Gasless Combustion Synthesis of Refractory Compounds

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GASLESS COMBUSTION SYNTHESIS OF REFRACTORY COMPOUNDS

Foreword

Gasless combustion synthesis technology for the preparation of refractory compounds is described in this volume. Processes and theory are discussed, with emphasis on recent Soviet technology; analytical combustion models are presented; and suggestions are made for future research directions.

Gasless combustion synthesis generally involves reactions of elemental constituents in condensed phases to form refractory, often ceramic, compositions. Gasless combustion's appeal, as opposed to conventional powder-compaction technology, is its potential for using the exothermic heat of reaction to form densified ceramic product shapes in a single step, thereby avoiding the need for subsequent processing by externally supplied heat. Process advantages claimed are low fabrication and capital investment costs, extremely high processing temperatures, relatively abrupt heatup and cooldown sequences, rapid processing, and relative product purity without the necessity of pure starting materials.

The major disadvantage of gasless combustion synthesis is that the processes may be difficult to control. The book describes analytical models which should aid in selecting favorable synthesis reactions, and predicting reaction temperatures, phase changes, and the speed of combustion.

Areas for future research opportunities include synthesis of ceramic matrix composites and complex (fracture tough) ceramic compounds, combination of synthesis reactions with isostatic pressing or with electric arc technology in hard surfacing operations, and the casting of composite materials in a zero-gravity environment.

The information in the book is from *Synthesis of Refractory Compounds with Gasless Combustion Reactions* prepared by William L. Frankhouser, Keith W. Brendley, Michael C. Kieszek, and Stephen T. Sullivan of System Planning Corporation for the U.S. Department of Defense, September 1983.

The table of contents is organized in such a way as to serve as a subject index and provides easy access to the information contained in the book.

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NOTICE

Contents and Subject Index

1. Introduction

The objective of this System Planning Corporation (SPC) study is to increase knowledge of reaction mechanisms in gasless combustion as used in development of new processes for synthesis of refractory materials. The materials under study normally are classified within the categories of structural materials as ceramics, cermets, or intermetallic compounds. Many are somewhat difficult to fabricate and usually costly in comparison to conventional metallic structurals.

Gasless combustion synthesis has recently received considerable attention as an alternative to conventional ceramic or powder metallurgy processing technology because of the unique process simplicity. Potential advantages of gasless combustion include low processing cost, conservation of energy (in production), low capital investment (for equipment), and high purity of product. With self-generation of intense thermal energy in synthesis reactions, the need for external process heating is minimized or eliminated completely. This characteristic has led to distinctive process descriptions, such as exothermic, self-propagating [Ref. 1], and self-sustaining [Ref. 2].

An understanding of the fundamental reaction mechanisms involved in gasless combustion is important in determining compositions and physical conditions that are compatible for synthesis of refractory products and properties. A reliable predictive capability will provide a control for selection of products and for optimizing processing variables and should eventually have an impact on achieving lower costs in industrial applications. Although a detailed molecular-scale description of the combustion mechanism may be useful, it is not a necessary precursor to successful commercial scale-up of gasless combustion processes. For example, laboratory data obtained from more macroscopic variables, such as particle size and density, can be used effectively in controlling reactions.

This report considers both theory and practice in gasless combustion synthesis. It begins with observations on the nature of the combustion process and continues with synthesis process adaptations and products. Much of the information provided for those discussions has been obtained from the Soviet literature, since materials synthesis by gasless combustion processing has been under intensive development in the Soviet Union for more than a decade. Lastly, combustion reaction phenomenology and analytical modeling of reaction mechanics are described. Analytical modeling of the combustion process will be useful as a quantitative predictive tool to support future laboratory research and development (R&D) in the United States.

2. The Nature of Gasless Combustion

A. A SIMPLE PROCESS FORM

A simple processing concept for gasless combustion synthesis of a refractory material is demonstrated in Figure 1. Precursor metallic and nonmetallic reactants are first mixed and lightly pressed together. After ignition with a short burst of electrical energy, the thermochemical reaction between the constituent materials (Ti and C) becomes self-sustaining, and a combustion wave propagates through the pressed mass to form the product (TiC). Ideally, this product form would be fully densified and in a readily usable shape. In that situation, the obvious advantages, when compared to more conventional processing methods, would be elimination of the need for either external heating or sophisticated processing equipment. As shown in Table 1, such process attributes are especially important when considering gasless combustion synthesis for potential industrial applications.

Another desirable attribute of gasless combustion synthesis is the extremely high reaction temperatures that can be generated. These high temperatures contribute to shorter reaction periods and completeness of reactions. High temperatures become even more significant when elimination of external heating is also possible. In fact, one investigator [Ref. 3] avers that gasless combustion synthesis can provide higher temperatures than any other industrial combustion process. His data, reproduced in part in Table 2, amply demonstrate this point, since most of the temperature range for gasless combustion synthesis and the maximum temperature exceed the other temperatures listed.

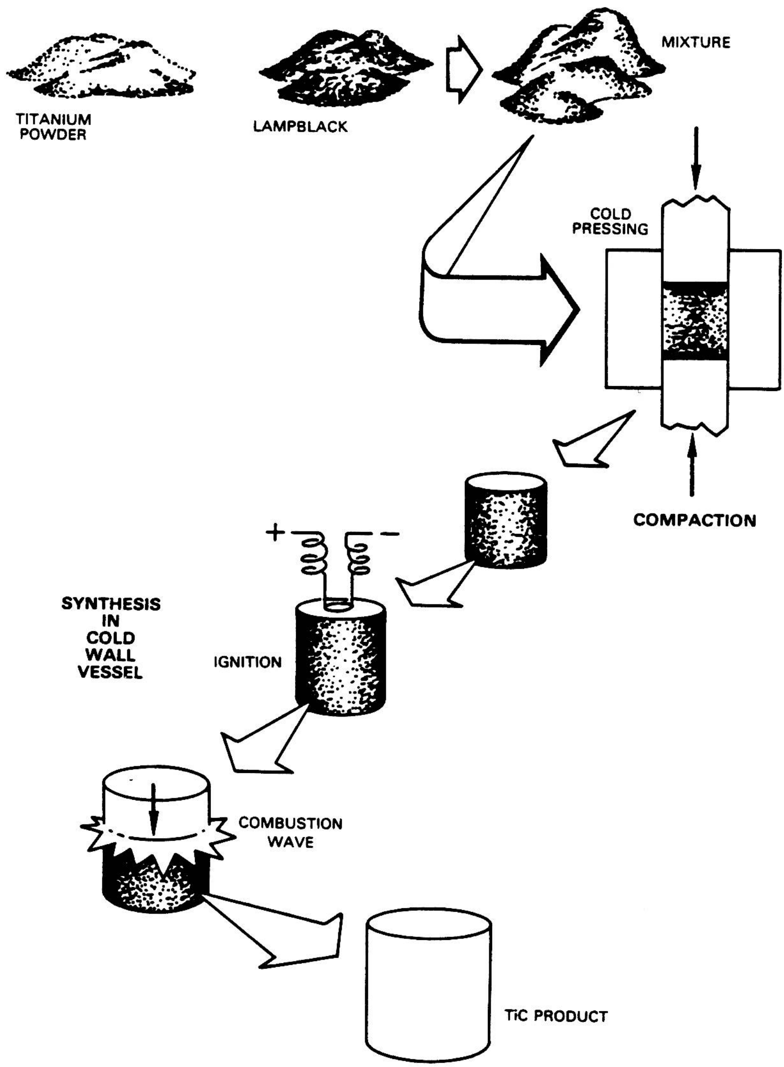

FIGURE 1.
GASLESS COMBUSTION SYNTHESIS IN SIMPLEST FORM

TABLE 1.

COMPARISON OF PROCESS ALTERNATIVES

	Process Step	Equipment: Conventional Powder Consolidation Technology	Equipment: Gasless Combustion Synthesis
1.	Powder preparation	Powder attrition, sizing blending, etc.	Same
2.	Cold compaction	Low-pressure press or cold-wall vessel	Same
3.	Product reaction, conditioning, shaping, etc.		
	• Pressure equipment	High-pressure press or hot-wall, high-pressure vessel	Reaction vessel with vacuum or modest pressure capability
	• Thermal equipment	Thermal adaptation to high-pressure press, high-temperature furnace, or both	High-temperature furnace, only if post-reaction thermal conditioning required

TABLE 2.

COMBUSTION TEMPERATURES FOR INDUSTRIAL PROCESSES

Process	Products	Combustion Temperatures (°C)
Combustion of hydrocarbons	Unsaturated hydrocarbons, industrial gas, carbon black	1,300-1,700
Gas-flame synthesis	Oxides	1,000-2,500
Oxidation treatment	Oxides	600-900
Blast furnace processing	Pig iron	1,600-1,900
Metallothermic processing	Ferroalloys and other master alloys	2,000-3,000
Gasless combustion synthesis	Refractory compounds	2,500-4,000

Another unique attribute of gasless combustion synthesis, when compared to more conventional processes, is localization of the combustion zone. With processes where external heating is required, heatups and cooldowns are considerably slower than with gasless combustion. Potential advantages attributable to short-time exposures in reacting, heating up, and cooling down are improved control over microstructures and properties and lessened extraneous contamination from both ambient atmospheres and containment materials. For example, Soviet researchers in gasless combustion synthesis claim that gasless combustion products are more pure chemically than starting materials, which is opposite to expectations for most conventional synthesis processes.

A final outstanding attribute of gasless combustion reactions is the potential versatility for synthesizing a variety of materials with distinctly different properties and in different forms with one basic process technology. For example, researchers already have synthesized many ceramic and intermetallic compounds and cermet materials, and the technology base undoubtedly can be extended to synthesis of composites and to materials with gradated compositions. To date, a number of materials have been synthesized in both massive and powder forms. Another possibility readily visualized for extending gasless combustion applications is to combine synthesis and bonding (e.g., ceramic-to-ceramic or metal-to-ceramic bonds) in one-step operations. Continuous production applications of the technology also can be surmised, for example, where a ceramic compound might be produced in powder form in a fluidized-bed reactor.

This versatility for production of a number of different compounds is demonstrated by the following generic form of a synthesis reaction between metallic (M) and nonmetallic (N) constituents:

$$\underbrace{\sum_{i=1}^{m} a_i M_i}_{\text{metal powders}} + \underbrace{\sum_{j=1}^{n} b_j N_j}_{\text{powder, liquid, or gas}} \longrightarrow \underbrace{P}_{\text{solid compound}}$$

Typically, the M elements in early Soviet research were transition metals from the A Groups in the periodic table, and the number of M and N elements was initially one [Ref. 3] (e.g., where titanium and carbon react to form titanium carbide). Later, reactions with one M and two N elements were examined by Soviet researchers (e.g. where titanium reacts with carbon and nitrogen to form a carbonitride), and other mixtures with two M and one N elements have been reacted (e.g. where titanium and chromium react with boron to form a diboride). More recently, Soviet researchers also have examined more complex compounds (e.g., where two M and N elements react, as exemplified by a reaction in which niobium and zirconium form a carbonitride).

This capability to produce complex compositions of ceramic compounds is especially intriguing, since some of these compounds may exhibit high-temperature superplasticity and unexpected fracture toughness at ambient temperatures [Ref. 4]. Gasless combustion synthesis of complex, fracture-tough compounds is of interest for two reasons. First, it is simple and fast (implying low production costs). Second, the relatively high rates of heatup and cooldown are supportive in maintaining the small grain sizes and discrete duplex phase combinations that may be one requirement for improving fracture toughness.

Other types of reactions also have been reported in which gasless combustion synthesis is combined with metallothermic (oxidation-reduction) reactions [Refs. 5 and 6]. A typical reaction might be:

$$MO_m + X \longrightarrow MX_n + X_kO_l \quad .$$

In this case, an oxide compound (MO_m) is reacted with an elemental oxidizer-reducer (X) to form a desired refractory product (MX_n) and a by product (X_kO_l). A specific example would be the reaction of molybdenum oxide with boron to form molybdenum boride (the product) and a slag that contains boron in the oxide form.

In other combined processes, a nonmetallic reactant (N) and reducer (R) might be introduced as separate elements, e.g.:

$$MO_m + N_n + R_p \longrightarrow MN_j + R_kO_l \quad .$$

The number of individual compounds already synthesized by Soviet researchers with gasless combustion processes is reported to be more than 100. Most of these have been intermetallic and ceramic compositions, and most of the latter type have been borides, carbides, nitrides, and silicides. In addition, they have synthesized complex combinations of these compounds and have produced some cermet materials. Other ceramic compounds synthesized include germanides, hydrides, phosphides, selenides, and sulfides. Aluminide and nickelide compounds also have been produced.

The Soviet view on potential applications for various compounds synthesized by gasless combustion reactions, which is illustrated in Table 3, demonstrates the broad range of potential industrial utilization that is anticipated. It also reveals considerable variation in types of materials, since both relatively hard and refractory compounds (like borides) and soft materials (like chalcogenides) are included; in addition, some have a high degree of chemical stability (like carbides), while others are characterized with much lesser stability (like some hydrides).

Now that the favorable attributes of gasless combustion synthesis and its potential versatility for industrial applications have been reviewed, a logical question is why it has not already been fully exploited. This probably can be attributed to the belief that combustion processes are difficult to control. Thus, when techniques were developed for synthesis of new materials, emphasis was placed on technologies that were better understood and considered to be more controllable. Interest in gasless combustion (solid-state) reactions for synthesis arose only after development of solid fuels as rocket propellants [Refs. 7 and 8]. As a result of that combustion R&D, the potential for gasless combustion in materials synthesis was recognized, and development has since proceeded to varying degrees in at least four countries for the last 17 years. Much of this development effort concentrated on understanding the basic combustion mechanisms and the underlying thermochemical properties of the materials used in the combustion process.

TABLE 3.

A SOVIET VIEW ON SOME APPLICATIONS FOR GASLESS COMBUSTION SYNTHESIS OF REFRACTORY COMPOUNDS[a]

Compounds	Applications						
	Hard Alloys[b]	High Temperature Structurals	Superhard Abrasives	Protective Coatings	Electrical and Electronic	Lubricants	Nuclear Energy
Borides	X	X	X	X	X		X
Carbides	X	X	X	X	X		X
Chalcogenides		X			X	X	
Hydrides							X
Intermetallic Compounds		X		X			
Nitrides	X	X	X	X	X	X	
Silicides		X		X	X		

[a]Source: Reference 3

[a]Cemented carbide and related tool industry products