best choice of the explosion time. The liner was set in motion by the products of slide detonation initiated at the upper point of the explosive charge at a certain time after passing the combustion wave. Shock waves were generated in the heated SHS products by a high-speed shock. The structure and properties of the materials were found to depend essentially on the detonation delay time, which was varied in the experiments between 30 and 300 sec. Some of the specimens were subsequently treated by heat in vacuum (10^{-3} Pa) at 1000°C for 300 min.

The microstructural properties of titanium carbide synthesized in the combustion mode and dynamically compacted were investigated by scanning electron microscopy, x-ray diffraction analysis, and other methods. Scanning electron microscopy has shown that the density and microstructural TiC properties strongly depend on the detonation delay time and, consequently, on the synthesized product temperature. As one can see from Fig. 3, with a long delay time the specimen density decreases. This trend may be ascribed to the fact that at large delay times the material under compaction ceases to be plastic since the brittle–ductile transition for TiC lies in the range of 800-1200°C. The data shown in Fig. 4 correlate with this fact. Figure 5 summarizes average grain sizes found in TiC specimens. The results show that production of high density fine-grained ceramics (1 μm grain size) is feasible. X-ray diffraction analysis has confirmed that the detonation delay time is of great importance since the parameter has a critical effect on the residual microstress level and the other microstructural properties of TiC.

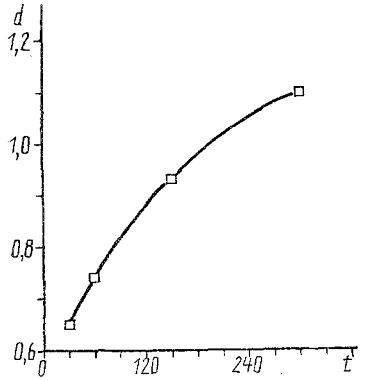

Fig. 5

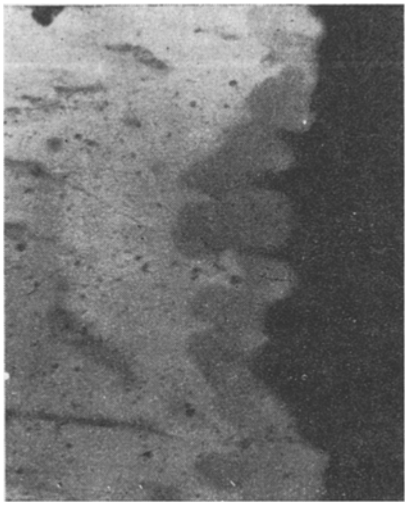

Fig. 6

Fig. 5. Average titanium carbide grain sizes d, μm, as a function of detonation delay time.

Fig. 6. Carbide film formed by the interaction of titanium particles and black particles under shock-wave conditions (COMPO specimen section), ×4000.

Interesting results are obtained if detonation is initiated at the time when the combustion wave has not yet reached the compacted charge edge. Then, in the same experiment with the same explosive loading parameters the effect of the shock wave on all SHS stages (that is, all synthesis zones, including the initial material region) can be observed. In [11] this situation was investigated in the Ti–C SHS system. The experiments have shown that the shock wave action on the initial SHS compositions gives different results, depending on the shock wave amplitude, the loading scheme, and the heat-removal conditions. As the pressure increases, other things being equal, compaction of the initial components and their deformation yielding metallographic textures are observed first, no chemical reactions take place at that time. As the amplitude increases, the shock wave activates the initial reactants, and a large number of defects is generated, crushing, intensive mixing, and heating of initial titanium and black particles occur. At that time the surface material layers react with the adjacent black particles to produce titanium carbide; however, after the advent of the rarefaction wave the reaction is stopped due to abrupt cooling of the system. A typical resulting structure is shown in Fig. 6. The titanium carbide film thickness (the gray region) is 2-3 μm, it separates titanium (the light region) and black (the dark region), there are no titanium melting zones, and the reaction is likely to occur in the solid phase.

As the peak pressure increases further, the conversion depth and the reactant temperature in the shock wave appear sufficient to compensate for the system cooling in the off-loading wave. "Quasivolumetric" initiation of the exothermic mixture occurs followed by the final thermal explosion reaction. Under certain conditions in locally initiated SHS systems under a shock wave loading, the cessation of the synthesis wave can be observed. The cessation of the chemical reaction may be ascribed in this case to a sudden increase of thermal conductivity of the material because of its compaction and, consequently, to enhanced heat removal. Analysis of specimens may be useful in studying the SHS mechanism with a correction for high-temperature action. This combustion wave quenching method was used in [14] to investigate the SHS mechanism in the Ti–N–O system.

It is noteworthy that the slightly modified schemes shown in Fig. 1 may be used for shock-wave compaction of the systems which react with intensive gas release. In particular, under such conditions dense $TaC-Al_2O_3$ and $TiC-Al_2O_3$ composites were produced from mixtures of tantalum and titanium oxides with aluminum and black. The specimen porosity was 2%. The carbide grain size was 2-3 μm, with the grains uniformly distributed within the oxide matrix. The articles produced from them were highly resistant in the heated oxygen and sulfuric acid environment.

Several attempts were made to produce high-density HTSC by combined SHS and dynamic compaction. The shock-wave loading scheme depicted in Fig. 1a was used. The ampoule design provided oxygen filtration through the reaction products of the $Y_2O_3-BaO_2-Cu$ exothermal composition. Systems with inner chemical oxygen sources were also tested. The electrophysical properties of HTSC produced in this way were at a level conventional for Y_{123}. Further studies along this line will probably give HTSC with high critical currents, up to 10^4 A/cm^2.

A combination of SHS with dynamic compaction allows SHS to be used as a pulse heater. This method may be used in some problems of high-pressure physics, particularly in diamond synthesis, which requires heating under pressure. In that case the materials and mixtures should be located (in tubes made of a refractory metal) within the reaction mixture, which, in turn, is placed into the store ampoule. The thermocouple measurements have shown that during SHS the material studied can be heated quickly (for seconds) to a very high temperature. Dynamic compaction of the SHS products and the material studied located in them can be realized at different stages: during the temperature rise, maximal heating or some time later when the temperature goes down. As was shown, pulse SHS heating can be used in various processes such as melting or vaporization of one or more components before compaction, thermal activation of the refractory component, etc., thus enhancing various physicochemical processes. In particular, as the studies have shown, in such conditions cubic boron nitride modification is formed but not a wurtsitelike one as is the case in ordinary shock wave compaction. In [23-25] the same pulse heating method was used. In those studies SHS in the Ti–C system served as a heat source to facilitate the shock wave compaction of SiC ceramics.

Summarizing all of the aforesaid, it may be stated that a combination of SHS with shock-wave compaction allows one to employ not easily realizable high-temperature pressure regions in the temperature–pressure system, both at high and low pressures. In experiments with matter conservation; however, serious limitations exist after pressure removal, since very high residual temperatures can convert the new synthesized phases into the ordinary ones. The limitations can be overcome, in principle, by quick quenching of the synthesized products or by providing conditions at which the products will be cooled at higher residual pressures.

In conclusion, it should be emphasized that the diversity of possible shock-wave aftereffects on the SHS systems provides prospects for their application in producing materials with various properties. As is known, the most important advantage of the SHS method is that it does not require an external power supply because the process is energized by inner resources. Since high pressures in explosive detonation can be achieved without expensive equipment, a combination of the two methods creating extreme conditions (high temperatures and high pressures) is of special practical interest. A combination of SHS and shock-wave treatment of the synthesized products (SHS/SWT) is a new effective method of producing new materials which cannot be reduced merely to compaction and moulding but also permits the high pressure to act on the structure formation of the material. However, effective control of the structure formation necessitates further systematic studies and perfection of the SHS/SWT method.

LITERATURE CITED

1. A. G. Merzhanov and I. P. Borovinskaya, Dokl. Akad. Nauk SSSR, **204**, No. 2 (1972).
2. A. G. Merzhanov, Self-Propagating High-Temperature Synthesis: Two Decades of Search and Findings (Preprint, Inst. Struct. Macrokinetics), Chernogolovka (1989).
3. D. S. Rainhart and D. Pearson, Explosive Treatment of Metals [Russian translation], Moscow (1990).
4. R. Prummer, Explosive Treatment of Power Metals [Russian translation], Moscow (1990).
5. V. M. Fedorov and Yu. A. Gordopolov, Studies of Explosive Compaction of SHS Ceramic HTSC (Preprint, Inst. Struct. Macrokinetic), Chernogolovka (1990).
6. V. M. Fedorov and Yu. A. Gordopolov, Shock-Wave Compacting of SHS Ceramic HTSP (Preprint, Inst. Struct. Macrokinetic), Chernogolovka (1990).
7. Yu. A. Gordopolov and V. M. Fedorov, Composite Materials of HTSC Ceramic Metal Stratified Titanium Produced by Explosive Compaction. Thermosynthesis Exhibition at the EEA USSR ("Resource Saving" Promotion Issue) (1990).
8. D. E. Maiden, G. Bianchini, H. Horing, and D. Kingman, Proc. DARPA/ARMY SHS Symp.. Daytona Beach, Florida (1985).
9. Yu. A. Gordopolov, R. M. Shikhverdiev, I. V. Molokov, Yu. V. Bogatov, I. P. Borovinskaya, and A. G. Merzhanov, Studies of Shock-Wave Loading of Heated Reaction Products in Combustion Wave Synthesis of Refractory Alloys (Preprint, Inst. Struct. Macrokinetics), Chernogolovka (1988).
10. Yu. A. Gordopolov, R. M. Shikhverdiev, I. V. Molokov, Yu. V. Bogatov, I. P. Borovinskaya, and A. G. Merzhanov, "The shock wave effect on the structure formation of combustion synthesized refractory hard alloys," 7th Int. Symp. on Explos. Treatment of Materials, Pardubice, Coll. Papers, Vol. 2 (1988).
11. Yu. A. Gordopolov, V. M. Fedorov, I. V. Molokov, R. M. Shikhverdiev, and A. G. Merzhanov, "Explosive treatment of SHS-products," 10th Int. Conf. High-Power Action on Materials. Lublana, Coll. Papers (1989).

12. Yu. A. Gordopolov, I. V. Molokov, R. M. Shikhverdiev, A. N. Pilyutin, O. Yu. Efimov, N. G. Zaripov, and L. V. Petrova, "Studies of shock-wave loading in combustion synthesis of refractory hard alloys," Proc. 16th All-Union Scientific Conf. Powder Metallurgy, Sverdlovsk (1989).
13. Yu. A. Gordopolov and A. G. Merzhanov, "The use of shock waves in the SHS research," Proc. 13th Int. Colloq. on Dynamics of Explosions and Reactive Systems, Nagoya (1991).
14. I. V. Molokov and A. S. Mukasyan, "Application of explosive action for SHS of gas–solid systems study," Proc. 1st Int. Symp. on SHS, Alma-Ata (1991).
15. R. M. Shikhverdiev, R. R. Kudashev, O. Yu. Efimov, N. G. Zaripov, and Yu. A. Gordopolov, "The shock-wave effect on Ti–C SHS system," Proc. 1st Int. Symp. on SHS, Alma-Ata (1991).
16. A. Niiler, L. J. Kecskes, T. Kottke, P. H. Netherwood, and R. F. Benck, Ballistic Research Laboratory Report No. RBL-TR-2951, Aberdeen Proving Ground (1988).
17. A. Niiler, L. J. Kecskes, and T. Kottke, in: Combustion and Plasma Synthesis of High-Temperature Materials. Z. A. Munir and J. B. Holt eds., VCH Publishers (1990).
18. A. Niiler, L. J. Kecskes, and T. Kottke, Proc. 1st U.S.–Japanese Workshop on Combustion Synthesis, Japan (1990).
19. H. A. Grebe, A. Advani, N. N. Thadhani, and T. Kottke, Proc. TMS Symp. on Reaction Synthesis of Materials, New Orleans (1991).
20. B. H. Rabin, G. E. Korth, and R. L. Williamson, J. Am. Ceram. Soc., **73**, No. 7 (1990).
21. G. A. Adadurov, Usp. Khim., **50**, No. 10 (1981).
22. G. A. Adadurov, Usp. Khim., **55**, No. 4 (1986).
23. T. Akashi and A. B. Sawaoka, Advan. Ceram. Mater., **3**, No.3 (1988).
24. T. Akashi and A. B. Sawaoka, Kogyo Kayaku, **49**, No. 4 (1988).
25. T. Akashi and A. B. Sawaoka, U. S. Patent, No. 4.655.830, Apr. 7, 1987.