Russians lead in ceramic production technologies

The Soviet Ministry of Tank Production found out about this revolutionary new technology, and classified it immediately. Robert Gallagher reports on the "ceramics gap."

After reports that Soviet facilities were producing finished ceramic cutting tools, heating elements, wire, plate, tubes, and other parts, as well as tons of ceramic powders, in a one-step process that takes a fraction of the time required by processes in the West, the U.S. Defense Department in 1983 commissioned the Systems Planning Corp. to investigate the technique, known in Russia as "self-propagating high-temperature synthesis," or as "gasless combustion synthesis" in the United States.

Modern ceramics are materials for the fabrication of parts for industrial, aerospace, and military equipment, that enable them to withstand higher temperatures and other stresses, or make them lighter. The space shuttle could not successfully reenter the Earth's atmosphere without the ceramic "tiles" that cover its surface. In industry, the use of modern ceramics will boost productivity by allowing the application of higher energy flux densities. However, among the bottlenecks to the widespread use of ceramics today, are the backward production methods in use in the West. The Russians have solved that production problem with a process that makes dominant Western methods look medieval.

Self-propagating high-temperature synthesis (SHS) involves igniting the energy-producing, exothermic reaction of molecular fusion of ceramic compounds, from powder mixtures of their elemental constituents. A small amount of energy (typically about 10 watt-hours), is applied at a high energy flux density (10^9 watts per square meter) through a tungsten wire, to ignite the reaction of formation of, for example, titanium carbide, from a mixture of titanium and carbon powders. If the powders are pressed into a desired shape, the result of the ignition will be a cutting tool or other finished product (**Figure 1**). U.S. national labs had looked at the process over a decade ago, but dismissed it then as unfeasible.

The national security issue

The reports written by Systems Planning Corp. and issued by the Defense Advanced Research Projects Agency (DARPA), document that the United States, Japan, and West Europe, now face a "ceramics gap" of significant national security importance. Self-propagating high-temperature synthesis of ceramic parts takes only minutes, and promises to completely eclipse existing U.S. ceramic part production methods, which presently require *days* to produce a single batch of parts, in an inefficient process little different from baking a cake.

A few years ago, the Soviet Ministry of Tank Production became interested in the new parts-production technology, and put the entire program

According to one DARPA report, recently reissued by Noyes Publications under the title, *Gasless Combustion Synthesis of Refractory Compounds,* SHS would benefit programs related to strategic defense, e.g., advanced space nuclear reactor fuels to power lasers, production of "lightweight, radiation protective armor" for satellites, etc. American ceramic powder and parts manufacturers interviewed by this writer, either had no awareness of the Soviet technology, or only very superficial knowledge of it.

The Russians have been working with the process for about 20 years, and according to the DARPA reports, now have nine plants in operation; each produces a thousand tons per year of titanium carbide, silcon nitride, and supercanthol

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The Soviet Ministry of Tank Production is interested in using the new ceramics technology for manufacture of precision cutting tools. Now the United States is in a race to catch up. Shown here: the Soviet T-72 tank, on parade in Moscow.

($MoSi_2$). The Russians know that they have caught the West flat-footed in this technology: They are presently licensing use in the West of a three-reactor unit which produces a continuous average output of 90 kilograms per hour of ceramic powders.

Soviet scientist A. G. Merzhanov has led the Soviet program since the 1960s, and has reportedly financed a good deal of the work himself, through sale of ceramic powders that his laboratory staff produces in a small plant, to other government industrial bodies.

Merzhanov now works directly with the Soviet Ministry of Tank Production, which is reportedly interested in the technology for machine tool applications. The Soviet program has apparently gone through two stages. First, from the 1960s to 1977, Merzhanov and his staff developed the production of ceramic powders. This is now a commercial industrial process in Russia. Since 1977, Merzhanov has placed his emphasis on combustion synthesis of finished parts and castings. In the course of this, he has developed a process for simultaneously producing parts of high quality, by surrounding them with a reaction process producing a ceramic powder. This process is known as the "chemical furnace."

Los Alamos National Laboratory has now confirmed the Russian claims, and other national labs have discovered that the ceramic powders produced in Russia are equal in quality to the best U.S. or Japanese powders, but with a production cost about two-thirds less. According to an industry newsletter, *High Tech Materials Alert,* the Japanese have begun to master the technology; Osaka University and Sumitomo Electric Industries are reportedly close to commercializing fabrication of engineering-quality ceramic parts, using self-propagating high-temperature synthesis under high pressure.

DARPA is apparently convinced that the process can be immediately commercialized in the United States, and that there is no need to await further research. Systems Planning Corp. has been entrusted with transferring the technology to U.S. industry.

Self-propagating high-temperature synthesis approximates a perfectly ordered industrial process. That is, it exploits properties of nature that can only be mastered under specific conditions of the ordering of technology. It has the unusual characteristic that it releases more energy than it consumes; in the process reactors that the Soviets are now building, thousands of times more energy. **Figure 2** shows the basic physical properties of self-propagating high-temperature synthesis, and some examples of the energy transformation rates of SHS processes (expressed in output per kilowatt-hour). These figures represent only those conditions attained so far. The potential energy transformation rate is unlimited.

One of the most impressive characteristics of self-propagating high-temperature synthesis, is its universality. The method can produce not only ceramic powders and parts, but also ceramic castings, and can be used for welding, industrial equipment repair at the factory site, and surface hardening of industrial equipment, such as turbine blades. **Figure 3** lists all SHS applications, with examples of the products and services provided.

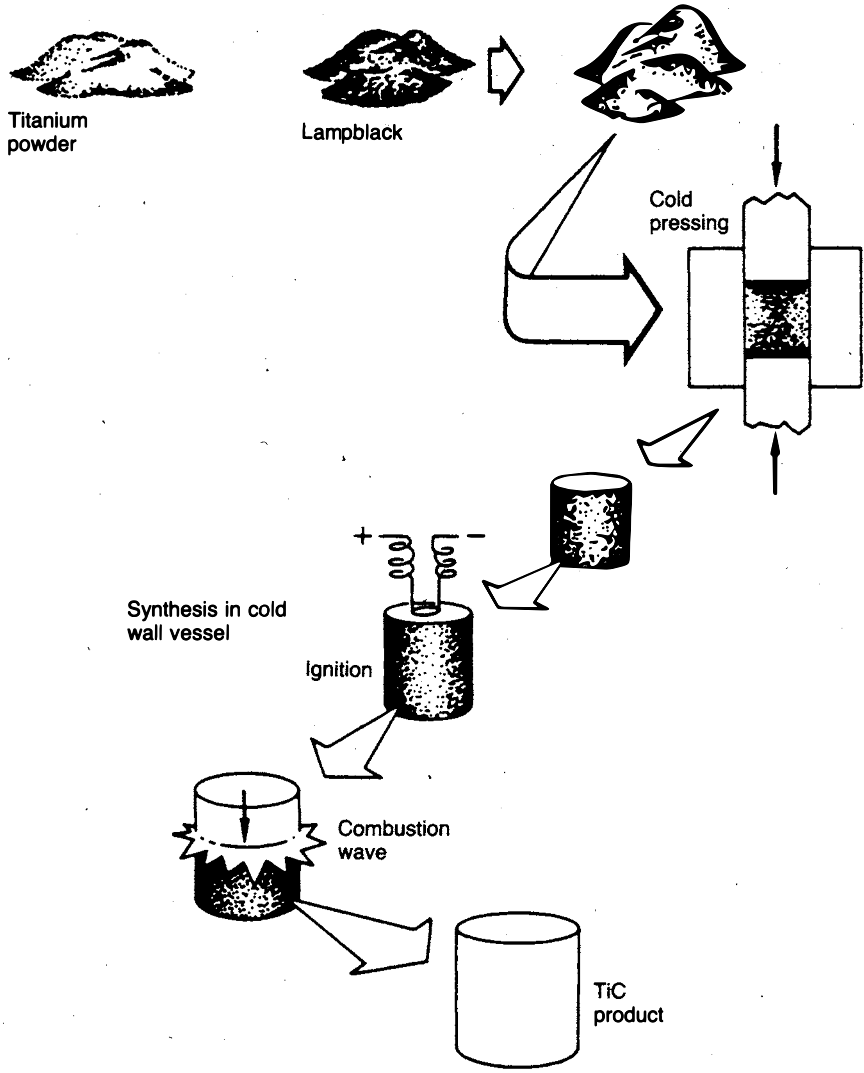
Present U.S. technology for both ceramic powder and parts production is antiquated. Typical processes for powder production use industrial furnaces that are run in batch cycles that take days. The compound is retrieved from the furnace in the form of a clinker that must then be ground and crushed to produce the end-product powder. This process introduces impurities from the grinding equipment, which must then be leached out chemically.

Typical of these, is the Acheson process for production of silicon carbide. In this process, invented a century ago by Edward Acheson, pure glass sand (silica) and high grade petroleum coke are mixed and poured into an electric "Acheson furnace." Current passed through the mixture between graphite electrodes, reacts the material to form a silicon carbide ingot. Sawdust must be mixed in with the silica and coke to provide pores for the escape of carbon monoxide gas. The process liberates 1.4 tons of carbon monoxide for every ton of silicon carbide produced. Early in a run, the furnace operator will take a long pole with a torch on the end, and hold it up to the side of the furnace, to ignite the CO and reduce the hazard of explosion or asphyxiation. A typical run takes 36 hours, and then the ingot must be cooled for 24 hours and ground into powder.

Ceramic part production technologies are in just as bad shape. The most advanced is known as injection molding. In this process, ceramic powders are molded with a wax into

FIGURE 1

Production of ceramic parts



Self-propagating high-temperature synthesis can produce finished ceramic parts in a simple and rapid process. First, powders of elements (such as titantium and carbon) are mixed in the ratio appropriate to a desired ceramic compound (e.g., titanium carbide). Then the powder mixture is pressed into the shape of the desired finished product. A small quantity of electricity is passed through the mixture to ignite the reaction of molecular fusion of the powder mixture; the reaction then propagates as a combustion wave through the shape. When the combustion is complete, the part is finished.

Source: W. Frankhouser et al., Gasless Combustion Synthesis of Refractory Compounds, *Noyes Publications, Park Ridge, N.J., 1985* the desired shape, in a machine similar to the kind used for plastic injection molding; this process takes about a minute. However, the part must then be processed through an oven for three days to remove the wax binder, and then be fired in a high-temperature furnace over a period of two days, before complete. Two of the days of the five-day cycle are required to allow semi-finished products to cool.

The Advanced Refractory method

Recently, Advanced Refractory Techonologies, Inc. of Buffalo, New York, has commercialized a more modern, *continuous* process for ceramic powder production. **Figure 4** shows that, in terms of labor productivity, the process developed by Advanced Refractory is competitive with SHS. It has the additional advantage that it does not require expensive powders of the elements to combine into the ceramic compound, but can use simple, abundant oxides (such as silica, or titania) in the feedstock for powder production.

In the case of silicon carbide powder production, as described in a lecture by Harvey Blakeley of Advanced Refractory:

> Silica sand and graphite are first mixed together with binders to form an intimate mixture. This feed is then introduced into an electric furnace at about 2,000°C. The feed material instantly reacts to form silicon carbide and carbon monoxide. The CO is exhausted out of the furnace, and burned much the same way as volatiles are at cracking plants in the refinery industry. The silicon carbide exits the furnace as additional feed is introduced.

Advanced Refractory has used their proprietary process to produce and market powders of:
boron carbide
silicon carbide

FIGURE 2
Physical parameters of self-propagating high-temperature synthesis

Basic physical parameters		**Output per kwh**
Energy flux density applied	2×10^9 W/m_2	Potentially infinite
Released (TiC)	10^8 W/m_2	
Ignition energy required	7-14 Whrs	
Energy released (TiC)	850 Whrs/kg	
Examples		
Ceramic powders		
Titanium carbide	3 tons (30 kg batches)	
The chemical furnance		
Tungsten carbide parts and titanium carbide powder	0.4 tons (batches of 3 1-kg parts and 1.5 kg powder)	

Sources: J. Holt & Z. Munir, "Combustion Synthesis of TiC," Los Alamos National Laboratory, pre-print, Dec. 1984; Systems Planning Corp., "Advanced Materials Technology Project Semi-Annual Technical Report," DARPA Report Nos. SPC 1059 June-Nov. 1984, SPC-1086 Dec.-May 1985; Frankhouser et al., Gasless Combustion Synthesis of Refractory Compounds.

FIGURE 3
Products produced by self-propagating high-temperature synthesis

1) Ceramic powders
titanium carbide
zirconium carbide
boron carbide
titanium carbonitride
silicon nitride
tungsten carbide
various hydride powders
sulfide and selenide powders

2) Finished ceramic parts
High-temperature industrial heating elements
Titanium nickelide wire, plate, tubes used aboard Soviet aircraft
Titanium carbide cutting tools

3) The chemical furnace: simultaneous production of ceramic and metal-alloy finished products and powders

Part compound	**Powder product**
Tungsten carbide	Titanium carbide
Tri-molybdenum silicide	Titanium silicide
Tantalum carbide	Titanium carbide
Tantalum dicarbide	Titanium carbide
Tri-niobium aluminum	Aluminum nickelide (pelletized)
Tri-niobium germanium	Aluminum nickelide (pelletized)
Copper aluminum	Titanium diboride
Di-copper aluminum	Titanium diboride

4) Gasless combustion ceramic castings
Bi-layer pipe
Castings of 94 different compounds have been made, including:
- chromium molybdenum carbide
- titantium nickelide
- borides (e.g., molybdenum boride)
- carbides (e.g., tungsten carbide)
- silicides of niobium, vanadium, etc.
- various complex compounds (e.g., molybdenum boronitride)

5) Explosive welding
Bonding of double-layer pipe

6) Industrial equipment repair

7) Surface-hardening with SHS coatings
Turbine blades

Source: Frankhouser et al.

FIGURE 4

Comparison of SHS with other existing ceramic powder and ceramic part manufacturing methods

	EFD (W/m²)	kg/kwh	Process Time	kg/ manhour	kg/ m³-hr.	kwh/ manhour
Ceramic powders						
SHS	10^9	3,000	Minutes	45	1,900	0.015
Advanced refractories	3×10^5	0.083	Minutes	30[1]	60	375
Acheson process	10^5	0.28[2]	3 days[2]		4	
Ceramic parts						
SHS	10^9	10,000	Minutes			
Injection molding	10^5	1	5 days			

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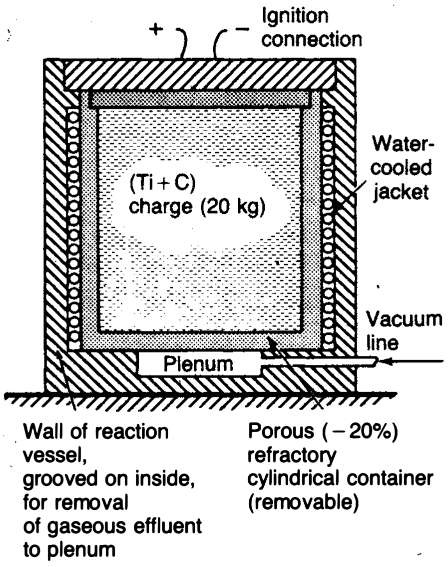
[1] Based on one operative tending six furnances, each with an average output of 5 kilograms per hour.

[2] Includes energy consumption and process time only up to production of silicon carbide ingots.

Sources: Advanced Refractories Inc.; Battelle Columbus Laboratories; "Breaking the Mold," Technology *magazine, Nov.-Dec. 1981; J. Holt & Z. Munir, "Combustion Synthesis of TiC"; Systems Planning Corp., DARPA Report Nos. SPC 1059, SPC-1086; Frankhouser et al.*

FIGURE 5

Soviet synthesis of titanium carbide powder



Self-propagating high-temperature synthesis was first developed in Russia for the production of ceramic powders. The process is similar to that for part production (Figure 1). First, powders of elements, such as titantium (Ti) and carbon (C), are mixed in the ratio appropriate to a desired ceramic compound (e.g., titanium carbide). Then the powder mixture is placed in a reaction vessel. A combustion wave of molecular fusion is ignited with a small quantity of electricity applied to the powder mixture through the walls of the vessel. When the combustion is complete, the ceramic powder is allowed to cool for a few minutes and then retrieved from the vessel.

Source: Frankhouser et al.

silicon nitride
titanium carbide
titanium diboride
zirconium carbide
zirconium diboride

Many of these materials are used for the fabrication of parts for nuclear power plants.

The Advanced Refractory unit furnace has a rated power of about 60 kilowatts with a volume of about three cubic feet. Depending on the ceramic powder being produced and other conditions, the unit can yield 1 to 10 kilograms of powder product per hour. Only a few hundred grams of material are inside the reactor at any one time. According to Keith Blakeley of Advanced Refractory, one operator could run six furnace modules, and each module can produce 25 tons per year with three work shifts in a five-day workweek. He adds that a fully automated plant could produce 2 million tons of powders per year, with a total workforce of only 15 persons, but present production volume would not require this.

Comparative advantages of SHS

Nonetheless, the data of physical economy shown in **Figure 4** show that when all criteria are taken into account, self-propagating high-temperature synthesis is a more advanced species of ceramic powder and part production.

1) Its *energy flux density* is orders of magnitude higher than other processes.

2) Its *energy transformation rate* (output per unit of energy consumption) is orders of magnitude greater than other processes.

3) Its *process time* for part production is orders of magnitude shorter than that of injection molding.

4) The reactor *throughput rate* is orders of magnitude greater than conventional processes, and even 30 times that of Advanced Refractory's.

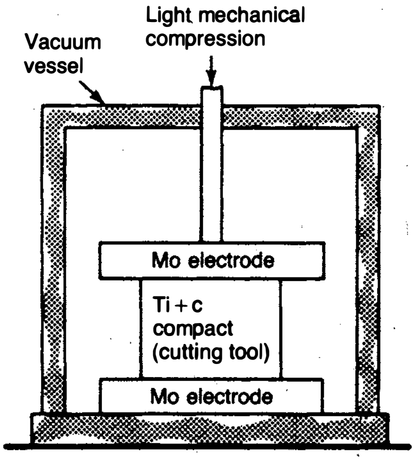
It is particularly interesting to note, that SHS provides an example of a process that is so highly organized, that the *energy applied per operative* declines dramatically, though the energy flux density applied increases.

Production of ceramic powders: The process begins with powders of the elements (or molecules) to react, mixed in an appropriate ratio, and placed into a reaction vessel filled with an inert, oxygen-free atmosphere. (For production of titanium carbide, a mixture of titanium and carbon powders is used.) Electrical energy (about 10 watt-hours) is applied to a portion of the material near the surface, through a tungsten wire or graphite strip (**Figure 5**). This small amount of energy excites the exothermic (energy-producing) reaction of formation of the molecular compound desired. The reaction then propagates completely through the mix. The energy *released* is about 850 watt-hours per kilogram of reacting material. It would be difficult to construct a case where the energy released was less than the energy applied. In fact, it is not out of the question that some electric power could be produced with SHS, in the course of producing ceramic materials and parts. The greater the quantity of the reactant, the faster the reaction proceeds and the purer the product.

One advantage of SHS, is that the reactants achieve a high temperature quickly and cool down quickly, as they

FIGURE 6

Increased pressure boosts quality of product

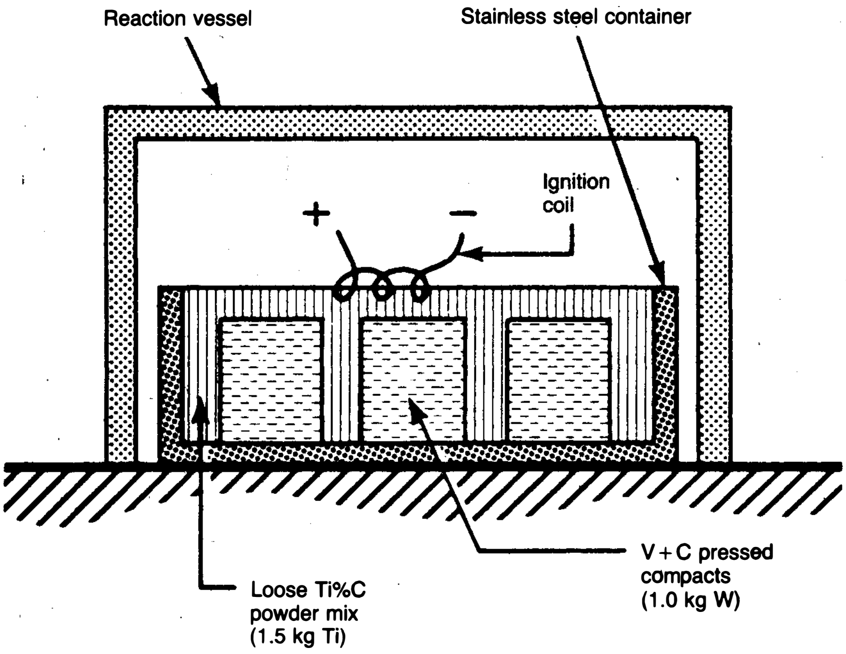


Mechanical application of light pressure in self-propagating high-temperature synthesis of ceramic parts, can improve the quality of the product. The figure shows two molybdenum electrodes applying pressure to a pressed shape of titanium (Ti) and carbon (C) powders for a cutting tool. The initiating current is also passed through the electrodes.

Source: Frankhouser et al.

FIGURE 7

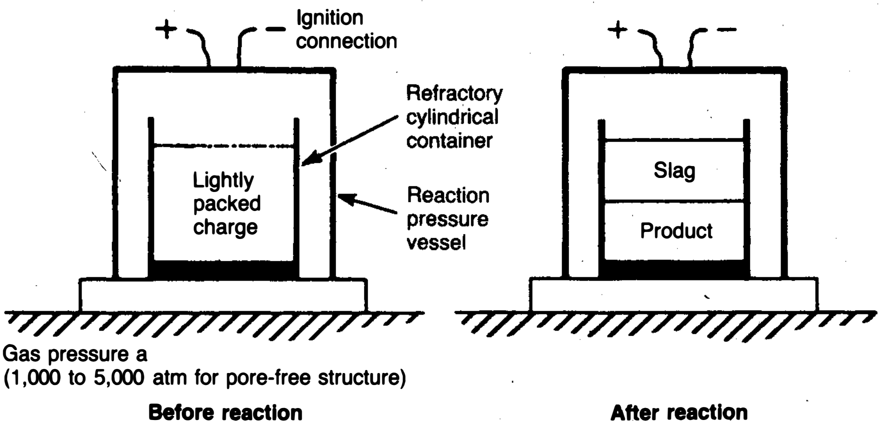
The 'chemical furnace'



The Russians have extended self-propagating high-temperature synthesis of ceramic parts to compounds whose reaction rate is relatively low, which presents some difficulties to ordinary SHS part production methods. The process, known as the "chemical furnace," combines ceramic powder and part production; pressed shapes of powders for parts are placed in a vessel, and then covered with a powder reactant mixture whose reaction proceeds faster than that of the powders making up the pressed parts. In the figure, three 1-kilogram titanium carbide shapes are surrounded by a 1.5-kg blanket of tungsten and carbon powders that is ignited, and reacts to form tungsten carbide, and drives the synthesis of the titanium carbide parts.

Source: Frankhouser et al.

FIGURE 8
Ceramic castings



Source: Frankhouser et al.

In addition to parts production, the SHS process that promises the biggest "payoff," is self-propagating high-temperature synthesis of ceramic or metal alloy castings. As shown in the figure, a reaction vessel is loaded with a mixture of a metal oxide (e.g., chromia), powders of elements the metal is desired to combine with (e.g., carbon and molybdenum) and a reducing agent (e.g., aluminum). SHS is initiated as usual, but the product is a casting. A slag of the oxidized reducing agent (in the case shown, alumina) floats above the product.

impart their energy to adjacent reacting material. This minimizes crystal grain growth, whereas in the slow-cool Acheson process, crystal growth is maximized.

SHS has produced powders in batches of tens of kilograms. The set of three 16-liter reactors referred to above, can provide a continuous output of 90 kilograms per hour, and require two operatives per shift to supervise the reactors and reload them. The three-reactor set occupies approximately six square meters of floor space. John Kiser, a former State Department official, licenses the reactors in the United States. Their size ranges from 2.5 to 30 liters. The powders are used for the fabrication of ceramic parts in the conventional way, or for lubricants, electrolytes, and for grinding and polishing applications. The Russians have replaced tungsten with SHS-produced titantium carbide in cutting tools, and also fabricate it into industrial diamonds. Silicon nitride is used for rocket nozzles and ceramic auto parts, and supercanthol for high-temperature industrial heating elements.

Finished parts: In this application, the elemental powders are pressed into the shape of a final product, as is done in powder metallurgy. The ignition energy is then applied to the surface of this so-called green compact part. The application of pressure to the combusting green compact may improve the quality of the result (**Figure 6**). With this technique, up to 96% theoretical densities have been achieved for titanium carbide tool bits. The larger the part, the faster the reaction rate and the better the quality of the product.

Parts produced with SHS include titanium nickelide wire, plate, and tubes used aboard Soviet aircraft for fuel and air lines; this material is produced in batches of hundreds of kilograms. High-temperature industrial heating elements are made from molybdenum silicide and titanium silicides. Other products are synthesized from borides, carbides, nitrides, ferroalloys, and master alloying compounds used in specialty steel-making. Because of classification restrictions, the details of physical economy for this process and for the chemical furnace are not available.

The chemical furnace: In this self-propagating high-temperature synthesis process, pressed powders for parts are placed in a vessel, and then covered with a powder reactant mixture whose reaction proceeds faster than that of the powders making up the pressed parts (**Figure 7**). In one example, three 1-kilogram titanium carbide "green compacts" are surrounded by a 1.5-kg blanket of tungsten and carbon that is ignited, and reacts to form tungsten carbide and drive the synthesis of the three titanium carbide parts. Other examples are shown in **Figure 3**.

Gasless combustion castings: Ceramic casting is the latest technology development in self-propagating high-temperature synthesis, and is apparently still in the research and development stage. In this process, SHS ignition of exothermic reactions produces a reaction of a metal oxide with carbon or some other material, while magnesium, aluminum, or zirconium serves as a reducing agent. The process produces a slag of alumina, magnesia, or zirconia, in molten form, above the cast product (**Figure 8**). Of course, this slag can itself be a useful material. **Figure 3** lists castings made with this process. Castings can be made without pores, if produced under elevated pressure or centrifugal conditions. Products produced with this method include bi-layer pipe. An appendix to *Gasless Combustion Synthesis of Refractory Compounds* lists 94 compounds of which the Russians have made castings.

Portable ceramic equipment repair technology: SHS electrodes and powders can be taken to the site of a ceramic fracture, and applied to repair the defect.