

ARMY RESEARCH LABORATORY



Upscaled Self-Propagating High-Temperature Synthesis (SHS)/Dynamic Compaction Processing

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Abstract

Titanium carbide (TiC) and titanium diboride (TiB₂) ceramics were formed from elemental powders using a Gleeble 1500 dynamic thermomechanical process simulator. In the first step of a two-step process, a self-propagating high-temperature synthesis (SHS) reaction was initiated by the passage of an electric current through the powdered green body. The temperature of the body was maintained at about 800° C, and the reaction rate was controlled by the application of a pressure of about 35 MPa. As verified by x-ray diffraction analysis, this procedure resulted in complete conversion from reactants into products having a range of densities from 72 to 75% of theoretical. In the second step, the current was increased to raise the temperature of the material, thereby sintering and densifying the product. TiC with 3 wt.-% nickel (Ni) was sintered to 95 to 98% of theoretical density, while TiC without Ni was sintered to 90% theoretical density. Although TiB₂ was successfully converted, efforts to fully densify the product were hindered by the limitations of the Gleeble 1500. The effects of the current and pressure levels on the product density and microstructure were examined. The advantages and limitations of this process are also discussed.

Acknowledgments

Xform would like to express its gratitude to Professor Roger Wright and the High Temperature Technology Program at Rensselaer, and to Duffers Scientific Associates for their contributions throughout the effort. Xform acknowledges the contributions and efforts of Dr. Theodore Schurman, Dr. Wojciech Misiolek, and Mr. Nicholas Sopchak of the Rensselaer Polytechnic Institute research team. Gratitude is also expressed to Professor Randall German and Mr. Karl Shaw for their contributions.

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Executive Summary

Titanium carbide (TiC) and titanium diboride (TiB₂) ceramics were formed from elemental powders by self-propagating high-temperature synthesis (SHS) by passing electrical current through the compact while the pressed powders were under a compressive load. With this developed technique, the reaction occurs in a controlled and steady manner allowing the graphite container surrounding the powders to remain at a low overall temperature during the reaction (e.g., 800° C for TiC). Pressure is applied during the reaction to aid densification and to achieve the controlled SHS reaction. The process works by passing electrical current through the conductive powders that are contained within a graphite tube. Extremely high current densities and heating are achieved locally at particle interfaces resulting from the high electrical resistance of the particle interfaces. This heating is sufficient to initiate the reaction locally for titanium (Ti) and graphite, or for Ti and boron (B), to form TiC or TiB₂, with the resultant release of heat. With this electrical current-induced SHS approach, the large, violent exothermic reaction associated with allowing the entire sample to reach the initiation temperature and to react to form a combustion synthesized product is avoided. When pressure is applied during current-induced SHS, the reaction will not self-propagate throughout the sample; the applied pressure increases thermal conduction and heat is extracted. The SHS reaction in this mode therefore stagnates, since this heat extraction keeps the neighboring elements from reaching the initiation temperature for compound formation and from reacting exothermically. As current continues to pass through the sample, new initiation sites continue to develop and react until all of the elemental powders have been transformed. Since outgassing associated with the exothermic transformation occurs locally during this method, there is time for the gas to escape from the compact and to not be entrapped. And because the reaction occurs stepwise and locally, there is no large outgassing volume; the vacuum level decreases within the reaction chamber, but vacuum is not lost completely as would be when the initiation temperature is reached in traditional SHS.

This approach provides an efficient and inherently safe process for forming materials by SHS. Because the elemental powders may be transformed to the product without the large release of heat

and associated tremendous gas liberation, a wider range of lower cost materials for containing the reaction is possible.

In this 6-mo effort, the electrical current-induced process was developed to form TiC and TiB₂ ceramics by SHS reactions in a controlled and safe manner by initiating the reaction locally at the high-resistance particle interfaces. Both TiC and TiB₂ 1.25-cm-diameter samples were formed from the elemental powders employing the two-step technique. As practiced, the transformation occurs first at roughly 800° C and then the temperature is raised to densify the sample. Following transformation, the product density is 72–75% of theoretical for the samples when 35 MPa (5 ksi) of pressure is applied. The current level is then raised to heat the sample to densify the transformed product. Densities of 95–98% of theoretical density were achieved for TiC with 3 wt.-% nickel (Ni) addition after producing the product at a temperature of 800° C and then heating to 1,400° C for less than 15 min for densification. Without Ni addition, it was necessary to heat to 2,000° C following transformation to TiC and hold for under 15 min to reach high densities. Despite this, TiC without Ni was sintered only to 90% theoretical. This approach was then applied to the formation of a 10-cm-diameter sample of TiC. A 2-kg mixture of Ti and graphite was transformed into TiC, keeping the temperature of the surrounding graphite tube from 700 to 900° C. The Gleeble thermomechanical apparatus employed for performing the transformation was not capable of operating at the conditions required for achieving high density following the transformation step. The density of the 10-cm-diameter sample following transformation with the electrical process with an applied pressure of 2.8 MPa (0.4 ksi) was 59% of theoretical. Formation of TiC was confirmed by x-ray. To achieve further densification, the transformed sample was subsequently hot pressed at 2,000° C and 21 MPa (3 ksi) at the General Electric Corporate Research and Development Center (Schenectady, NY). The final density after hot pressing was 84% of theoretical, and the microhardness measured 16.5 GPa. Ideally, the approach of passing additional current through the sample for sintering would have been employed to densify the 10-cm-diameter sample. However, constraints on the present apparatus could not be resolved in a timely and cost-effective manner. This necessitated the use of conventional hot pressing to densify the transformed TiC. Additionally,

the use of current to sinter samples appears to aid densification and therefore appears superior to conventional furnace heating.

Additional work to be performed includes determining the effect of pressure on the density of the ceramic following transformation. A pressure of 2.8 MPa on the 10-cm-diameter sample resulted in 59% density after transformation, and 35 MPa on the 1.25-cm-diameter sample resulted in 73% density after transformation. The effects of higher pressures, such as 350 MPa, during the transformation need to be explored. It may be possible with higher applied pressures during the transformation to reduce this method to a one-step process for achieving high densities.

A Gleeble thermomechanical apparatus was employed in this research, but the equipment that would be used in a manufacturing environment would consist simply of a power supply system capable of supplying 450–800 A/cm² (3,000–5,000 A/in²), a vacuum system and chamber for carrying out the reaction, and a press for applying pressure. An apparatus would be built to supply current into a mixture of elemental powders while simultaneously applying pressure. Such a system would be inexpensive and would provide a safe and effective means for generating TiC and TiB₂ ceramics by SHS.

Based on the current-induced process, an invention disclosure was filed by Dr. Theodore Schurman and Mr. Nicholas Sopchak entitled, "Low Enthalpy Power Controlled Synthesis." The process was demonstrated to synthesize TiC, TiB₂, and nickel aluminides (NiAl) from elemental powders while passing current through a powder compact while under pressure.

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1. Background

Research has demonstrated that the use of certain ceramics can enhance the performance of Army vehicle armors against attack by depleted uranium shells. Hard ceramic materials on the outside of tanks can prevent kinetic energy projectiles from coming into contact with the tank and rendering it inoperable. Use of these materials by the U.S. Army, however, is affected by their high cost. Producing monolithic low-porosity ceramics from titanium carbide (TiC) and titanium diboride (TiB₂) proves to be slow, expensive, inhomogeneous, and unreliable with standard powder processing approaches such as hot pressing.

Prior research at the U.S. Army Ballistic Research Laboratory (BRL)* has shown that mixtures of elemental powders can be used to generate a ceramic compound through exothermic reactions such as self-propagating high-temperature synthesis (SHS). Along with compound synthesis, the excess heat from the reaction provides an opportunity for densification and net shaping through application of an external stress (e.g., Dynamic Compaction). In experiments conducted at BRL, the product after combustion synthesis (CS) is porous and is at a very high temperature, exceeding 2,500° C; the porosity is eliminated by the use of a pressure wave that is generated using explosives. This two-step process consisting of first synthesizing a ceramic material and then consolidating to high density is referred to as Combustion Synthesis/Dynamic Compaction. This method has the potential of being a low-cost manufacturing process; the objective of this Phase I Small Business Innovation Research (SBIR) effort was to develop this method into a viable manufacturing process.

Reactive synthesis processing has been successively applied to the formation of intermetallics and ceramics [1-10]. The basic concept is to combine mixed elemental powders and to initiate a self-sustaining exothermic reaction. Generally, materials formed using this technique have low processing costs. However, many ceramics synthesized using reactive techniques are inherently

* The U.S. Army Ballistic Research Laboratory was deactivated on 30 September 1992 and subsequently became a part of the U.S. Army Research Laboratory (ARL) on 1 October 1992.

resistant to high-temperature consolidation, and consequently, traditional, ceramic fabrication approaches prove less than ideal. Many of the reactively processed materials exhibit unique microstructures and properties, in part, due to their self-purification during the exothermic reaction. Reactive sintering techniques have progressed to the point where densities of 97% of theoretical may be obtained with intermetallics such as nickel aluminides (NiAl) [1-4], however, TiC and TiB₂ have not been densified using reactive sintering processing. Near full density has been achieved through consolidation only, while the newly synthesized phase still contains its latent heat of reaction [5, 9, 11-20].

This Phase I effort was intended to develop a cost-effective approach employed to mass produce ceramic components. The proposed approach included a thermomechanical simulator that would be used to heat the powder mixture by resistance heating to the initiation temperature through passage of current and then, at a predetermined time following CS, load the sample in compression at high strain rates to achieve dynamic compaction.

This approach has the advantage of separating the CS parameters (i.e., particle size, heating rate, green density, degassing, and so on) from the dynamic compaction parameters (i.e., time delay, pressure, strain rate, peak stress). This method provides a means for sequencing the reaction and compaction steps and providing the ability for direct current heating during compaction. The proposed approach of heating the compacted mixture of elemental powders by resistance heating is attractive because it has the advantages of being inherently safer, since there are no explosive materials involved, and of possessing rapid cycle times. A further objective of Phase I work would be to explore the several variables influencing reactive synthesis and dynamic compaction to isolate those conditions giving the most suitable products.

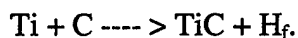
2. Introduction

As stated, the objective of this project was to study the feasibility of SHS followed by compaction to achieve high-density ceramic materials such as TiC and TiB₂. The final product, in

the form of cylindrical samples 10 cm in diameter \times 2.5 cm thick, was expected to reach densities of 95% and 98% of the theoretical values for TiC and TiB₂, respectively. The mechanical properties, measured by microhardness, had to be comparable to the values for the same materials manufactured by traditional hot pressing of TiC and TiB₂ powders.

The thrust of this investigation was to develop an efficient low-cost potential manufacturing process for producing dense TiC and TiB₂ ceramics employing SHS. Reactive sintering techniques have been successfully applied to the fabrication of several materials, such as borides, carbides, nitrides, silicides, intermetallics, and composites [21–25]. In some systems, the final density after reactive sintering is only on the order of 60% of theoretical density—utilization of additional densification techniques is necessary to increase the final density. To enhance the densification mechanism, experiments were planned employing reactive sintering with subsequent pressurization.

Underlying Principles. The CS of intermetallic compounds from mixed elemental powders is a new fabrication route for high-performance, high-temperature alloys. The SHS or reactive sintering reaction relies on the exothermic heat associated with compound formation to induce a transient liquid phase. Several compounds have been formed, including aluminides, silicides, hydrides, oxides, carbides, nitrides, and borides. Control over the transient liquid phase and the characteristics of the final product are possible through the heating rate, green density, degassing procedure, particle size, particle size ratio, powder homogeneity, and stoichiometry. For this effort, a large heat release from a combustion reaction was used to generate a thermal spike that forms a transient liquid phase. Consider a mixture of titanium (Ti) and carbon (C) powders. These powders will form a stoichiometric compound TiC with the release of heat H_f ,



The reaction from elemental powders results in the formation of a compound, in this case TiC, and the release of excess heat. Such reactions are thermally activated events with the rate of reaction dependent on the temperature,

$$dy/dt = (1 - y)^n k_0 \exp(-E/RT),$$

where y is the fraction of reactant transformed, t is the time, n is the order of the reaction (usually 1 or 2), k_0 is the frequency factor, E is the activation energy for the reaction, R is the gas constant, and T is the absolute temperature. The reaction energy concept indicates that an activation energy E is needed to initiate diffusion across the interface between contacting particles. The probability that a given atomic vibration will gather sufficient energy to undergo such a step varies in proportion to $\exp(-E/RT)$. However, once an atomic jump has become activated, there is a large energy return of H_f . Depending on the heat capacity of the material, this energy release creates a temperature increase, termed adiabatic heating. In turn, adiabatic heating leads to faster rates of reaction because of the strong rate sensitivity as expressed by the Arrhenius temperature dependence. This is especially true if a liquid should form. Such reactions are termed as autocatalytic, because when initiated, the reaction proceeds in a spontaneous manner without external heat input.

Generally, these reactions are known by such names as self-combustion, SHS, or reactive synthesis. Much research has occurred in the Soviet Union with such synthesis techniques. Reactive sintering is actually a variant of CS where simultaneous sintering densification is combined with the CS reaction. Reactive sintering occurs by mixing elemental powders in approximately the stoichiometric ratio. These powders are degassed to remove contaminants. The material is then reacted to induce formation of the compound. A transient liquid phase forms in most cases.

The parameters that influence CS fall into two categories: those that are inherent to the system thermodynamics (such as heat capacity, activation energy, and heat of formation) and those that are adjustable through the processing conditions (such as particle size, heating rate, green density, and composition). The heat of formation, initial compact temperature, and heat capacity of the materials determine the temperature rise in the reaction zone. The actual maximum temperature achieved is determined by an energy balance using the appropriate heat capacities and melting enthalpies. The adiabatic temperature, T_a , represents the maximum possible temperature attainable in the reaction zone. It can be estimated using energy balance calculations,

$$H_f = C_p dT + H_m$$

with

$$dT = T_a - T_i,$$

where H_f is the enthalpy of formation of the compound, dT is the temperature rise from the initiation temperature T_i to the adiabatic temperature T_a , C_p represents the heat capacity for the various components, and H_m is the appropriate collection of melting enthalpies. The maximum temperature depends on the particular combination of reactant and compound melting events. Each melting event consumes energy and lowers the maximum temperature, while higher initiation temperatures and higher reaction heats raise the maximum temperature. Diffusional homogenization is aided by having the maximum temperature approach the compound melting temperature. Control of the maximum temperature is possible through adjustments to the processing parameters, including the initiation temperature. Generally, the most desirable situations have temperature increases of 1,500° C. TiC has an adiabatic temperature of 3,210° C, while the adiabatic temperature for TiB₂ is 3,190° C.

Several experiments have been conducted to delineate the important factors affecting CS of TiC and TiB₂ [5, 9, 11–20]. These factors include particle size, green density, degassing procedure, compact size, reaction dilution, and atmosphere effects. Several densification guidelines have emerged from previous work to include the alignment of the pressing direction with the reaction front and the occurrence of optimal densification if pressurization takes place within 1–2 s after the SHS reaction. From this basis, sequential SHS/Dynamic Compaction processing was planned.

3. Approach

The experimental portion of this effort was conducted at Rensselaer Polytechnic Institute in conjunction with the Rensselaer High Temperature Technology Program, which is a New-York-State-funded program whose aim, in part, is to assist small companies in technological development. This work on processing of TiC and TiB₂ ceramics fits in with the program's

high-temperature materials processing studies. The program is under the administration of Dr. Roger Wright, Professor of Materials Engineering at Rensselaer. The Rensselaer research team on this effort consisted of Dr. Wojciech Misiolek, Research Assistant Professor, and Dr. Theodore Schurman, Post Doctoral Research Associate, both in the Materials Engineering Department, and Mr. Nicholas Sopchak, a senior in Materials Engineering. Dr. Misiolek's field of expertise is powder processing and material flow and design. He has past experience in reactive sintering and pressure reactive sintering based on work with intermetallics and intermetallic matrix composites; Dr. Misiolek was a researcher with Professor Randall German at Rensselaer. Mr. Sopchak has worked as an undergraduate in powder metallurgy for Professor German and has experience in intermetallic thermomechanical processing. Dr. Schurman received his doctorate from Rensselaer in 1991 and has considerable experience on the Gleeble 1500 thermomechanical process simulator.

Pressure-assisted reactive sintering studies were performed on the dynamic thermomechanical process simulator Gleeble 1500. This instrument is capable of heating specimens at $1,000^{\circ}\text{C/s}$ and holding steady-state equilibrium temperatures within $\pm 1^{\circ}\text{C}$. Thermocouples or an infrared pyrometer provide signals for accurate feedback control of temperature. The Gleeble 1500 can operate in air or can be used with an environmental chamber. Working with the environmental chamber allows a choice of desired atmosphere or vacuum. The Gleeble 1500 mechanical system at Rensselaer is capable of applying up to 9 tons of force in tension or compression. The jaws can be programmed to move at a speed from 0.00002 to 1,000 mm/s. Strain gages and displacement transducers provide feedback, which allows accurate execution and repeatability of the simulation program. Important process variables, such as force, stroke, strain, and strain rate are monitored during the simulation. The Gleeble 1500 may be controlled either by computer or manual control. It is also possible to operate the apparatus with a combination of computer and manual control to provide maximum versatility in the simulation experiment. The unit may be operated in load control or stroke control mode. In load control mode, the force is measured by load cells and kept constant while stroke is adjusted to maintain the desired force. Similarly, in stroke control, the force is adjusted to achieve the desired stroke change. Ten volts (AC) are applied across the sample, and current is adjusted causing the sample to heat by resistance heating. Roughly 25% of the heat is lost from the sample by radiation and by lengthwise conduction through the water-cooled copper jaws.

When operating the Gleeble in temperature control mode, temperature is monitored and power is adjusted to match the programmed schedule. There is a significant problem when this mode is used for studying the exothermic reactions. Because of the exothermic reaction, the sample's temperature rises and the instrument attempts to compensate for the temperature rise by reducing the power being delivered to maintain a constant heating rate. The consequence is that the exothermic reaction is masked. An adjustment was made during the effort by Duffers Scientific Associates of Poestenkill, NY, the manufacturer of the Gleeble, to allow the instrument to be run in power control mode. In this mode, a constant power level is supplied to the sample and thus the exothermic reaction does not result in a reduction of the electrical current being delivered to the sample. A second modification was made to the mechanical system, allowing the vacuum gauge to trigger application of the applied force. Since vast outgassing would take place during the exothermic reaction, timing for applying force may be based on when the amount of outgassing causes the vacuum to degrade above a given preset level. The vacuum gage is employed to trigger the application of force when vacuum starts to deteriorate because of immense outgassing.

The initial approach was to start by fabricating 1.25-cm-diameter \times 2.5-cm-thick samples of TiB_2 and TiC . The reason for this was to conserve material and to establish the proper process parameters for scaleup to the 10-cm-diameter samples. A special die for fabricating cylindrical samples 1.25 cm in diameter and 2.5 cm thick was designed and built for this study. The die was made from a graphite tube, 1.25-cm inside diameter (ID), 1.78-cm outside diameter (OD), and 8.8-cm length. G540 grade graphite was chosen for the die material because of its properties at room and elevated temperatures (compressive strength of 98 MPa [14 ksi] at room temperature). With no reinforcement around the graphite die, a maximum force of roughly 70 MPa (10 ksi) may be applied at room temperature and a maximum force of 6,700 N (1,500 lbf) may be applied at 1,500° C. The source for the graphite was Southern Graphite USA, Inc., in East Windsor, CT. A schematic of the die design is shown in Figure 1. Powders of TiC and TiB_2 were to be contained in the graphite tube, and the graphite was to be supported by two split alumina tubes that were pressed against the graphite tube. The two ceramic tubes measured 1.78-cm ID \times 2.5-cm OD and 2.5-cm ID \times 3.1-cm OD, respectively, and both tubes were 7.5 cm in length. The alumina and graphite tubes were contained

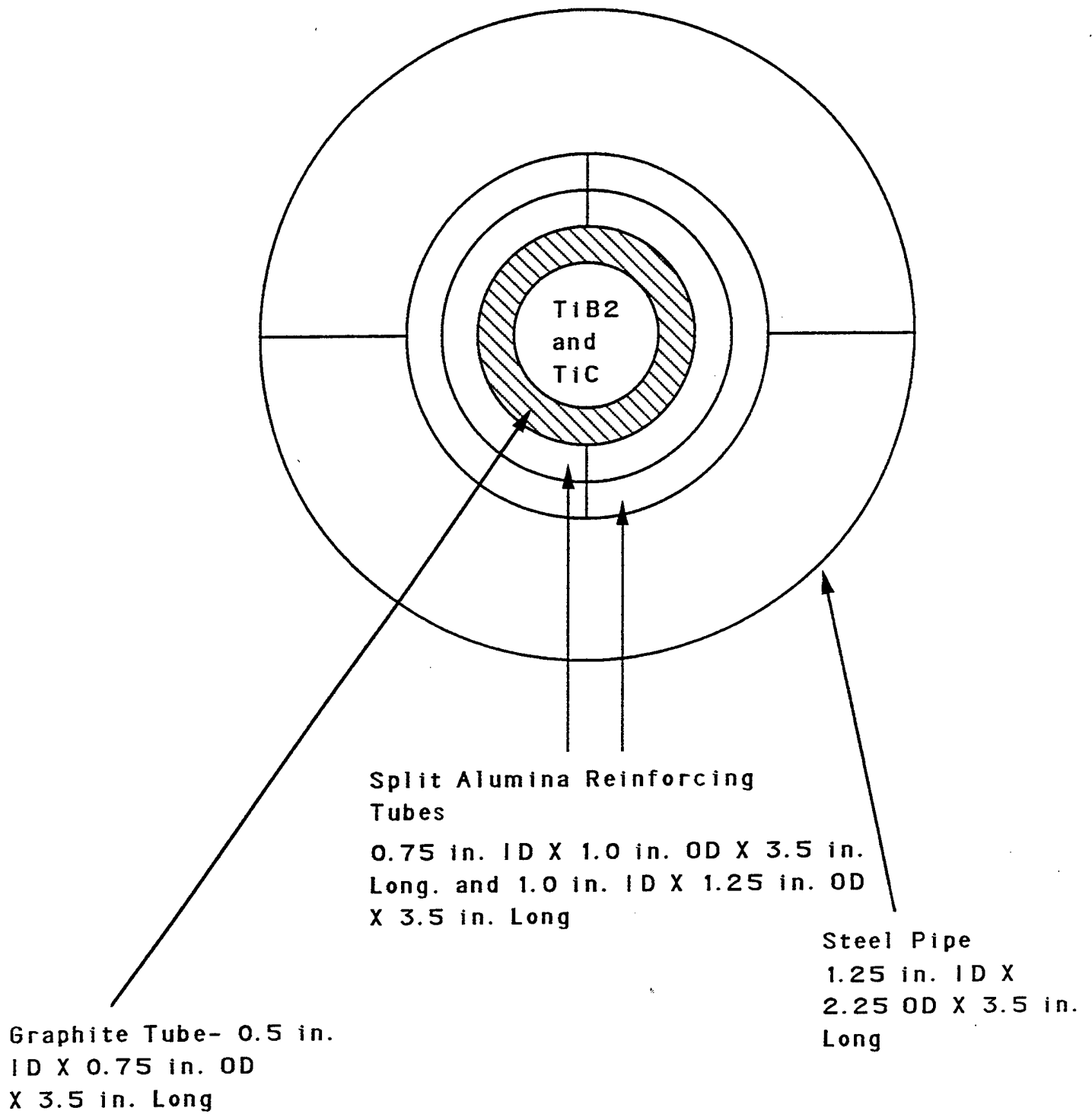


Figure 1. Die Design, Axial View.

by a steel pipe, which was also split down its long axis and fixtured around the other tubes using hose clamps. The entire die assembly was fitted between the jaws of the Gleeble and within the vacuum chamber of the system. The anvils were made from tungsten carbide (WC), which contains roughly 6 wt.-% cobalt (Co). The material has its service temperature limited by creep at about 1,100° C. Graphite end plugs were placed between anvils and powder compact to prevent sintering of the densified sample to the WC-Co anvils. When the Gleeble operated in compression, one of its jaws was fixed while the other jaw moved to apply the loading on the sample. Figure 2 shows a side view of the die assembly and clearly indicates the position of the anvils against the graphite plugs. The initial WC-Co anvils measured 1.26 cm in diameter to ensure a good fit within the graphite tube. Grafoil (thin sheets of graphite material) was also obtained to be placed on the inside of the graphite tube to prevent sticking of either the TiC or TiB₂ against the walls of the tube.

4. Reactive Sintering/Dynamic Compaction

4.1 Material Preparation. Elemental Ti and graphite or Ti and B powders were weighed in proportion to form TiC and TiB₂, respectively. The powders purchased for these experiments are shown in Table 1. Their scanning electron micrographs (SEMs) showing particle morphology are presented in Figures 3, 4, 5, 6, and 7. The TiC system was evaluated first for reactive sintering and dynamic compaction studies. It was decided to study the TiC system first and then apply the gained knowledge and experience to the TiB₂ system.

As shown in Table 1, the Ti powder was received from Micron Metals and the graphite powder used was the Micro 250 synthetic graphite from Asbury Graphite Mills. The Ti powder was reported by the vendor as being -325 mesh, but particle size analysis showed the powder to be an average of 44 μm in diameter. The powder was sieved through a 325-mesh screen to obtain actual -325 mesh powder. The mean particle sizes are shown in Table 2. The particle size distributions are plotted in Figures 8-12.

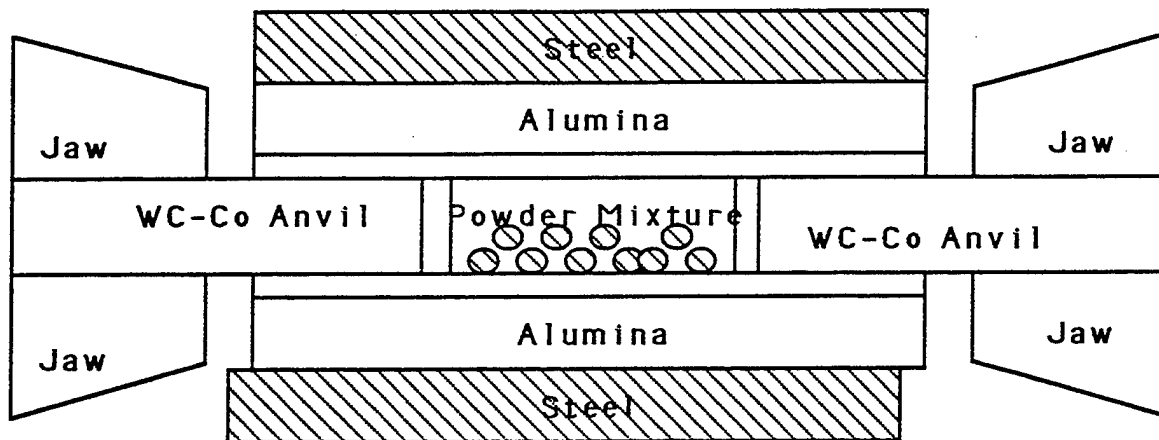


Figure 2. Die Assembly, Side View.

Table 1. Listing of Powders Employed in Study

Powder Name	Vendor	Designation	Size	Cost (per/lb)	Quantity (in house)
Boron (amorphous)	Hermann Starck	Grade I lot 1/91	0.84 μm	\$135.00	0.5 kg
Boron (crystalline)	Hermann Starck	Lot 288/91	-325 mesh	\$370.00	0.5 kg
Graphite (natural)	Asbury Graphite Mills	Micro 850	4.22 μm	\$6.40	10 lb
Graphite (synthetic)	Asbury Graphite Mills	Micro 250	4.27 μm	\$6.20	10 lb
Nickel	Novamet	123	12.81 μm	\$9.24	11 lb
Nickel	Novamet	4SP	11.81 μm	\$9.34	11 lb
Ti	Micron Metals	Ti-020	-325 mesh ^a	\$28.00	20 lb

^a Size given by vendor.

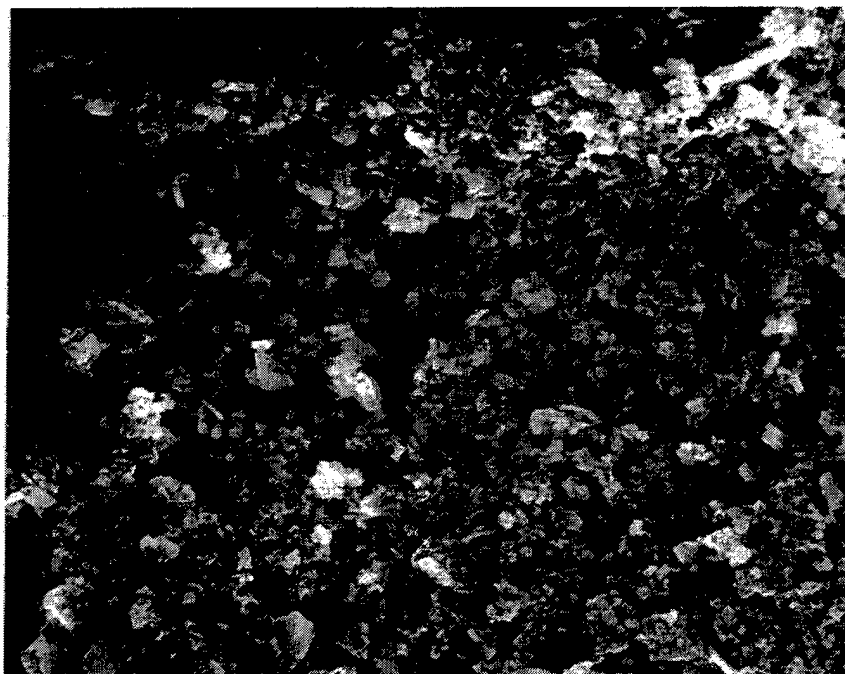


Figure 3. SEM of Amorphous Boron Powder.

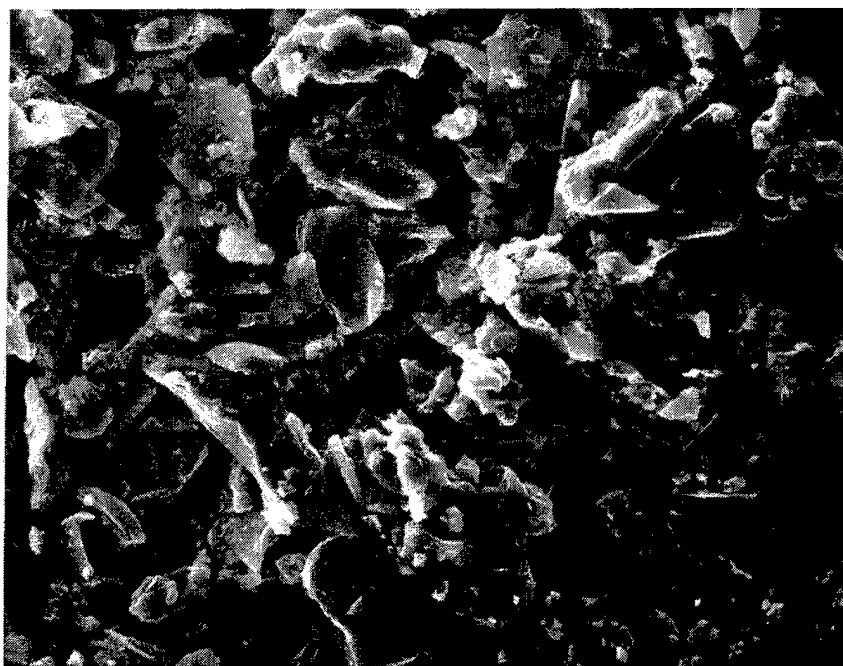
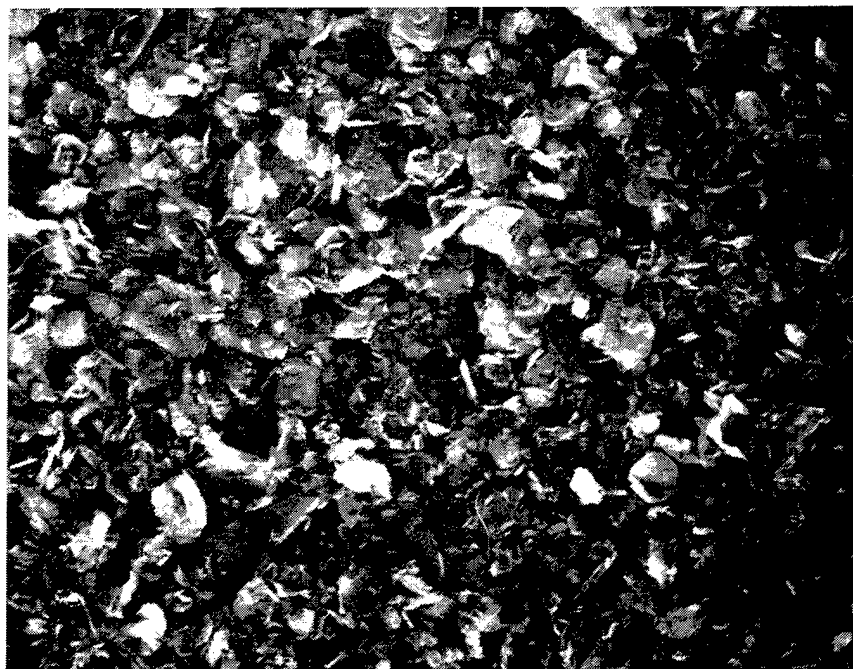


Figure 4. SEM of Crystalline Boron Powder.



10 μm

Figure 5. SEM of Natural Graphite Powder.



10 μm

Figure 6. SEM of Synthetic Graphite Powder.

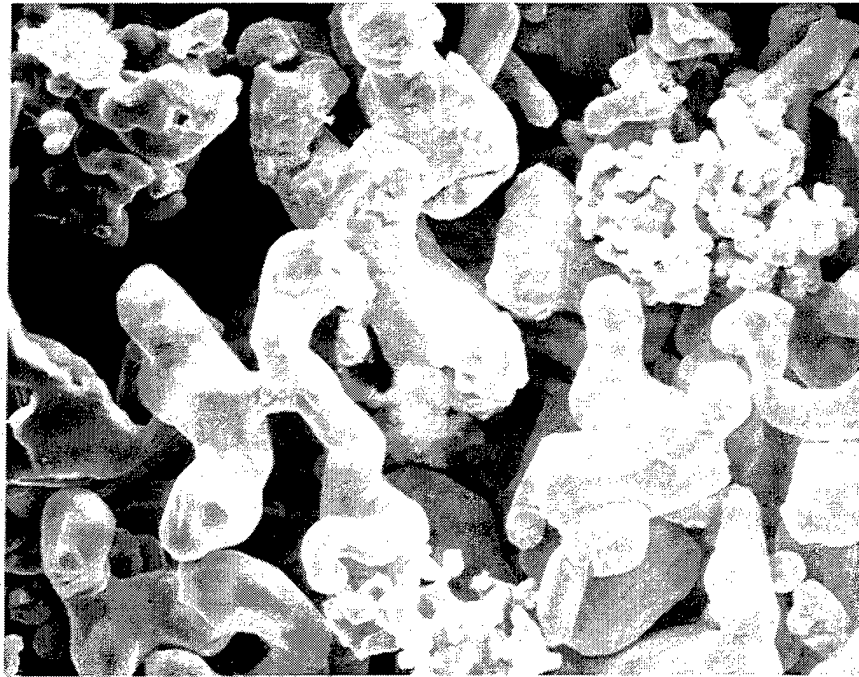


Figure 7. SEM of Titanium Powder.

Table 2. Mean Particle Sizes of Powder

Powder (mean)	Particle Size (μm)
Crystalline B	18.0
Amorphous B	2.10
Graphite 250 (Synthetic)	6.17
Graphite 850 (Natural)	8.74
Ti	34 (after sieving)

Based on the theoretical density of the ceramic product and a desired final dimension of 2.5-cm long \times 1.25-cm-diameter, 15.8 g of Ti and graphite powder were added to the graphite die. Knowing the starting amount of material, it was possible to monitor densification during heating and reactive sintering by following stroke displacement. After weighing and combining, the powders

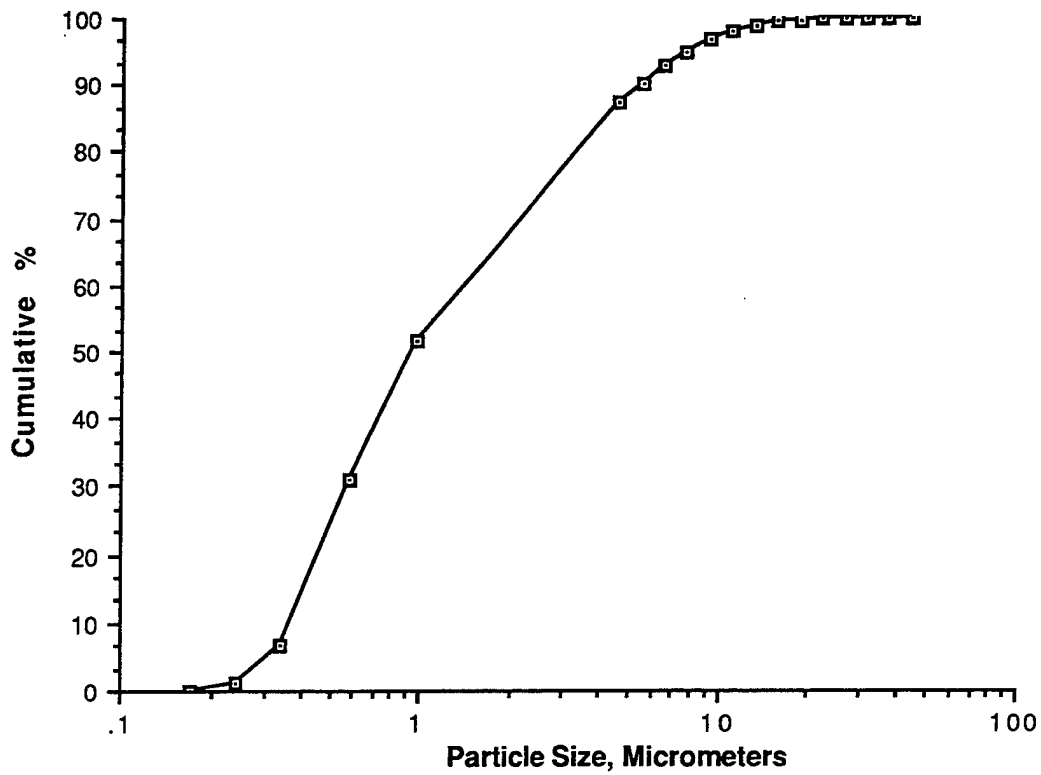


Figure 8. Particle Size Distribution for Amorphous Boron.

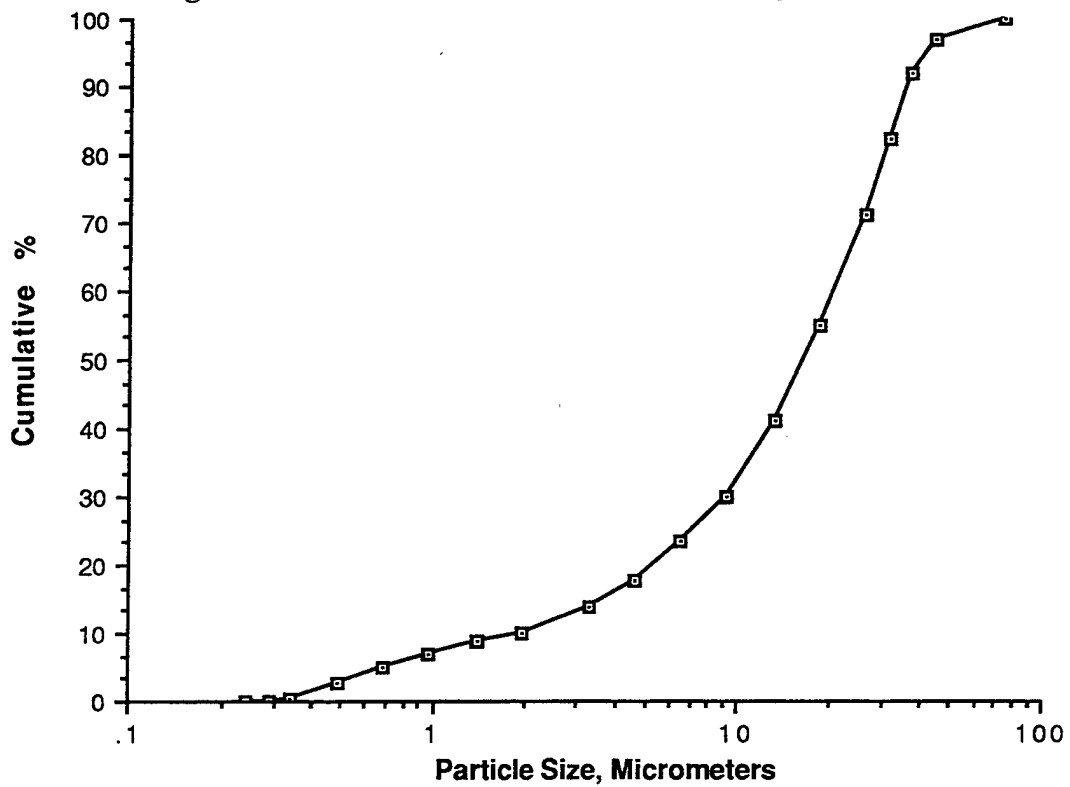


Figure 9. Particle Size Distribution for Crystalline Boron.

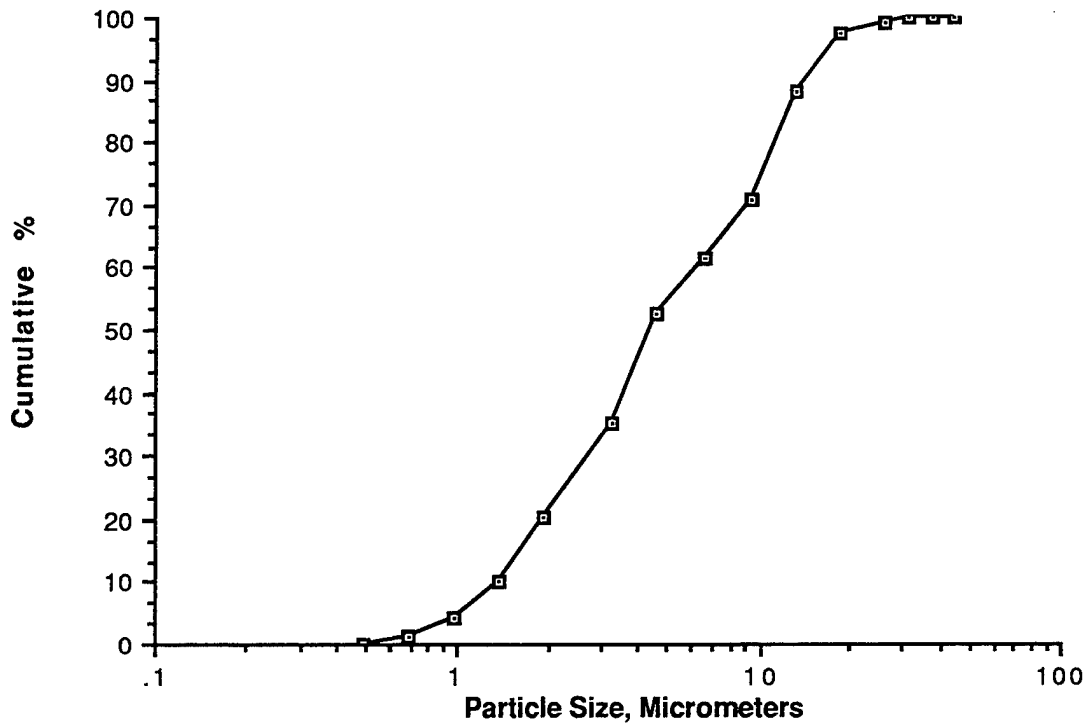


Figure 10. Particle Size Distribution for Synthetic Graphite.

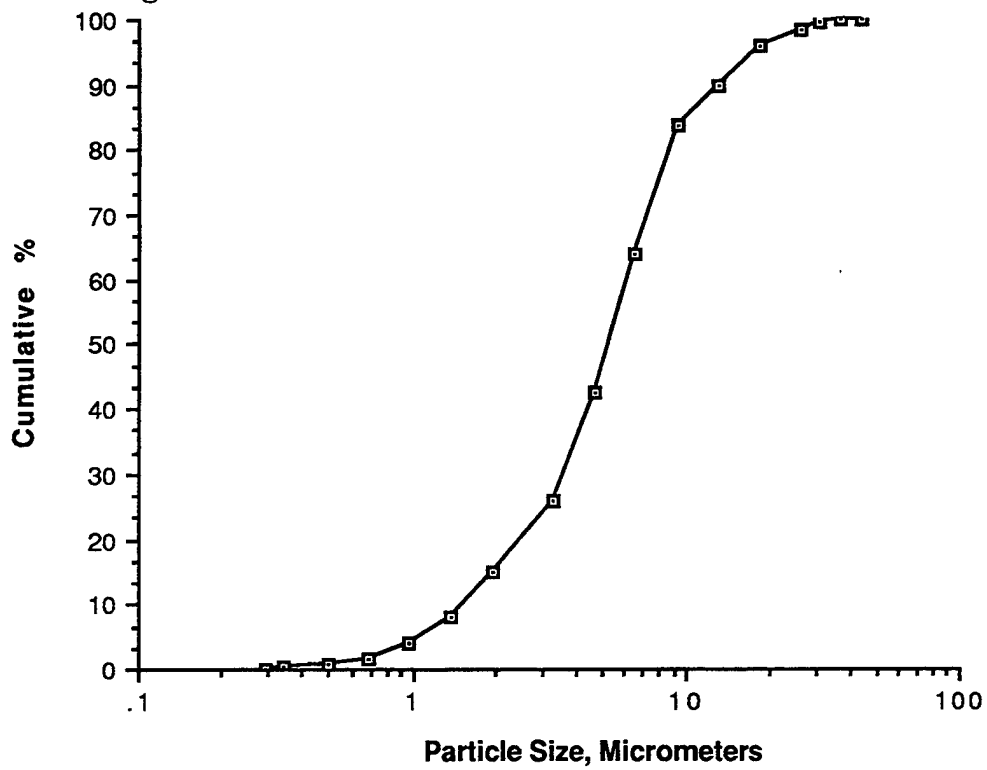


Figure 11. Particle Size Distribution for Natural Graphite.

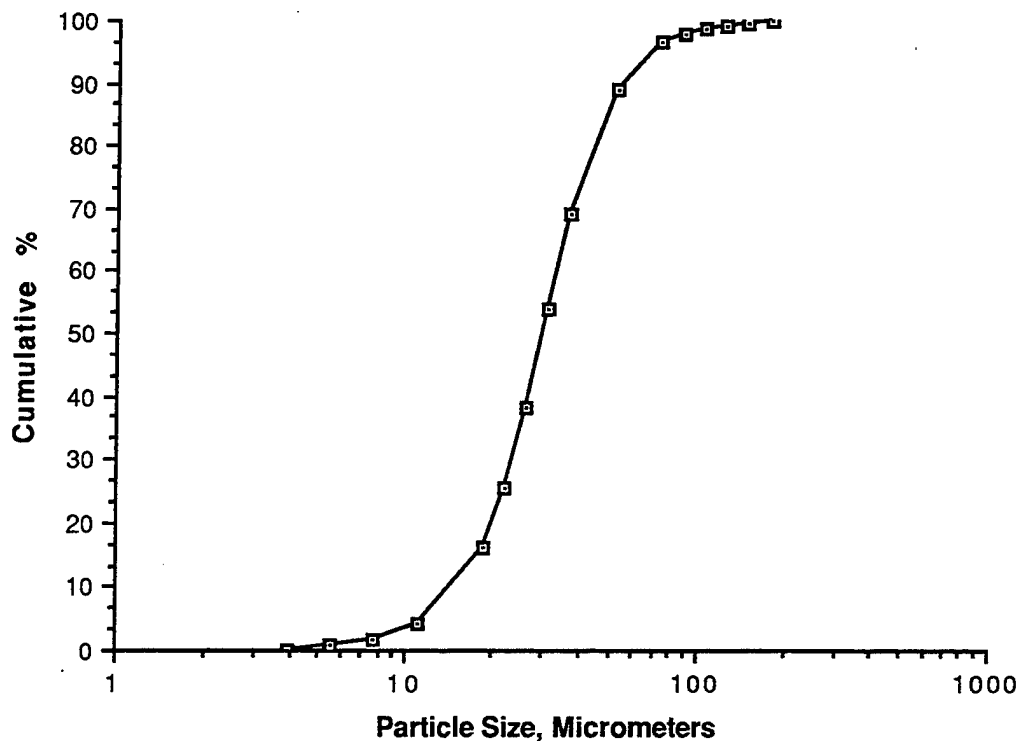


Figure 12. Particle Size Distribution for Titanium.

were mixed together in a Turbula mixer for 30 min and then the powder mixture was loaded into the graphite die and pressed on a hydraulic press using double-action compaction to form a 60% dense green sample. Roughly 35 MPa (5 ksi) of pressure was employed for greening the sample. The loaded die was moved from the hydraulic press to the Gleeble 1500 testing machine. No Ni powder was added to the TiC for the first set of testing.

4.2 Experimental Procedure. Both sample material and the die were resistance heated by the flowing current. Heating rates were limited by cracking of the die because of thermal expansion mismatch. High heating rates can lead to die cracking because of the thermal expansion difference between the sample and the die material. (The die may also crack during rapid cooling after completed densification because of thermal shock.)

The Gleeble 1500 could not be run initially due to the fact that the system was temperature controlled through the reading from the chromel-alumel thermocouple. The thermocouple would melt after the Ti and graphite mixture went exothermic and the electrical system triggering the hydraulic load system would be shut down. Duffers Scientific Associates installed a power control module that allowed the machine to be run in power control mode and did not rely on feedback from the thermocouple.

Once the module was added, an experiment was performed using the roughing pump and diffusion pump to draw high vacuum within the chamber containing the die assembly and sample. A chromel-alumel thermocouple was attached to the graphite tube using a cement-based sealant. Degassing of the powders was performed at 600° C for 30 min and then the temperature was increased at a rate of 10° C/s. The large exotherm associated with reactive sintering was observed between 800 and 1,100° C during rapid heating. Outgassing from the reaction would crack the graphite die. The actual initiation temperature varied and sometimes would not be reached, therefore preventing CS. While operating in power control mode, a tungsten-rhenium thermocouple was embedded in the powders and the sample was heated to allow the sample to reach the initiation temperature for CS. The thermocouple would eventually fail, which indicated that the exotherm had to have exceeded the 2,400° C melting temperature of the thermocouple. The WC anvils melted during this experiment, which also indicated that a significant amount of heat was being lost longitudinally through the anvils.

Experiments were continued using the graphite die surrounded by a split steel die to allow application of high pressures. Outgassing from the reaction shattered the graphite die when it was used unsupported. A thermocouple was welded to the steel, and the steel was in direct contact with the graphite tube. Force was applied using manual control after onset of CS. Densities less than 80% were being obtained with this approach, as force was probably being applied too late. It was then that the vacuum gauge was added for triggering the hydraulic system of the Gleeble. Timing of the compaction was associated with a given amount of outgassing. A value such as 10 or 50 × 10⁻³ Torr would be preset so that when this value was exceeded as the chamber started to lose

vacuum, load would be applied to achieve dynamic compaction. With this approach, it still was not possible to achieve densities greater than 80% of theoretical. The maximum temperature recorded on the outside of the graphite tube after the exothermic reaction was 1,400° C, which indicated that most of the heat loss was occurring longitudinally and not radially. Heat loss from the compact was such that, when load was applied, not enough of the latent heat from the CS reaction was remaining in the sample to keep the compact at a sufficient temperature for dynamic compaction to achieve high densities.

A significant heat loss was occurring due to radiation, direct conduction, and electronic conduction. Radiation loss is estimated to be up to 25% of the entire heat lost. Loss due to conduction longitudinally is significant and accounts for the bulk of the remaining heat loss. Samples processed by this method must be electrically conductive for resistance heating to occur, and consequently, unwanted thermal conductivity in the form of heat loss to the jaws of the testing machine also takes place. This described heat loss can lower the temperature of the sample in a very short time after the reaction such that further densification is greatly limited. With the resistance heating approach, the amount of heat loss longitudinally may be reduced by employing materials of varying electrical resistances between the anvil and sample. The sample will take longer to heat, but loss of heat through conduction will also be reduced. Heat loss will still occur, and it is uncertain if adiabatic conditions will be approximated enough for there to be enough heat remaining in the sample to obtain high densities at the time the load is applied.

It was observed in these studies that when the pressure was greater than 35 MPa during heating to the initiation temperature, the sample would not self-propagate, which is consistent with the literature findings that increasing the pressure of the compacted powder mixture prior to ignition can significantly retard the combustion. Most likely, developed enthalpy is dissipated quickly and the critical enthalpy for combustion is not reached.

The greatest densities achieved using reactive sintering and dynamic compaction were 82%. Further attempts at processing TiC using compaction following reactive sintering were suspended

based on success at getting TiC to form at low temperature without observation of the large exotherm. Early in the effort, tests were conducted heating the powder mixture while applying force, and though the large exotherm typically associated with CS was not observed, the vacuum level would decrease within the chamber but vacuum would not be lost completely. This change in vacuum level would occur from 700 to 900° C, as measured on the graphite die. Associated with the decrease in vacuum was an associated stroke change that would eventually cease. Stopping the test at this point generated a compact that was roughly 73% dense, and x-ray analysis confirmed that the Ti and graphite had reacted to form TiC.

5. Current-Induced SHS

5.1 1.25-cm-Diameter Evaluation Studies. The "steady" current-induced SHS technique was developed in this study. During degassing under compaction stress ranging from 17.5 to 35 MPa, some densification took place as the sample heated. Stroke change leveled off at 600° C, and following degassing, densification would resume again at 700° C. Stroke change would be observed for approximately 15 min after which time densification would cease. X-ray diffraction confirmed 100% transformation to TiC. Figure 13 shows a typical plot of stroke change as a function of temperature and pressure during current-induced SHS. This plot is from the 10-cm-diameter sample, but it is also representative of the 1.25-cm-diameter samples. The time for transformation of the 10-cm-diameter sample to TiC was longer than for the 1.25-cm-diameter samples because of the larger mass and caution employed to keep the samples from self-propagating. Further testing helped to understand the mechanism for the reaction.

The current-induced process transforms the elemental powders to TiC in a controlled manner, maintaining low overall temperatures and without the onset of the violent exothermic reaction. Both TiC and TiB₂ have been formed using this process without the gross temperature of the containing graphite die exceeding 800° C. To reiterate, the process works as follows: electrical current is passed through the electrically conductive elemental powders. Very high current densities are developed locally at particle interfaces. Heating results from the electrical resistance of the particle

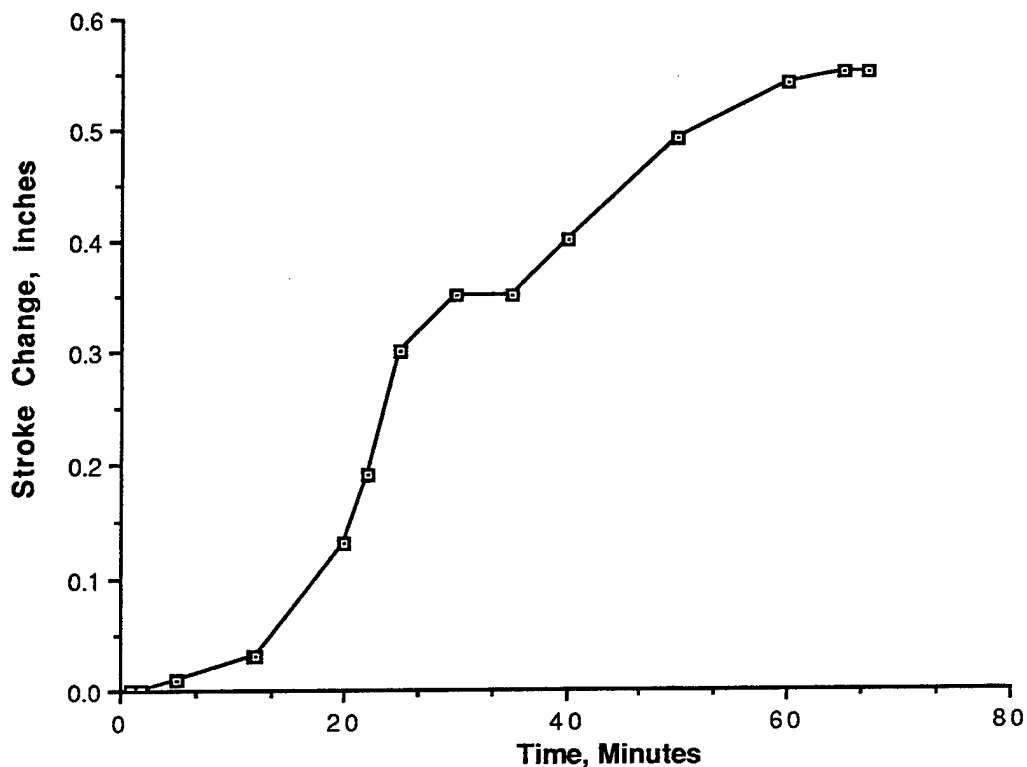


Figure 13. 10-cm TiC Transformation Plot.

interfaces. This heat is sufficient to cause transformation locally. However, the reaction stagnates and does not self-propagate since heat is conducted/radiated from the system faster than neighboring elements could reach the critical temperature for CS. As current continues to flow into the compact, the electrical resistance of the regions that have reacted decreases while untransformed regions continue to react and stagnate until eventually all of the elemental powders have been transformed.

Transformation occurs faster at 800° C than at 700° C. Increasing the current to raise the temperature can cause the remaining unreacted powders to go exothermic. (Recall—the current-induced technique employed an unsupported graphite die, so if a large volume of the powder was allowed to self-propagate, degassing would have shattered the die.) As pressure is increased from 17.5 MPa to 35 MPa, the time for complete transformation is reduced. The density of samples following this reaction is consistently 73% of theoretical. The presence of 3 wt.-% Ni does not change the transformation process.

The TiC material was densified to 95–97% by electrically heating the sample after synthesis using the steady current-induced SHS technique. With 3 wt.-% Ni added to TiC and with 35 MPa pressure, densification occurs at 1,300° C. The maximum sintering temperature examined for TiC with 3 wt.-% Ni was 1,500° C, and a 97% density was obtained at 56 MPa (8 ksi). The time at temperature was approximately 15 min. Using current to heat the compact appears to significantly reduce the time needed for densification. Microhardness testing could not be performed without cracking the Ni-based matrix. The Vickers hardness at 500-gf load was approximately 19 GPa, and the Ni-based matrix was cracked from the indentation.

TiC without Ni would transform at 700–800° C but would not densify at the combination of 1,500° C and 56 MPa. The material would creep at 1,700° C and 35 MPa, but the density rate would eventually stagnate. As the density increased, higher temperatures and pressures were required to further densify the compact.

TiB₂ showed the same transformation temperature as TiC with the current-induced process at 800° C using 35 MPa of pressure but did not demonstrate the same densification as TiC at 1,500° C and 56 MPa. The Gleeble begins to overheat as more current is brought to the compact to raise its temperature above 1,500° C. Because of this overheating, we could not explore temperatures at which densification would occur for TiB₂. Limitation of the present apparatus prevented additional high-temperature processing for the TiB₂ system.

Figures 14–17 show the x-ray diffraction patterns for TiC and TiB₂. Except for Figure 17, the analyses are for 1.25-cm-diameter samples. Analysis shown in Figure 14 is from a sample that was identified as A5 and was the first in which the current-induced transformation was noted. X-ray analysis of the sample verified that TiC had been produced from the elemental powders. Sample A5 was 72% dense after transformation. Figure 15 shows the x-ray diffraction pattern for a sample that was brought to 1,500° C following transformation and sintered to 96% density. This sample contained 3 wt.-% Ni. The TiB₂ sample that was transformed to approximately 73% density by the current-induced transformation process was analyzed and confirmed to be TiB₂ by x-ray diffraction.

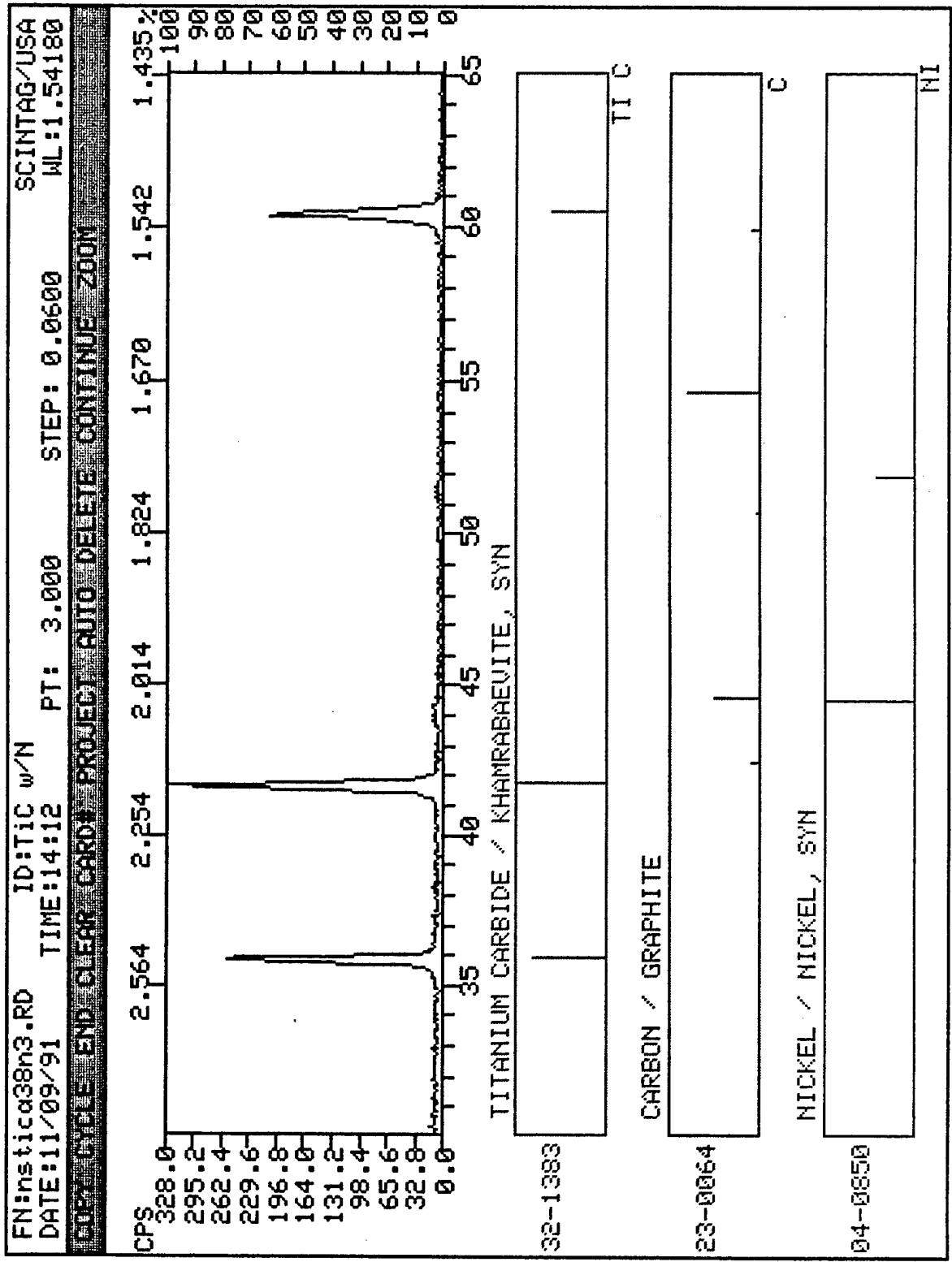


Figure 15. X-ray Diffraction for TiC, 95% Dense.

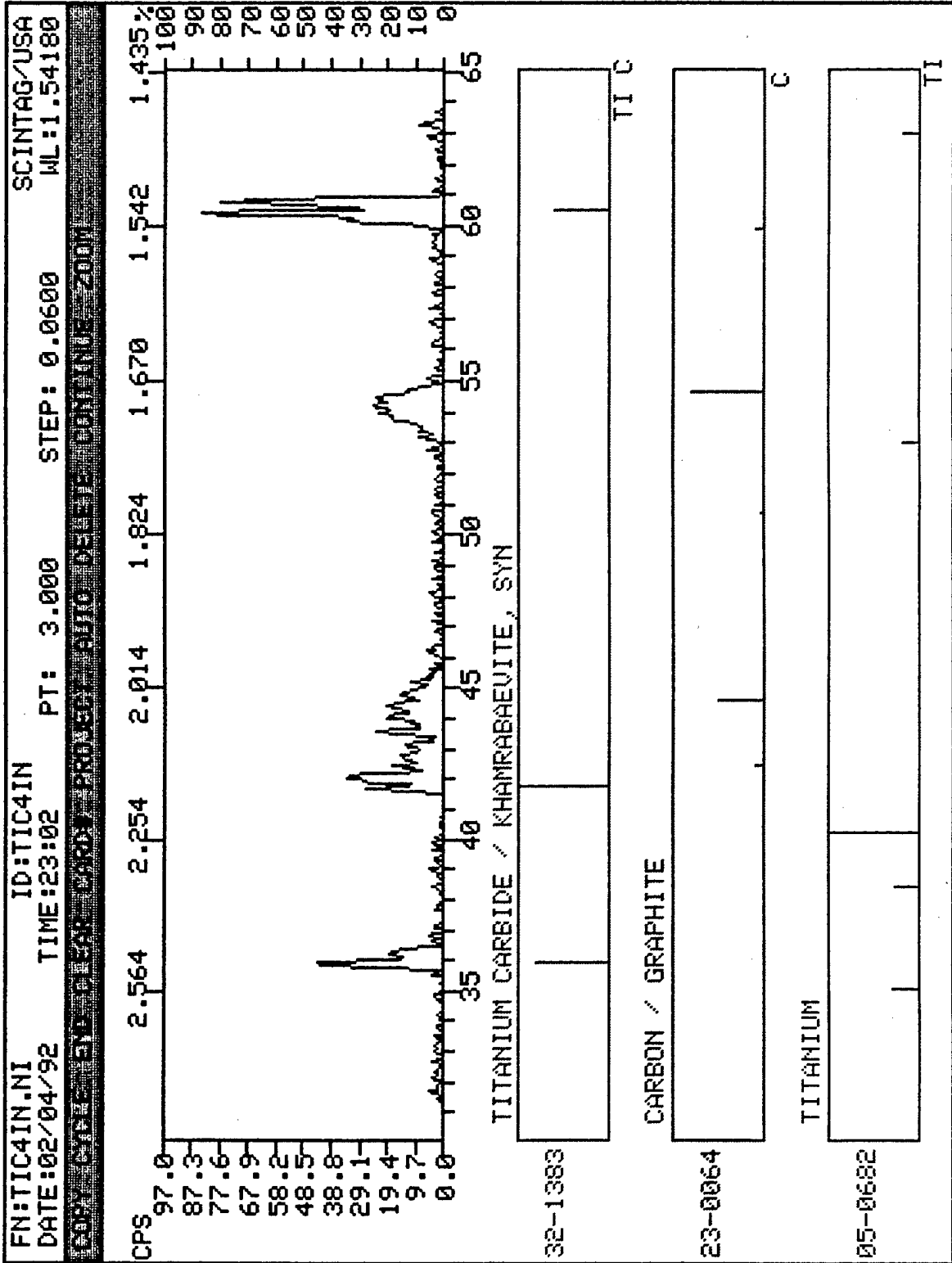


Figure 17. X-ray Diffraction for TiC, 84% Dense.

The TiB_2 sample is shown in Figure 16. Figure 17 is the pattern for the 10-cm-diameter sample of TiC that was transformed and hot pressed to 84% density.

5.2 10-cm-Diameter Disk. It was necessary to demonstrate that the controlled SHS approach could be applied to the fabrication of large shapes. The Gleeble 1500 at Rensselaer was employed for the transformation from elemental powders to TiC; Ni was not used in this sample. It was not possible to densify the 10-cm sample on the Gleeble following transformation because of overheating resulting when running current levels required to densify such a large sample.

The die material was again ordered from Southern Graphite; the dimensions of the die and anvils are shown below. During the current-induced SHS studies, graphite anvils were used to compact the sample; graphite anvils were also used for processing the 10-cm-diameter TiC.

Grade SG-2

Die: 12.5-cm OD \times 10-cm ID \times 8.8-cm long

Anvil: 10-cm OD \times 8.8-cm long

A picture of the graphite die and graphite anvils that were used for scale-up to 10-cm diameter is shown in Figure 18.

Powders were weighed out for making two 10-cm-diameter TiC samples, one TiC sample with 3 wt.-% Ni, and one TiB_2 sample. The mixtures are in Table 3 for the three combinations.

Because of limited availability of the Gleeble 1500, we were not able to run more than one 10-cm-diameter sample. TiC with no Ni addition was selected for the test. The die was loaded with powder and greened at 14 MPa (2 ksi) before being loaded in the Gleeble. The optical pyrometer was again used to measure the temperature of the graphite die during the test. The graphite anvils were positioned against the powder and again no backing support was placed around the graphite

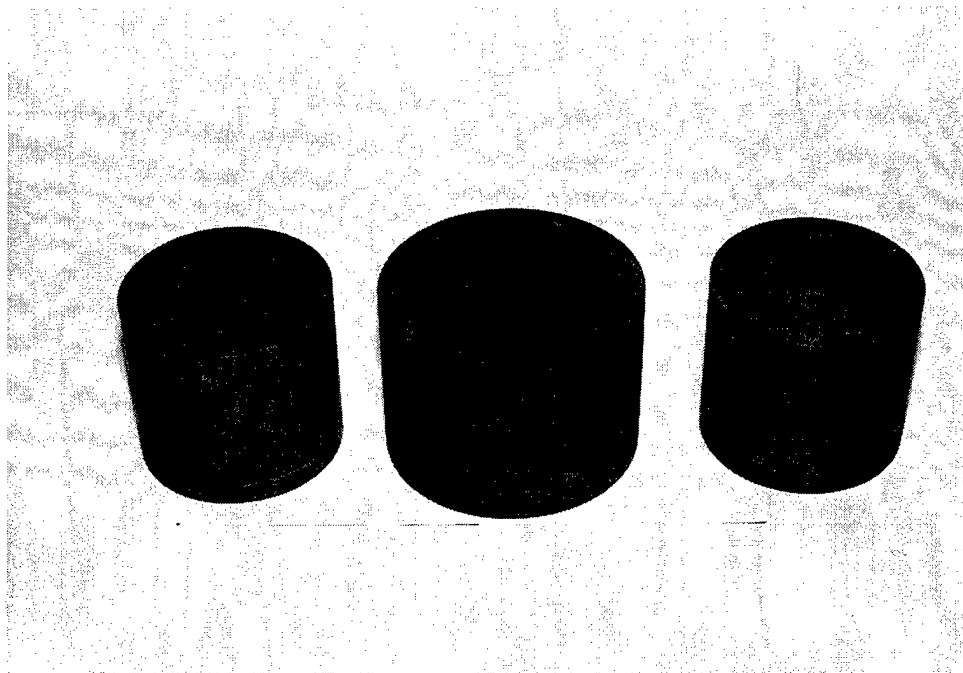


Figure 18. Graphite Die and Anvils for 10-cm Sample.

Table 3. Powder Amounts for Scale-Up to 10-cm-Diameter Sample

Compound	Amount of Powder Added			
	Ti (g)	C (g)	Ni (g)	B (g)
TiC	807.28	201.82	—	—
TiC/3 wt.-% Ni	783.06	195.77	15.13	—
TiB ₂	639.93	—	—	290.88

die. The sample was heated slowly to ensure that the powder would not initiate in a self-propagating exothermic manner. The sample began to densify at 700° C, and the temperature during transformation was as high as 800° C with roughly 4,000 A running through the sample. Pressure on the sample was 2.8 MPa (0.4 ksi). Because of the manner in which the die was positioned in the Gleeble, only the bottom half of the anvil was actually being compressed; use of additional pressure

would have increased the possibility of having the die rupture. Time for transformation was approximately 30 min, and the density after transformation was 59%. Figure 13 shows the plot of temperature, load, and stroke change during transformation to TiC. This sample was then taken to General Electric in Schenectady, NY, where it was hot pressed at 2,000° C and roughly 21 MPa (3 ksi). At that facility, die design limited pressures to 21 MPa. Density after hot pressing was 84% of theoretical. Data for the hot pressing experiment appear in Table 4.

Table 4. Hot Pressing Data for 10-cm-Diameter Sample

Time (hr:mm)	Temperature (° C)	Deflection (mm)	Pressure (MPa)	Vacuum (μ m of Hg)
13:20	—	0.0	0.8	8
14:05	820	-1.96	0.8	16
14:25	1,145	-2.3	2.8	23
14:45	1,420	-2.1	2.8	60
14:54	1,515	-1.14	5.6	110
15:24	1,755	-0.76	5.6	150
15:32	1,775	-0.78	5.6	90
16:00	1,920	0.13	5.6	48
16:22	2,010	2.8	8.0	42
16:46	2,050	5.5	8.0	42

Following transformation to TiC on the Gleeble, the faces of the sample were slightly uneven. As a result, the faces were machined flat at General Electric prior to the hot pressing experiment. The sample was easily machined without cracking and then placed in the graphite die for hot pressing. The sample after hot pressing was cracked, which most likely occurred during cooling. The structure of the 10-cm sample was identical to the 1.25-cm-diameter samples in that there were regions of unreacted agglomerated graphite. Ball milling would be applied for future mixing experiments to eliminate these islands of graphite.

6. Discussion

Attempts to achieve high density by initiating the CS reaction with passing current through the sample to provide resistance heating and subsequently dynamically compacting the sample proved unsuccessful. Notable heat loss was reported in the longitudinal direction in comparison with the radial direction of the graphite die that was used for this experiment. Because of this heat loss, adiabatic conditions were not closely approximated such that when pressure was applied, the temperature of the sample was too low to densify to high densities. Densification was limited to 80% with reactive sintering followed by dynamic compaction.

However, it was found that by passing current through the powder to provide resistance heating, high temperatures are achieved locally and the elemental powders actually do transform to product by a variation of traditional SHS. In this case, pressure was being applied while current was passing through the sample and transformation to product occurred locally without a large exotherm and gas release. This process was termed the slow and steady technique because it provided transformation of reactants to products in a controlled and safe manner. X-ray analysis revealed that the reaction occurred to completion. The current-induced SHS process demonstrated much more control over the transformation than was possible with traditional SHS processing. The transformation rate may be increased by performing the process at a higher current level. But the use of higher current increases the risk of the elemental powders reacting and producing a combustion wave through the remaining unreacted powders. The degassing associated with such a combustion wave will destroy an unsupported graphite die and damage the sample.

In this effort, basically a two-step process was practiced. In the first step, the elemental powders were converted to product, which was roughly 73% dense after transformation. The second step involved increasing the current level to heat the sample to a temperature sufficient to sinter to high density. Further densification of transformed material was noticed at higher temperatures, such as 1,300° C. Ni acted not only as a sintering aid but also allowed deformation of the porous material. A creep mechanism led TiC to final high density, such as 97% of theoretical value. Without Ni in

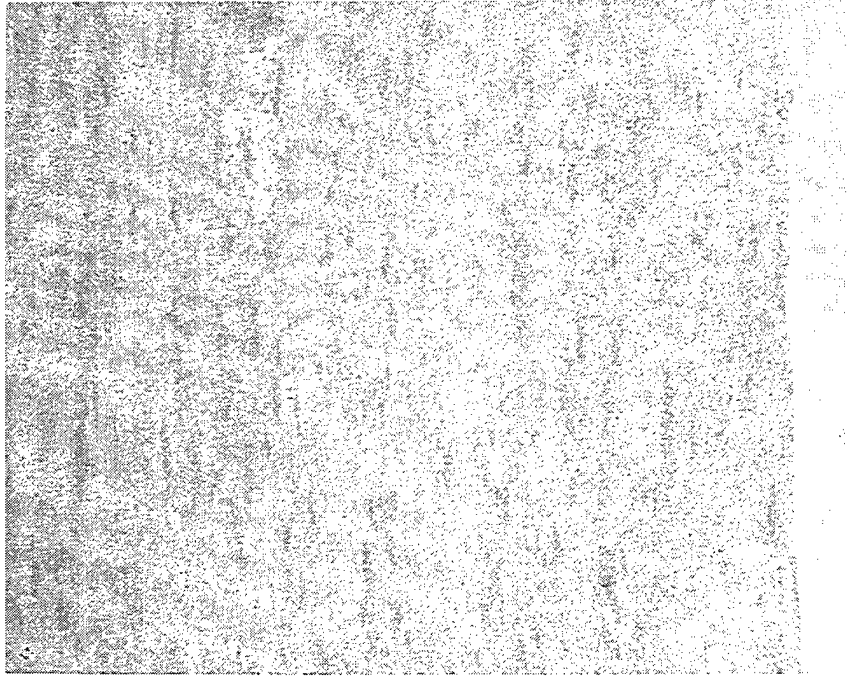
the Ti and graphite powder mixture, the first step of the process was unchanged but higher temperatures were required for densification. Only 90% dense material was obtained at temperatures such as 2,200° C and under a pressure of 56 MPa.

Table 5 shows the A5, A11, A38, A40, A41, and A45 sample densities. Samples A5, A11, and A40 were stopped following transformation; the others were sintered following transformation by increasing the current level. The sintering time needed to go from roughly 70% density (at 35 MPa) was on the order of 15 min. A low magnification optical micrograph of sample A5 appears in Figure 19. It shows regions of graphite, which may be attributed to poor mixing. Figures 20 and 21 show the microstructure for sample A38, which is 95% dense and contains 3 wt.-% Ni addition. This microstructure is representative of samples with Ni addition that were sintered to high density by raising the current level following transformation.

Table 5. Density Measurements (TiC 3 wt.-% Ni)

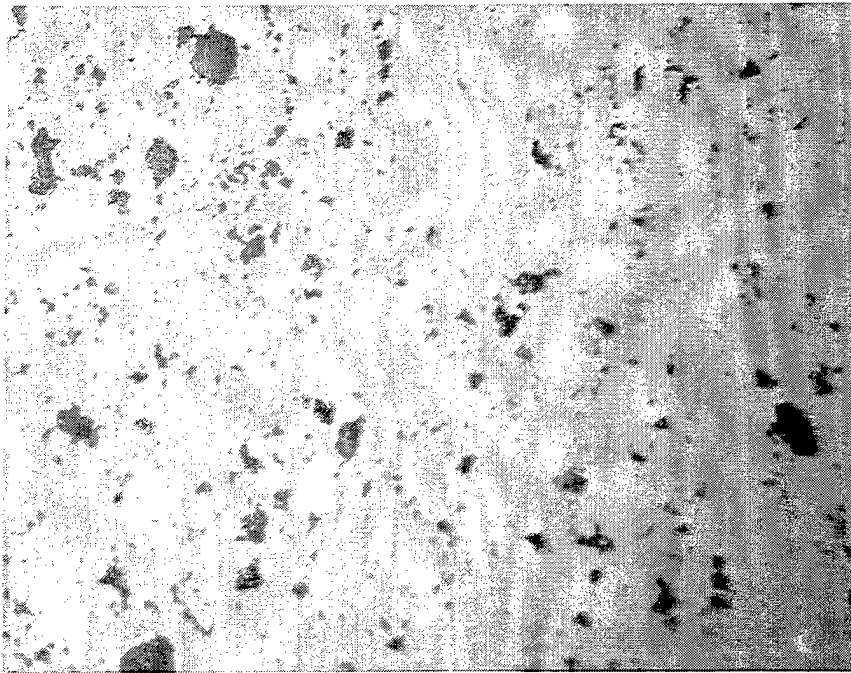
Sample	Process Conditions	Density (g/cm ³)	Theoretical (%)
A5	Transformed at 900° C, 17.5 MPa	3.52	72
A11	Transformed at 900° C, 35 MPa	3.68	75
A40	Transformed at 800° C, 35 MPa	3.47	71
A38	Transformed at 800° C, 35 MPa Sintered at 1,400° C, 15 min, 35 MPa	4.66	95
A41	Transformed at 800° C, 35 MPa Sintered at 1,400° C, 15 min, 35 MPa	4.60	94
A45	Transformed at 800° C, 56 MPa Sintered at 1,400° C, 15 min, 56 MPa	4.76	97

In experiments with Ti and B powders, transformation of the initial mixture into TiB₂ proved that this approach has universal value even though process parameters have to be considered individually for each material. Though not part of this SBIR effort, this approach was also successively demonstrated on the NiAl system. For NiAl, full density was achieved and the sample hardness was comparable to conventionally processed NiAl.



360 μm

Figure 19. Sample A5 Microstructure, 72% Dense.



25 μm

Figure 20. Sample A38 Microstructure, 95% Dense.

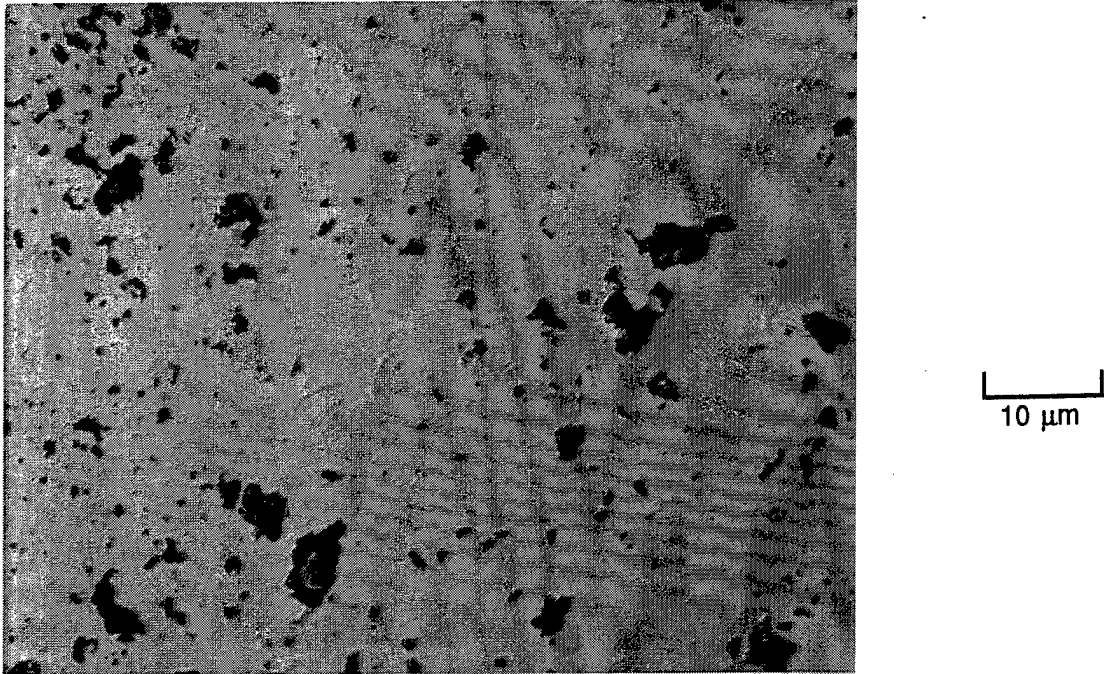


Figure 21. Sample A38 Microstructure, 95% Dense; Enlarged View.

Additional work that should be performed includes transforming elemental powders with the electrical current technique with a very high stress applied; a test is planned at Duffers Scientific using 700-MPa (100 ksi) pressure during transformation. The goal would be to transform and fully densify in one step. Additionally, the powders for this test would be ball milled to determine whether a more uniform microstructure results.

7. Summary

In this effort, an approach employing current-induced reactive sintering was developed and shown to be a viable method for producing TiC and TiB_2 by CS. Applying pressure to a powder mixture of Ti and C or Ti and B, while passing current through the mixture, resulted in the formation of a product by CS with the reaction proceeding in a slow and steady fashion without a large

exotherm or violent outgassing. This approach demonstrated that CS may be performed while applying pressure to a green compact. Combustion synthesis occurred in a very controlled fashion, and the large exotherm was avoided. In this SBIR effort, the process was demonstrated with TiC, TiC with 3 wt.-% Ni, TiB₂, and, to determine the generality of the process, NiAl.

Although it has been shown that excellent shape control is achievable with this technique, further work needs to be performed to assess the effect of pressure during transformation. Specifically, it should be determined whether application of large pressures in the samples will generate 95% theoretical densities or greater after transformation.

Attempts to obtain high densities using dynamic compaction after reactive sintering were unsuccessful because of large longitudinal heat losses. Renewed attempts to employ current resistance heating to initiate the SHS reaction followed by compaction must focus on a means to prevent large heat losses so that adiabatic conditions are more closely approximated.

The current-induced reactive sintering process may be inexpensively scaled to a manufacturing setup and would not require the same tooling or safety considerations as those for traditional SHS. Further development is required to determine maximum densities that may be achieved as a function of pressure as well as to optimize the process parameters such as current level to reduce the time required to form the synthesized product.

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13. ABSTRACT (Maximum 200 words) Titanium carbide (TiC) and titanium diboride (TiB ₂) ceramics were formed from elemental powders using a Gleeble 1500 dynamic thermomechanical process simulator. In the first step of a two-step process, a self-propagating high-temperature synthesis (SHS) reaction was initiated by the passage of an electric current through the powdered green body. The temperature of the body was maintained at about 800° C, and the reaction rate was controlled by the application of a pressure of about 35 MPa. As verified by x-ray diffraction analysis, this procedure resulted in complete conversion from reactants into products having a range of densities from 72 to 75% of theoretical. In the second step, the current was increased to raise the temperature of the material, thereby sintering and densifying the product. TiC with 3 wt.-% nickel (Ni) was sintered to 95 to 98% of theoretical density, while TiC without Ni was sintered to 90% theoretical density. Although TiB ₂ was successfully converted, efforts to fully densify the product were hindered by the limitations of the Gleeble 1500. The effects of the current and pressure levels on the product density and microstructure were examined. The advantages and limitations of this process are also discussed.				
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