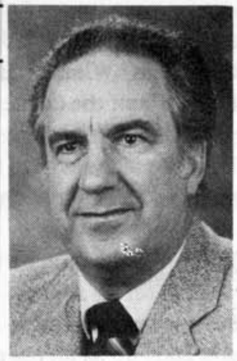
Interview: Birch Holt



The commercial potential and applications of SHS

Birch Holt is the Lawrence Livermore National Laboratory principal investigator of the program in self-propagating high-temperature synthesis (SHS).

EIR: Suppose a company or a government agency such as the state of Illinois decided to build a ceramics industry based on this technology. How would they begin a program to build a pilot plant, based on either the Russian work or the work that's been done at Livermore and Los Alamos? What would they need to do this, in manpower and equipment?
Holt: We feel that in our combustion synthesis research, which has been going on for about five years, and which has been funded by DARPA, that we have reached a place where some of the ideas can be commercialized.

EIR: Please give examples of ceramic compounds that could be produced and what applications.
Holt: For example, alpha-silicon nitride, aluminum nitride, titanium nitride, and hafnium nitride, are all produced by a process which is different from what the Russians have done. We have received or have applied for patents on this process (see **Figure 3**). Composite powders such as titanium carbide-alumina, and titanium nitride-alumina, are other good examples of materials that we believe can be produced more economically.

Silicon nitrides will be used in materials for ceramic engines. Aluminum nitride is used for electronic substrates. The sialons (silica aluminum-oxide nitride) are also used for ceramic engine applications. The composites have applications for cutting tools, grinding media, abrasives, and armor.

We are looking forward to an industrial technology transfer period. We have held one meeting with industry, and we are holding another meeting on June 5, in which we are telling industrial people about the work that has been done here at the laboratory, and pointing out the different products and processes which might have immediate applications to industry. There is still much research to be done on combustion synthesis of these refractory materials. We hope to form a consortium which will bridge the gap with industry. Again, how long it's going to take, and how much money, all depends on the particular chemical system.

EIR: What are some of the original applications of SHS developed at LLNL?
Holt: We have done a lot of work with the nitrides. Nitride materials are used in electronic devices, as high-temperature crucibles for melting metals, and as cutting tools and grinding media. To produce silicon nitride or aluminum nitride powders by the SHS process had required the application of 1,000 times atmosphere pressure for nitrogen gas to achieve complete combustion and conversion of the metal to a nitride. We have succeeded in lowering the required pressure to 100 atmospheres. Second, we have been able to produce aluminum nitride in solid form, directly from aluminum and nitrogen. Third, we developed an entirely new approach for the synthesis of metal nitrides by using solid sources of nitrogen. We mixed titanium powder with sodium azide, NaN_3. The mixture easily ignites and burns to completion in a few seconds to produce pure titanium nitride powder. Due to the generation of high temperatures, the sodium is vaporized during the reaction. With this experimental procedure, we have obtained 100% yields of TiN, HfN, and ZrN. We extended this method to the synthesis of solid solution. Titanium carbo-nitride and various composite systems such as zirconium boride-zirconium nitride, and titanium-nitride-alumina. The titanium carbo-nitride has applications as a hard, high-temperature, and corrosion-resistant material. The zirconium boride-zirconium nitride product is a superplastic material, while titanium-nitride-alumina can be used in cutting tools.

EIR: How have the ceramic companies responded to the LLNL program?
Holt: Some companies are already doing work in combustion synthesis. It looks like some are also willing to sponsor further research and development. However, in general the response has been sluggish, and the ceramic companies aren't paying sufficient attention.

EIR: Let's take a specific example. Suppose a company wanted to set up a pilot plant to produce silicon nitride parts. You mentioned the ceramic engine application. There is also an application in machine tools. How would they go about doing that? What would they need to do?

Holt: First, the concept that we've developed in the laboratory has to be evaluated as to the economics of the process. If those are favorable, then it has to be taken to the pilot plant stage and developed there, and then on to full production.

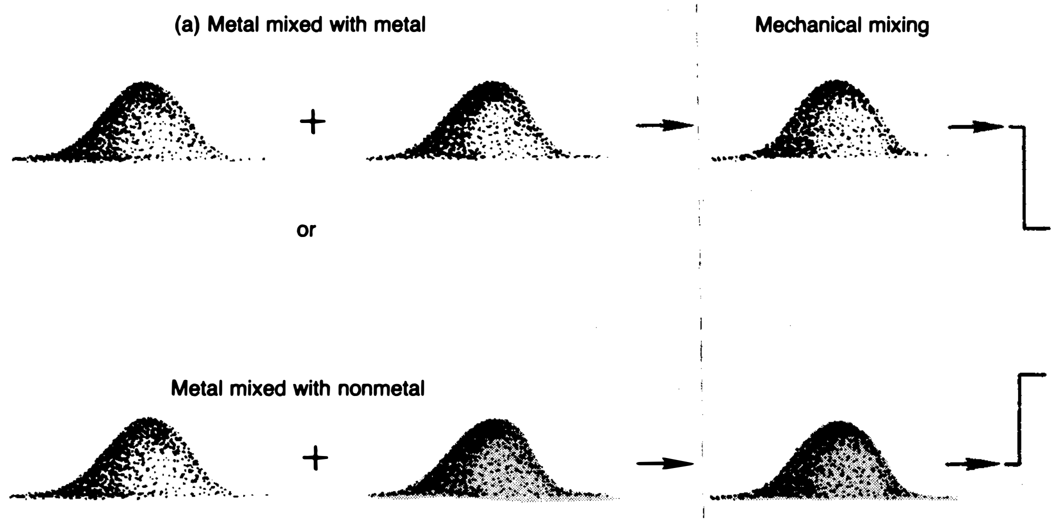
EIR: What would be involved in the pilot-plant stage? You want to set up a plant—and I'm talking about a pilot plant, a demonstration plant—-where it begins like a big laboratory, and ends up as an operating small plant. We could take two examples: One would be the production of titanium carbide powder, which is something that I would guess is pretty much nailed down; and the other example would be the one we just discussed, production of silica nitride parts.

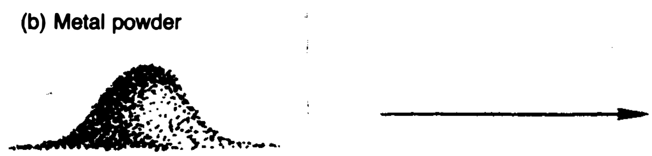
Holt: The Russians have pretty well outlined what they have done with titanium and carbon; they have used titanium metal and carbon black, as the two reactants. And they react them in large containers, and produce kilogram batches. They use refractory containers, which can withstand high temperatures. They have been able to control the process so that they can get full reaction of the mixture.

Some question whether the process would be economical if you use titanium, because it's more expensive, rather than titanium oxide. However, you can start with titanium oxide (TiO_2), and magnesium and carbon to make titanium carbide and magnesium oxide and then leach out the magnesium oxide. Then you'd have a fine grain titanium carbide. So, you can get around using the more expensive elements, by going to other reactions.

FIGURE 3

Sequence of operations in combustion synthesis





The relatively simple process begins with the preparation of the reactants. The reactants can be (a) mixtures of two metal powders or of metal and nonmetal powders or (b) a metal powder that can be combined with reactive gases. The powders are cold pressed into a cylinder or may be ignited as loose powder. After a heated tungsten coil ignites the surface, the combustion wave moves rapidly through the material as the product is synthesized.

EIR: How would the magnesium oxide be leached out?
Holt: With hydrochloric acid.

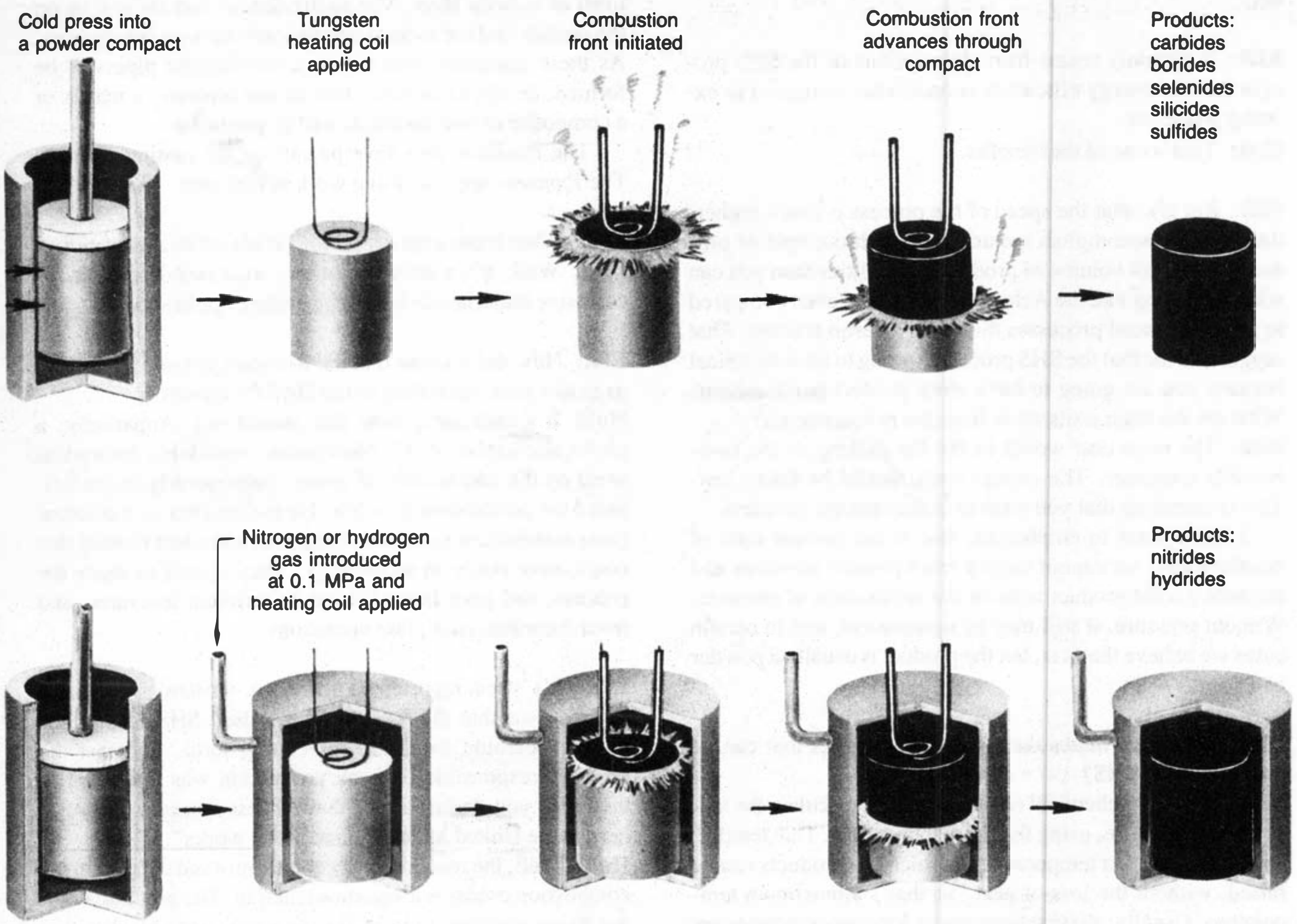
EIR: Is that easily enough done?
Holt: Yes, that should be an economical process.

There are investigators in our country, who are working on similar reactions. Raymond Cutler at Ceramatec is working on the silica, magnesium, and carbon reaction to produce a silicon carbide-magnesium oxide composite. The magnesium oxide is leached out leaving a submicron silicon carbide.

EIR: So it seems some companies are already getting into this.
Holt: There are some industrial companies now doing work in combustion synthesis, but there is not very much information available.

EIR: Let me ask you how long does it take to leach out this magnesium oxide? Is that a quick process? Does it take hours or days?
Holt: No, it's a fairly quick process.

EIR: So the process you have outlined is clearly a nice way to make titanium carbide powder without having to begin with titanium metal. And if somebody could do that then they would be in a fairly good spot competitively.
Holt: Let me mention another process, which may be even more economical. That is the synthesis of ceramic composite



materials. For example, you can produce titanium carbide-aluminum oxide composites. If one starts with titanium oxide, aluminum, and carbon, the reaction produces titanium carbide-aluminum oxide, which is a cutting tool material.

Now, if you react these ingredients in the usual SHS process, the product is a powder, not a dense product. We have been able to densify in the same operation by using high pressure techiques.

The greatest benefit would be to be able to densify using chemical means instead of having to apply pressure. I don't believe anyone has been able to develop that process so far. In general, composite materials are one of the more promising areas, nearest to commercialization.

In all cases, if you want to make a ceramic product like silicon nitride, for example, you have to look at the SHS process and see how it would compare with the conventional way of making silicon nitride. In some instances, conventional ways may still be the best for making the powder. Each individual chemical system has to be examined on its own merits. I think that there are certain systems, where even making a powder with the SHS process, would be economical.

EIR: It certainly seems from descriptions of the SHS process that the energy efficiency is enormous compared to existing processes.
Holt: That's one of the benefits.

EIR: But also that the speed of the process is much higher, that you can accomplish a much greater throughput of production per unit volume of production facilities than you can with something like the Acheson process and even compared to more advanced processes than the Acheson process. That suggests to me that the SHS process is going to be economical because you are going to have more product per manhour. What are the main costs aside from the raw materials?
Holt: The main cost would be for the making of the combustible container. The capital costs should be fairly low. This is assuming that you want to make ceramic powders.

I really want to emphasize, that at the present state of development, we cannot simply react powder mixtures and produce a solid product without the application of pressure. Without pressure, it still may be economical, and in certain cases we believe that it is, but the product is usually a powder or a porous solid.

EIR: What determines the variety of products that can be produced with SHS?
Holt: For every chemical reaction, we can calculate the adiabatic temperature, using thermodynamic data. That temperature is the highest temperature to which the products can be raised, without the loss of heat. So that's a maximum temperature. Usually, these temperatures for many reactions are very high, in the range of 2,000 to 4,000° centigrade. With most of these reactions, the temperatures are below the melting points of the refractory products. If they are below the melting point temperature, then the process by which they are densified is by the application of pressure. If the combustion temperature happens to be above the melting point temperature of the product, then the product will be molten or fused. It's possible, then, to ca

Now, we have not done any work on casting; the Russians have done considerable work on that process. They claim that they can cast monolithic bodies.

Most of the research with castings has been done by the Russians with thermite-type reactions. They mix an oxide with a reductant metal, such as aluminum, and with carbon. For example, we might have a mixture of molybdenum oxide, aluminum, and carbon. They would be mixed together and then ignited. They will burn very vigorously and the products are molybdenum carbide and aluminum oxide. The combustion temperature is above the melting-point of both of those materials. If they are ignited in a centrifuge, or in a horizontal refractory tube which is rotating at a rapid speed, then the centrifugal force will push the heavier material, to form an outside layer. The molybdenum carbide will be on the outside and the molten alumina will form an inside layer. As these materials cool down, a two-layered pipe will be formed. In other reactions, that do not separate, a matrix or a composite of two materials will be produced.

The Russians also have patents on the casting process. The Japanese are also doing work in that area.

EIR: What is this pipe useful for? What are its applications?
Holt: Well, it's a refractory pipe, so it could be used for corrosive materials or high-temperature applications.

EIR: How did it occur that the Russians got so far ahead of us in this area, according to the DARPA reports?
Holt: It's interesting how this started out. Apparently, a physical chemist, A. G. Merzhanov, was doing theoretical work on the combustion of gases. Subsequently he investigated the combustion of solids. He realized that as a result of these combustion reactions, there was a product formed that could have utility in technology. They started to study the process, and later farmed it out to different institutes, and from there into pilot plant operations.

EIR: It's been reported in the book written by William Frankhauser that the Russians have used SHS to produce titanium carbide tool bits, for cutting tools, and that the ministry responsible for tank production was interested in this. Can you describe how that process works, or how we here in the United States assume that it works?
Holt: Well, the reaction between titanium and carbon, in the combustion mode, is a vigorous reaction. The product, without doing anything to it, is always a very porous solid, or a powder; it is not a solid. So they have used the titanium

carbide as an abrasive material, or grinding material. There isn't much information in the Russian literature about their making the actual tool bits; they show pictures of them, where they have densified the material into the final product.

As stated before, we have been looking at techniques by which you can both synthesize and densify the materials, such as titanium and carbon, by the application of pressure, applied either simultaneously to the reaction or right after the reaction, while the products are still at high temperature.

EIR: In the SHS process, you apply a certain amount of energy to a mixture that's been prepared to be transformed into a ceramic powder, but you end up releasing a lot more energy than you applied, correct?
Holt: Yes.

EIR: In fact, I did a calculation that shows that you'd really have to go to a lot of trouble to set up a situation where you would release less energy than you applied?
Holt: You can't do that, the reaction would not be self-sustaining.

EIR: It wouldn't propagate and. . .
Holt: you wouldn't be able to ignite it.

EIR: What are the problems in producing silicon carbide or boron carbide, both of which are very important ceramic materials?
Holt: Both reactions are very weak exothermally. You can't ignite these because the adiabatic temperature for silicon carbide is only about 1,500° centigrade, and for boron carbide is 850° centigrade. So you can't get them to ignite in the same way as you can titanium and carbon. Because the chemical heats available from their reactions are not high enough, it is impossible for them to occur in a self-propagating mode.

EIR: Boron carbide is one of the materials used in nuclear power reactors. Is there any way these problems can be circumvented in the SHS process?
Holt: You circumvent those problems in one of several ways. First of all, you could raise the initial temperature. This would require the heating up of the reaction beforehand. Instead of reacting at room temperature, you'd react at some higher temperature. That would require a furnace, and that decreases the advantage of the process.

Another thing that you could do is to drive it with another reaction. This is what the Russians refer to as a "chemical furnace." They surround a reactant which has a low exothermicity with one which has a very high exothermicity. For example, put boron and carbon in a crucible made up of titanium and carbon, ignite the titanium and carbon, then you can drive the boron carbide reaction using the energy released by the titanium carbide reaction, and making boron carbide and titanium carbide (see **Figure 4**).

Boron carbide could also be synthesized in a thermite-type reaction, involving boron oxide and magnesium and carbon, which combust to form boron carbide and magnesium oxide.

EIR: And so you produce two products?
Holt: Yes.

EIR: What other advances do you expect might come out of the SHS process?
Holt: One of the biggest applications in which we want to do some work, is the formation of new materials. Inherent in the process are high temperatures and very high heating rates, and those are the very characteristics that could be used in the formation of metastable or nonequilibrium materials. One focus for research would be the ability of these inherent characteristics of the process to form metastable or nonequilibrium crystal phases. The Russians refer to one of those, cubic tantalum nitride, which was formed by this process before it was formed by high pressure. But this is really a high pressure form. That was the first indication that SHS does have applications to making new materials. Because of the high temperatures that are realized in the reactions, and particularly the high rates of heatings, which may vary from 10^3 to 10^6 degrees centigrade per second, and with the possibility of controlled cooling, then it is possible to form new phases. This should be a very worthwhile avenue of research.

FIGURE 4
Schematic representation of Soviet "chemical furnace" synthesis