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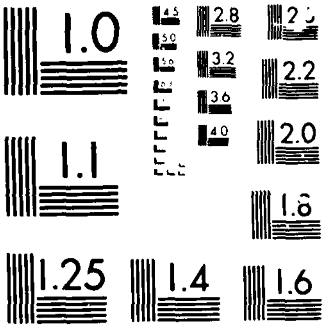
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SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS): CURRENT STATUS AND FUTURE PROSPECTS

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MATERIALS CHARACTERIZATION DIVISION

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ABSTRACT

Self-propagating high-temperature synthesis (SHS) is a rather unique and intriguing method for preparing refractory materials. Its major advantages over conventional methods include the generation of temperatures in excess of 2500'C without the need for high temperature furnaces, rapid processing times, and self-purification of volatiles.

Past work in this area has focused primarily on the reaction process using combustion engineering approaches. Efforts are now underway in the United States and internationally to focus on the production of materials by this process. Hence, focus is shifting from the process to the product, and studies are taking on a materials science approach. The combination of combustion technology and materials science will provide for a rapid evolution of this technology. Considering this, it is anticipated that SHS processing will be used to commercially produce a variety of advanced ceramic and ceramic composite materials in the near future.

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SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS): CURRENT STATUS AND FUTURE PROSPECTS

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1.0 INTRODUCTION

Conventional ceramic processing normally consists of two stages: first, a powder having the desired physical and chemical characteristics is prepared, then it is heated to promote interparticle bonding (sintering) and densification. This generally requires high temperatures (1200-2000'C) and controlled atmospheres (vacuum - high pressure). Often the sintering stage may require up to several days to carry out.

An alternative method termed "Self-Propagating High-Temperature Synthesis (SHS)" is described in this review. The process utilizes the heat generated by an exothermic reaction between precursor components to densify the resulting reaction products. The heat generated by these reactions is capable of producing temperatures in excess of 2500'C. Since the heat is "self-generated," high temperature furnaces are not required. Processing times are on the order of seconds/minutes rather than hours/days as in conventional processes. In addition to these attributes, products produced by SHS tend to be of higher purity than the starting materials since the high temperatures vaporize the volatile contaminants. Further, intractable borides and carbides can be produced by this technique.

2.0 SHS TECHNOLOGY

2.1 Definitions

2.1.1 Pyrochemical Technology

Many chemical reactions are accompanied by the release of heat and are referred to as exothermic reactions. If enough heat is generated, the reaction may be self-sustaining after initiation. Burning wood is a typical example.

Self-sustaining exothermic reactions are included in the broad field of pyrochemical technology. The various reactions are further classified according to their energy output, reaction or burning rate and volume of emitted gas (1-3). Table 1 illustrates the differences between four categories of self-sustaining exothermic reactions: burning, pyrotechnics, propellants, and explosives.

Table 1. PYROCHEMICAL TECHNOLOGIES COMPARISONS

	COAL/AIR	PYROTECHNICS	PROPELLANTS	EXPLOSIVES
BURNING RATE (cm/s)	10^{-6}	10^{-2}	10^{-2}	$1\text{-}10\times10^{3}$
ENERGY OUTPUT (J/g)	10^{4}	10^{3}	10^{3}	10^{3}
GAS VOLUME (cm^3/g)	-	10-100	10^{2}-10^{3}	10^{3}

2.1.2 SHS Technology

Pyrotechnic reactions produce solid reaction products with smaller amounts of gas than explosives and propellants (10 cm^3/g compared to 1000 cm^3/g) and are often referred to as "gasless" reactions. Common sparklers used on Independence Day are typical examples. These reactions can be further classified as follows:

I. Thermite Type: Oxidation-Reduction Reaction

Example: $2Al + Fe_2O_3 = Al_2O_3 + 2Fe$

II. Compound Formation from its Elements:

Example: $Ti + 2B = TiB_2$

III. Combinations of I and II Above:

When these reactions are used to synthesize materials they have been called Self-Propagating High-Temperature Synthesis (SHS) reactions.

2.1.3 Process Versus Product

The major aspect of SHS which contrasts with other self-sustaining exothermic reactions is that SHS reactions are carried out to produce a desired solid PRODUCT. Other pyrochemical technologies generally utilize aspects of the reaction PROCESS, such as generating heat, radiation or gases. There has been much work done by pyrochemical and chemical engineers on studying the reaction process itself. This has resulted in a thorough understanding of the effects of various processing variables (e.g., composition, particle size, etc.) on the reaction processes (e.g., reaction rate, adiabatic temperatures). In contrast, SHS technology is relatively new, and the effects of processing variables on product-properties are not yet optimized or even well understood.

2.2 Requirements for SHS Reactions

Three basic requirements must be met in order to produce a self-propagating reaction. First, the reaction must be strongly exothermic. Heats of reaction on the order of 40 kcal/mole are generally sufficient. Table 2 (4) lists heat of formations for several compounds reacted from their elemental constituents. Secondly, a liquid phase should form during the reaction in order to enhance diffusion. The optimum condition occurs when the calculated adiabatic temperature (T_{ad}) is at or above the melting point (T_{mp}) of the desired product. Table 2 lists calculated adiabatic temperatures and melting points for a variety of compounds. Generally, when the

Table 2. THERMODYNAMIC INFORMATION ON PHASES PRODUCED BY "SHS"

Phase	Tmp (K)	Tad (K)	Enthalpy Change H_{298} (Kcal/mole)	Heat of Formation Q (cal/g)
TiB_2	3190	3190*	66.8	962
TiC	3210	3210*	44.13	736
SiC	3100	1800	16.5	412
B_4C	2620	1000	13.8	250
WC	3070	1000	8.4	43
AlN	2500	2900*	64.0	1560
Si_3N_4	2170	4300*	176.0	1260
TiN	3220	4900*	80.75	1300

*Tad > Tmp
Information from Reference 4

calculated adiabatic temperature is less than the melting point of the compound, self-propagating reactions will not occur without preheating prior to initiation (5) unless a low temperature eutectic exists.

Finally, in order for the reaction wave to propagate, the rate of heat dissipation must be less than the rate of heat generation; otherwise the reaction will be quenched. Heat dissipation is largely affected by particle size, bulk density, and surface/volume ratio. Hardt has reported that the powders should be fine enough to limit heat transfer into the unreacted material (6).

2.3 SHS Reaction Character

In principle, there are two different methods for producing an SHS reaction. One is to initiate the reaction locally and produce a propagating reaction-wave, while the second is to react the entire bulk material instantaneously. These methods will be discussed separately.

2.3.1 Propagating Reactions

An example of using a propagating reaction for material synthesis is shown in Figure 1. Generally, powders of the reactants are mixed for the proper stoichiometric ratio and then pelletized at room temperature. The reaction is initiated at an outer surface by supplying a short intense burst of energy (e.g., spark, laser, heat, etc.). A reaction wave then propagates through the compact. Complete reaction of the sample occurs within a matter of seconds. Many reactions can be carried out in air. Since an inert atmosphere eliminates surface oxidation, most reactions are carried out in controlled environments.

Studies have been done to evaluate the structure of the reaction zone in a propagating reaction (7). Figure 2 shows the four zones which occur under equilibrium adiabatic conditions. More complex structures occur for nonequilibrium

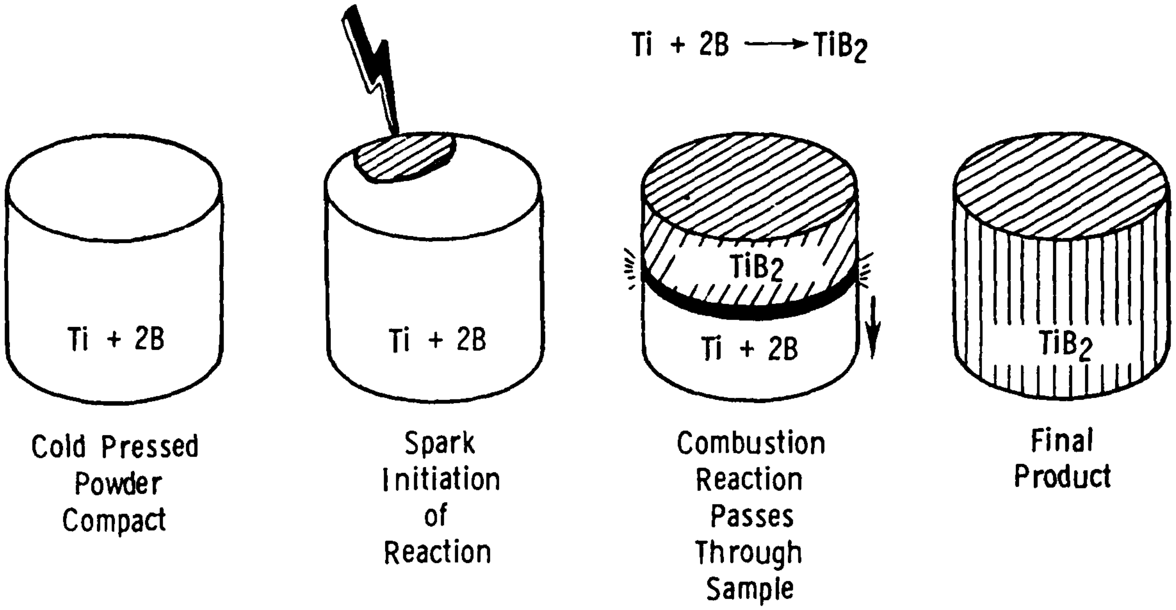

Figure 1. SHS reaction scheme.

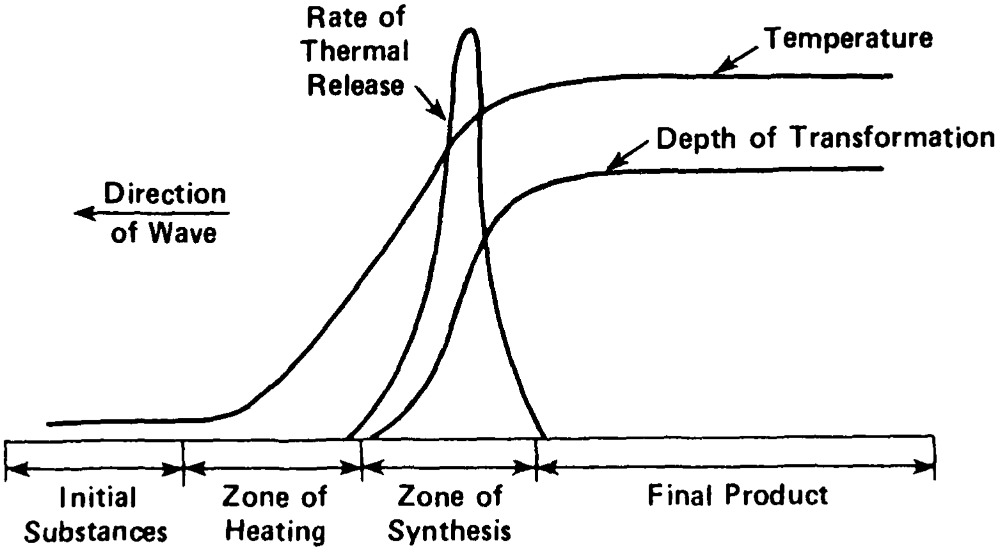

Figure 2. Equilibrium adiabatic structure of synthesis wave (References 7 and 13).

conditions. In addition to changes in the wave structure, the mode of propagation can vary depending on whether equilibrium or nonequilibrium conditions occur. Some of these include pulsating, spiraling, and fingering modes. A good review of the Soviet studies on conditions which cause the variety of wave structures and propagating modes has been published by Frankhouser (8).

2.3.2 Bulk Reactions

There have also been studies involved with bulk initiation of an SHS reaction. In this case the powder mixture is rapidly heated in a conventional furnace until the exothermic reaction is initiated. As in the propagating case, the reaction-generated heat increases the temperature of the compact to >2500'C. Thus, an advantage of this technique is using conventional furnaces to obtain very high temperatures (>2500'C). Many of these studies have been done under pressure to enhance sample densification (9-11).

2.4 SHS Reaction Products

2.4.1 Physical Character

The products of SHS reactions range from sintered bodies to extremely porous "foam-like" material. The sintered materials are generally only about 50% dense unless pressure is applied during the reaction process. With the aid of pressure, densities greater than 95% theoretical have been obtained for a variety of materials (9-11).

When densification is desired one must consider the porosity generated by these reactions. Table 3 lists several compounds along with the volume changes which occur when reacting from their elemental constituents. For example, if a titanium and boron powder mixture were packed such that no porosity remained, then reacted to produce TiB_2, the product would contain 22% void space. This aspect of SHS is a major factor for making the production of dense bodies difficult. The foam-like material which forms can have greater than 70% porosity. Generally, samples will expand during reaction. This expansion is a result of volatilization and/or the diffusion process (12).

Table 3. VOLUME CHANGES WHEN COMPOUNDS ARE FORMED FROM THEIR ELEMENTS*

$MoSi_2$	-40.6	NbC	-17.4
SiC	-28.4	ZrC	-17.0
$TiSi_2$	-27.5	Cr_3C_2	-16.9
TiC	-24.1	WC	-16.3
TiSi	-22.9	CaB_6	-15.8
TiB_2	-22.3	B_4C	- 7.9
ZrB_2	-20.4	AlB_{12}	- 6.1
TaC	-18.1	BeB_{12}	- 4.2

*Courtesy of Dr. Roy Rice,
U.S. Naval Research Laboratory

2.4.2 Chemical Characteristics

Research workers in the Soviet Union have reported the production of over 200 different compounds including solid solutions and metastable phases (13). Table 4 (7) is a partial listing. In addition to single-phase products, multiphase products can also be produced; these are typical of "thermite-type" reactions. Table 5 lists a variety of thermite-type reactions used to produce multiphase products. The major advantage of these reactions is the use of lower cost reactants (e.g., oxides versus metals). Early studies by Walton (14) demonstrated the use of these reactions to produce cermets. They may also be used to produce interesting ceramic-matrix composites with unique microstructures.

Table 4. SOME REFRACTORY COMPOUNDS PRODUCED BY SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS)

STRONGLY EXOTHERMIC	
CARBIDES:	TiC, ZrC, HfC, VC, NbC, Ta_2C
BORIDES:	TiB_2. ZrB_2, HfB_2, VB_2. NbB_2, TaB_2, MoB
NITRIDES:	AlN, BN, Si_3N_4, TiN, ZrN, Ta_2N
SILICIDES:	$TiSi_3$, ZrSi, $MoSi_2$
CHALCOGENIDES:	MgS, $NbSe_2$, $TaSe_2$, MoS_2, WS_2
HYDRIDES:	TiH_2, ZrH_2, NdH_2, CsH_2, IH_2
ALUMINIDES:	NiAL, CoAl
WEAKLY EXOTHERMIC	
CARBIDES:	B_4C, Al_4C_3, SiC, Mo_2C
BORIDES:	MoB_4, Mo_2B, W_2B_5
GERMANIDE:	$NbGe_2$

Information from Reference 7

Table 5. EXAMPLES OF THERMITE TYPE REACTIONS USED IN SHS PROCESSING

		REFERENCE
METAL + OXIDE PRODUCT		
Cr_2O_3+ 2 AL	2CR + AL_2O_3	16
Fe_2O_3 + 2 AL	2Fe + AL_2O_3	16
OXIDE + BORIDE OR CARBIDE PRODUCT		
TiO_2 + B_2O_3 + 3 1/3 AL	TiB_2 + 1 2/3 Al_2O_3	16
SiO_2 + C + 1 1/3 AL	SiC + 2/3 AL_2O_3	16
BORIDE + CARBIDE PRODUCT		
B_4C + 3Ti	$2TiB_2$ + TiC	30,22
B_4C + 3Zr	2ZrB2 + ZrC	30

3.0 RESEARCH PRIOR TO 1980

3.1 Soviet Union

Soviet investigators first began to publish results from their SHS activities in 1967, following the discovery by A. G. Merzhanov at the Institute of Chemical Physics in Chernogolovka that condensed phase combustion reactions can readily produce refractory materials. Since that time the Soviets have focused on investigating the reaction process and evaluating which compounds can be produced. In their reports there is minimal property data on the final products. Several good reviews on the Soviet studies have been written, in particular Crider (13), Frankhouser (8), and Merzhanov (7).

3.2 United States

Past studies on self-propagating reactions in the United States have focused on utilizing properties of the reaction process. Examples include their use as igniters, fuses, flares, propellants, and local heat sources (e.g., batteries, welding). These investigations consisted of both experimental and theoretical studies; see for example Hardt (6,15). At MTL, early work focused on the $Zr-BaCrO_4$ reaction used in heat paper for thermal batteries. Specifically, the effect of the physical characteristics of fine (<10 m) zirconium powder on the reaction kinetics was investigated (16).

Two early product-oriented studies in the U.S. were carried out by Walton (14) and Shepard and Croft (9). The former studied thermite reactions to produce cermet composites. The latter utilized "impulse-resistance sintering" combined with pressure to produce dense materials in the Ti-B-C system.

3.3 Australia

In 1968 Stringer (10) reported on a technique he termed "reaction pressing," which consisted of conventionally heating the reactants until the exotherm occurred, while simultaneously applying pressure. He had success in producing dense ZrB_2 and $MoSi_2$ materials. His report notes the importance of starting-powder characteristics on this process, in particular particle size and volatile content.

4.0 CURRENT RESEARCH EFFORTS

4.1 United States

4.1.1 Funding Sources

The United States Department of Defense has taken an active interest in promoting and financially supporting SHS technology. This is due to their belief that SHS is a viable method for producing advanced ceramic materials, especially intractable borides and carbides. Recently, a workshop (17) on SHS sponsored by the Defense Advanced Research Projects Agency (DARPA) and the Army Research Office (ARO), and organized by the U.S. Army Materials Technology Laboratory (MTL) was held. The workshop succeeded in bringing together for the first time all the U.S. SHS researchers. A list of all the known organizations doing work in SHS is given in Table 6. Some of these organizations are subcontractors to a three-year program (started July 1984) funded by DARPA to Lawrence Livermore National Laboratory for $1.6 million; MTL is the monitor of this program.

Table 6. CURRENT KNOWN UNITED STATES SHS EFFORTS

DEPARTMENT OF DEFENSE	PRINCIPAL INVESTIGATORS
U.S. ARMY MATERIALS TECHNOLOGY LABORATORY	McCAULEY, CORBIN, MOON
ARMY BALLISTIC RESEARCH LABORATORY	NIILER
ARMY FOREIGN SCIENCE AND TECHNOLOGY CENTER	CRIDER
NAVAL RESEARCH LABORATORY	RICE
DEPARTMENT OF ENERGY	
LOS ALAMOS NATIONAL LABORATORY	BEHRENS
LAWRENCE LIVERMORE NATIONAL LABORATORY	HOLT
ACADEMIA	
UNIVERSITY OF CALIFORNIA-DAVIS	MUNIR, PHILPOT
GEORGIA INSTITUTE OF TECHNOLOGY	WALTON, LOGAN
RICE UNIVERSITY	MARGRAVE
STATE UNIVERSITY OF NEW YORK-BUFFALO	HLAVACEK
INDUSTRY	
CERAMETEC	CUTLER
GENERAL ELECTRIC	ZAVITSANOS
SYSTEM PLANNING CORPORATION	FRANKHOUSER
LOCKHEED	HARDT
N. J. DAMASKOS, INC.	SENFT
FUNDING SUPPORT	
U. S. ARMY RESEARCH OFFICE (ARO)	
DEFENSE ADVANCED RESEARCH PROJECTS AGENCY (DARPA)	
U.S. ARMY MATERIALS TECHNOLOGY LABORATORY (MTL)	

4.1.2 USA Research

Since 1980, American efforts have focused on using SHS for materials synthesis and processing, two examples being the studies of McCauley et al. (18) and Holt (19). One aspect of current research involves the analysis of the SHS "reaction process" information, generated by combustion researchers, in terms of materials synthesis and processing. Conditions which may optimize the reaction process (e.g., propagation rate, etc.) do not necessarily provide optimum conditions for usable final products. The other aspect of recent U.S. efforts involves experimental research focused on materials synthesis and processing. The previously mentioned DARPA contract to Lawrence Livermore National Laboratory is a major effort in this direction. Other studies currently underway include the production of powders (20), dense bodies (11,21), and the influence of starting powder characteristics (22). The most effective mechanism for rapid advancement in the use of SHS for materials processing will involve the dedicated collaboration of pyrotechnic engineers and theoreticians with materials scientists. The Army/DARPA workshop was a first attempt at providing a mechanism for this interaction.

4.2 Foreign Studies

Recently, the Japanese have reported on a technique called a "centrifugal thermite process" (23). This method utilizes a thermite-type SHS reaction to coat the interior of metal tubes with ceramics. They have had success in bonding an Al_2O_3 layer to the interior of steel tubes. Another SHS technique recently reported is termed "high-pressure self-combustion sintering" (24). This technique combines exothermic reactions with extremely high pressures to produce dense ceramics. They have reported success in producing 95% dense TiB_2 with a 5- m grain size.

Currently, the Soviet Union has over 30 organizations investigating SHS reactions and is mass-producing TiC abrasive materials (13). Silicon nitride, TiB_2 and B_4C powders appear to be at pilot-plant stage and are available in the United States through a firm specializing in Eastern Bloc Technology Transfer (25). There is no published evidence on the Soviets producing dense materials directly by SHS.

A recent publication from a team at the Industrial Materials Research Institute of the National Research Council of Canada indicates success in producing cermet (ceramic and metallic phases) powders (26). These powders were subsequently used in a hot-isostatic pressing operation to produce dense TiB_2 material. They suggest that SHS produces a powder having the sintering aid (metal) distributed on a much finer scale than conventional mixing.

5.0 FUTURE EFFORTS

Interest in SHS in the United States and world-wide is rapidly growing. This is primarily due to the perceived potential for cost-and-energy reduction in producing powders and sintered final products of a variety of refractory materials, especially intractable borides and carbides. SHS may also be advantageous because it can be utilized to produce equilibrium and nonequilibrium single phase, multiphase and composite materials of high purity and unique microstructural characteristics.

Many other ceramic materials-processing techniques involve exothermic reactions. Carbothermal reduction of Al_2O_3 to AlN is one example, while the formation of reaction bonded silicon nitride (RBSN) by the nitridation of silicon is another. The single-step reaction sintering of ALON (27) from a powder mixture of Al_2O_3 and AlN also involves an exothermic reaction. In these processes, the mechanisms surrounding the exothermic reactions have been ignored in the various models which simulate the processes. At best, empirical techniques are used to prevent runaway or self-sustaining reactions. It is now clear that a unified model must be developed to simulate the sintering of powder systems that involve exothermic reactions. This will only be possible by the combined efforts of pyrochemical (chemical) engineers and materials scientists working together. Derivation of accurate analytical and atomistic models for SHS systems can be used to predict optimum conditions for SHS reactions, and also be used to improve the sintering of nonSHS systems that contain an exothermic reaction. A recent report by Coble (28) addresses the role of chemical reactions on "activating" the sintering process.

Besides accurate modeling of SHS reactions, major experimental efforts must be initiated on relating the precise, total characteristics of starting powders and phase equilibria considerations (formation of liquid and vapor phases and melt recrystallization) to the kinetics of the process and, in particular, the characteristics of the final product. Implicit in this is a detailed understanding of the thermal balance and heat transfer mechanisms. These considerations will become even more important when scale-up of the SHS processes commences.

The utilization of pressure applied via a centrifuge process, gravity, intensified atmosphere or inert solid material (hot pressing, etc.) is a direct way of achieving low porosity material by SHS. However, since the major benefit of SHS is in cost reduction, every effort should be expended in minimizing the complexity of the processing apparatus. It is the authors' opinion that low porosity materials can eventually be produced via pressureless-SHS through optimization of the processing variables. This can be achieved only through detailed understanding of the SHS process. Therefore, techniques must be derived to quantitatively analyze the in-process (during reaction) characteristics of the reactions. Analysis of only starting materials and final products ignore transient characteristics which are probably extremely important.

In summary, the future focus for a major effort in SHS will involve the combined efforts of pyrochemical engineers and materials scientists in the following areas:

a. analytical and atomistic models,

b. final-product relationships to starting materials, phase equilibria and melt-recrystallization phenomena,

c. thermal balance and heat transfer mechanisms, and

d. in-process characterization techniques.

6.0 SUMMARY

Self-propagating High-Temperature Synthesis (SHS) is a rather unique and intriguing method for preparing refractory materials. Its major advantages over conventional methods include the generation of temperatures in excess of 2500'C without the need for high temperature furnaces, rapid processing times, and self-purification of volatiles.

Past work in this area has focused primarily on the reaction process using combustion engineering approaches. Efforts are now underway in the United States and internationally to focus on the production of materials by this process. Hence, focus is shifting from the process to the product, and studies are taking on a materials science approach. The combination of combustion technology and materials science will provide for a rapid evolution of this technology. Considering this, it is anticipated that SHS processing will be used to commercially produce a variety of advanced ceramic and ceramic composite materials in the near future. Recently, (29) TiB_2 has been produced by this technique without pressure that is analogous to the state-of-the-art for RBSN in the late 1960's.

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