ADVANCED CERAMICS RESEARCH

SEMI-ANNUAL REPORT #3

FIBROUS MONOLITH WEAR RESISTANT COMPONENTS FOR THE MINING INDUSTRY

3RD TECHNICAL SEMI-ANNUAL REPORT

Reporting Period: 2/23/02 to 8/22/02

Prepared by:

Mark J. Rigali (Principal Investigator)

Mike L. Fulcher (Research Engineer)

Kenneth L. Knittel (Research Engineer)

Phone: 520-434-6365

FAX: 520-573-2057

Submittal Date: 10/1/2002

Contract # DE-FC26-01NT41051

Advanced Ceramics Research Inc.
3292 East Hemisphere Loop Dr.
Tucson, AZ 85706-5013

Submitted to:

Morgan Mosser

NETL ADD Document Control BLDG. 921

U.S. Department of Energy

National Energy Technology Laboratory

P.O. Box 10940

Pittsburgh PA 15236-0940

DISCLAIMER

“This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.”

ABSTRACT

During the reporting period, work continued on development of formulations using the materials down-selected from the initially identified contenders for the fibrous monolith wear resistant components. The FM systems studied were: WC-Co/WC-Co, WC-Co/Co, diamond/WC-Co, and $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3\text{-TiCN}$. Extrudable formulations for the materials listed were developed during the first twelve months of this effort, and work during the reporting period was focused on the development of optimized binder removal processes. A two-stage binder removal process was developed that resulted in prototype parts free of voids and other internal defects. In addition, changes in the binder removal atmosphere resulted in the apparent elimination of residual carbon, an important consideration when consolidating WC-Co containing systems. Using the improved binder removal processes, parts were consolidated by both sintering and hot pressing to >99% theoretical density. Samples of these materials were sent to Kyocera for mechanical evaluations. Fabrication of drill bit inserts was begun, and binder removal begun during the reporting period. A total of 24 green inserts were fabricated, and will be consolidated and delivered for field testing during the upcoming reporting period.

TABLE OF CONTENTS

DISCLAIMER	2
ABSTRACT	3
TABLE OF CONTENTS	4
INTRODUCTION	5
EXECUTIVE SUMMARY	9
PROGRAM MANAGEMENT	10
EXPERIMENTAL	11
PLANS FOR THE NEXT REPORTING PERIOD	24
REFERENCES	25
APPENDIX A	26

INTRODUCTION

This program addresses the mining industry's need for improved components for wear resistance. The cost/performance ratio drives the application of components and materials used in mining applications. The mining industry traditionally had little use for advanced wear resistant materials due to their high cost relative to their improved durability. The goal of this program is to offer advanced wear resistant materials, in the form of fibrous monolith composites, which will overcome the cost/performance barrier traditionally associated with advanced materials and significantly increase the wear life of targeted components. Materials systems that exhibit promise as a crosscutting technology where resistance to wear is important will also be developed. Research will be performed on other applications, such as metal cutting tools, as crosscutting technologies are developed and translated into other industries.

The program is a collaborative effort of component manufacturers, end users, a national laboratory, and universities. The program will target three particular wear components which offer a broad cross-section of wear conditions and environments encountered in the mining industry. These components are: 1) drill bit inserts used for drilling blast holes and oil and gas wells, 2) dozer teeth used in a variety of earth-moving equipment, and 3) hydro cyclone apex cones, used in cyclone separators for sizing of crushed ore. As the program progresses these target items will be evaluated for appropriateness to the goals of the program. The program team will design fibrous monolith structures or coatings into existing components. The program team members will fabricate, inspect, and test the components in real operating environments. Team members will also develop process workbooks for fabricating fibrous monoliths, non-destructive evaluation of components, and modeling of composite/component behavior under typical stress and wear conditions. This body of knowledge will be used as a basis for future work.

Fibrous Monolith Composites

Fibrous monoliths (FMs) are a new and very versatile class of structural ceramics. They have mechanical properties similar to CFCCs, including very high fracture energies, damage tolerance, and graceful failures but can be produced at a significantly lower cost. Since they are monolithic ceramics, FMs are prepared using a simple process in which ceramic and/or metal powders are blended with thermoplastics and melt extruded to form a flexible bi-component 'green' fiber (**Figure 1**). These fibers can be compacted into the 'green' state to create the fabric of polycrystalline cells after sintering. The process is widely applicable, allowing the cell/cell boundary bi-component fibers to be made from any thermodynamically compatible set of materials available as sinterable powders. The scale of the macro-structure is determined by the green fiber diameter (cell size) and coating thickness (cell boundary). Once the green composite fiber is fabricated it can be wound or braided into the shape of the desired component using any conventional composite architecture. The thermoplastic binder is removed in a binder burnout step and is then hot pressed or sintered to obtain a fully dense component.

Figure 1. Illustration of the Fibrous Monolith co-extrusion process. Ceramic and/or metal powders are blended separately with thermoplastics and plasticizers. The resulting mixtures are pressed into shells and rods. The shells and rods laminated to form a composite feedrod that is then placed in a heated die and co-extruded. The resulting green coaxial filament is laid-up, wound or woven into the desired component. The component is then delubed to remove the plastics and then hot pressed or sintered to densify the composite.

When viewed perpendicular to the fiber direction after densification, the two phases that make up the architecture of a FM composite are a primary phase that appears as a hexagonal polycrystalline cell, separated by a thin and continuous secondary phase (cell boundaries) as shown **Figure 2**. Volume fractions of the two phases in an FM composite that result in the best composite properties are typically 75 to 90 % for the primary phase (polycrystalline cell), and 10 to 25% for the continuous phase (cell boundary). The cell phase is typically a structural ceramic, such as ZrC, HfC, TaC, Si₃N₄, SiC, ZrB₂, HfB₂, ZrO₂, or Al₂O₃, while the cell boundary phase is typically either a ductile metal, such as W-Re, Re Ni, Ni-Cr, Nb, or a weakly-bonded, low-shear-strength material such as graphite or hexagonal BN.

Past research has shown that the low shear strength cell boundaries such as BN and graphite accommodate the expansions and contractions during thermal cycling of the FM composite components, resulting in improved thermal shock resistance. From the mechanical behavior viewpoint, the BN or graphite cell boundaries enables non-catastrophic failure due to stress delocalization and crack deflection mechanisms (**Figure 3**). This has been successfully demonstrated previously at both room and elevated temperatures. In addition, the presence of a ductile or relatively ductile cell boundary phase greatly increases the damage tolerance and wear resistance of the Fibrous Monolith composite. For example, a Diamond-based FM composite with a relatively ductile WC-Co interface forms a very wear resistant and damage tolerant composite that can be applied as a coating to drill bit inserts for use in rock drilling applications for oil, gas, and ore deposit exploration and production (**Figure 4**).

Figure 2. Schematic of a typical uniaxial Fibrous Monolith microstructure shown perpendicular to principal fiber direction.

Figure 3. Typical flexural stress-strain curve for a silicon nitride/BN FM material.

Figure 4. ACR's Diamond/ WC-Co FM composite applied as a coating on the surface of a WC drill bit insert (100x). Note the isolation of the darker material (Diamond) into discrete cells by the lighter contrast phase (WC-Co).

EXECUTIVE SUMMARY

During the reporting period, work was performed to develop binder removal processes for WC-Co, Al₂O₃, and diamond based FM material systems. A comprehensive study into potential binder removal methodologies for the WC-Co based FM systems led to the development of a dual binder thermoplastic formulation for these materials, and a complimentary two stage binder removal process. Use of this process has resulted in the fabrication of defect free sintered WC-Co FM bodies, with minimal free carbon porosity and densities as high as 99.5% of theoretical. For the Al₂O₃ and diamond based systems, binder removal work focused on developing processes that produced parts with minimal defects that could be reasonably healed through hot pressing or other high pressure consolidation processes. Al₂O₃ based FM test coupons fabricated using the new two-stage binder removal process were consolidated by hot pressing to 99.6% theoretical density. Diamond/WC-Co circular inserts were also fabricated and delivered to Phoenix Crystal for consolidation.

The component fabrication effort remained focused on drill bit inserts, conical and radial tool inserts and wear plates/inserts for earth moving equipment. Twenty-four 7/8" drill bit inserts (WC-Co(6%)/WC-Co(16%) FM) have been processed through binder removal, using the newly developed two-stage binder removal process, and are currently being consolidated. Delivery of these inserts for field testing is scheduled for the end of October. Extruded WC-Co(6%)/WC-Co(16%) 10 mm round feed stock was also fabricated, and test pieces consolidated by sintering to >99% of theoretical density. This feed stock will be used to machine point attack and other insert tooling. In addition, Al₂O₃/Al₂O₃-TiCN FM test coupons have been fabricated, and are being sectioned into rectangular inserts for evaluations of metal cutting performance.

Meetings with Kyocera Corporation took place in April, at the Kyocera Sendai plant. ACR participants included program PI Dr. Mark J. Rigali (Manager of Composite Ceramics), Mike Fulcher, (Research Engineer) along with ACM personnel Joe Halloran (Development Engineer). On the Kyocera side the participants were Hiromi Fujioka Materials Development, Junichi Imada Manager, Yoshio Nagato Vice-department Manager, Tatsuyuki Nakaoka Materials Development, Kenji Noda Materials Development, Daisuke Shibata Materials Development. Both Kyocera and ACR personnel presented results of materials development for WC-Co based FMs, as well as other fibrous monolith material systems of interest to both parties.

PROGRAM MANAGEMENT

The integration of partners into the program has required travel to facilities in Utah and Japan in order to build relationships and work toward agreement on the pursuit of materials, approaches and intended outcomes for the Fibrous Monolith Wear Resistant Components.

Dr. Zak Fang, University of Utah

A subcontract was put in place during the reporting period with Dr. Zak Fang, professor at the University of Utah in Salt Lake City. Dr. Fang is formerly of Smith International, and was an active participant in the development of diamond/WC-Co Fibrous Monolith materials for oil and gas drilling applications. Dr. Fang is well recognized as an expert in the field of WC-Co and other hardmetal materials, and has been enlisted to support the program in the area of consolidation process development. Several meetings were held with Dr. Fang over the course of the reporting period, both in Utah and at ACR's facilities.

Dr. Greg Hilmas, University of Missouri-Rolla

A subcontract was put in place during the reporting period with Dr. Greg Hilmas, professor at the University of Missouri-Rolla. Dr. Hilmas is formerly of ACR, and was an active participant in the development of fibrous monolith material technology, including diamond/WC-Co Fibrous Monolith materials for oil and gas drilling applications. Dr. Hilmas is well recognized as an expert in the field of fibrous monolith materials, and has been enlisted to support the program in the area of formulation and binder removal process development. Several meetings were held with Dr. Hilmas over the course of the reporting period, both in Missouri and at ACR's facilities.

Kyocera Corporation

Meetings with Kyocera Corporation took place April 2002, at the Kyocera Sendai plant and at the Kyocera Kokubu plant. ACR participants included Mike Fulcher, (Research Engineer) and program PI Dr. Mark J. Rigali (Manager of Composite Ceramics). Joe Halloran, of Advanced Ceramics Manufacturing was also in attendance.

Those present from the Kyocera were Hiromi Fujioka (Materials Development), Junichi Imada (Manager), Yoshio Nagato (Vice-department Manager), Tatsuyuki Nakaoka (Materials Development), Kenji Noda (Materials Development), and Daisuke Shibata (Materials Development). Tours of the cutting tools production facility and analytical research laboratory were conducted. Presentations by Kyocera Sendai personnel included topics on WC-Co, Si₃N₄/BN and diamond/WC-Co FM development. Lengthy discussions were held on the topics of formulation and green processing, with emphasis on material flow behavior and its effects on FM processing.

Dr. Mark Rigali made a presentation about the state of research and materials systems up to that point. The tests planned to evaluate the FM materials were discussed. Processing improvements, such as continuous co-extrusion, were also discussed, including aspects such as technical difficulties and possible equipment availability. Samples of some of the fibrous monolith billets produced to date were forwarded to Kyocera per these discussions. The characterization results appear in Section 5.

EXPERIMENTAL

Task 2. Develop Compositions of Fibrous Monoliths

During the previous reporting period, materials were down-selected from the original trade study based on the results of preliminary consolidation investigations. The down-selected material systems are listed in **Table 1**. Efforts during the reporting period were focused on the development of these material systems for mining applications.

Table 1 – Down-Selected Core and Interface Materials for FM Development

Core Material	Interface Materials
Tungsten Carbide-Co(6%)	Cobalt metal
Tungsten Carbide-Co(6%)	Tungsten Carbide-Co(16%)
Diamond	Tungsten Carbide-Co(14%)
Alumina	Alumina-TiCN

Task 3. Develop Fabrication Process Parameters of Fibrous Monoliths

Fabrication process parameters for fibrous monoliths include thermoplastic blending, core and shell molding, core and shell co-extrusion, coupon fabrication, and binder removal. Extrudable formulations for all the materials listed in **Table 1** were developed during the first twelve months of this effort, and work during the current reporting period focused on the development of optimized binder burnout conditions. The initial criterion used to evaluate binder removal processes was the presence of physical defects in the test parts after binder removal. These defects typically are in the form of cracks and internal bloating, which can result in distortion and diminished mechanical integrity of the parts after processing. In addition to physical defects, it was discovered that residual carbon, often referred to as carbon “porosity”, was an additional criterion by which the binder removal processes could be evaluated. A review of the literature was conducted, and potential binder removal processes were identified. Three distinct binder removal processes were evaluated during the reporting period. These processes were 1) high temperature vacuum binder removal, 2) high temperature binder removal in an inert atmosphere, and 3) a two-stage, low temperature vacuum followed by high temperature binder removal in a reducing (Ar/H₂) atmosphere. Detailed discussions of these evaluations are presented in the following section of this report.

ACR’s standard binder removal profile, which was originally designed for FM systems including Si₃N₄/BN, consists of a series of heating ramps and soaks to 600 °C in an N₂ atmosphere, designed to allow the gradual removal of binders from the part. Parts to be hot pressed require enclosure in graphite die so that the loads required for consolidation can be applied. Parts are typically enclosed prior to binder removal, which helps preserve mechanical integrity during processing. Parts to be pressureless sintered are typically placed in a crucible for binder removal. The ramp rates and temperatures are based on the TGA/DSC analyses of the thermoplastic polymers most commonly used to form extrudable material blends. Due to cost barriers with respect to tooling in the mining industry, a focus

of this program has been to develop consolidation techniques that will be cost competitive with those currently being used in industry, such as pressureless sintering. This focus necessitates the development of appropriate binder removal profiles that eliminate defects and allow for the use of low cost consolidation techniques.

High Temperature Binder Removal in Vacuum

One candidate process identified during the literature review was binder removal in vacuum at temperatures up to 500 °C. This process consisted of a constant temperature ramp (0.5 – 5 °C/min) to a maximum temperature of 500 °C in a roughing pump vacuum atmosphere ($\sim 10^{-3}$ torr). The relative simplicity of this process made it an ideal candidate for investigations on this program.

Test coupons of WC-Co(6%)/Co ~ 1 in² using a polymer binder mixture (EEA/EAA/MPEG) were prepared for high temperature vacuum binder removal experiments. Coupons were run at 0.5, 1 and 2 °C/minute to a set point of 500 °C. Photographs of the coupons before and after binder removal are presented in **Figures 5-7**. As evidenced in the photographs, significant cracking of the coupons parallel to the filament direction was observed following binder removal, even at the lowest heating rate of 0.5 °C/minute. In addition, the test samples were coated with a black powdery residue following binder removal. It was postulated that the polymer breakdown products were escaping the part but not leaving the furnace, due to the low mass flow rates in the vacuum furnace during binder removal, and these residual polymers were being carbonized at high temperature, resulting in the observed char. This char would then settle on the parts in a thin layer as it was formed. Due to the cracking and char residues seen during preliminary investigations, it was determined that the high temperature vacuum process would not be suitable for binder removal, and no further work was performed on this process.

Figure 5 – WC-Co(6%)/Co FM test sample before (left) and after (right) binder removal in vacuum (10^{-3} torr) with a heating rate of 0.5 °C/minute to a set point of 500 °C.

Figure 6 – WC-Co(6%)/Co FM test sample before (left) and after (right) binder removal in vacuum (10^{-3} torr) with a heating rate of $1.0\text{ }^{\circ}\text{C}/\text{minute}$ to a set point of $500\text{ }^{\circ}\text{C}$.

Figure 7 – WC-Co(6%)/Co FM test sample before (left) and after (right) binder removal in vacuum (10^{-3} torr) with a heating rate of $2.0\text{ }^{\circ}\text{C}/\text{minute}$ to a set point of $500\text{ }^{\circ}\text{C}$.

High Temperature Binder Removal in Inert Atmosphere

ACR has considerable experience with the removal of polymer binder mixtures at high temperatures in inert atmospheres (N_2). This type of process is in practice as the standard binder removal process for the majority of our ceramic part production. Investigations were undertaken to develop a heating profile that could be used to remove binder from parts without creating defects that could not be corrected during sintering. To simplify binder removal, thermoplastic blends containing only one polymer (EEA) were used to fabricate FM parts for evaluation. Cylinders 9 mm in diameter and approximately 10 mm tall were fabricated from both the bulk core (WC-Co (6%)) and shell (WC-Co (16%)) thermoplastic blends, as well as from co-extruded FM. TGA/DSC data for the breakdown of EEA in a N_2 atmosphere was used to establish a baseline heating profile, from which minor adjustments were made to improve the mechanical quality of the parts after binder removal.

The binder was removed in a 3" diameter tube furnace under a flowing Ar atmosphere (2 standard cubic feet per minute). Photographs of parts processed using the experimental binder removal heating profiles are presented in **Figures 8-9**. Following several iterations of heating profile adjustments, a profile that routinely produced apparently defect free WC-Co FM cylinders was developed. This profile is given below in **Table 2**. Through discussions with engineers at Kyocera, carbon content was identified as an important measure of the effectiveness of binder removal, as well as the presence of physical defects. A phase diagram for WC-Co (Gurland, 1951) referenced by Kyocera showed that the carbon content for WC-Co materials must be very tightly controlled, and that residual carbon from binder removal must be limited to below ± 0.05 wt%. Samples of cylinders processed using this profile were sent for carbon analysis in order to baseline the carbon content and provide direction for further binder removal work. The measured carbon content for the samples was in excess of 7 wt%, which was well above the carbon content for the baseline WC-Co (6%) material of 5.75 wt%. Reports in the literature suggested that H₂ gas could be used to "correct" the carbon content in WC-Co samples by reducing free carbon residue from binder removal into methane (CH₄). A gas mixture consisting of 90% Ar, 10% H₂ by volume was obtained, and samples run using the most promising profiles developed using a pure Ar atmosphere. After binder removal, these samples were similar in appearance to the samples run in Ar shown in **Figures 8-9**. When analyzed for carbon, however, the samples run in the Ar/H₂ atmosphere had a carbon content of 5.88 wt%, much closer to the baseline material at 5.75%. Parts were then prepared for preliminary sintering experiments, and the binders removed in an Ar/H₂ atmosphere. The parts were sintered at 1300 °C for 30 minutes under vacuum, then cross-sectioned and polished for examination. Cross sectioning of the parts revealed that, despite the absence of defects visible on the outside of the parts, significant cracking and voiding was still present inside the parts. The presence of internal defects prompted a review of the work-to-date with respect to thermoplastic blend formulation and binder removal, and the development of a WC-Co binder system and binder removal profile that would eliminate physical defects.

Figure 8 – WC-Co monolithic and FM test samples processed using binder removal profile “A” (left) and “B” (right) in a 3” diameter tube furnace under a flowing Ar atmosphere.

Figure 9 – WC-Co monolithic and FM test samples processed using binder removal profile “C” (left) and “E” (right) in a 3” diameter tube furnace under a flowing Ar atmosphere.

Table 2 – High Temperature Inert Gas Atmosphere Binder Removal Profile

Start Temp	End Temp	Heating Rate	Soak Time
RT	325 °C	30 °C/hr	8.0 Hours
325 °C	600 °C	30 °C/hr	3.0 Hours
600 °C	RT	Unforced Cooling	N/a

Two Stage Binder Removal Process

Based on the results of the high temperature vacuum and inert atmosphere binder removal evaluations, it was decided to re-evaluate the use of a dual polymer binder system with respect to the fabrication of defect free parts. A review of the scientific literature on binder removal from ceramic bodies suggested the use of two polymer binder systems for green processing of ceramics. Typically, one of the binders is removed at lower temperatures, which creates pathways for diffusion of breakdown products from the second binder at higher temperatures. For FM processing, the challenge was to develop co-binder systems that are compatible and suitable for co-extrusion.

During the previous reporting period, work at ACR was performed on co-binder systems because of the availability of WC-Co powders containing ~2 wt% paraffin wax, which is a common raw material used to fabricate monolithic WC-Co inserts. Systems using this material were developed and evaluated using the high temperature vacuum binder removal process, but the significant cracking and carbon char formation was observed. Samples of these systems were also evaluated using a high temperature inert gas binder removal process, however, significant bloating was observed in parts after binder removal and this system was dropped from consideration. In addition to the challenges associated with binder removal, the wt% paraffin wax varied significantly from batch to batch, making it very difficult to develop a universal thermoplastic formulation for this material. In order to eliminate the

batch variability of the wax content of the WC-Co powders, formulations were developed where a measured amount of wax (Calwax paraffin, Chevron) was added to wax-free powders, along with the second binder component (EVA, DuPont). These formulations were then used to fabricate test articles for binder removal experiments. The main challenge in earlier evaluations was the formation of bloats and defects during the low temperature (<200 °C) phase of the binder removal profile, where a majority of the wax is extracted from the part. In order to facilitate wax removal at the lower temperatures, a profile was developed based on TGA data provided by the wax supplier, and parts were processed in a low temperature vacuum oven at approximately 10^{-3} torr. After several iterations, a profile was developed that removed a significant of the wax within a part without creating mechanical defects. This profile is given in **Table 3**. As expected, the percentage of wax removed using this profile is strongly dependent on both the surface area and effective diameter of the part. For example, smaller cylindrical parts (~1 cm diameter) typically lose 80-90% of the total wax mass, while larger cylindrical parts (~2.5 cm diameter) typically lose 50-60% of the total wax mass using this profile in a vacuum atmosphere.

Table 3 – Low Temperature Vacuum Atmosphere Wax Removal Profile

Start Temp	End Temp	Heating Rate	Soak Time
RT	50 °C	4.0 °C/hr	2.0 Hours
50 °C	100 °C	2.5 °C/hr	4.0 Hours
100 °C	160 °C	3.0 °C/hr	4.0 Hours
160 °C	200 °C	3.3 °C/hr	12 Hours
200 °C	RT	Unforced Cooling	N/a

Following the wax removal process, the remaining binder was removed in the tube furnace under a flowing Ar/H₂ atmosphere, which was shown in earlier binder removal studies to significantly reduce free carbon levels. The heating profile for the second binder removal process is similar to the profile in **Table 2**, with one soak at 325 °C and a second soak at 550 °C. The 325 °C soak is to breakdown the polymer binder into smaller, more volatile, segments and residual carbon, and the 550 °C soak is to remove free carbon by reduction with H₂. The two-stage binder removal process has become the standard process for fabricating WC-Co containing parts, and has been successfully used to fabricate parts (e.g. test coupons, rod stock, inserts) that have sintered density in excess of 99%.

Task 4. Densification Process Development

Densification studies are being performed in order to optimize conditions and develop processes for the fabrication of fully dense ceramic parts. Incomplete densification can be detrimental to hardness, fracture toughness and transverse rupture strength, which are all important factors determining the performance of the mining components under development. The densification processes studied during the reporting period include uniaxial hot pressing and pressureless sintering, which are used extensively in industry for densifying ceramic materials. Consolidation experiments were performed on the WC-Co

based and Al_2O_3 based systems during the reporting period. The results for the systems are presented below.

WC-Co based systems

Full densification of the WC-Co materials is critical to the performance of these materials in applications for drill bit inserts, wear surfaces, and hydrocyclone cones. As mentioned above, processes being evaluated for consolidation of this system are hot pressing and sintering, with each having associated unique benefits. Sintering is the most cost effective consolidation process, and can be used to fabricate large batches of parts. Hot pressing is limited to a smaller batch size, however, increased pressures can allow for lower processing temperatures than possible with sintering. It is also possible to form near net shape parts so little post-process machining will be needed. For example, prototype drill bit inserts can be formed so they will need only outside diameter grinding to be application ready.

Hot Pressed Samples

Initial hot pressing experiments were used to establish processing conditions that would produce dense monolithic WC-Co coupons. Results for these experiments were reported previously (2nd Semi-Annual Report). Using conditions established to produce dense monolithic WC-Co coupons, efforts in the current reporting period focused on the densification of WC(6%)Co/WC(16%)Co FMs. Coupons were hot pressed at a range of temperatures from 1200 to 1300°C with pressures ranging from 2 to 6 ksi for times between 5 and 60 minutes. A complete listing of the hot pressed samples prepared during the reporting period is given in **Appendix A Section 2 Table 2 WC(6%)Co/WC(16%)Co – based Hot Pressed Samples**. Photographs of the WC-Co-based FM test coupons are presented in **Appendix A, Section 2**.

For an initial evaluation of hot pressing conditions and their effect on degree of consolidation, test coupons were consolidated at 1250, 1275 and 1300°C and 2, 4, and 6 ksi. All the coupons were processed using ACR's standard binder removal process. The hot pressing conditions and associated densities are shown in **Table 4 – WC(6%)Co/WC(16%)Co – based Hot Pressed Samples**. Densities for coupons hot pressed at 1300 °C were not as high as were seen for lower temperature samples with higher pressure. This density difference was attributed to the increased liquid phase mobility of Co metal at the higher temperature and subsequent formation of voids. Coupons hot pressed at 1250°C and a 60 minute hold showed increased density between 2 and 4 ksi, but decreased density at 6 ksi, suggesting that excessive pressures may have a negative effect. This may also be due to increased liquid phase mobility of Co metal at the higher pressure and subsequent formation of voids, as was suggested for the coupons pressed at 1300 °C. The coupon hot pressed at 1275 °C and 4 ksi has the highest density of all the test coupons fabricated, at 99.3% of the calculated theoretical density. Based on this result, these conditions were selected as the baseline for future hot pressing experiments.

To determine the effect of soak time on density and mechanical properties, test coupons were prepared using the two-stage binder removal process discussed earlier in **Task 3**. These coupons were then hot pressed at 1275 °C and 4 ksi, and soak times of 6, 30 and 60 minutes. The measured densities and hardness are given in **Table 5 –**

WC(6%)Co/WC(16%)Co – based 1275°C Hot Pressed Samples. Hardness was measured on the Rockwell A scale using testing equipment available at ACR. Increasing soak time was found to result in an increase in measured density; however, the hardness was highest for the sample hot pressed for 30 minutes. In order to confirm this observation, samples of these test coupons were sent to Kyocera for hardness, toughness and transverse rupture strength measurements. Results from those measurements will be presented along with additional discussion of this experiment in the upcoming technical report.

Table 4 – WC(6%)Co/WC(16%)Co – based 1300°C Hot Pressed Samples

Composition or FM Combination 82.5%core/17.5%shell (volume/volume)	Temperature °C (Pressure ksi, Time min)	Measured Bulk Density (g/cc)	Theoretical Density (g/cc)	% Full Theoretical Density
WC Co(6%) / WC Co(16%)	1300(2 ksi, 8 min)	13.839	14.77	93.7
WC Co(6%) / WC Co(16%)	1300(2 ksi, 60 min)	14.112	14.77	95.5
WC Co(6%) / WC Co(16%)	1300(2 ksi, 60 min)	14.154	14.77	95.8
WC Co(6%) / WC Co(16%)	1275(4 ksi, 60 min)	14.672	14.77	99.3
WC Co(6%) / WC Co(16%)	1250(2 ksi, 60 min)	14.069	14.77	95.2
WC Co(6%) / WC Co(16%)	1250(4 ksi, 60 min)	14.367	14.77	97.2
WC Co(6%) / WC Co(16%)	1250(6 ksi, 60 min)	14.094	14.77	95.4

Table 5 – WC(6%)Co/WC(16%)Co – based 1275°C, 4ksi Hot Pressed Sample Hardness

Composition or FM Combination 82.5%core/17.5%shell (volume/volume)	Time	Measured Bulk Density (g/cc)	Theoretical Density (g/cc)	% Full Theoretical Density	Hardness (Ra)
WC Co(6%) / WC Co(16%)	6 min	14.398	14.77	97.5	85.2
WC Co(6%) / WC Co(16%)	30 min	14.409	14.77	97.5	90.4
WC Co(6%) / WC Co(16%)	60 min	14.513	14.77	98.2	83.6

Based on the data given in **Tables 3 and 4**, relatively high density can be achieved by hot pressing at 1275 °C and 4 ksi for 60 minutes. During the next reporting period, plans for further refinement of hot pressing conditions include more detailed evaluation of the effect of pressure, temperature and soak time, using the above discussed data as a baseline for the development of experimental conditions. As conditions are verified to result in improved density and mechanical properties, they will be implemented in the processing of prototypes by hot pressing.

Sintered Samples

Sintering experiments to optimize conditions were not performed during the reporting period, as work to eliminate binder removal defects was deemed necessary to provide

suitable samples for sintering evaluation. Sintering was carried out to evaluate progress of the binder burnout work performed under **Task 3**. Sintered samples were used to evaluate porosity and voiding using sample cross-sections and visual observation. As improved binder removal systems and processes were developed, densities of the sintered parts increased. The results in **Table 6 WC-Co – based Sintered Samples Summary** are representative of progress made with respect to binder removal in the WC-Co based FM systems. Photographs of the sintered FM samples can be found in **Appendix A, Section 2**. During the next reporting period, as the issues with binder removal defects are resolved, experiments will be planned to optimize sintering conditions with respect to temperature, time and atmosphere. Work to evaluate sintering conditions will also be carried out by Dr. Zak Fang at the university of Utah as a subcontract to this program.

Table 6 WC-Co – based Sintered Samples Summary

Composition or FM Combination 82.5% core/17.5% shell (volume/volume)	Measured			% Full Theoretical Density
	Temperature °C (ATM)	Bulk Density (g/cc)	Theoretical Density (g/cc)	
WC(6%)Co	1300(N ₂)	13.513	14.95	90.4
WC(6%)Co	1300(N ₂)	14.429	14.95	96.5
WC(14%)Co	1300(N ₂)	12.978	14.13	91.8
WC(14%)Co	1300(N ₂)	13.947	14.13	98.7
WC(16%)Co	1300(N ₂)	12.564	13.94	90.1
WC(16%)Co	1300(N ₂)	13.533	13.94	97.1
WC(6%)Co/Co	1300(N ₂)	12.524	13.89	90.2
WC(6%)Co/Co	1300(N ₂)	13.053	13.89	94.0
WC(6%)Co/WC(16%)Co	1300(N ₂)	13.225	14.77	89.5
WC(6%)Co/WC(16%)Co	1300(Vacuum)	14.603	14.77	98.8

Al₂O₃-based Systems

The Al₂O₃ based systems are being pursued at the request of Kennametal, an ACR industrial partner for this program. In addition to the mining applications, such as roof bit inserts, Kennametal is interested in the FM systems as a way to potentially improve material performance over the currently available monolithic metal cutting inserts. Alumina based materials are currently in use for machining cast gray iron. It has been proposed that the FM structure will create a more durable, longer lasting machine tool insert than available with conventional monolithic materials. While there is widespread use of this machining technique, substantial market share is currently dominated by two or three manufacturers.

In order to better understand consolidation conditions for Al₂O₃-based fibrous monolith composites, monolithic test coupons were first prepared using Al₂O₃ powder with and without performance enhancing additives. The Al₂O₃ powder achieved a density of 100.3%, Al₂O₃-TiCN powder consolidated to 99.9% and Al₂O₃/Al₂O₃-TiCN FM to 99.6%. The TiCN is added to the Al₂O₃ to enhance the toughness of the Al₂O₃. The FM structure will

be the focus of continuing efforts. In reviewing **Table 7 - Al₂O₃ – based Samples** consolidation of the Al₂O₃-TiCN powder was used as a development bed for the densification of the FM structure. With increasing pressure and temperature the density generally increased. The highest density (99.9%) was seen for the Al₂O₃-TiCN powder hot pressed at 1650°C and 4 ksi.

Table 7 - Al₂O₃ – based Samples

Composition or FM Combination 82.5%core/17.5%shell (volume/volume)	Temperature °C (Pressure ksi)	Measured Bulk Density	Theoretical Density (g/cc)	% Full Theoretical Density
Al ₂ O ₃ powder	1650(5 ksi)	3.972	3.96	100.3
Al ₂ O ₃ -TiCN powder	1550(5ksi)	4.175	4.39	95.1
Al ₂ O ₃ -TiCN powder	1550(4ksi)	4.223	4.39	96.2
Al ₂ O ₃ -TiCN powder	1600(4ksi)	4.348	4.39	99.1
Al ₂ O ₃ -TiCN powder	1650(4ksi)	4.383	4.39	99.9

All samples where hot pressed for 1 hour.

The FM coupons were hot pressed using the information from the powder billets. Increasing pressure with constant temperature, then increasing temperature at the same pressure allowed higher and higher densities for the FM coupons, as shown in **Table 8 - Al₂O₃/Al₂O₃-TiCN– based FM Samples**. The highest densities seen were for the coupons hot pressed at 1650°C and 5 ksi.

Table 8 - Al₂O₃/Al₂O₃-TiCN– based FM Samples

Composition or FM Combination 82.5%core/17.5%shell (volume/volume)	Temperature °C (Pressure ksi)	Measured Bulk Density	Theoretical Density (g/cc)	% Full Theoretical Density
Al ₂ O ₃ / Al ₂ O ₃ –TiCN	1600 (4 ksi)	2.609	4.03	64.7
Al ₂ O ₃ / Al ₂ O ₃ –TiCN	1600(5 ksi)	3.863	4.03	95.9
Al ₂ O ₃ / Al ₂ O ₃ –TiCN	1650(5 ksi)	4.007	4.03	99.4
Al ₂ O ₃ / Al ₂ O ₃ –TiCN	1650(5 ksi)	4.016	4.03	99.6

All samples where hot pressed for 1 hour.

The mechanical properties evaluated to date on a powder coupon (1650°C and 4 ksi) and of a FM coupon (1650°C and 5 ksi) showed differences in the hardness (1960 Kgf/mm² for the powder versus 1620 Kgf/mm²) but very similar fracture toughness (3 MPa/m² for the powder versus 2.7 MPa/m²). The two coupons that were hot pressed to very high densities are to be machined for functional evaluations to determine how the composite structure will affect the mechanical performance. Photographs of the Al₂O₃ based coupons are presented in **Appendix A, Section 1**. They are identified as HP 908, HP 927 and HP 940. These samples correlate to Al₂O₃ / Al₂O₃ –TiCN 1600°C 5 ksi, Al₂O₃ powder 1650°C 5 ksi and

Al₂O₃ / Al₂O₃ –TiCN 1650°C 5 ksi respectively, identified in **Table 7 - Al₂O₃ – based Samples** above. The Al₂O₃ / Al₂O₃ –TiCN FM coupons both had a dark lustrous appearance. The alumina coupon had a grey, dull appearance.

Diamond based

No consolidation of diamond-based materials took place during this reporting period, due to focus on the removal of binders from these systems without defects. Residual organic materials interfere with the consolidation of the diamond materials by limiting the intimate contact between the diamond and the metallic binder phase present such as cobalt. In a more fundamental issue, the carbon residue from the decomposition of the polymer can also interfere with the diamond consolidation reaction. During the next reporting period, work to consolidate diamond-based FMs onto tungsten carbide blanks and roller cone drill bit inserts will be undertaken. In addition, the consolidation of diamond coatings onto roof bit inserts will be performed once appropriate cans are fabricated. The goal, during the next reporting period, is to produce acceptable coated inserts for roller bits and roof bits for field testing. Once binder removal issues have been resolved, the consolidation of these coatings will be the focus of effort with respect to this system. The consolidation supplier, Phoenix Crystal, has a wealth of experience and knowledge in this field, and will be performing the consolidation development for the diamond-based systems.

Task 5. Fabrication of Laboratory Test Samples

Testing underway

Samples of WC-Co based and Al₂O₃ based FM coupons were submitted for hardness and fracture toughness testing using the Vickers indentation method. The samples were sent to Kyocera for evaluation at their facility in Kokubu, Kagoshima, Japan. The samples in both groups were selected due to their relatively high densities. The samples sent for testing were oriented with the fibers parallel to the test surface. The test results from the samples are presented in **Table 9 – Kyocera Test Sample Physical Properties**.

The hardness of the monolithic samples compares very favorably with data on the WC-Co powder reported in the literature (6% Co – 1700, 14% Co – 1000-1100, and 16% Co – 900-1000 HV). In the case of the FM sample with the highest density (99.3), the hardness is lower than would be expected using the hardness value based on the bulk phase cobalt concentration, however, the fracture toughness is very close to expected based on the same calculation. The lower than expected hardness values are most likely not representative of the overall composite hardness, since the hardness test uses an indentation method that produces an indent significantly larger than the average cell core size. For that same reason, the toughness values are also most likely not representative of the overall composite.

Investigation of the Al₂O₃-TiCN materials has continued with two samples tested at Kyocera, one each of a powder and an FM coupon. The high density and comparable fracture toughness of the two are excellent with the difference in hardness reflecting the composite nature of the FM tested. Again, as with the WC-Co FM, the bulk properties of the FM material may be the source of the difference. Additional samples of the FM materials are to be fabricated for testing during the next reporting period.

Continuing hardness and toughness testing of the FM samples and analysis by scanning electron microscopy has been performed to determine if changes to the processing conditions have improved the diffusion seen on earlier samples. Again, samples with high density (now >95% theoretical) were chosen for analysis. The images obtained appear at the end of this report in the **Appendix B, Section 1**. As before, elemental analysis through SEM showed various levels of Co diffusion in all of the samples evaluated. Limiting cobalt diffusion and migration across the core/interface boundary, in order to preserve the desired FM structure, will be a principal area of focus for consolidation optimization work during the upcoming reporting period.

Table 9 – Kyocera Test Sample Physical Properties

Formulation Shell/Core	Temperature °C (Time, Pressure)	Hardness HV	Fracture toughness MPa(m) ^{-1/2}	% Full Theoretical Density
Al ₂ O ₃ –TiCN powder	1650(1 hr, 4 ksi)	1960	3	99.8
Al ₂ O ₃ /Al ₂ O ₃ –TiCN	1650(1 hr, 5 ksi)	1620	2.7	99.6
WC(3%)Co	1300(1 hr, 2 ksi)	1140	12	95.4
<i>WC(6%)Co</i>	<i>1300(1 hr, 2 ksi)</i>	<i>1700</i>	<i>9.3</i>	<i>100.3</i>
<i>WC(14%)Co</i>	<i>1300(1 hr, 2 ksi)</i>	<i>1650</i>	<i>14.9</i>	<i>101.0</i>
<i>WC(16%)Co</i>	<i>1300(1 hr, 2 ksi)</i>	<i>1090</i>	<i>22</i>	<i>101.7</i>
<i>WC(6%)Co/Co</i>	<i>1200(1 hr, 2 ksi)</i>	<i>600</i>	<i>17.9</i>	<i>84.5</i>
WC(6%)Co/Co	1300(1 hr, 2 ksi)	1680	16.7	100.5
<i>WC(3%)Co/WC(6%)Co</i>	<i>1400(1 hr, 2 ksi)</i>	<i>1160</i>	<i>15.2</i>	<i>91.5</i>
<i>WC(3%)Co/WC(6%)Co</i>	<i>1400(1 hr, 2 ksi)</i>	<i>1110</i>	<i>12.5</i>	<i>92.1</i>
<i>WC(6%)Co/WC(14%)Co</i>	<i>1300(1 hr, 2 ksi)</i>	<i>1390</i>	<i>11.5</i>	<i>94.7</i>
WC(6%)Co/WC(16%)Co	1300(0 hr, 2 ksi)	1140	15.8	93.7
WC(6%)Co/WC(16%)Co	1200(1 hr, 6 ksi)	1300	11.7	95.2
WC(6%)Co/WC(16%)Co	1250(1 hr, 2 ksi)	1220	15.6	95.2
WC(6%)Co/WC(16%)Co	1250(1 hr, 6 ksi)	1320	14	95.4
WC(6%)Co/WC(16%)Co	1300(1 hr, 2 ksi)	1450	10.7	95.5
WC(6%)Co/WC(16%)Co	1250(1 hr, 4 ksi)	1450	10.7	97.2
WC(6%)Co/WC(16%)Co	1275(1 hr, 4 ksi)	1530	10.4	99.3

Italicized samples were presented in the previous report and are repeated here only for comparison

Task 6. Fabrication of Drill Bit Inserts

With the development of improved thermoplastic blends and binder removal processes, work was begun during the reporting period to fabricate large drill bit inserts for field testing. Twenty-four green drill bit inserts were fabricated, and binder removal begun during the reporting period. **Figure 10** shows one of the green inserts fabricated during the reporting period. Due to the size of the inserts (0.87 inch diameter), hot pressing was selected as the consolidation method to eliminate the bundle boundary separations still seen after binder removal in larger parts. A graphite die for hot pressed was designed, with the capacity to press as few as 4 and as many as 17 individual inserts in a run. Inserts for field

testing will be consolidated during the next reporting period, using the best hot pressing conditions identified in **Task 4**. These parts will then be sent out for centerless grinding, where they will be machined to the final insert dimensions, and then delivered for field testing to Superior Rock Bit Company, Virginia, MN. Frank Klima of Superior has agreed to provide field testing of inserts for no charge.

As additional improvements are made to the binder removal and sintering processes, inserts will be fabricated for consolidation by sintering. Consolidation by sintering represents a considerable cost benefit, when compared to hot pressing, and is the current practice in industry for consolidation WC-Co monolithic inserts. For sintering to be effective, however, the binder-free parts must not contain defects large enough to be preserved through consolidation. It is expected that sintered inserts suitable for field testing will be fabricated during the upcoming reporting period.

Figure 10. WC-Co FM green drill bit insert for fabrication of hot pressed field test prototypes.

PLANS FOR THE NEXT REPORTING PERIOD

1. Complete the development of fabrication process parameters of Fibrous Monolith compositions selected for the drill bit insert application (Task 3).
2. Continue binder removal process optimization of Fibrous Monolith compositions selected for the mining drill bit insert application (Task 3).
3. Continue densification process optimization of Fibrous Monolith compositions selected for the mining drill bit insert application (Task 4).
4. Complete design and assembly of high stress abrasion wear tester and begin in house testing of WC-Co FM materials (Task 5).
5. Complete fabrication of Fibrous Monolith drill bit inserts for evaluation of mechanical properties by field testing (Task 6).
6. Complete design, fabrication and consolidation, and deliver WC-Co based /dozer grader blade inserts for field testing (Task 7).
7. Initiate discussion with Krebs and begin work on design requirements for hydro-cyclone apex cone wear parts (Task 8).

REFERENCES

1. S. Baskaran and J. W. Halloran, *J. Am. Ceram. Soc.*, 76 [9] 2217 (1993). S. Baskaran and J. W. Halloran, *J. Am. Ceram. Soc.*, 77 [5] 1249 (1994).
2. G.E. Hilmas, A. Brady, U. Abdali, G. Zywicki and J.W. Halloran, "Fibrous Monoliths: Non-Brittle Fracture from Powder Processed Ceramics," *Mat. Sci. & Eng. A.*, 195, 263-268 1995.
3. G.E. Hilmas, A. Brady and J.W. Halloran, "SiC and Si₃N₄ Fibrous Monoliths: Non-Brittle Fracture From Powder Processed Ceramics Produced by Coextrusion,"; pp. 609-614 in Ceramic Transactions-Vol. 51 *Ceramic Processing Science and Technology*. Edited by H. Hausner and G. Messing, American Ceramic Society Westerville, OH, 1995.
4. "Development of Advanced Fibrous Monoliths," Advanced Materials Partnership program, a DARPA funded, DOE managed program, Cooperative Agreement No. DE-FC02-96CH10861 between DARPA and ACR.
5. June-Ho Park, Yong-Ho Lee, Young-Hag Koh and Hyoun-Ee Kim, "Effect of Hot-Pressing Temperature on Densification and Mechanical Properties of Titanium Diboride with Silicon Nitride as a Sintering Aid" *J. Am. Ceram. Soc.*, 83, [6], (2000).
6. June-Ho Park, Yong-Ho Lee, Young-Hag Koh and Hyoun-Ee Kim, "Effect of Hot-Pressing Temperature on Densification and Mechanical Properties of Titanium Diboride with Silicon Nitride as a Sintering Aid" *J. Am. Ceram. Soc.*, 83, [6], (2000).
7. Z. Zak Fang, et al., "Fracture Resistant Super Hard Materials and Hardmetals Composite With Functionally Designed Microstructure" *Int. J. Refractory Metals & Hard Materials*, 19, 453-459, (2001).

APPENDIX A

Section 1

Al₂O₃ powder 1650°C 5 ksi

Al₂O₃ / Al₂O₃ TiCN 1600°C 5 ksi

Al₂O₃ / Al₂O₃ TiCN 1600°C 5 ksi

Section 2

WC(6%)Co / WC(16%)Co Sintered Blanks

WC(6%)Co / WC(16%)Co Sintered Insert

WC(6%)Co / WC(16%)Co Sintered Insert

WC(6%)Co / WC(16%)Co Sintered Coupon

Section 3

**WC(6%)Co / WC(16%)Co insert
for hot pressing**

**WC(6%)Co / WC(16%)Co insert
for sintering**