

Innovative Processing and Synthesis of Ceramics, Glasses, and Composites

Edited by

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Preface

An international symposium, "Innovative Processing and Synthesis of Ceramics, Glasses, and Composites" was held during the 99th Annual Meeting of the American Ceramic Society in Cincinnati, OH, May 4-7, 1997. The purpose of this symposium was to provide an international forum for scientists, engineers, and technologists to facilitate exchange of ideas, information, and technology on advanced methods and approaches for processing and synthesis of ceramics, glasses, and composites. A total of 102 papers, including nine invited talks, was presented in the form of oral and poster presentations indicating high interest in the scientifically and technologically important field of ceramic processing. Authors from Belgium, Brazil, Canada, Chile, China, Germany, India, Israel, Italy, Japan, Korea, Poland, Sweden, Taiwan, Turkey, and the United States participated. The speakers represented universities, industry, and government research laboratories.

These proceedings contain 32 contributions on various aspects of synthesis and processing of ceramics, glasses, and composites that were discussed at the symposium. Latest developments in combustion synthesis, reaction forming/bonding, mechanical alloying, oxidation of metallic precursors, sol-gel and microwave processing, electrophoresis, and CVI techniques are described. Papers describing preparation of oxide and non-oxide ceramics in the form of powders, thin films, fibers, laminates, composites, etc. are included in this volume. Each manuscript was peer reviewed using the American Ceramic Society review process.

The editors wish to extend their gratitude and appreciation to all the authors for their cooperation and contributions, to the session chairs for their time and efforts in keeping the sessions on schedule, and to all the reviewers for their useful comments and suggestions. Financial support of the American Ceramic Society is gratefully acknowledged. Thanks are due to the staff of the meetings and publications departments of the American Ceramic Society for their invaluable assistance. Finally, we are grateful to Sarah Godby of the American Ceramic Society for efficiently coordinating the on-site review of the manuscripts and her cheerful assistance and cooperation throughout the production process of this volume.

We hope that this volume will serve as a valuable reference for the researchers as well as the technologists interested in innovative approaches for synthesis and processing of ceramics, glasses, and composites.

Narottam P. Bansal
Kathryn V. Logan
J.P. Singh

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Combustion Synthesis

COMBUSTION SYNTHESIS OF CERAMICS AND COMPOSITES

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ABSTRACT

Combustion synthesis provides an attractive alternative to conventional methods of producing advanced materials such as ceramics, intermetallics and compounds therein. Examples of materials synthesized using this process include borides, carbides, nitrides, silicides as well as oxides. This paper will review some recent research directions in this interesting field of synthesis of materials. Mention will be made of some of the products that could be produced using such reactions. Finally the application of a variant process called the "Auto Ignition" process for synthesizing nanoceramics powders will be described.

INTRODUCTION

Self-propagating High-temperature Synthesis (SHS) technique is being used all over the world not only in synthesizing many advanced materials but also in various industrial applications. Other terminologies used to describe the process include Combustion Synthesis (CS), Gasless Combustion, etc. The current interest in the topic can be credited to the pioneering work of Merzhanov and his group in Russia starting in the early seventies [1]. However, contrary to the popular belief, the process itself has a much longer history. The earliest mention of a combustion phenomenon in materials synthesis can be found in 1825. Berzelius reported that Zr metal powders burn to form the corresponding oxide [2]. The thermodynamics of the process was explained by Goldschmidt in 1895 [3]. In fact, Goldschmidt can be rightly called the originator of the aluminothermic process, a sub group of SHS reactions. During the next 200 years, there were some sporadic industrial discoveries utilizing the combustion phenomena [4,5]. In spite of those discoveries, there was no widespread scientific interest in the process until the vigorous research initiated by Merzhanov and his colleagues.

In this country, it is generally believed that the work in this field started with support from ARPA in the mid eighties. However, long before that, in 1959, Walton and his colleagues started utilizing the aluminothermic processes for synthesizing cermets [6]. This activity went on for several decades. As the SHS related activities took firm root in this country, many excellent reviews started

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appearing in the literature. Frankhouser et al. published an extensive monograph on the subject [7]. This monograph was interesting in that it has an industrial bias and is a balanced review of the work done in the then Soviet Union and elsewhere in the West. Soon after that, two of Munir's reviews were published [9,10]. Ref.

[9] is a shorter version of the comprehensive one [10]. These two reviews together describe the important aspects of the then Soviet work, which by then was already two decades old. Yi and Moore [11] as well as Merzhanov [12] reviewed the very similar topic. The paper by Koizumi is an important contribution in reviewing the Japanese work [13]. A short paper by Hlavacek [14] points out the historic aspects of the process and mentions the earliest work by Berzelius, Goldschmidt and others. Other reviews also appeared in the literature including the most recent ones by Moore and Feng [15-17]. However, in spite of almost ten reviews in the field within the last decade (i.e. almost one review per year), the contents of the reviews have not progressed much further since the publication of the seminal paper by Munir and Anselmi-Tamburini [9]. Since some of the information contained in ref. 9 were actually quoted from earlier Russian references, it is believed that the data needed a second examination in view of the more recent reports. Furthermore, as active practitioners of the science and technology of this process, we feel that there have been some interesting developments in the field, which need proper attention and dissemination. Finally, in spite of a great deal of applications in the industries, the number of skeptics either in this country or elsewhere in the world are numerous. Hence, there is a need for reviewing some of the recent interesting developments in the field. The present attempt is not going to be comprehensive. In stead, it will be an evolutionary step towards a broader review. Therefore, the focus here will be towards the synthesis of newer materials and developments of new techniques with a view towards ultimate application. Unless, the SHS community can show large scale applications of SHS, skepticism will still remain. We would like to point out that the industrial applications of SHS are by no means insignificant in this country. But elsewhere in the world, particularly in Russia, in other countries of the CIS, in Europe (notably Spain), and in Asia (specifically in Japan, China, Korea, Taiwan and India), the industrial applications have been substantial.

This review will start off with a discussion of the thermodynamic aspects of the process. This will be followed by some specific examples of materials development e.g. nitrides, silicides, metal matrix composites as well as oxides.

THERMODYNAMIC CONSIDERATIONS

Once ignited, high temperatures can be achieved in very short times due to the highly exothermic nature of the reactions. The enthalpy of the synthesis reaction for the propagating case, $\Delta H_{\text{reaction}}$, is equal to $\Delta H_{f,298}$, the standard enthalpy of formation of the product. For an adiabatic reaction with the reaction temperature denoted by T_{ad} , the heating of the product from 298K to T_{ad} takes place in response to the input of $\Delta H_{\text{reaction}}$. Depending upon whether T_{ad} is smaller than, equal to, or larger than the product melting temperature T_m , the following three cases arise.

$$-\Delta H_{f,298} = \int_{298}^{T_{ad}} C_{p(\text{product})} dT, \text{ if } T_{ad} < T_m \quad (1)$$

$$-\Delta H_{f,298} = \int_{298}^{T_{ad}} C_{p(\text{product})} dT + \nu \Delta H_m, \text{ if } T_{ad} = T_m \quad (2)$$

$$-\Delta H_{f,298} = \int_{298}^{T_{mp}} C_{p(\text{product})} dT + \Delta H_m + \int_{T_{mp}}^{T_{ad}} C_{p(\text{liquid})} dT \quad (3)$$

if $T_{ad} > T_m$

where ν is the fraction of the liquid phase in the mixture of liquid and solid phases since both of them are expected to exist at the melting point.

For many compounds, the thermodynamic data required to calculate T_{ad} , are available in the literature. However, it is pointed out that, agreement between the experimentally obtained data and theoretically calculated values is lacking. This is because the reactions are not truly adiabatic. At best, the calculations predict the upper limit of T_{ad} . Nevertheless, such calculations provide important guidelines for maintaining the exothermic state of the reactions. Based on the observations of a number of reactions [10,16], it has been found that there is a linear correlation between $\Delta H_{f,298}/C_{p,298}$ and T_{ad} . It has been suggested in the literature that the reaction will not be self sustained if $\Delta H_{f,298}/C_{p,298} < 2,000\text{C}$ (or T_{ad} values are less than $1,800\text{C}$).

Table 1 shows the results of T_{ad} calculations for various silicides. $\Delta H_{f,298}$ for the materials under consideration were obtained from refs 18 and 19. C_p (in kJoule/mole K) is written as $a + bT + cT^2$, where the coefficients a, b and c are taken from ref.18 and are listed in Table 1. Depending on a particular case (i.e. when there is substantial melting), the calculations may require a value of $C_{p(\text{liquid})}$, which is taken as $33.74.n \text{ Joule/mole.K}$, where n is the number of atoms in a molecule and is equal to 8, for example, in Ti_5Si_3 [20]. Table 2 lists the as predicted values of the various silicides to those reported in ref 15, which are based on the Russian data. It is seen that, the values are available only in some cases. Of those cases where comparable data exist, the agreement is quite good in many cases, while there are substantial differences in the predicted values of T_{ad} in the cases of TiSi and CrSi_2 .

Tables 3 and 4 show similarly calculated T_{ad} values for various carbides as well as borides. Again there are agreements as well as discrepancies between our data and the Russian predictions. Notable differences exist in the cases of ZrC and HfC . Also, VC is reported to have a very high T_{ad} value in excess of 3500K in refs 9, 10 and 16, which we believe is in error. According to our calculations, that value is moderately high. Similar comments can be also made in the cases of various borides. Notable differences exist in the cases of CrB_2 and MoB .

At this point several comments can be made. First, since these predictions serve as important guidelines, the new values should be carefully considered before initiating any reaction. Second, combustion of stoichiometric TiB composition seems to be interesting. Even though the predictions favor reactions with even higher exothermicity compared to the TiB₂ reaction, in practice such reactions are quite sluggish. This is because a large quantity of unreacted Ti remains within the system. This possibility can be exploited in fabricating metal matrix composites, as will be described in later. Third, it is seen that, the formation of several compounds are quite sluggish (i.e. have T_{ad} temperatures in the range of 1000K). There are many strategies that are followed in initiating reactions in such cases. Common methods to ignite such reactions are the "Explosion Mode", the "Chemical Oven" and using ternary reactions with several different phases taking part in the reaction. A recent advancement in this field is the use of "Field Assisted Combustion Synthesis (FACS)", which will also be described. Fourth, T_{ad} calculations in the cases of nitrides have not been discussed since it is felt that the "Azide" process has better capabilities, which will be discussed later. Finally, the thermodynamics of the "Auto Ignition" or "Combustion Synthesis in the Auto Ignition" mode will also be described at the appropriate place.

KINETIC CONSIDERATIONS

In order to understand the kinetics of the process, a cylindrical compact is placed vertically in a reaction chamber and ignited at the top. A self-supporting reaction wave is initiated under suitable conditions and its steady speed of combustion is measured. Of interest is the dependence of such variables of the experiment as: the specimen diameter; specimen composition; size of the particles which are pressed; and the extent of dilution with an inert component such as the reaction product itself. These are well documented in ref 9,10,16 and 17.

Azatyán [21] has derived an expression for the rate of propagation of a planar combustion front based upon an elementary model of the process. In this model, the calculations are performed assuming an uniform radial distribution (a planar front). With the additional assumptions that there exists a single heat source and the only heat loss from the body is conductive and radiative, the generalized form of Fourier's one dimensional heat equation takes the form

$$C_p \rho \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + Q_p \phi(T, \eta) - 2 \frac{\alpha}{r} (T - T_o) - 2 \epsilon \frac{\sigma}{r} (T^4 - T_o^4)$$

(4)

$$\phi(T, \eta) = \frac{\partial \eta}{\partial t}$$

(5)

where C_p is the heat capacity, ρ the density, T the temperature, T_0 the ambient temperature, η the fraction reacted, t the time, k the thermal conductivity, x the axial distance, Q the heat of reaction, α the heat transfer coefficient, r the sample radius, ϵ the emissivity coefficient, σ the Stefan Boltzman constant and ϕ is the kinetic function.

Neglecting the transient effects from the ignition surfaces and the heat losses, the above equation can be rewritten as-

$$C_p \rho \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial x^2} + Q \rho \Phi(T, \eta) \quad (6)$$

The solution to the above equation can be written as

$$u^2 = \sigma_n \frac{k}{Q \rho} \frac{RT_{ad}^2}{E} K_o \exp\left(-\frac{E}{RT_{ad}}\right) \quad (7)$$

where σ_n is a constant depending upon the order of the reaction. The apparent activation energy of the reaction can be found from a graph of $\ln(u/T_{ad})$ vs $1/T_{ad}$.

FIELD ACTIVATED COMBUSTION SYNTHESIS

During the discussion on the thermodynamic calculation, it was mentioned that frequently, the reactions are quite sluggish and do not propagate in a self sustaining manner. Several alternate methods for propagating such reaction were also suggested. But, these alternative methods lead to other undesirable phases. A specific example of this phenomenon is the combustion of $MoSi_2$ in the Mo-Si binary system. As noted earlier, the T_{ad} value for $MoSi_2$ formation is in the threshold of self propagation. In order to enhance the propagating reaction, the explosion mode can be tried which leads the formation Mo_5Si_3 , which generally does not have the high temperature oxidation resistance of $MoSi_2$. To alleviate this problem, Munir and his co-workers ignited CS reactions in the presence of electric fields [22-30]. The idea here is to create localized Joule heating in the reaction zone. This was found to be true by monitoring the voltage, current and the resistance of the sample, which essentially remained constant during propagation. Second, the dependence of wave propagation on the field was clearly demonstrated by turning off the field. The propagation ceased when the field was shut off. Third, the propagation velocity was directly related to the magnitude of the field. Fourth, there is a threshold value of the field below which combustion did not take place. Fifth, at relatively high values of the field combustion took place spontaneously. Finally, actual mechanisms for such reactions can be studied by turning off the field and stopping the propagating reaction any time.

Such reactions are easy to model by adding Joule heating term of mE^2 to the right hand side of equation (6). Feng and Munir modeled such reaction using a

two dimensional version of the modified equation (6) [26]. Results from such model are shown in Figure 1. The graphs show profiles of current densities near the top, center and the bottom of the sample. The profiles show that a planar front is moving through the sample. The experimental configuration, which is modeled is shown in Figure 2. The system consists of spring loaded graphite electrodes between which the powder compact is placed. The compact is ignited from the side.

Table 5 shows some of the materials produced by the FACS process. Gedevarishvili and Munir studied the SHS reactions in $\text{MoSi}_2\text{-SiC}$ system [22]. In such a case, the formation of both constituents are sluggish. However, beyond a threshold voltage, a desirable compositions of $\text{MoSi}_2\text{-SiC}$ composite were produced. The threshold field level decreased as more and more Si and C were incorporated into the system. Feng and Munir used the process to react Si and C to form SiC. The threshold voltage was 9.5v and for voltage greater than 30v. simultaneous combustion occur [23,27].

Shon and Munir reported FACS processing of $\text{MoSi}_2\text{-ZrO}_2$ and $\text{MoSi}_2\text{-Nb}$ composites [24]. The secondary phases are added to enhance the mechanical properties with the application of field, without the formation of undesirable phases.

In the absence of the field, however, the reactions do not self sustain and undesirable phases form. The same comment can also be made in the case of $\text{B}_4\text{C-TiB}_2$ composites. While the formation of B_4C is sluggish, the reaction to form TiB_2 is highly energetic. Under normal circumstance, thermodynamics predicts the propagating reactions only in restrictive compositions. However, with FACS, propagating reactions can take place easily [29]. FACS is also useful in producing W_5Si_3 with a T_{ad} of 954K. Normally, a propagating reaction is not expected here. Therefore, a high voltage is necessary.

THE "AZIDE" PROCESS

Nitrides are typically formed by igniting a reaction between a metal and nitrogen gas. There are two competitive processes that take place during such reactions: the kinetics of reaction and permeation of the gas. Typically, permeation of gas is the rate controlling step. The conversion efficiency can be increased by making use of two strategies: to increase permeation by increasing the porosity of the compact and by increasing the gas pressure. Frequently, the formation of a molten phase adversely affects the permeation of gas. Inclusion of diluents helps to reduce T_{ad} values. This does not allow a molten metal to form. In spite of these strategies, the conversion to the final nitride may not be significant. For example, if the initial starting materials are low melting, it is extremely difficult to control their melting. A case in point is the synthesis of AlN by SHS, during which substantial melting of Al is a problem.

Solid-state nitrogen sources can solve this problem. One such source of nitrogen is sodium azide, NaN_3 . The material is cheap, readily available, and is unstable. Holt pioneered the "Azide Process" for making nitrides by the SHS process [31,32]. Originally, the process was developed for making nuclear fuels

[31,32]. Typical reactions are written in the following along with the respective Tad values.



During the process, the nitrides form and metallic sodium vaporizes. In the case of the second reaction, CaO is leached from the product and is expected to offer much better control.

Similar ideas can be used in making important ceramic materials as well which are described by the following equations:

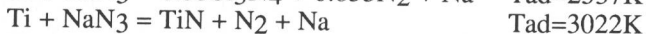
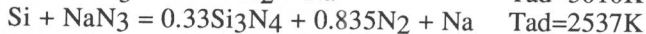
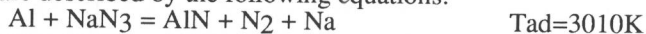


Table 6 shows the Tad values calculated in the case of the "Azide" process vs. the conventional gaseous N₂ reactions. In some cases the calculated Tad values for the "Azide" process are lower (e.g. in the cases of TiN, Si₃N₄) than the conventional situation, while in other cases the Tad values by the "Azide" process are higher. Nevertheless, generation of N₂ in-situ is an important advantage so much so that over pressure of N₂ is not required [31-33].

In spite of these potential advantages, the growth in this field has not been significant. Recently, Amosov et al. used this process for synthesizing several nitrides [33]. They reported that NH₄Cl when incorporated into the powder mixture sometimes catalyzes the reactions. Lee and Chang explained the catalytic effect of NH₄Cl on the basis of vapor phase decomposition of NH₄Cl, formation of SiCl_x followed by the nitridation of SiCl_x to form Si₃N₄ [34]. The maximum temperature of combustion was about 2123K, which is much lesser than the Tad value calculated. Since vapor phase reactions took place, the product contained loose powders, whiskers as well as platelets.

Lee et al also used the "Azide" process to synthesize AlN powder. As predicted by the thermodynamic calculations, the Tad for such reactions are higher than that for the formation of Si₃N₄. In order to counteract the fragmentation of processed pellet, a casket of Ti and C powder was built around the Al and NaN₃ mix. The actual change of Al and NaN₃ was ignited by the combustion reaction between Ti and C. The conversion was reasonably high. Similar to the Si₃N₄ reaction, gas phase reactions also took part in AlN formation.

SHS REACTIONS IN SYNTHESIZING Ti₃SiC₂

Recently, considerable attention has been focused on Ti₃SiC₂ due to its reported plastic behavior [36-43]. A complete understanding of the mechanical properties can be obtained only if bulk samples of Ti₃SiC₂ can be synthesized. Such samples have been obtained by sintering (or) hot pressing Ti₃SiC₂ powders obtained by combustion synthesis. Combustion synthesis yields powders that contain up to 10 - 30 vol% TiC impurities. These powders have to be subsequently pulverized and hot pressed to obtain bulk samples for testing. As opposed to this two-stage process, we have reactively hot pressed Ti, Si and C powders at 1400 C and 40 MPa for 90 minutes and obtained bulk samples [44].

XRD indicates the presence of Ti_3SiC_2 with TiC content of 10 vol%. The hardness of Ti_3SiC_2 at room temperature is 4.1 GPa and decreases to GPa beyond 1000 C. This suggests significant yielding of the compound beyond 1000 C. As a result, it should be possible to fabricate complex shapes by extrusion, forging, injection molding etc., A fracture toughness of $6.15 \pm 0.4 \text{ MPa}\cdot\text{m}^{1/2}$ was obtained from chevron - notched specimens. The fracture surface revealed a layered profile and cleavage planes (Fig. 3).

Despite possessing superb mechanical properties, Ti_3SiC_2 lacks sufficient resistance to oxidation. Composite with SiC was investigated to improve the resistance to oxidation. Solid state displacement reaction between TiC and Si was utilized to fabricate $\text{Ti}_3\text{SiC}_2/\text{SiC}$ composites. The composite microstructure revealed a uniform distribution of SiC in a Ti_3SiC_2 matrix (Fig. 4). Two morphologies of SiC were identified: blocky and needle shaped.

The composite when subjected to oxidation in air at 1000C, registered a weight gain of the order of a few milligrams after 10 hours. A very thin oxide layer was formed. Therefore, our objective to improve the oxidation resistance was successful [45]

The effect of SiC on mechanical properties was also investigated. A hardness of 4.74 GPa was obtained. The increase in hardness can be attributed to the addition of SiC. Cracks from Vickers indent when examined using SEM provided evidence of crack bridging and crack deflection (Fig. 5). The bend strength of the composite was 405 MPa. The fracture surface showed fracture around SiC particles as well as a layered Ti_3SiC_2 matrix.

CONTROLLED REACTIONS IN THE Ti-B BINARY SYSTEM

Another example of utility of thermodynamic predictions in controlling vigorous combustion reactions is in the Ti-B binary system. It is generally believed that the formation of single phase TiB_2 is highly exothermic [7-11]. A low melting ternary element such as Fe or Cu may be incorporated to control the reaction between Ti and B [47]. Addition of extra elements, however, gives rise to other undesirable phases, rendering the interpretation of mechanisms and evaluation of properties difficult. Therefore, control of the reaction can be sought by simply shifting to a composition away from the TiB_2 stoichiometry [48,49]. In the following, the results of this work are presented.

First, a thermodynamic study was carried out to investigate how the exothermic nature changed. Pertinent thermodynamic properties of TiB and TiB_2 are showed in Table 7. Fig. 6 shows the variations of T_{ad} with respect to the free Ti acting as a diluent. Phase changes affect the temperature of the system and consequently the reaction rate. The reaction $(1+x)\text{Ti} + 2\text{B} \rightarrow \text{TiB}_2 + x\text{Ti}$, for instance, absorbs the latent of fusion of 100.4 kJ/mol, while maintaining T_{ad} close to the melting temperature. This continues up to an addition of .65 mole of Ti, as depicted in line 2 of Fig. 6. T_{ad} in the reaction $(1+x)\text{Ti} + \text{B} \rightarrow \text{TiB} + x\text{Ti}$ drops drastically with the addition of Ti.