

TECHNICAL REPORT

FIBROUS MONOLITH WEAR RESISTANT COMPONENTS FOR THE MINING INDUSTRY

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ABSTRACT

The work performed on this program was to develop wear resistant, tough FM composite materials with efforts focused on WC-Co based FM systems. The materials were developed for use in mining industry wear applications. Components of interest were drill bit inserts for drilling blast holes. Other component applications investigated included wear plates for a variety of equipment such as pit shovels, wear surfaces for conveyors, milling media for ball milling operations, hydrocyclone cones, grader blades and dozer teeth. Cross-cutting technologies investigated included hot metal extrusion dies, drill bits for circuit board fabrication, cutting tools for cast iron and aluminum machining.

An important part of the work was identification of the standard materials used in drilling applications. A materials trade study to determine those metals and ceramics used for mining applications provided guidance for the most important materials to be investigated. WC-Co and diamond combinations were shown to have the most desirable properties. Other considerations such as fabrication technique and the ability to consolidate shifted the focus away from diamond materials and toward WC-Co.

Cooperating partners such as Kennametal and Kyocera assisted with supplies, evaluations of material systems, fabricated parts and suggestions for cross-cutting technology applications for FM architectures. Kennametal provided the raw materials (WC-Co and Al-TiCN powders) for the extent of the material evaluations. Kyocera shared their research into various FM systems and provided laboratory testing of fabricated materials.

Field testing provided by partners Superior Rock Bit and Brady Mining and Construction provided insight into the performance of the fabricated materials under actual operational conditions. Additional field testing of cross-cutting technology, the extrusion of hot metals, at Extruded Metals showed the potential for additional market development.

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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.

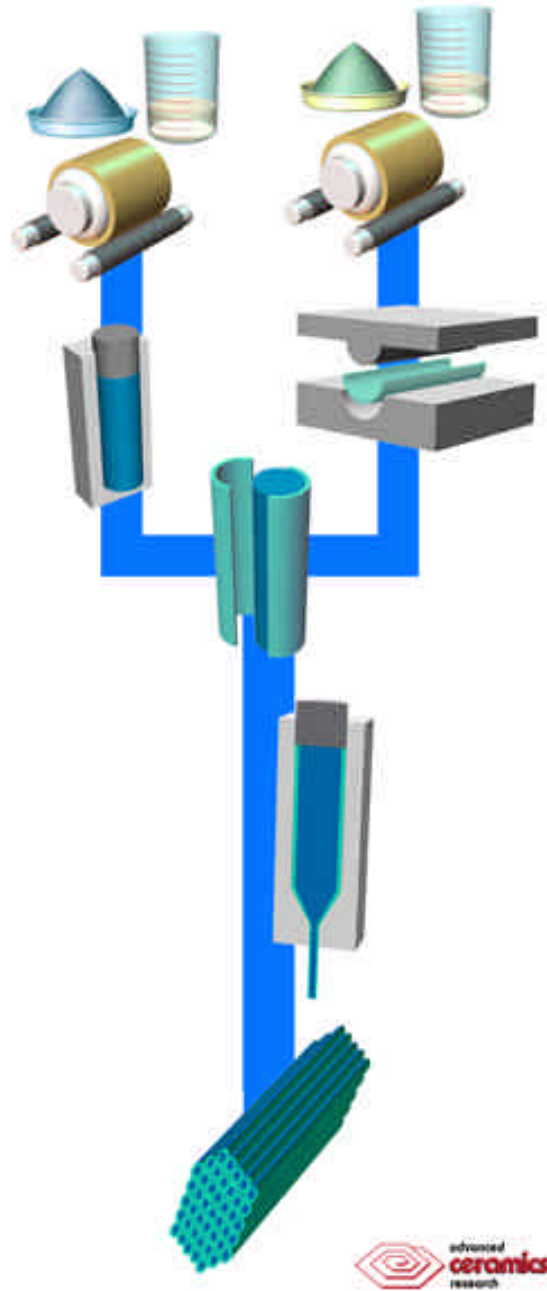


Figure 1. Illustration of the Fibrous Monolith co-extrusion process. Ceramic and/or metal powders are blended separately with thermoplastics and plasticizers. The resulting mixtures are pressed into shells and rods. The shells and rods laminated to form a composite feedrod that is then placed in a heated 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 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**).

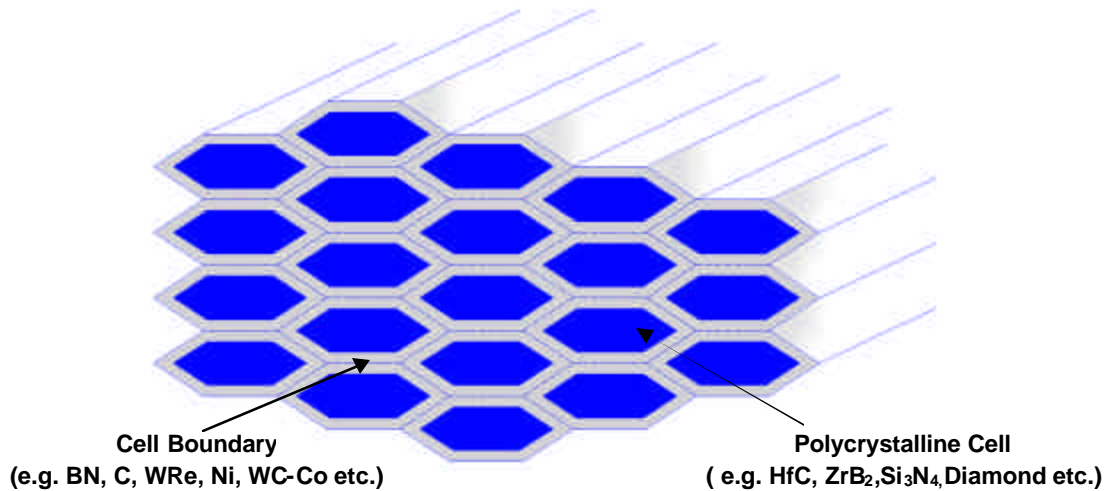


Figure 2. Schematic of a typical uniaxial Fibrous Monolith microstructure shown perpendicular to principal fiber direction.

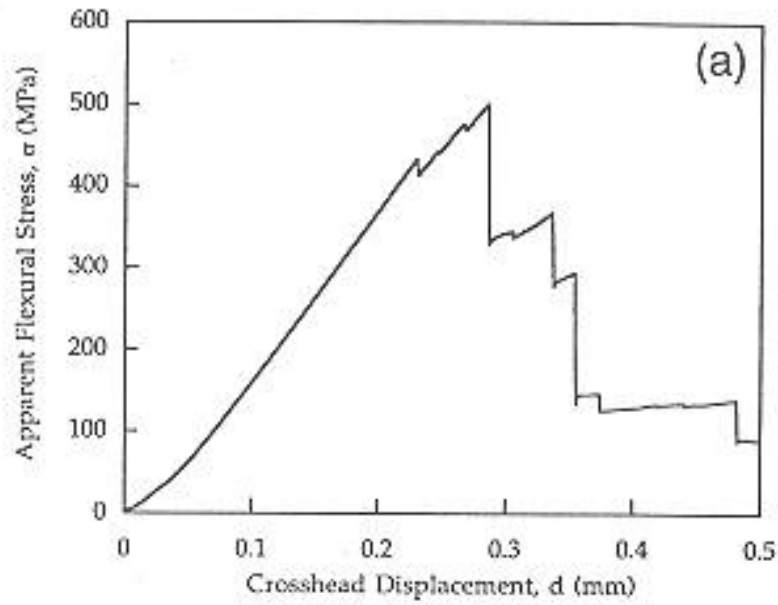


Figure 3. Typical flexural stress-strain curve for a silicon nitride/BN FM material.

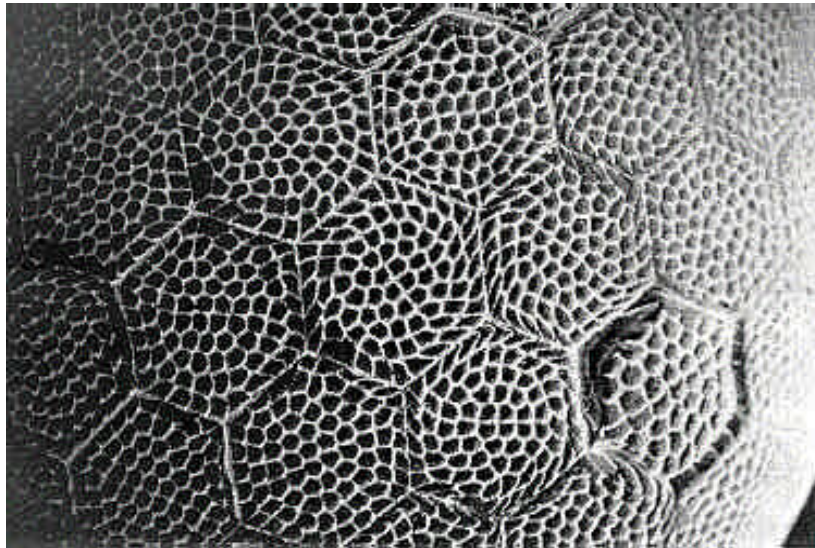


Figure 4. ACR's Diamond/ WC-Co FM composite applied as a coating on the surface of a WC drill bit insert (100x). Note the isolation of the darker material (Diamond) into discrete cells by the lighter contrast phase (WC-Co).

EXECUTIVE SUMMARY

The program to develop wear resistant materials for the mining industry is described in detail under the EXPERIMENTAL section. The summary presented here covers the materials and process development, the industrial partnerships and relationships developed, and the field testing operations performed on materials developed with the financial assistance provided for this program.

A set of materials property data for potential wear resistant materials was collected and analyzed. The materials of interest included but were not limited to: Diamond, Tungsten Carbide and Cemented Tungsten Carbides, Carbides of Boron, Silicon, Titanium and Aluminum, Diborides of Titanium and Aluminum, Nitrides of Aluminum, Silicon, Titanium, and Boron, Aluminum Oxide, Tungsten, Titanium, Iron, Cobalt and Metal Alloys. These materials are designated for use as 'core' and 'shell' materials in the Fibrous Monolith structure. The material properties of hardness, stiffness, tensile strength, transverse rupture strength, toughness, thermal conductivity, coefficient of thermal expansion and cost were selected as determining factors for material choice. Data for these four properties were normalized, and weighting factors were assigned for each property to establish priority and evaluate the effects of priority fluctuation. Materials were then given a score based on the normalized parameters and weighting values. Using the initial estimates for parameter priority, the highest-ranking material was tungsten carbide, with diamond as the second ranked material. Several materials were included in the trade study, and five were selected as promising 'core' materials to include in this effort. These materials are tungsten carbide, diamond, boron carbide, and titanium diboride. Work was also completed on the trade study to evaluate 'shell' materials. The selected shell materials include tungsten carbide-cobalt, tungsten-metal alloys, molybdenum-metal alloys, and high-strength-steel alloys.

Efforts to develop, fabricate, and consolidate FM compositions utilizing the selected core and shell materials have been completed. Several FM systems including diamond/WC-Co, TiB_2 /WC-Co, B_4C /WC-Co, and WC-Co/W-Ni-Fe were fabricated and consolidated. Early results indicated that the diamond/WC-Co and WC-Co/W-Ni-Fe FM systems have excellent potential as effective wear-resistant coatings for the mining drill bit insert application.

In parallel with the composite development and fabrication effort, a test matrix for the evaluation of these composites for drill bit inserts application was also compiled. The test matrix was developed with input from several sources including searches of the National Institute of Standards Technology ASTM literature database (www.astm.org), previous research performed in cooperation between ACR and Argonne National Laboratory and reviews of drill bit manufacturer's datasheets

Work on the development of formulations using the materials identified as contenders for the fibrous monolith wear resistant component was performed. The FM structures fabricated were: diamond/WC-Co, B_4C /WC-Co, TiB_2 /WC-Co, WC-Co/WC-Co. Results of our densification studies on these systems lead to the down-selection of WC-Co/WC-Co, WC-Co/Co and diamond/WC-Co for further development for mining applications

including drill bit inserts, roof bit inserts, radial tools, conical tools and wear plates (WC-Co based system only) for earth moving equipment.

Our component fabrication effort focused on drill bit inserts, conical and radial tool inserts and wear plates/inserts for earth moving equipment. The conical tool prototypes of Kennametal design were fabricated using the WC-Co/WC-Co FM system. Kennametal was also interested in diamond /WC-Co coated roof bit inserts and provided ACR with WC substrates for the development of coated inserts. The drill bit insert prototypes were fabricated using diamond/WC-Co coatings and the grader blade insert plates fabricated using the WC-Co/WC-Co FM system.

ACR Inc. visited Dennis Tool of Houston TX and Phoenix Crystal of Ann Arbor, Michigan to discuss the possibility of teaming to consolidate diamond/WC-Co composite coatings. Diamond-based composites require special high-pressure consolidation equipment and Phoenix Crystal has expressed an interest in providing diamond powder preparation and consolidation services, to enable the mass-production of a low cost diamond-based FM composite products including drill bit inserts and point attack tools. After considering our options in teaming with these companies, ACR decided to team with Phoenix Crystal. ACR and Phoenix Crystal agreed to perform consolidation of diamond/WC-Co FM coated inserts to verify their consolidation process and produce test pieces to be pressed into mining drill bits for field testing. Samples of diamond/WC-Co coated domed and flat WC inserts were sent to Phoenix Crystal for consolidation in February of 2002. Results of insert fabrication were of poor quality. Repeated experiments did not improve the initial results. Due to a lack of interest on the part of Phoenix Crystal this line of inquiry was discontinued.

A broad range of materials were investigated with fabrication of FM's using 3% cores and 16%, 20% and 25% shells. These and FM's with 6% cores and 16%, 20% and 25% shells were subjected to hardness, toughness and wear testing to identify constructions with the best performance characteristics. In addition, experiments to identify ideal solids loading for the WC-Co materials were completed during the reporting period. The work performed will improve the green material handling and forming as well as give a solid foundation for work with any FM material in the future.

Component materials have been identified for the fabrication of a wide variety of FM parts. The higher wear resistance and superior fracture toughness seen for the 3% core and 25% shell FM's are expected to give better performance at a reasonable cost compared to the current commercial WC-Co materials.

Work was performed to develop binder removal processes for WC-Co, Al_2O_3 , 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%. For the Al_2O_3 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. Al_2O_3 based FM test coupons fabricated using the new two-stage binder removal process were consolidated by hot

pressing to 99.6%. Diamond/WC-Co circular inserts were also fabricated and delivered to Phoenix Crystal for consolidation.

Fifty seven 7/8" drill bit inserts (WC-Co(6%)/WC-Co(16%) FM) were fabricated, twenty four were made using the newly developed two-stage binder removal process. 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 was for machine point attack and other insert tooling. In addition, $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3\text{-TiCN}$ FM test coupons have been fabricated, and finished as rectangular inserts for evaluations of metal cutting performance.

Work was performed to characterize the two-stage binder removal process for WC-Co based FM material systems. Use of this process has resulted in the fabrication of defect free sintered WC-Co FM bodies, with minimal free carbon porosity and densities approaching 100% theoretical. In addition, shrinkage of the monolithic core and shell materials used in the WC-Co based FM system was measured, and differences in material shrinkage were identified as a potential cause of cell boundary cracking observed in sintered parts. Re-formulation of material blends for this system was begun, with the goal of eliminating mechanical stresses during sintering by matching the volumetric shrinkage of the core and shell materials. This development allowed fabrication of prototype components for field-testing using the pressureless sintering.

Kyocera Industrial Ceramics in Kyoto, Japan was visited, with the purpose of negotiating and signing the subcontract for Kyocera's participation on this program. An assessment was made on the testing and manufacturing capabilities of Kyocera and how such capabilities can be integrated into our development effort. Tours were conducted of Kyocera's machine tool production plant in Sendai, Japan, as well as their research and development facilities in Kagoshima, Japan. Kyocera's facilities include substantial materials characterization and testing capabilities at room and elevated temperatures, and manufacturing capabilities of thousands of parts/hr, all of which were made available to us for use on this program as part of Kyocera's in-kind program cost share contribution. The Kyocera subcontract and the details of Kyocera's participation on this program were discussed and agreed upon during the two-day meeting.

Technical exchange meetings with Kyocera Corporation took place November, 2001, at the Kyocera Sendai plant and at the Kyocera Kokubu, April, 2002 also at the Kyocera Sendai plant, December, 2002 at ACR and 2003 again at Kyocera Sendai and Kokubu. ACR participants included product development engineers, research engineers, and program principle investigator. On the Kyocera side the participants were the materials development attorney, department manager, vice-department manager, and materials development engineers. Both Kyocera and ACR personnel presented results of materials development for diamond/WC-Co and WC-Co/WC-Co systems as well as production scale-up issues for fibrous monolith composites. Kyocera also presented the first results of mechanical testing on WC and TiB_2 fibrous monolith composite systems fabricated by ACR.

The component fabrication efforts at ACR focused on production of field test components for a number of industrial partners. Brady Mining and Construction Supply, St. Louis, MO expressed interest in field testing of FM drill buttons in the drill bits they manufacture for

drilling holes 3 inches diameter and less. Parts were fabricated and tested. Center Rock, Inc., Berlin, PA as well as Superior Rock Bit, Virginia, MN both expressed a desire to evaluate FM drill bit inserts in their tri-cone roller bits. Superior evaluated FM inserts during the previous reporting period. Both are currently using powder compacts and are interested in improved performance available with the FM inserts. Master Craft Extrusion Tools, Northport, MI has worked with ACR to develop FM extrusion dies for the hot metal and plastics extrusion industries. While this was not a mining related industry, was an ideal application of the extremely wear resistant and high toughness FM's developed under this program. FM extrusion dies were fabricated and tested. The operators of the Phelps-Dodge Sierrita mine outside of Tucson, AZ have provided a ground engagement tool (GET) for retrofit with wear buttons. The Robbins Group, Seattle, WA has provided a replaceable component (bucket lip) for retrofit and evaluation of wear plates. They are interested in improved life for the component since down-time and replacement expenses are major issues for any large scale mining operation. Plates were fabricated and installed for field testing.

PROGRAM MANAGEMENT

Task 1. Program management

Prepare and deliver management plan

Advanced Ceramics Research program management (PM) wrote a Project Management Plan for managing the program. The management plan included project milestones, schedules (including timelines), project coordination (including subcontract management), technical targets, deliverables, decision points, and go/no-go decision criteria. The Project Management Plan was submitted as a topical report.

Travel

ACR program management and technical staff have traveled to support the program including establishing and monitoring subcontracts (both funded and cost share), monitoring laboratory and field tests, and participating in program reviews.

The integration of industrial partners into the program has required travel to facilities in Michigan, Pennsylvania, Texas and Utah in addition to 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.

Subcontract Management

ACR program management prepared statements of work and placed subcontracts with the appropriate suppliers to complete the program tasks. ACR program management monitored progress of all subcontractors to assure performance to the agreed upon statement of work including cost share components. Subcontractors on the program included:

- Advanced Ceramics Manufacturing
- Kennametal Incorporated
- Kyocera Corporation
- University of Arizona

Kyocera Corporation

During the week of April 9th to the 13th 2001 ACR Inc Chief Operating Officer Mark Angier, Vice President of Marketing and Sales Matthew Pobloske, and Manager of Composite Ceramics Mark J. Rigali visited Kyocera Industrial Ceramics in Kyoto, Japan. The purpose of this trip was to negotiate and sign the subcontract for Kyocera's participation on this program. In addition, we had the opportunity to assess the testing and manufacturing capabilities of Kyocera and how such capabilities can be integrated into our development effort on this program.

The visit began with tours of Kyocera's machine tool production plant in Sendai, Japan as well as their research and development facilities in Kagoshima, Japan. Kyocera's R&D facilities include tremendous materials characterization and testing capabilities at room and elevated temperatures, all of which will be made available to us for use on this program as part of Kyocera's in-kind program cost share contribution. The machine tool manufacturing line allows Kyocera to manufacture thousands of ceramic inserts per hour. Resources in both facilities were available for composite development work on this program.

On April 11th and 12th 2001 ACR representatives met with Kyocera executives Director and General Manager of the Legal Affairs Group Minoru Fujiyoshi, Manager of the Corporate Development Group Michio Ito, Deputy General Manager of Cutting Tools Division Eiji Umegae, and Legal Counsel Takeshi Kawano. The Kyocera subcontract and the details of Kyocera's participation on this program were discussed and agreed upon during the two-day meeting. Kyocera agreed to participate by evaluating new compositions of fibrous monoliths for wear resistant applications and developing and applying testing and characterization techniques for fibrous monolith components. On Friday April 13th Kennametal's Vice President and Chief Technical Officer David B. Arnold joined discussions regarding potential 3-way collaborations between Kyocera, ACR Inc. and Kennametal. This collaboration would involve the utilization of Kennametal's Rapid Omni-Directional Compaction Process (ROC Process) in the production of FM-based cutting tools. Kyocera and ACR Inc evaluated the potential of this process in the fabrication of wear resistant composite tooling. ACR was interesting in pursuing the ROC process as a consolidation tool but we were not able to achieve an arrangement acceptable to Kennametal.

Continuing meetings with Kyocera Corporation took place November 2001, April 2002, and December 2002 at the Kyocera Sendai, Kyocera Kokubu plants and at the ACR facilities in Tucson, Arizona. A variety of staff from Kyocera, ACR, and ACM participated in these technical exchanges. The technical exchanges included tours of the various Kyocera and ACR facilities along with discussions of issues developed since previous meetings. At the repeated meetings the continued testing 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. Other fabrication techniques such as Rapid Prototyping were discussed, as well as material systems of interest for future exploration. It was indicated to Kyocera that ACR wanted to include rapid prototyping as a part of this and future development projects. Presentations by Kyocera Sendai personnel included 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.

Development of an industrial research relationship with the technical staff at Kyocera at Sendai and the research facility at Kokubu has led to opportunities for development of the FM technology into areas of cutting tools and electronic materials. Researchers at Kyocera have developed applications for diamond/diamond composites and silicon nitride/boron nitride cutting tools. Ideas for applications such as tailored FM's for fiber optics property manipulation were also suggested and investigated by Kyocera researchers. The connection with a large firm like Kyocera has also given ACR the opportunity to use highly sophisticated analytical equipment not normally available to a small firm. Kyocera's measurements of mechanical and chemical properties of the FM's gave ACR a broader picture of the materials we had fabricated. They also provided needed insight to the actual structure of the FM's evaluated.

Tribocor, Inc.

ACR Inc. also visited Tribocor Inc. of Houston TX to discuss the possibility of teaming to consolidate diamond/WC-Co composite coatings. Since diamond-based composites require special high pressure consolidation equipment and Tribocor had expressed an interest in

providing diamond powder preparation and consolidation services to enable the mass-production of low cost diamond-based FM composite products such as drill bit inserts and point attack tools. Tribacor agreed to perform consolidation of diamond/WC-Co FM coated inserts to verify their consolidation process and produce test pieces to be pressed into mining drill bits for field testing. Tribacor had agreed but no samples were processed by them during the period of this contract.

ACR thought that collaboration with a diamond consolidation facility would allow development of specialized diamond/tungsten carbide FM's superior to those developed previously. The efforts to do so with Tribacor proved fruitless.

Dennis Tool Company

A meeting with Dennis Tool Company took place on October 2001. A range of ACR and Dennis Tool staff took part. Dennis Tool expressed interest in working with ACR on the development of diamond/WC-Co coatings for drill bit inserts as well as WC-based FM roof bits and water jet nozzles. Unfortunately Mahlon Dennis expressed concern in working with ACR because of our strong relationship with Smith international because of Dennis Tool's close ties to Smith competitor Hughes Christiansen. For this reason ACR decided to seek an alternative supplier of high-pressure consolidation services.

Phoenix Crystal

As an alternative to Dennis Tool and Tribacor Inc., ACR met with Phoenix Crystal President Dr. Bob Frushour in February 2002. Discussions with Bob Frushour regarding the consolidation of diamond/WC-Co FM composites onto insert blanks lead to a "handshake" agreement for Phoenix to consolidate samples. Samples were then fabricated and sent to Phoenix Crystal (Ann Arbor, Michigan) for consolidation experiments towards the end of February. In addition some unique diamond-based FM composites were conceived for fabrication, consolidation and evaluation over the next several months. Phoenix agreed to contribute the costs of high-pressure consolidation as cost share for this program. Problems with the consolidation of the samples sent to Phoenix Crystal led to a loss of interest by them and few additional samples processed.

Phoenix Crystal thought that development of a diamond/tungsten carbide cobalt system would be beneficial to both ACR and them. They saw the concept for an FM structure as innovation that would allow them to enter new markets with higher performance than existing materials and lowers costs. Once the duration of the effort became known they did not seem committed to the long term development effort that was needed.

Dr. Zak Fang, University of Utah

A subcontract was put in place 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 was enlisted to support the program in the area of consolidation process development. Several meetings were held with Dr. Fang over the course of the program in Utah, Missouri, and at ACR's facilities.

Dr. Fang's contributions to densification and suggestions for lines of inquiry, led to solutions to sintering problems such as cobalt migration and achieving higher densities. The

assistance he provided allowed quicker development of sintering profiles and development of preferred microstructures.

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 also held with Dr. Hilmas over the course of the program, in Missouri, Utah, and at ACR's facilities.

EXPERIMENTAL

Task 2. Develop Compositions of fibrous monoliths

a. Conduct material trade studies to select best materials for evaluation

Advanced Ceramics Research technical staff, in conjunction with the program team members, conducted trade studies to determine the best material candidates for high wear resistant fibrous monolith applications. Material candidates included a wide range of ceramic and metal materials that demonstrated the desired properties. Trade studies evaluated the materials based on the desired features for each of the three applications, for example impact toughness, high-temperature capability, and compressive strength.

Published mechanical and thermal properties data on a variety of materials for development as wear resistant and damage tolerant composites for mining industry applications were used to compile a materials property database for the mining drill bit insert application. The information was used to select the best materials for this application. Factors such as cost and ability to process as FMs were considered in addition to material properties such as density, melting point, ultimate tensile strength, toughness, thermal conductivity and transverse rupture strength. Materials of interest include but were not limited to:

1. Diamond
2. Tungsten Carbide and Cemented Tungsten Carbides
3. Carbides of Boron, Silicon, Titanium and Aluminum
4. Diborides of Titanium and Aluminum
5. Nitrides of Aluminum, Silicon, Titanium, and Boron
6. Aluminum Oxide
7. Tungsten, Titanium, Iron, Cobalt and Metal Alloys

Core Material Trade Study

A set of material property data for potential wear resistant materials was gathered. These materials represented the initial candidates for developing fibrous monolith (FM) drill bits for use in the mining industry. A trade study matrix used the material properties considered most important for the drill bit application, specifically hardness, toughness, thermal conductivity, and cost. Each of these properties was normalized to the maximum value contained in the data set. All properties were ranked between 0 and 1, where 1 was the most desirable value. Because the cost values are inversely proportional to their desirability, the normalized cost number was subtracted from 1 so that the ranking order was consistent with the other parameters. To obtain an overall score for each material, we summed the normalized parameters after applying a percentage-weighting factor for each parameter. This method allowed some flexibility to adjust the weighing factors according to the priority of the property. For materials that had a range of properties, the maximum and minimum values were input to show a possible range of expected performance in the trade study. Those materials with a range of values reported in the literature are listed as individual maximum and minimum rows in the trade matrix.

Based on experience and discussions with mining industry members, the initial weighting factors were set to the following values:

Parameter	Weight
Hardness	35%
Toughness	25%
Thermal Conductivity	15%
Cost	25%

As expected, the top ranked material using these weighing factors was tungsten carbide, with diamond as the second ranked material. The fact that the most commonly used material, tungsten carbide, and diamond are so closely ranked may have been an indication that the importance of cost was underestimated in our initial determination of the mining industry's perception of parameter weighting factors. There was a significant gap in the material scores after tungsten carbide and diamond, indicating that these two materials were clearly superior to the others when using these weighting factors. The top ten materials are listed in the following table with their weighted score.

Rank	Material	Score
1	WC maximum	0.543
2	Diamond maximum	0.543
3	WC/Co 10.1% 2.84 micron	0.409
4	Diamond minimum	0.402
5	B ₄ C maximum	0.394
6	TiB ₂ maximum	0.383
7	TiC maximum	0.381
8	SiC alpha maximum	0.380
9	B ₄ C minimum	0.377
10	WC/Co 10.1% 0.98 micron	0.376

To study the influence of cost on the material selection decision, the weighting factors were adjusted by increasing the performance parameters and decreasing the importance of cost, and vice versa. The following table lists the parameters used to study cost sensitivity.

Parameter	Performance Sensitive	Balanced	Cost Sensitive
Hardness	40%	35%	30%
Toughness	30%	25%	20%
Thermal Conductivity	20%	15%	10%
Cost	10%	25%	40%

With maximum emphasis on the importance of cost (40%), tungsten carbide was clearly above the other materials as the obvious material choice. This was not surprising, since in the cost sensitive mining industry tungsten carbide is the most common wear resistant material. As the importance of the performance parameters was increased, diamond became the obvious material choice. As a wear resistant material, diamond has found a niche in the mining and drilling marketplace. High end drilling operations that can afford larger investments required to access resources, such as oil and gas drilling, utilize diamond drill bits. It should be mentioned, however, that diamond is only utilized where the most demanding drilling environments necessitate a high performance bit.

Performance Sensitive					Cost Sensitive	
<i>Balanced</i>						
Rank	Material	Score	Material	Score	Material	Score
1	Diamond maximum	0.651	WC maximum	0.543	WC maximum	0.625
2	Diamond minimum	0.490	Diamond maximum	0.543	B ₄ C maximum	0.504
3	WC maximum	0.460	WC/Co 10.1% 2.84 micron	0.409	WC/Co 10.1% 2.84 micron	0.498
4	TiB ₂ maximum	0.321	Diamond minimum	0.402	SiC alpha maximum	0.497
5	WC/Co 10.1% 2.84 micron	0.320	B ₄ C maximum	0.394	TiC maximum	0.495
6	B ₄ C maximum	0.285	TiB ₂ maximum	0.383	ZrO ₂ cubic maximum	0.491
7	WC/Co 10.1% 0.98 micron	0.280	TiC maximum	0.381	B ₄ C minimum	0.489
8	WC/Co 5.1%	0.277	SiC alpha maximum	0.380	Al ₂ O ₃ maximum	0.488
9	WC/Co 7.6%	0.275	B ₄ C minimum	0.377	WC minimum	0.485
10	TiC maximum	0.267	WC/Co 10.1% 0.98 micron	0.376	ZrO ₂ cubic minimum	0.480

One of the main benefits of the fibrous monolith composite structure is its increased toughness. Hardness is desired for wear resistance, but very hard materials tend to fail catastrophically. By using the FM composite structure ACR plans to increase toughness and improve the overall performance of the wear components. For this reason it was decided to use the trade study matrix to look at the relationship between hardness and toughness. As with the cost analysis, where the importance of cost was adjusted up and down, the importance of hardness and toughness were adjusted up and down. Starting with an equal weighting of importance, the importance of hardness was increased while toughness was decreased and all other parameters were held constant. The weighting factors are listed in the following table.

Parameter	Balanced	Harder	Hardest
Hardness	30%	40%	50%
Toughness	30%	20%	10%
Thermal Conductivity	15%	15%	15%
Cost	25%	25%	25%

It is clear that as the hardness parameter becomes more important in the trade study, diamond moves to become the overwhelming choice. The mining industry's current choice,

tungsten carbide, is a distant second when hardness is the most important factor. Boron carbide is another material with good scores in this hardness versus toughness trade. Even though boron carbide scores drop as the importance of hardness increases, it does not drop as rapidly as all the other materials in the study, thus holding it's ranking at 4th in all three cases.

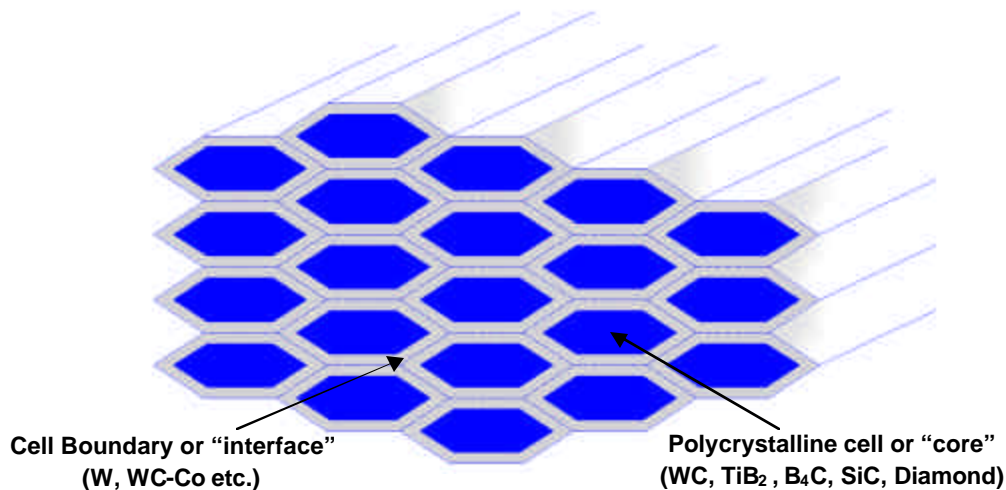
Balanced			Harder		Hardest	
Rank	Material	Score	Material	Score	Material	Score
1	WC maximum	0.585	Diamond maximum	0.584	Diamond maximum	0.667
2	Diamond maximum	0.501	WC maximum	0.500	Diamond minimum	0.466
3	WC/Co 10% 2.84 micron	0.438	Diamond minimum	0.423	WC maximum	0.415
4	B ₄ C maximum	0.399	B ₄ C maximum	0.390	B ₄ C maximum	0.381
5	WC/Co 10% 0.98 micron	0.396	TiC maximum	0.381	TiC maximum	0.380
6	ZrO ₂ cubic partially stabilized	0.392	WC/Co 10.1% 2.84 micron	0.380	SiC alpha maximum	0.375
7	WC/Co 5.1%	0.392	TiB ₂ maximum	0.378	TiB ₂ maximum	0.369
8	WC/Co 7.6%	0.390	SiC alpha maximum	0.378	B ₄ C minimum	0.357
9	TiB ₂ maximum	0.388	B ₄ C minimum	0.370	Cr ₂ O ₃ maximum	0.354
10	B ₄ C minimum	0.383	Al ₂ O ₃ maximum	0.362	Cr ₂ O ₃ minimum	0.353

After reviewing these results, the materials for this phase of the program were narrowed to 5 choices. ACR will work with at least three of these materials when attempting to develop FM systems based on these core materials. The five materials are:

- 1) Tungsten carbide
- 2) Boron carbide
- 3) Titanium diboride
- 4) Diamond
- 5) Silicon Carbide

Tungsten carbide is such a widely used material that ACR would want to use this material in early trails even if the material had not ranked high in the trade study. Since boron carbide was the next best material when cost sensitivity is concerned it should also be included in the early trails. Titanium diboride was one of the highest ranked materials in performance so it should be included. Diamond is typically a high cost material, but the overwhelming

indications that expected performance would exceed all other materials dictates that it be included. Diamond has an added difficulty due to the high pressure processing requirements. In spite of this hurdle, ACR wants to keep this material on the initial list in the event that ACR gains access to diamond consolidation equipment through one of the program partners. Silicon carbide is included since the material scored well in the cost/sensitivity trade. However, it may be a more appropriate material for apex cones in the next phase of the program. For this reason, silicon carbide is included in the list and will be tested in this phase if one of the other materials fall out.



In addition to the Fibrous Monolith potential core materials, an interface trade study to select appropriate interface materials to be used with the selected core materials has been completed. The material requirements included high ultimate tensile strength, high ductility and/or toughness, a matched coefficient of thermal expansion, thermal conductivity and compatibility of the interface's sintering/consolidation temperature with the selected core materials. Cost will be considered, although FM composites are not as cost sensitive to interface selection because the interface typically makes up a much smaller portion of the composite (10-20 volume %).

Because of the success of the diamond/WC-Co FM system in the oil and gas drill bit insert application, and the high rating of both the WC and diamond in the core trade study, the first system selected for development in the mining drill bit insert is diamond/WC-Co. Diamond/WC-Co FM inserts were fabricated and sent to Kennametal for evaluation. Parts were consolidated but further testing was not pursued.

Interface materials were selected by considering hardness, elastic modulus, ultimate tensile strength and thermal conductivity. Based on the results of the trade study, the materials listed below were selected for development into FM systems and evaluation.

Table 2a – Core and Interface Materials for FM Development

Core Material	Interface Materials
Tungsten carbide	Tungsten Carbide Cobalt, Cobalt
Boron carbide	Tungsten Carbide Cobalt
Titanium diboride	Tungsten Carbide Cobalt
Diamond	Tungsten Carbide Cobalt

The trade study focused ACR efforts on a specific group of materials. While the materials investigated were defined by those listed in **Table 2a**, the range of processing conditions condition were limited by the technology available for consolidation. That technology is discussed in detail for Task 4. The results of the densification efforts clearly define the difficulties overcome and those that still remain to be resolved.

b. Composition development

Advanced Ceramics Research technical staff selected the most promising materials for further develop and design efforts. Selection was based on the required material properties for each of the applications studied during the program.

Preliminary efforts focused on fabrication of a set of Fibrous Monolith coupons and components for testing and evaluation in the mining and machine tool applications (**Figure 2a**). The material combinations pursued are listed below.

1. Silicon Nitride/Boron Nitride ($\text{Si}_3\text{N}_4/\text{BN}$)
2. Zirconium Diboride/Boron Nitride (ZrB_2/BN)
3. Hafnium Carbide/Tungsten-3.6%Rhenium alloy (HfC/WRe)
4. Titanium Diboride/Alumina ($\text{TiB}_2/\text{Al}_2\text{O}_3$)



Figure 2a. 3" x 0.5 x 0.5" ZrB₂/BN (left) and TiB₂/Al₂O₃ Fibrous Monolith coupons fabricated for testing and evaluation. The photo at left shows a 0.25" thick slice cut from the FM coupon.

Test results on the coupons for the metal machine tool application were disappointing. The FM insert samples all chipped during preparation for testing and as a result we were unable to produce any testable inserts from any of the samples. The BN and WRe interfaces may be

too brittle for metal cutting tools. After careful consideration of materials for machine tool applications, ACR obtained samples of the Al_2O_3 and TiCN powders typically used in Al_2O_3 -TiCN composite metal cutting tools. These powders were used to fabricate Al_2O_3 /TiCN FMs for direct comparison to Al_2O_3 -TiCN products in the cutting tool industry. Some success was seen with the production of improved metal cutting tool inserts using Non-Aqueous Gel Casting technology.

In addition to the test coupons, there is considerable interest by the cutting tool and mining industries in the Diamond/Tungsten Carbide-Cobalt FM system originally developed for Smith International Inc. (SII) as a coating for oil and gas drill bit inserts on a DOE funded program [5] to produce toughened coatings for drill bit inserts used in oil and gas exploration. With the cooperation of SII, one dozen 3/8-inch WC drill bit inserts coated with Diamond/Tungsten Carbide-6% Cobalt Fibrous Monolith (**Figure 2b**) were fabricated for testing and evaluation for mining applications.



Figure 2b. Diamond/WC-Co Fibrous Monolith coating (left) and a consolidated Diamond WC-Co coating on a 3/8" WC oil drill bit insert.

ACR investigated material sources and potential benefits of WC-based FM systems with core to shell cobalt ratios other than 6%:16%. Because the difference in mechanical properties between the core and shell are what give FM materials their enhanced wear resistance properties, it was thought that increasing the cobalt ratio from the current 6%:16% to 6%:20%, 6%:30% as well as 3%/6%, 3%/16%, 3%/20%, 3%/25% would result in a subsequent increase in wear resistance. Samples of WC-based FM materials with some of these ratios were made for testing. Representative samples appear in **Figure 2c** below.



Figure 2c – Representative coupons fabricated with 82.5% core WC(3%)Co/ 17.5% shell WC(16%)Co on the left and 82.5% core WC(3%)Co/ 17.5% shell WC(20%)Co on the right

Compositional development work focused on broadening the material properties database to cover a wider range of WC-Co based FM compositions. Expansion of the investigation to include additional compositions was brought about as a result of field testing by Superior Rock Bit with the 6%/16% FM drill inserts. Wear resistance for this material system was extremely high, but the relatively low fracture toughness caused the parts to fail much more quickly than the WC(8%)Co powder compacts commonly used by Superior for inserts. Mechanical properties characterization of FMs using WC(3%)Co was also performed with testing in roof bits fabricated by Brady Mining and Construction Supply. Wear plates were also fabricated with WC(3%)Co FM's for testing by the Robbins Group in a bucket lip application.

The compositions developed and densified at this stage of the program broadened the materials background for ACR. Work with materials such as WC-Co, diamond, TiB₂, B₄C for wear applications, while not entirely new, did broaden our understanding of the materials systems and difficulties of incorporating divergent materials with very different properties. Theory provided the background for the investigation; the fabrication and densification told us the difficult reality. Fabrication of materials with high wear resistance was accomplished; the combination of high wear resistance and fracture toughness was more elusive. The performance of the FM components will be improved with the changes to core/shell composition based on the field test results.

Task 3. Development of fibrous monolith fabrication process parameters

a. Fabrication process optimization

Advanced Ceramics Research technical staff, in conjunction with the program team members, performed fabrication process development tests to improve the yield and cycle time required to process fibrous monolith materials.

Upon completion of the trade study, the selected materials were obtained and suitable thermoplastic-ceramic blends were developed for fibrous monolith co-extrusion. This development process was iterative with repeated attempts to achieve an extrudable blend for

a given thermoplastic-ceramic FM system. The process involved blending individual ceramic powders with thermoplastic, melt-spinnable polymer binders, and plasticizers in a high shear mixer, to form a smooth uniformly suspended mixture. Since the mixers used have fixed volume reservoirs, the recipes devised to produce batches of the thermoplastic/ceramic blends were formulated on a volumetric, as opposed to a mass, basis. A typical blend consisted of 50 to 62 vol. % of ceramic powder, 38 to 50 vol. % of thermoplastics, and 0 to 12 vol. % of plasticizers. The core and interface of a fibrous monolith composite were blended separately and pressed into feedrod and shells respectively then warm-laminated to form a green composite feedrod. 'Green' composite feedrods with core/shell volumes in the ratios: 90/10, 82.5/17.5, 80/20, 70/30, 60/40 and 50/50 can be made. The composite feedrods were extruded to form a coaxial FM filament. Production of thermoplastic/ceramic blends of the cores and shells with the appropriate rheological properties preserves the extruded filament core/shell volume ratio of the original feedrod. The filaments were then laid-up in the desired architecture, warm laminated and delubed in a burnout furnace to remove the polymers. After binder burnout the samples were consolidated using pressureless sintering or uniaxial hot pressing to form the final dense component.

Initial development work used formulations for boron carbide, titanium diboride, tungsten carbide, and a tungsten-nickel-iron alloy in **Tables 3a-3d**. Previous work by ACR and the University of Michigan [5] had shown that a core/shell volume ratio of 82.5%/17.5% co-extruded to 2 mm provides the best combination of composite strength and toughness in applications where wear resistance is required. For this reason these parameters were selected to begin our development efforts on this program.

Table 3a. Co-extrudable Boron Carbide-Polymer 'Core' recipes.

Working B₄C Brabender Recipes		
Type	B₄C 'Core' material	
Recipe No.	ECT-01	
Material	Density (g/cc)	Volume %
B ₄ C	2.520	50.00
Polymers	1.000	40.00
Plasticizer	1.000	10.00
		100.00

Co-extrusion of the FM systems (**Table 3b**) was performed; 2 mm filament was cut into 3" lengths, and then laid-up uniaxially in a 1" x 3" die to form ~0.5 inch thick 1" x 3" FM coupons. These coupons were debound then densified by hot pressing. The establishment of optimal consolidation conditions for hot pressing used systematic variation of temperature, pressure and addition of sintering aids were needed.

Once the work to develop suitable thermoplastic blends of the materials had been completed all steps of green processing were scrutinized to identify areas where improvements could be made. These areas included thermoplastic blending, core and shell molding, core and shell co-extrusion, coupon fabrication, and binder removal. The development of optimized binder burnout conditions focused on understanding the breakdown and removal of materials under vacuum conditions using thermal gravimetric

analysis (TGA). Preliminary vacuum TGA measurements gave an indication of the need for further analytical work for systems complicated by combinations of materials such as binders, plasticizers and modifiers. The removal of binders with no distortion to the green blank was a critical step to achieve high density. Any potential improvements in these areas were thoroughly investigated, both theoretically and experimentally, prior to implementation for the FM fabrication process.

ACR's standard binder removal profile consisted of a series of heating ramps and soaks to 600 °C in an N₂ atmosphere. The design allowed the gradual removal of binders from a green part. Parts to be hot pressed require closed graphite die so that the loads required for consolidation can be applied. Parts are typically enclosed prior to binder removal, which helps preserve structure 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 Thermal Gravimetric Analysis/Differential Scanning Calorimetry (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. Because of this, the development of appropriate binder removal profiles that created no defects and allowed for the use of low cost consolidation techniques were important.

The initial criterion used to evaluate the binder removal processes was the presence of physical defects in the parts after binder removal. These defects were in the form of cracks and internal bloating, which can result in distortion and diminished mechanical integrity of the parts after processing. It was discovered that residual carbon was an additional criterion by which the binder removal processes could be evaluated. The three binder removal processes evaluated 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.

Table 3b. Co-extrudable Titanium Diboride ‘Core’ recipes.

Working TiB₂ Brabender Recipes		
Type	TiB₂ 'Core' material	
Recipe No.	ECT-02	
Material	Density (g/cc)	Volume %
TiB ₂	4.520	55.00
Polymers	1.000	40.00
Plasticizer	1.000	5.00
		100.00
Type	TiB₂ + (10% Ni Sintering Aid) ‘Core’ material	
Recipe No.	ECT – 05	
Material	Density (g/cc)	Volume %
TiB ₂ + 10vol% Ni	4.918	55.00
Polymers	1.000	36.00
Plasticizer	1.000	9.00
		100.00
Type	TiB₂ + (5% Al₂O₃ Sintering Aid) ‘Core’ material	
Recipe No.	ECT – 05	
Material	Density (g/cc)	Volume %
TiB ₂	4.520	50.00
Al ₂ O ₃	3.990	5.00
Polymers	0.930	37.00
Plasticizer	1.100	8.00
	2.892	100.00

Table 3c. Co-extrudable Tungsten Carbide-Polymer ‘Core’ and ‘Shell’ recipes.

Working WC Brabender Recipes		
Type	WC-3%Co ‘Core’ material	
Recipe No.	ECT-06	
Material	Density (g/cc)	Volume %
WC-3%Co	14.950	50.00
Polymers	1.000	42.00
Plasticizer	1.000	8.00
		100.00
Type	WC-6%Co ‘Shell’ material	
Recipe No.	ECT-07	
Material	Density (g/cc)	Volume %
WC-6%Co	14.960	50.00
Polymers	1.000	45.00
Plasticizer	1.000	5.00
		100.00

Table 3d. Co-extrudable Tungsten-Nickel-Iron alloy ‘Shell’ recipe.

Working W-Ni-Fe Brabender Recipes		
Type	W-Ni-Fe ‘Shell’ material	
Recipe No.	ECT-01	
Material	Density (g/cc)	Volume %
W-Ni-Fe	15.42	54.00
Polymers	1.000	34.00
Plasticizer	1.000	12.00
		100.00

High Temperature Binder Removal in Vacuum

The first binder removal program used vacuum at temperatures up to 500 °C. The program called for a constant temperature ramp (0.5 – 5 °C/min) to a maximum temperature of 500 °C in a 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 were prepared using a polymer binder mixture (EEA/EAA/MPEG) 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 3a-3c**. As seen 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 thought 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. 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, 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 3a – 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 3b – 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 °C/minute to a set point of 500 °C.

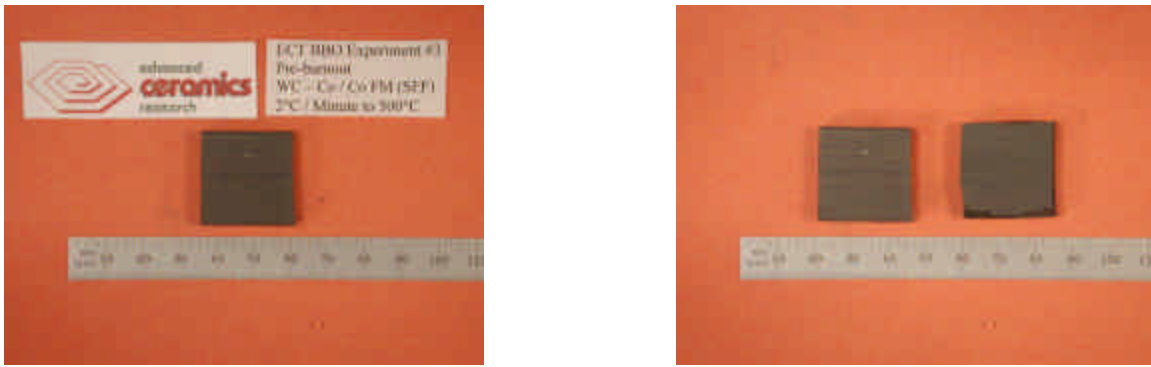


Figure 3c – WC-Co(6%)/Co FM test sample before (left) and after (right) binder removal in vacuum (10^{-3} torr) with a heating rate of $2.0^{\circ}\text{C}/\text{minute}$ to a set point of 500°C .

High Temperature Binder Removal in Inert Atmosphere

Since ACR has considerable experience with the removal of polymer binder mixtures at high temperatures in inert atmospheres (N_2), this is the standard binder removal process for the majority of our ceramic part production. Experiments were performed to develop a heating profile to remove binder without creating defects correctable 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(6%)Co) and shell (WC(16%)Co) blends, and from co-extruded WC(6%)Co/WC(16%)Co 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 removal was performed in a 3" diameter tube furnace under flowing Ar (2 standard cubic feet per minute). Photographs of parts processed using the experimental binder removal heating profiles are presented in **Figures 3d-3e**. Following several iterations, a profile that routinely produced visually defect free WC-Co FM cylinders was identified. This profile is given below in **Table 3e**. In consultation 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) used 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 below ± 0.05 wt%. Samples processed using this profile were sent for carbon analysis to determine baseline carbon content and provide direction for further binder removal work. The measured carbon content for the samples exceeded 7 wt%, well above the carbon content for the baseline WC(6%)Co material of 5.75 wt%. H_2 gas is used to "correct" the carbon content in WC-Co samples by reducing free carbon residue from binder removal into methane (CH_4). Using a gas mixture consisting of 90% Ar, 10% H_2 by volume, samples were run using the most promising profiles developed with a pure Ar atmosphere. After binder removal, these samples were similar in appearance to the samples run in Ar shown in **Figures 3d-3e**. When analyzed for carbon the samples run in the Ar/ H_2 atmosphere had a carbon content of 5.88 wt%, much closer to the baseline material at 5.75%. Parts were made for preliminary sintering experiments, and the binders removed in an Ar/ H_2 atmosphere. The parts were sintered at 1300°C for 30 minutes under vacuum, cross-sectioned, and

polished for examination. Cross sectioning of the parts revealed that, despite the absence of defects visible on the outside, significant cracking and voiding was still present inside. 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 internal physical defects.



Figure 3d – 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.

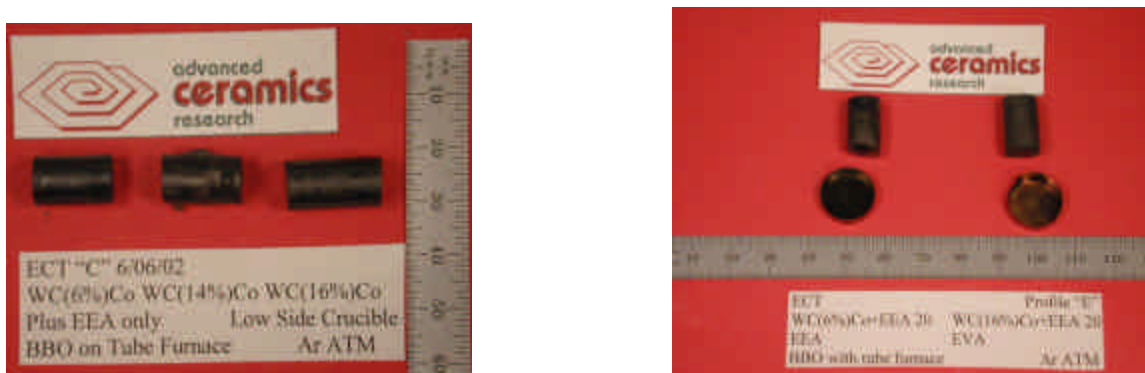


Figure 3e – WC-Co monolithic and FM test samples processed using binder removal profile “C” (left) and “E” (right) in a 3” diameter tube furnace under a flowing Ar atmosphere.

Table 3e – 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, a re-evaluation of dual polymer binder system was made in an effort to fabricate

defect free parts. A literature review on binder removal suggested the use of two polymer binder systems for green processing. Typically, one of the binders is removed at lower temperatures creating pathways for diffusion of breakdown products from the second binder at higher temperatures. For FM processing, the challenge was to develop binder systems that are compatible and suitable for co-extrusion.

Previous work at ACR performed on co-binder systems was because of available WC-Co powders containing ~2 wt% paraffin wax. It 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 cracking and char formation were observed. Samples were also evaluated using a high temperature inert gas binder removal process but 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 difficult to develop a universal thermoplastic formulation for this material. In order to eliminate the batch variability of the wax, formulations were developed where a measured amount of wax (Calwax paraffin, Chevron) was added to wax-free powders, along with a second binder component (EVA, DuPont). Test articles for binder removal experiments. The main challenge in earlier evaluations were bloats and defects during the low temperature (<200 °C) phase. This is 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 experiments, a profile was developed that removed a significant amount of wax without creating mechanical defects. This profile is given in **Table 3f**. The percentage of wax removed using this profile is strongly dependent on both the surface area and effective diameter of the part. 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 3f – 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 a tube furnace under flowing Ar/H₂, which was shown to significantly reduce free carbon levels. The heating profile for the second binder removal process is similar to the profile in **Table 3e**, 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 is now the ACR standard for fabricating WC-Co containing parts, and has been used to

fabricate parts (e.g. test coupons, rod stock, inserts) that have sintered densities exceeding 99%.

In order to further characterize and optimize the two-stage binder removal process, experiments to both calculate and measure free carbon levels in WC-Co FM samples with varying final soak (550°C) times were performed. The final soak temperature was selected based on literature, which suggested that at 550°C the kinetics for carbon reduction by H₂ were most favorable. WC-Co FM cylindrical samples 10 mm in diameter and 10 mm tall were fabricated and used for characterization experiments. The low temperature vacuum stage of the binder removal process was held constant, and the final soak time of the high temperature stage (**Table 3g**) was varied from 4 to 24 hours in increments of 4 hours. The free carbon was then calculated using the weight of each sample, and the known binder formulation and loading. A chart of the calculated percentage of organic material removed is shown in **Figure 3f**. The data demonstrated the expected trend, where the calculated percentage removal of organic material from the FM samples decreased with decreasing final soak times.

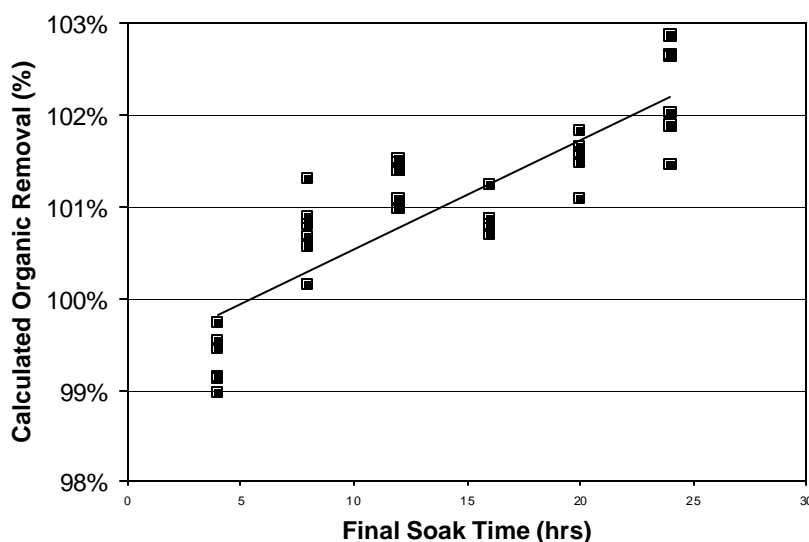


Figure 3f – Calculated organic removal from WC-Co FM samples with varying binder removal profile final soak (550 °C) time in Ar/H₂ atmosphere.

While the trend of decreasing organic removal with decreasing final soak times was expected based on published literature and past experience, the calculated values of greater than 100% organic removal were unexpected. There are several possible explanations for this observation, including measurement error, formulation error, or potential loss of Co from the samples during binder removal. Calculations made using monolithic WC-Co(6%) and WC-Co(16%) material samples fabricated to determine material shrinkage during sintering (see **Task 4**) have shown that in samples of core material weight loss during binder removal is essentially 100%, however, the weight loss in the shell material was significantly higher at 102.5%. Because the shell material has significantly more cobalt than the core material, it appears as if cobalt loss is the likely cause of the extra weight loss in both the monolithic and FM samples. A cobalt loss of 0.01 g during binder removal would account for the increase in calculated organic removal percentage seen for the binder removal process with a 24 hour

final soak time. This is approximately 1.5% of the total cobalt in each sample, and is not expected to have a major impact on the mechanical or wear properties of the WC-based FM system. Such loss may also be expected in conventional monolithic cemented carbides as well.

Melt Rheology

In order to further enhance understanding of the green processing of raw materials for FM structures, a study was undertaken to characterize the rheology of the polymer/powder mixtures. It was based on suggestions from a text on powder injection molding (PIM), [8]. The rheological studies were performed on samples with solids loadings from 10 to 60% of core (WC(6%)Co) and shell (WC(16%)Co) materials. Measurements were made using capillary rheometry with an Instron model 3211 capillary rheometer. The shell and core materials were both evaluated with the goal of improved green processing, binder removal and improved process robustness. **Figure 3g** below shows relative viscosity versus solids loading for both core and shell materials measured at an extrusion velocity of 2.5 millimeters (0.1 inch) per minute.

For the core and shell materials the relative viscosity is fairly consistent. At lower extrusion velocity, shown in **Figure 3h**, it is clear that the lower extrusion velocity of 0.0762 millimeters (0.03 inches) per minute has a more divergent effect on the viscosities of the two materials. This is important since the materials are co-extruded and when forming the architecture for the FM, if one material is more resistant to extrusion the material will separate forming voids, thin areas or even stripping the shell material. For the 58% solids loading range used it appears that extrusion speed should be at least 2.5 millimeters (0.1 inch) per minute.

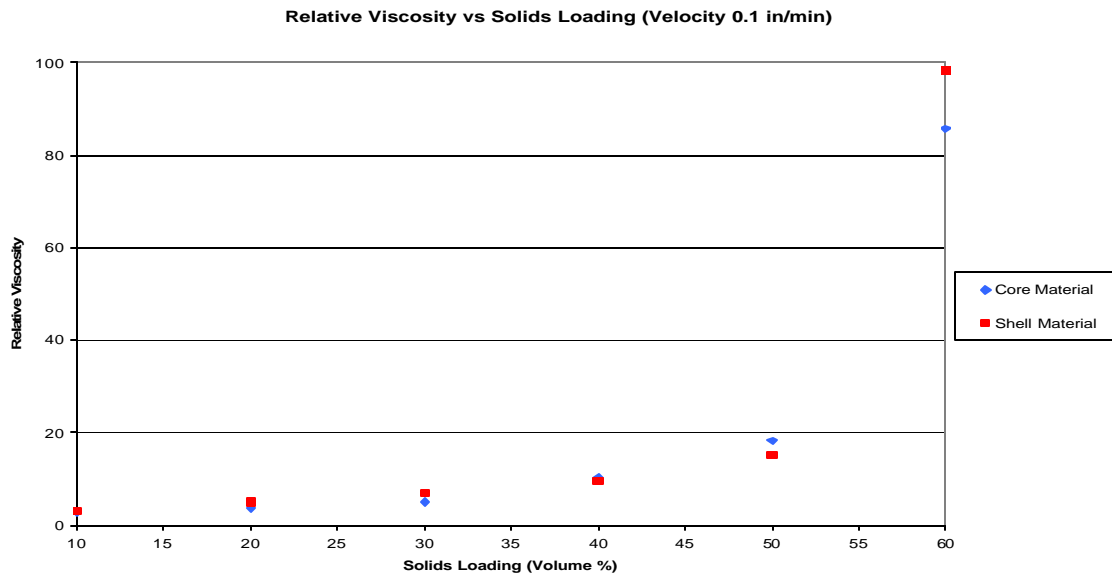


Figure 3g– Relative viscosity versus solids loading (velocity 0.1 in/min)

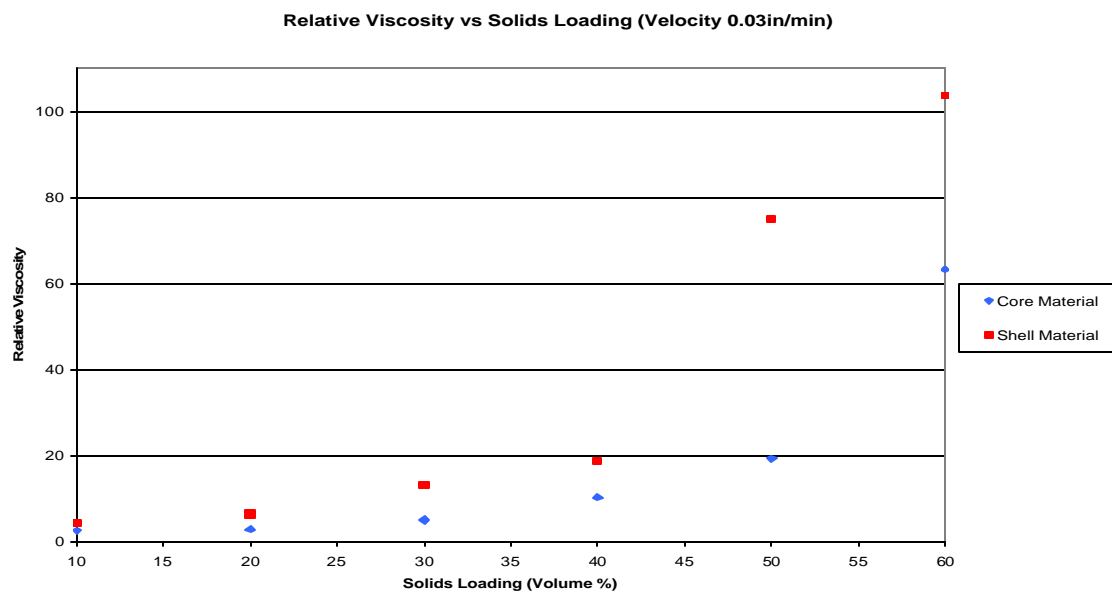


Figure 3h – Relative viscosity versus solids loading (velocity 0.03 in/min)

Another issue addressed with the rheometry study was the ideal solids loading for the core and shell materials (WC(6%)Co/WC(16%)Co). Plots of the Force versus Rheometer speeds (shown in **Figure 3i** and **Figure 3j**) for the core and shell, respectively, show the dramatic increase in the force for solids loading at 60%. All levels below that (50%, 40%, etc.) show much lower force generated from the varying extrusion speeds. The 58% solids loading was arrived at through long and difficult trial and error based on the performance of the material through the mixing, pressing, extruding, forming and densification. We now have a verified

experimental basis for solids loading and extrusion speeds. The same modeling will simplify the development of alternate formulations and systems for other materials.

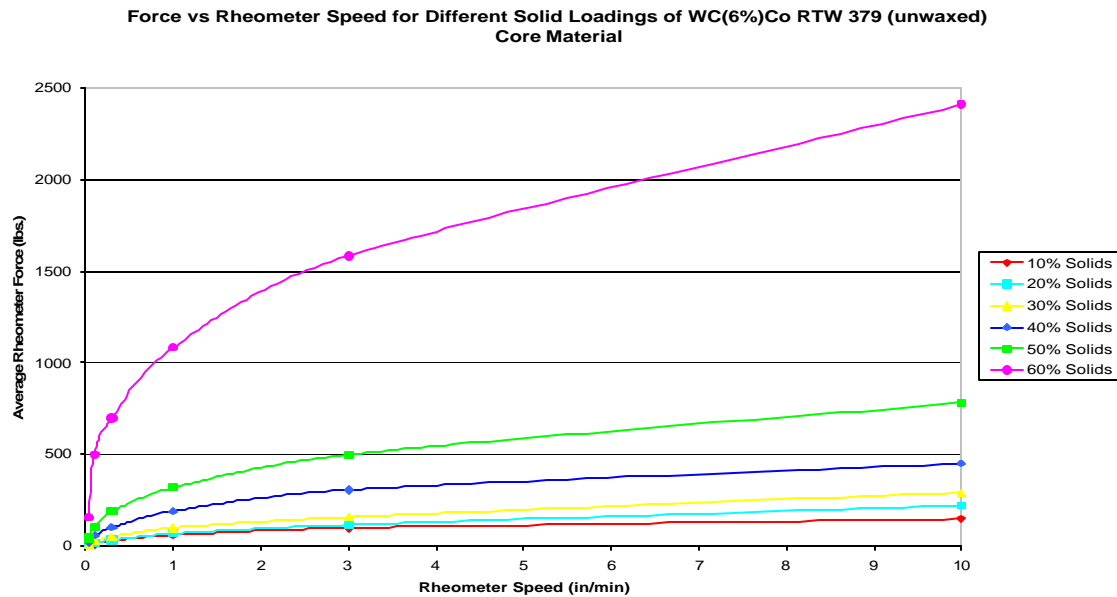


Figure 3i – Force versus rheometer speed for different solids loadings of WC(6%)Co RTW 379 (unwaxed) core material.

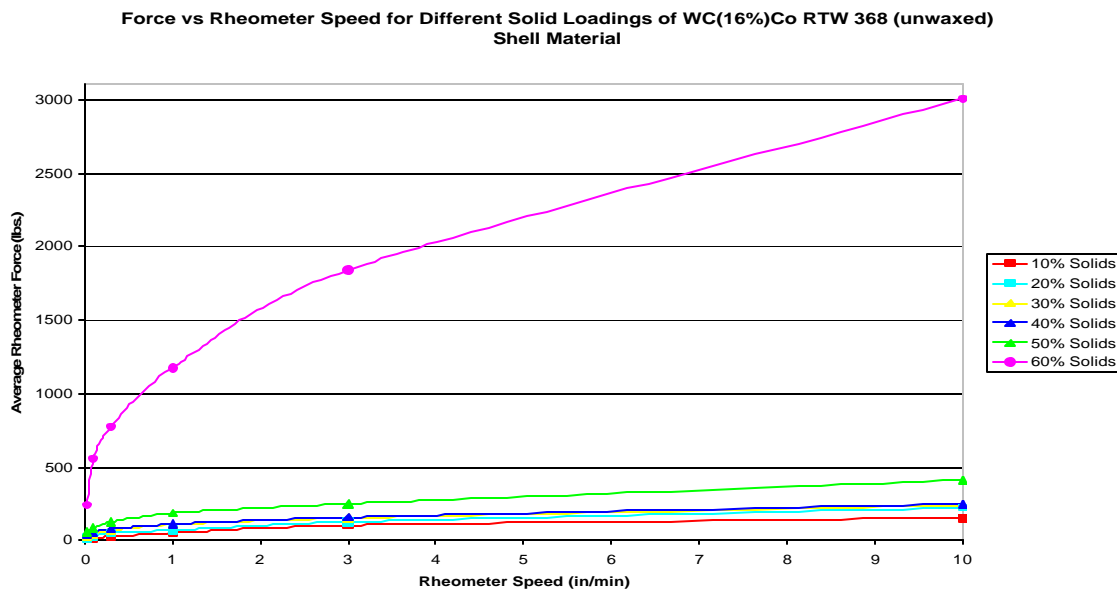


Figure 3j – Force versus rheometer speed for different solid loadings of WC(16%)Co RTW 368 (waxed) shell material

Based on the rheological analysis, for the 58% solids loading range used extrusion speed should be at least 2.5 millimeters (0.1 inch) per minute. With the experimental results we have a verified experimental basis for solids loading and extrusion speeds. This information

will bridge all rheological systems since the same modeling will simplify the development of alternate formulations and systems for other materials.

Work performed at UMR

Dr. Hilmas, an associate professor at UMR, formerly worked at 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.

UMR has made progress on this program in two areas. The first of these was development of powder binder compositions that can be successfully co-extruded and burned out to remove the organic binder in the components. The powder binder blends to be used had to serve three basic functions. Primarily, the binder system had to be able to accommodate a high (>55%vol) solids loading and still be able to form a homogeneous blend. The binder system that was chosen is able to accommodate 60% (volume) solids. Secondly, the powder/binder system had to provide successful co-extrusions of FM architectures. With the developed binder system, UMR was able to manufacture FM structures using the co-extrusion process. UMR has also been able to develop a binder burnout profile that completely removed the polymer with no externally visible defects.

The second part of UMR's effort focused on production of laminated samples using alternating layers of the core and shell material from the co-extrusion process. This study was undertaken to develop a better understanding of the role of Co content on the mechanical behavior of the WC-Co FM systems. The high wear resistance of the WC-Co based FM material system in the mining tool bit application depends specifically on the manner in which cracks interact with the core/shell materials and the interface between them. In order to study this aspect of the structure, it was determined that laminate samples would provide a good method to test how cracks would interact with the core and shell and the interface. In order to produce these samples, sheets of material were pressed using compositions similar to those used for co-extrusion. These sheets were then laminated together into large disks or squares. Sample bars were then cut from the larger laminates followed by burnout and sintering. All samples that were sintered show some form of minor cracking, either visible on the outside, or in the center of the bar after sectioning. By forming samples with alternating layers of WC-Co and cell boundary materials such as cobalt and tungsten iron nickel (W-Fe-Ni) investigations of W-Ni-Fe and Co cell boundaries were performed. Mechanical evaluations show that the composite materials provide a weaker plane for crack deflection as shown in **Figure 3k**.

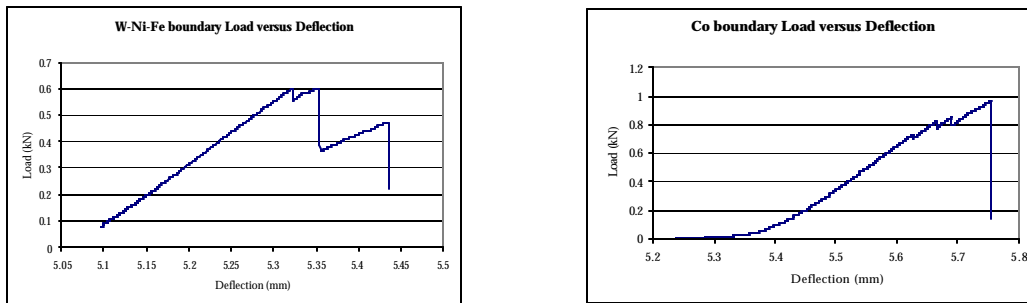


Figure 3k — Load versus deflection plots for W-Ni-Fe (left) and Co (right) demonstrating the crack deflecting properties in the layered composite material (i.e. WC-Co/W-Ni-Fe and WC-Co/Co).

The plots in **Figure 3k** show what has been identified as ideal composite material behavior with the ability of the material to deflect cracks as the more brittle elements fail and the tougher material (either Co or W-Ni-Fe) absorbs the energy to stop propagation through the material.

UMR performed characterization of the hardness and density for a range of sintering temperatures from 1225°C to 1350°C. To identify the possible interaction of WC-Co with firing setters, the parts have been sintered on alumina and graphite coated alumina. No reaction was identified with either setter type.

The third area of investigation at UMR was the removal of binders from the WC-Co coupons using solvent in place of heat and vacuum. The focus of binder removal were the materials which leave the green parts at low temperature such as wax and heavy mineral oil (HMO). Using the loss of weight as an indicator, success was seen with acetone and MEK mixtures for the wax (85% weight loss) and acetone only for the HMO (95% weight loss). The removal of the low temperature organics was confirmed with TGA. The formulations used by UMR were switched to HMO since efforts to extract were successful. It was also found to be quicker to perform burnout on parts where solvent extraction had been used.

A combined investigation of the effects of normal process, solvent extraction and sintering on alumina or graphite setters was performed on standard FM samples. (**Table 3g**) The normal binder removal process using alumina or graphite setters varied roughly 3% for densities, favoring the graphite setter. The solvent extraction process showed a much smaller deviation in the density. The density differential for the graphite versus the alumina is less than .5%. Similar results are seen for the hardnesses with normal process giving greater hardness for the graphite setter and the solvent extraction giving a small improvement with the alumina setter (.3%). Differences in the densities and hardnesses show most of the properties as better using the graphite setters.

The overarching concern for the materials being processed was to achieve the highest density possible. With the highest possible density, the balance of the properties could be addressed and optimized.

Table 3g – Results of solvent and conventional binder removal experiments at UMR

Conditions	Properties	Setter	
		Alumina	Graphite
Normal Processing	Density	95.03%	97.89%
	Hardness	1734.00	1791.00
Solvent Extraction	Density	95.50%	96.00%
	Hardness	1761.00	1755.00

The significant contributions of UMR to the progress of this program with development of binder compositions and study of core/shell interactions has broadened the understanding of the WC-Co systems selected as most important for wear resistant mining applications.

Task 4. Densification Process Development

a. Densification Process Optimization

Advanced Ceramics Research technical staff and the program team members performed densification process development tests to improve the yield and cycle time required to process fibrous monolith materials.

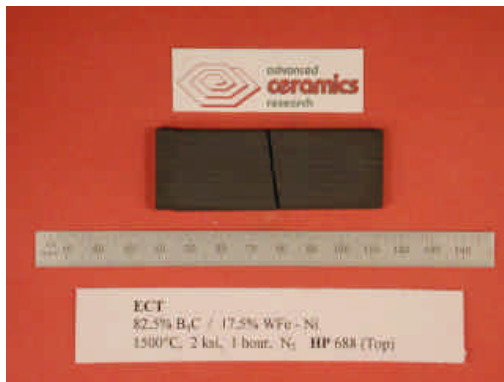
Densification studies were being performed to optimize conditions and develop processes for the fabrication of fully dense parts. Incomplete densification can be detrimental to hardness, fracture toughness and transverse rupture strength, all important factors for the performance of mining components. The densification processes included uniaxial hot pressing, pressureless sintering, and hot isostatic pressing. Sample fabrication started with 1" x 3" powder billets, progressed to uniaxial Fibrous Monolith billets, FM drill inserts, and FM wear plates of various compositions. The initial FM parts are shown in **Table 4a** and illustrated in the photographs below:

Table 4a – FM Composition, consolidation, and density

FM Composition 82.5% core / 17.5% shell (volume/volume)	Temperature (° C)*	Pressure (PSI)	Measured Bulk Density (g/cc)	Theoretical Density (g/cc)	% Full Theoretical Density
TiB ₂ / WC-6%Co	1500	2000	4.348	6.080	71.5
B ₄ C / W-Ni-Fe	1500	2000	3.685	4.535	81.3
TiB ₂ -10%Ni / WC-6%Co	1500	2000	4.155	6.541	63.5
TiB ₂ -5%Al ₂ O ₃ / WC-6%Co	1500	2000	4.803	6.184	77.7
WC-6%Co / W-Ni-Fe	1550	2000	14.562	15.032	96.9
TiB ₂ / WC-6%Co	1550	2000	4.817	6.541	73.6
TiB ₂ -5%Al ₂ O ₃ / WC-6%Co	1600	2000	4.386	6.168	71.1
TiB ₂ -10%Ni / WC-6%Co	1600	2000	3.984	6.541	60.9

*All samples were hot-pressed for 1 hour at the temperatures denoted.

Figure 4a. Photo-archive of FM Coupons Listed in Table 5 above.



82.5% B₄C / 17.5% W-Ni-Fe



82.5% TiB₂ / 17.5% WC-6%Co



82.5% TiB₂-5%Ni / 17.5% WC-6%Co



82.5% TiB₂-5%Al₂O₃ / 17.5% WC-6%Co



82.5% TiB₂ / 17.5% WC-6%Co



82.5% WC-6%Co / 17.5% W-Ni-Fe



82.5% TiB₂-Ni / 17.5% WC-Co (6%)



82.5% TiB₂-Al₂O₃ / 17.5% WC-Co

Physical characterization of the hot pressed FM composites was performed using optical microscopy and Archimedes density measurements (as reported in **Table 4a** above). The physical appearance of fabricated billets varied widely due to the constituent materials and range of sintering temperatures. The poorest billets were only partially consolidated with friable structures easily broken in the hand. The best billets were dense with metallic luster and some cell structure intact. The sample in the first group with the highest measured theoretical density is the WC-6%Co / W-Ni-Fe FM sample hot pressed at 1550°C. Because of its hardness, the sample proved to be extremely difficult to polish in preparation for microscopic observations. It was possible to obtain a photomicrograph showing the presence of a distinct FM cellular structure. The high density, high apparent hardness, and presence of a distinct FM structure made the WC-6%Co / W-Ni-Fe system look very promising for mining wear applications, especially as a coating for WC drill bit inserts. Attempts to repeat fabrication of the same system, however, did not show the same result.

Examination of the other systems listed above revealed they all have well defined FM structures. However, the presence of voids and pores is indicated by their low measured densities, between 60 and 80%, as well as the observation of pores and voids in the samples during optical microscopy. Efforts to obtain fully dense TiB₂ and B₄C-based FM systems by refining the consolidation pressure, temperature and sintering aids continued as these systems also had considerable promise in improving the wear-life of a variety of mining components.

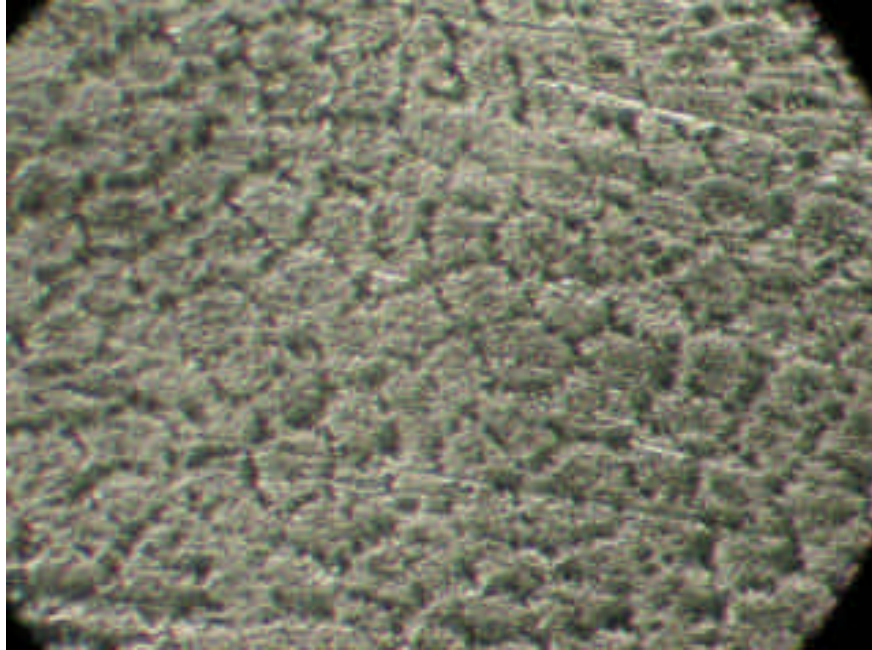


Figure 4b. Photomicrograph of WC-6%Co / W-Ni-Fe FM system consolidated at 1550 C. The hexagonal WC-6%C cells (gray) are isolated by thin W-Ni-Fe boundaries. Note that the rough polish of the sample partially obscures the FM structure.

B₄C-based Systems

In order to better understand the required consolidation conditions for the B₄C-based fibrous monolith composites, monolithic test coupons were first prepared using B₄C powder with and without sintering enhancing additives. Additives used, which were reported in the literature to enhance the sintering of B₄C, included SiB₆ and Co. Sintering additives were expected to be necessary based on the high melting point of B₄C (2450°C), and experimental sintering temperatures (>2000°C) reported in the literature. A list of the powder coupons prepared, and their measured Archimedes densities, is given in **Table 4b**.

Table 4b - B₄C – based Monolithic Samples

Composition or FM Combination 82.5% core/ 17.5% shell (volume / volume)	Temperature (° C)*	Measured Bulk Density (g/cc)	Theoretical Density (g/cc)	% Full Theoretical Density
B ₄ C	2200	2.441	2.52	96.9
B ₄ C	2100	2.149	2.52	85.3
B ₄ C	1800	1.413	2.52	56.1
B ₄ C(6%)Co	1800	1.685	2.904	58.0
B ₄ C(6%)Co	1800	1.718	2.904	59.2
B ₄ C-SiB ₆	2200	2.434	2.516	96.7
B ₄ C -SiB ₆	2100	2.316	2.516	92.1

*All samples were hot pressed for 1 hour (at soak temperature) and 2000 psi.

As anticipated, hot pressing temperatures of 2200 °C were required to produce test coupons approaching 100% theoretical density, even with the presence of additives to promote sintering.

Following the consolidation of the powder test coupons, B₄C-based FM test coupons were fabricated, using B₄C (with and without additives) as the core phase, and W, WC-Co(3%), WC-Co(6%) or WFeNi as the interface phase. WFeNi was an experimental material that had been considered for use in tooling applications on previous ACR development efforts. Experience suggested that the use of a lower melting point interface phase would reduce the consolidation temperature required for the B₄C-based FM systems. This is compared to the powder test coupon data which suggested that hot pressing temperatures of 2200 °C or higher would be needed to consolidate B₄C-based FM composites to full density. In addition to consolidation by hot pressing, one test coupon (B₄C/W) was consolidated by hot isostatic pressing (HIP) for comparison. A list of the B₄C FM test coupons prepared, and their measured Archimedes densities, is given in **Table 4c**.

Despite the relatively high consolidation temperature (~2000 °C), none of the test coupons fabricated had densities high enough to be considered as usable materials for our target applications. In some cases the high consolidation temperature resulted in the mobilization and subsequent migration of the lower melting point interface material to the outer surface of the test coupon. It is expected, if a suitable interface material could be found, that hot pressing temperatures of 2200 °C were required to produce test coupons approaching 100% theoretical density, similar to those required for the monolithic samples. Because of the high consolidation temperatures required for the B₄C based systems, as well as the lack of a suitable tougher interface material that can withstand the high temperatures, B₄C-based FM systems were excluded from further investigation.

Table 4c - B₄C – based Fibrous Monolith Samples

Composition or FM Combination 82.5% core/ 17.5% shell (volume / volume)	Temperature (° C)*	Measured Bulk Density (g/cc)	Theoretical Density (g/cc)	% Full Theoretical Density
B ₄ C / W	2000	3.277	5.457	60.1
B ₄ C / W (HIP, 15 ksi)	2000	2.435	5.457	44.6
B ₄ C / WC(3-4%)Co	2000	2.913	4.695	62.0
B ₄ C / WC(6%)Co	1600	3.00	4.756	63.1
B ₄ C / WC(6%)Co	1700	2.14	4.756	45.0
B ₄ C-SiB ₆ / WC(6%)Co	2000	2.79	4.693	59.5
B ₄ C(5%)Al ₂ O ₃ / WC(6%)Co	2000	3.572	4.756	75.1
B ₄ C / WFeNi	1500	3.685	4.535	81.3

* All samples except (HIP) were hot pressed for 1 hour (at temperature) and 2000 psi.

TiB₂-based Samples

To develop an understanding of the necessary consolidation conditions for TiB₂-based FM systems, monolithic test coupons were first prepared using TiB₂ powder with and without

sintering additives. Additives used in powder and FM versions, reported in the literature to enhance the sintering of TiB_2 , included Al_2O_3 , Ni, Co, and Si_3N_4 [6]. Sintering additives were expected to be necessary based on the high melting point of TiB_2 (2980 °C). The two powder coupons prepared, along with their Archimedes densities, are given in **Table 4d**.

Table 4d - TiB_2 – based Monolithic Samples.

Composition or FM Combination 82.5% core/ 17.5% shell (volume / volume)	Temperature (° C)*	Measured Bulk Density (g/cc)	Theoretical Density (g/cc)	% Full Theoretical Density
TiB_2	1800	2.88	4.52	63.7
TiB_2 -(6%)Co	1800	4.18	4.74	88.2

*All samples were hot pressed for 1 hour (at soak temperature) and 2000 psi.

As anticipated, hot pressing temperatures of 1800 °C were not sufficient to produce test coupons approaching 100% theoretical density, although the presence of additives did appear to promote densification.

Following the consolidation of the powder test coupons, TiB_2 -based FM test coupons were fabricated, using TiB_2 (with and without additives) as the core phase, and W, WC-Co(3%), or WC-Co(6%) as the interface. As seen for the B_4C -based FM systems, experience suggested that the use of a lower melting point interface would reduce the consolidation temperature required for the TiB_2 -based FM systems. A list of the FM test coupons prepared, and their measured Archimedes densities, is given in **Table 4e**.

Table 4e – TiB₂ – based Fibrous Monolith Samples

Composition or FM Combination 82.5% core/ 17.5% shell (volume / volume)	Temperature (° C)*	Measured Bulk Density (g/cc)	Theoretical Density (g/cc)	% Full Theoretical Density
TiB ₂ / W	2000	5.65	7.08	79.8
TiB ₂ / WC(3-4%)Co	1900	3.76	6.32	59.5
TiB ₂ / WC(3-4%)Co	2000	5.10	6.32	80.7
TiB ₂ / WC(3-4%)Co	2100	5.46	6.32	86.3
TiB ₂ / WC(6%)Co	1600	5.47	6.21	88.1
TiB ₂ / WC(6%)Co	1550	4.82	6.54	73.6
TiB ₂ / WC(6%)Co	1500	4.35	6.08	71.5
TiB ₂ (2.5%)Si ₃ N ₄ /WC(3-4%)Co	1600	3.87	6.32	61.2
TiB ₂ / WC(6%)Co	1700	1.72	6.21	27.6
TiB ₂ / WC(6%)Co with wax	2000	nd	nd	nd
TiB ₂ / WC(6%)Co (7.62 x 7.62 cm)	2100	5.61	6.21	90.3
TiB ₂ (5%)Al ₂ O ₃ /WC(6%)Co	1500	4.80	6.18	77.7
TiB ₂ (5%)Al ₂ O ₃ /WC(6%)Co	1600	4.31	6.18	69.8
TiB ₂ (5%)Al ₂ O ₃ /WC(6%)Co	1800	5.09	6.18	82.3
TiB ₂ (5%)Al ₂ O ₃ /WC(6%)Co	2000	5.43	6.18	87.8
TiB ₂ (10%)Ni/WC(6%)Co	1500	4.16	6.54	63.5
TiB ₂ (10%)Ni/WC(6%)Co	1600	3.98	6.54	60.9
TiB ₂ (5%)Ni/WC(6%)Co	1800	5.61	6.39	87.7
TiB ₂ (10%)Ni/WC(6%)Co	2000	5.53	6.39	84.6
TiB ₂ (2.5%)Si ₃ N ₄ /WC(6%)Co	1600	3.96	6.32	62.7
TiB ₂ (2.5%)Si ₃ N ₄ /WC(6%)Co	1800	5.02	6.32	79.4
TiB ₂ (2.5%)Si ₃ N ₄ /WC(6%)Co	1850	4.98	6.32	78.7
TiB ₂ (2.5%)Si ₃ N ₄ /WC(6%)Co	1900	4.88	6.32	77.3

*All samples were hot pressed for 1 hour at 2000 psi.

The TiB₂-based FM test coupons had significantly higher densities than the B₄C-based FM coupons, at roughly the same consolidation temperatures (>2000 °C). The highest achieved density of 90.3% for TiB₂/WC-Co(6%) at 2100°C, however, is still well short of the >99% density required to be considered as usable materials for our target applications. It is conceivable that increasing the consolidation temperature to 2200 °C or higher would result in coupons with acceptable densities, however, these processing temperatures are not desirable due to increased operating costs and reduced throughput for manufacturing. Because of this, TiB₂-based FM systems have been excluded from further investigation. As with other materials, investigation of this material may be pursued at a later date if high temperature application interface materials are identified, and if cost considerations make this a desired material for use in mining applications.

Al₂O₃-based Systems

Al₂O₃ based FM materials are being pursued at the request of Kyocera, an industrial partner on this program and Kennametal, a customer of ACR. In addition to the mining

applications, such as roof bit inserts, Kennametal is interested in the FM systems as a way to 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 three manufacturers.

In order to better understand consolidation conditions for Al_2O_3 -based fibrous monolith composites, monolithic test coupons were first prepared using Al_2O_3 powder with and without performance enhancing additives. The Al_2O_3 powder achieved a density of 100.3%, Al_2O_3 -TiCN powder consolidated to 99.9% and $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ -TiCN FM to 99.6%. The TiCN is added to the Al_2O_3 to enhance the toughness of the Al_2O_3 . The FM structure will be the focus of continuing efforts. In reviewing **Table 4f** consolidation of the Al_2O_3 -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 Al_2O_3 -TiCN powder hot pressed at 1650°C and 4 ksi.

Table 4f - Al_2O_3 – 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_2O_3 powder	1650(5 ksi)	3.972	3.96	100.3
Al_2O_3 -TiCN powder	1550(5ksi)	4.175	4.39	95.1
Al_2O_3 -TiCN powder	1550(4ksi)	4.223	4.39	96.2
Al_2O_3 -TiCN powder	1600(4ksi)	4.348	4.39	99.1
Al_2O_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 information generated with 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 4g**. The highest densities seen were for FM the coupons hot pressed at 1650°C and 5 ksi.

Table 4g - $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ -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_2O_3 / Al_2O_3 -TiCN	1600 (4 ksi)	2.609	4.03	64.7
Al_2O_3 / Al_2O_3 -TiCN	1600(5 ksi)	3.863	4.03	95.9
Al_2O_3 / Al_2O_3 -TiCN	1650(5 ksi)	4.007	4.03	99.4
Al_2O_3 / Al_2O_3 -TiCN	1650(5 ksi)	4.016	4.03	99.6

All samples where hot pressed for 1 hour.

The mechanical properties evaluated on one of the powder coupons (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. 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 4f** above. The Al₂O₃ / Al₂O₃-TiCN FM coupons both had a dark lustrous appearance. The alumina coupon had a dull grey appearance.

Al₂O₃ based FM materials have also been pursued for extrusion dies for use in the hot forming of materials such as brass, aluminum and filled plastics. The industrial partner, Master Craft Extrusion Tools of Northport, MI, has strong interest as a supplier to the extrusion industry. The Al₂O₃-based materials are being pursued after an effort to develop Si₃N₄-based material for the same application was abandoned due to poor performance. In addition to an Al₂O₃-based FM, other materials fabricated by non-aqueous gel casting are being investigated for this application. Materials such as Al₂O₃, Al₂O₃-TiCN, silicon carbide and silicon nitride have been successfully gel casted and sintered for this application. The images in **Figure 4c** below show an Al₂O₃/Al₂O₃-TiCN extrusion die and a sample of the roughly 6300 feet of brass extruded with it.



Figure 4c – Al₂O₃ / Al₂O₃-TiCN FM extrusion die prior to machining (left) and approximately 1200 feet of 1” extruded brass rod (right).

The extrusion blank was machined and fitted into an extrusion die set by Master Craft Extrusion Tools, Inc. The brass extrusion was performed at Extruded Metals, Inc. of Belding MI. It clearly demonstrated the opportunity for FM materials in the cross cutting field of hot metal extrusion.

WC-Co-based Systems

The largest body of work was pursued on the WC-Co systems. This was due to its current level of acceptance as a wear resistant material for the mining industry and the relative ease of processing commercial powders. The WC-Co-based FM test coupons had significantly higher densities than the B₄C-based or TiB₂-based FM coupons, and were consolidated at significantly lower temperatures. The relatively high densities obtained with the WC-Co

based FM composites are very close to the densities required to be considered for use in mining tools or other related applications. Densities approaching full theoretical have been achieved on a consistent basis. The relatively low consolidation temperature, compared to the B_4C and TiB_2 -based FM systems, and the high measured densities have resulted in the down-selection of the WC-Co-based FM system as the most promising material system for our targeted mining applications. For this reason, efforts on this program were focused on the development of WC-Co-based FMs for mining applications.

Sintered Samples

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 4f** are representative of progress made with respect to binder removal in the WC-Co based FM systems. Work to evaluate sintering conditions has also been carried out by Dr. Zak Fang at the University of Utah as a subcontract to this program.

Table 4f WC-Co – based Sintered Samples Summary

Composition or FM Combination 82.5% core/17.5% shell (volume/volume)	Temperature °C (ATM)	Measured Bulk Density (g/cc)	Theoretical Density (g/cc)	% Full Theoretical Density
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

Relatively high densities were achieved for powder and FM samples (WC(14%)Co and WC(6%)Co/WC(16%)Co) at 1300°C and either a nitrogen or vacuum atmosphere.

Hot Pressed Samples

As was done for the B_4C and TiB_2 FM systems, monolithic WC-Co test coupons were first prepared using WC-Co powder with varying Co percentages, so that the conditions for consolidation could be more fully understood. A list of the powder coupons prepared, and their measured Archimedes densities, is given in **Table 4g**.

Table 4g – WC-Co – based Monolithic Samples.

Composition or FM Combination 82.5% core/ 17.5% shell (volume / volume)	Temperature (° C)*	Measured Bulk Density (g/cc)	Theoretical Density (g/cc)	% Full Theoretical Density
WC-Co(3-4%)	1300	14.269	14.96	95.381
WC-Co(6%)	1300	14.999	14.95	100.3
WC-Co(14%)	1300	14.270	14.13	101.0
WC-Co(16%)	1300	14.174	13.94	101.7

*All samples were hot pressed for 1 hour (at temperature) and 2000 psi.

For the monolithic WC-Co powders, with 3 to 16% Co, a hot pressing temperature of 1300 °C was sufficient to produce test coupons at or near full theoretical density.

Following the consolidation of the powder test coupons, WC-Co-based FM test coupons were fabricated, using WC-Co (with varying cobalt content) as the core phase, and WC-Co or Co as the interface phase. Data from the monolithic test coupons suggested that these systems could be fully densified at or below 1300 °C. A list of the FM test coupons prepared, and their measured Archimedes densities, are given in **Table 4h**.

Table 4h – WC-Co – based Fibrous Monolith Samples

Composition or FM Combination 82.5% core/ 17.5% shell (volume / volume)	Temperature (° C)*	Measured Bulk Density (g/cc)	Theoretical Density (g/cc)	% Full Theoretical Density
WC(3-4%)Co / Co	1450	13.692	13.90	98.5
WC(3-4%)Co / WC(6%)Co	1450	13.815	14.96	92.4
WC(6%)Co / Co	1300	12.644	13.89	91.0
WC(6%)Co / Co	1300 (4KSI)	14.006	13.89	100.8
WC(3-4%)Co / WC(6%)Co	1400	13.578	14.96	90.8
WC(3-4%)Co / WC(6%)Co	1400	13.691	14.96	91.5
WC(3-4%)Co / WC(6%)Co	1400	13.784	14.96	92.1
WC(6%)Co / Co	1200	11.734	13.89	84.5
WC(6%)Co / WC(14%)Co	1300	14.017	14.81	94.7
WC(6%)Co / WC(16%)Co	1300	14.112	14.77	95.5

*All samples were hot pressed for 1 hour (at temperature) and 2000 psi (except as noted).

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. 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 as developed in **Task 3**. The hot pressing conditions and associated densities are shown in **Table 4**. 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, 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 under **Task 3**. These were then hot pressed at 1275 °C and 4 ksi, and soak times of 6, 30 and 60 minutes. Measured density and hardness are given in **Table 4j**. Hardness was measured on the Rockwell A scale using testing equipment available at ACR. Increased 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.

Table 4i – 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 4j – 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 Table 4i, relatively high density can be achieved by hot pressing at 1275 °C and 4 ksi for 60 minutes.

Diamond based

Polycrystalline diamond coated (PCD) tools are an attractive alternative to WC-Co based tools in mining and drilling applications when operating costs dictate that service life be maximized and/or conditions require the hardest of materials. Diamond based FM systems offer a significant advantage over PCD coated tools, by providing increased coating toughness, as compared to the hard, but very brittle, PCD coatings demonstrated previously [5,7]. Similar to PCD coated tools, and in order to reduce tool cost, diamond based FM coatings are typically applied to the wear surface of a WC-Co substrate, minimizing the total amount of diamond in the tool.

Extrudable thermoplastic diamond/polymer blends were developed, and a diamond/WC-Co FM rod was fabricated and sectioned into thin (~0.025-0.050”) disks. The disks were applied to WC-Co blanks, canned and the binders removed. The coated blanks were then consolidated at Phoenix Crystal. Micrographs of the surface of one of the consolidated inserts are presented in **Figure 4c**.

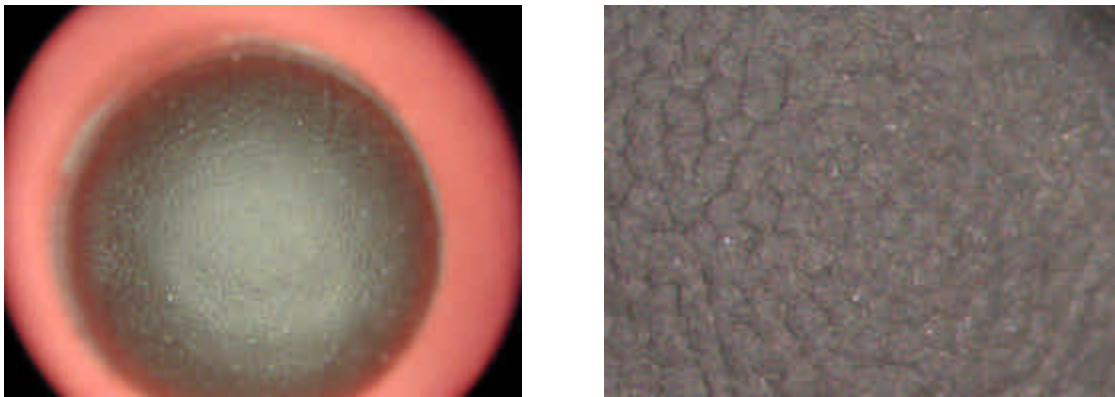


Figure 4c – Surface of Diamond/WCCo FM coated drill bit insert at 10X (left) and 50X(right).

ACR had planned to continue optimization of the coating formulation and consolidation conditions. The consolidation supplier, Phoenix Crystal, has a wealth of experience and knowledge in this field, and performed the consolidation development for the diamond-based systems but there were difficulties with the consolidator-Phoenix Crystal. After several groups of samples were consolidated Phoenix Crystal was not satisfied with the quality and additional samples were not fabricated.

University of Utah

Experiments to optimize pressureless sintering for the WC-Co based FM were designed and carried out both at ACR and the University of Utah by Dr. Zak Fang. This process is used extensively in industry for densification of WC-Co based materials. Specific experiments carried out included time, temperature, and heating rate evaluations, as well as measurements of individual material shrinkage during sintering at various temperatures.

Using samples fabricated for the binder removal study discussed in **Task 3**, evaluations of sintering rate, soak time and temperature were performed. Initial sintering experiments were carried out using an alumina crucible and cover containing a small alumina boat filled with Co metal. The reservoir of Co metal was used to prevent excessive evaporation of cobalt from the WC-Co FM parts during sintering by creating a partial pressure of Co at the sintering temperatures. Results of initial experiments confirmed the expectation that part density increased with increasing soak temperatures and time, and appeared to be unaffected by the heating rate of the furnace during sintering. Upon cross sectioning of the sintered samples, a significant number of parts contained small cracks, which at first appeared to be associated with bundle boundary separations during binder removal. Bundle boundary separations are typically caused by poor or incomplete lamination of the individual filament during lamination of the green part. Observation of the cracks at 100X, however, showed that the cracks were actually along both the filament and cell boundaries (**Figure 4d**). Because the cell boundaries are formed at a relatively high pressure (~10X green lamination) during the second pass extrusion process, cracks along the cell boundaries are most likely not formed during binder removal, and likely formed due to excessive mechanical or thermal stresses during sintering. Additionally, after several sintering runs it was observed that the alumina crucible was cracked and had a high surface roughness that was not present when the crucible was first used. Based on discussions with Dr. Fang, it was suggested that the alumina crucible was dissolving at the sintering temperatures of the WC-Co FM, and use of the alumina crucible was halted.

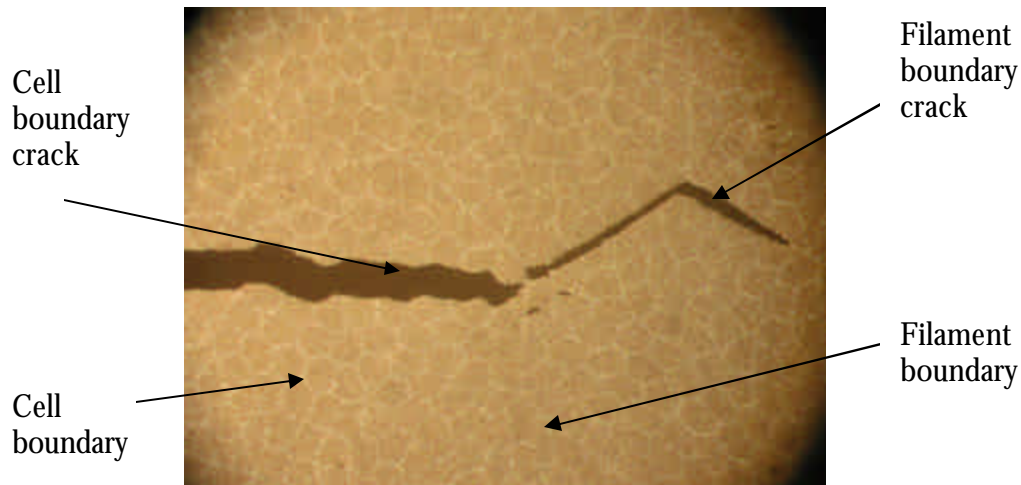


Figure 4d – Examples of cell and filament boundary cracking in sintered WC-Co based FM samples.

To determine if the use of the alumina crucible was the root cause for the cracks observed after sintering, a new graphite crucible was purchased. The new sintering set-up was identical to the old, with graphite replacing alumina. A small number of parts were sintered in the graphite crucible, at two different heating rates. The two heating rates used were the standard fast heating rate (2700 °C/hr) used for earlier sintering experiments at ACR, and a rate (300 °C/hr) suggested by Dr. Fang (see discussion of U of Utah work) that produced crack free samples. A summary of these results is presented in **Table 4k**. Based on the

observance of cracks in one of the samples sintered using the highest heating rate, it was determined that the cracks seen in parts from earlier sintering runs were not due to the use of the alumina crucible. The defects in the alumina crucible, surface roughening and cracking, were probably due to exaggerated grain growth brought on by repeated heating cycles.

Table 4k – WC-Co FM samples sintered using different heating rates

Sample #	Heating Rate (°C/hr)	Soak Temp.	Soak Time	Density	Cracks
1	300	1350 °C	60 minutes	14.61	No
2	300	1350 °C	60 minutes	14.65	No
3	2700	1350 °C	60 minutes	14.62	No
4	2700	1350 °C	60 minutes	14.54	Yes

Once the alumina crucible had been eliminated as a possible source for the boundary cracking observed in sintered WC-Co based FM samples, it was suggested that the cracks were a result of mechanical stresses caused by a difference in shrinkage between the core and shell materials during sintering. This idea is based on comments from WC-Co material suppliers, in this case Kennametal, with respect to differences in material shrinkage with differing Co percentage. Corroboration for this concept was the observation of large domains of cobalt (called “pools”) in samples sintered at the University of Utah with the slower heating rate (see discussion below), which are most likely cracks that have been healed by the flow of cobalt during the longer sintering run. To verify that the shrinkage of monolithic WC-Co(6%) and WC-Co(16%) were different, an experiment to measure the individual shrinkage of core and shell materials was run. Samples of monolithic WC-Co(6%) and WC-Co(16%) 10 mm in diameter and 10 mm high were prepared, using the standard EVA-wax formulations and the recently developed two-stage binder removal process. These samples were then sintered at varying temperatures using the rapid heating profile, with the volume measured by water immersion and compared with the green material volume measured in the same way. Data on the shrinkage of the two monolithic materials is presented in **Figure 4e**.

From **Figure 4e**, it is clear that at all the sintering temperatures investigated, the shrinkage of the shell material is significantly (2-2.5%) higher than that of the core material. In the current green formulation, the solids loading for both materials was 58%, which would result in a shrinkage of 42% assuming ideal mixing of the powders and polymer. The shrinkage of the core material is very close to 42%, however the ~45% shrinkage of the shell material may be enough to cause significant mechanical stresses and cracking of the FM parts during sintering.

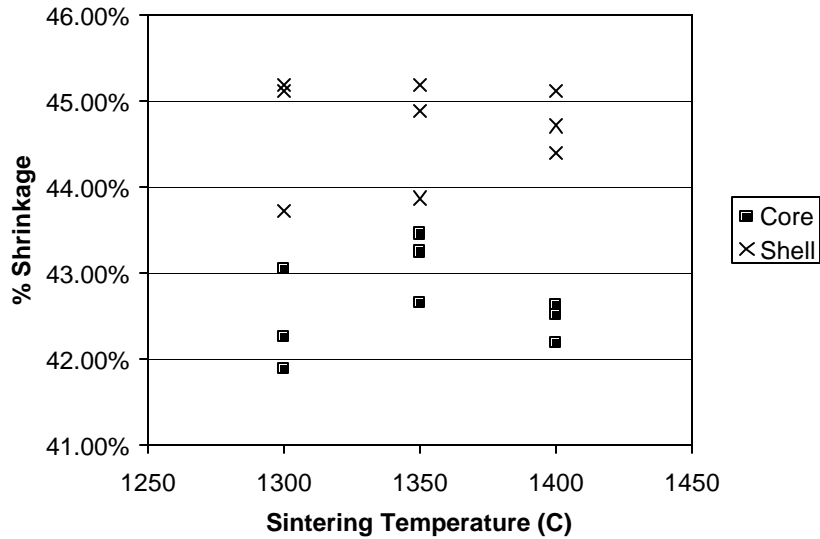


Figure 4e – Shrinkage measurements on monolithic WC(6%)Co and WC(16%)Co

Cobalt diffusion studies at University of Utah

While it is known that diffusion of cobalt across the cell/boundary interface is a function of the sintering temperature, the role of various process and material parameters (e.g. particle size and porosity) on the diffusion kinetics of cobalt needs to be further investigated and understood. Preliminary experimental studies of the sintering behavior of WC-16%Co/WC-6%Co FM composite were carried out. Samples were sintered in a vacuum furnace at different sintering temperatures, using a profile with one, two or three elevated soak temperatures. Sintered samples showed an increase in density with sintering temperature. Micro-hardness measurements also showed an increase in Vickers hardness values with sintering temperature. At sintering temperature of 1320 °C and above, a difference in micro hardness values of about 100 between cell and boundary was observed, with the cell having higher values compared with the boundary. Similar to the micro hardness values, the macro hardness values also showed an increase with sintering temperature. In all cases, the cellular structure of the FM (WC-16%Co/WC-6%Co) was preserved during liquid phase sintering. Additional studies were performed on the influence of cobalt concentration on the sintering behavior and microstructural evolution of WC-Co fibrous monolithic composites. While previous studies were performed on the behavior of different grain sizes of WC-Co in boundary regions of the cells, samples used in this study have the same grain size WC-Co particles in both cell and boundary regions of the structure. Using the earlier work as background, the influence of particle size and sintering behavior on microstructure evolution was examined.

Sintering temperatures were investigated for their effect on the homogenization of the core and shell materials (WC(3%)Co core with WC(20%)Co shell or WC(25%)Co shell). Samples were exposed to three different temperatures and the effect on their density and microstructure compared. The behavior predicted in the literature was observed, that is, as the temperature increased the density and the homogeneity increased. Homogeneity was determined as the difference in the Co concentration of the shell and core after sintering

(?C) divided by the difference in the Co core and shell before sintering (? Co). The temperatures investigated were 1230°C, 1270°C and 1350°C. Fully homogenized shell/core was observed at 1350°C and 60 minutes while 26% homogenization was observed for 1230°C and 60 minutes.

The qualitative and quantitative results obtained from this study provided a general framework on which continued sintering experiments were based. Additional sintering experiments done using selected particle size and cobalt concentration differences between the cell and boundary regions of the structure were used to generate an empirical relationship between the migration of cobalt, sintering temperature, and sintering time across the microstructure.

Task 5. Fabrication of Test Samples

a. Fabricate Fibrous Monolith Samples

Best process methods available were used (based on tasks 2, 3, and 4), the technical staff, worked with the program team fabricated material samples for laboratory testing.

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 as part of Kyocera's cost share commitment. 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 both groups of samples have been returned and are shown in **Table 5a**.

Table 5a – 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
WC(6%)Co	1300(1 hr, 2 ksi)	1700	9.3	100.3
WC(14%)Co	1300(1 hr, 2 ksi)	1650	14.9	101.0
WC(16%)Co	1300(1 hr, 2 ksi)	1090	22	101.7
WC(6%)Co/Co	1200(1 hr, 2 ksi)	600	17.9	84.5
WC(6%)Co/Co	1300(1 hr, 2 ksi)	1680	16.7	100.5
WC(3%)Co/WC(6%)Co	1400(1 hr, 2 ksi)	1160	15.2	91.5
WC(3%)Co/WC(6%)Co	1400(1 hr, 2 ksi)	1110	12.5	92.1
WC(6%)Co/WC(14%)Co	1300(1 hr, 2 ksi)	1390	11.5	94.7
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

Hardness of the monolithic samples compared 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 samples, the hardness of all samples was slightly lower than would be expected using the hardness value based on the bulk phase cobalt concentration, however, the fracture toughness is higher than would be expected based on the same calculation. 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 the same reason, the toughness values are also not representative of the overall composite toughness. Since a test could not be identified that would give a better indication of hardness or toughness of the FM composites all development work was evaluated for these characteristics using the indentation test method.

In addition to the hardness and toughness testing of the WC-Co FM samples, analysis by scanning electron microscope was carried out to resolve structures and concentrations of the constituents in the cell and boundary locations. Samples with high density (>90% theoretical) were chosen for analysis. This group of samples contained several of the samples forwarded to Kyocera for mechanical testing. Elemental analysis using 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, was an area of focus for consolidation optimization work. Refer to the previous task, Task 4, for details.

Investigation of the Al₂O₃-TiCN materials was pursued 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 were 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.

Cutting tool tests on Al₂O₃ based monolithic and FM systems were performed at Competitive Engineering in Tucson, AZ during the reporting period. This work coordinated by Advanced Ceramic Manufacturing (ACM) as part of the industrial cost share commitment to this program. Several rectangular test inserts were prepared, using both ACR and ACM material formulations, and compared with a baseline Kennametal K090 Al₂O₃-TiC commercially available insert. Results of the testing indicated that both the monolithic (~50% of K090) and FM (~20% of K090) systems still require additional development work to meet the baseline performance established using the K090 insert.

WC-Co based FM systems

ACR completed fabrication of an abrasion testing system based on ASTM Standard B661 for testing high stress abrasion resistance, and input from Dr. Fang at the University of Utah. A photo of the testing machine appears in **Figure 5a**. Samples of ACR's hot pressed WC-Co based drill bit inserts, as well as commercial available WC-Co bit inserts, have been fabricated and tested using this machine. The high stress abrasion tester has been used to evaluate a range of samples. Coupons fabricated from 3%, 6%, 16%, 20% and 25% powder and FMs with 3% and 6% cores and shells of 16%, 20% and 25% were tested.



Figure 5a – High stress abrasion testing machine.

Powder results

As a baseline for the mechanical evaluation of Fibrous Monolith (FM) parts, hot pressed powder coupons with a variety of WC-Co compositions were prepared and evaluated. The

WC-Co powders were obtained from the Rogers Tools Works (RTW) division of Kennametal. The powder compositions ranged from WC(3%)Co to WC(25%)Co. Particle sizes for the as-received powder ranged from 2-5 μm to 3-9 μm . Typical high stress abrasion tested coupons appear in **Figure 5b**. The test results are shown in **Figure 5c** below. It is clear from the data that lower cobalt (Co) compositions improve the wear resistance of the coupons. This correlates well with the published data and the experience throughout the industry.



Figure 5b – Typical high stress abrasion wear tested samples, WC(3%)Co/WC(20%)Co FM left and WC(20%)Co powder coupon right.

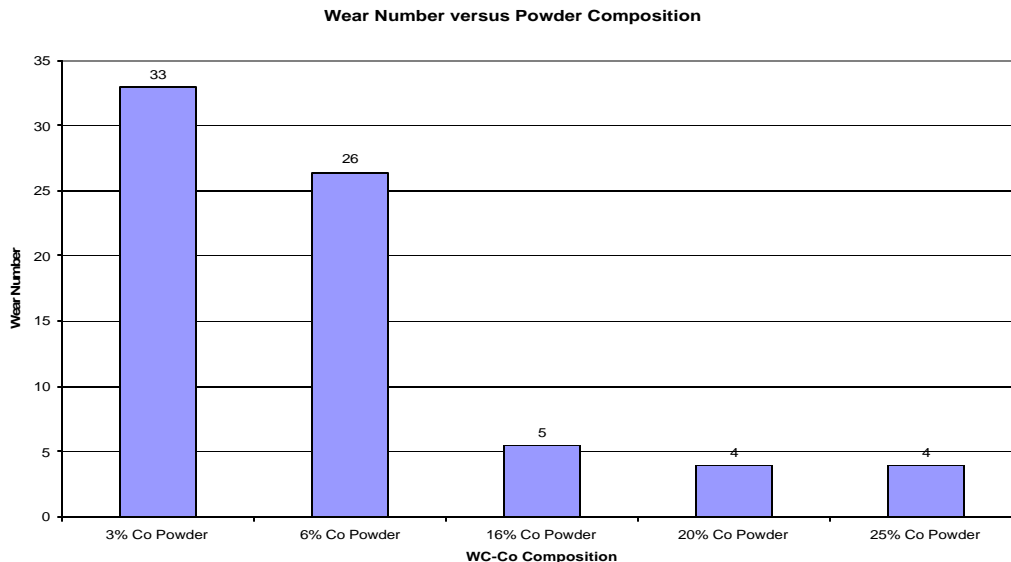


Figure 5c – Wear number versus powder composition as tested by ASTM-B611

3% FM core results

The testing of the FM structures has been focused on identifying the combination of core and shell with highest wear resistance and best fracture toughness. The powder evaluations suggested the best combination of core and shell to achieve this goal. The core and shell combinations were tested for abrasion resistance, hardness and fracture toughness in an attempt to identify the best combination. Combined results for the wear resistance and hardness appear in **Figure 5d** below.

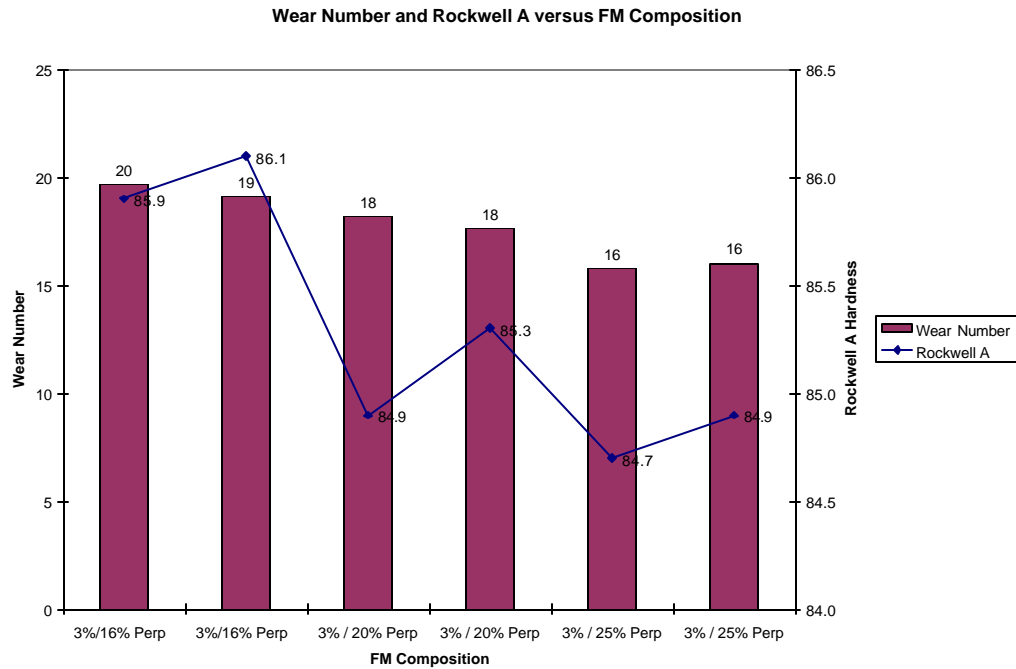


Figure 5d – Wear number and Rockwell A versus FM composition

Wear resistance of WC-Co based FM's with WC(3%)Co cores, shown as bars in **Figure 5d**, decreased with increasing shell cobalt (Co) content. The decrease in wear resistance correlate well with the increase in bulk material Co percentage, a result of increasing the shell material Co percentage from 16% to 25%. Hardness testing also correlated to the bulk Co content. Rockwell A (R_A) hardnesses ranged from 84.8 to 86, corresponding to bulk concentrations of 6.3% Co and 5.3% Co, respectively. While increasing Co content negatively impacts the macro hardness of the coupon, fracture toughness is enhanced as the cobalt content increases, as seen in **Figure 5e**. In addition, microhardness measurements by Kyocera demonstrate that the hardness of each discrete phase are consistent with values reported for the individual materials. For example, the bulk hardness of 3/20 FM was 85.1 (R_A), but the microhardness on the 3% was 92.3 (R_A) and the 20% shell was 84.9 (R_A). For the FM coupons fabricated with WC(3%)Co cores the increasing cobalt content is associated with higher fracture toughness, with the highest toughness was seen in the FM with the WC(25%)Co shell.

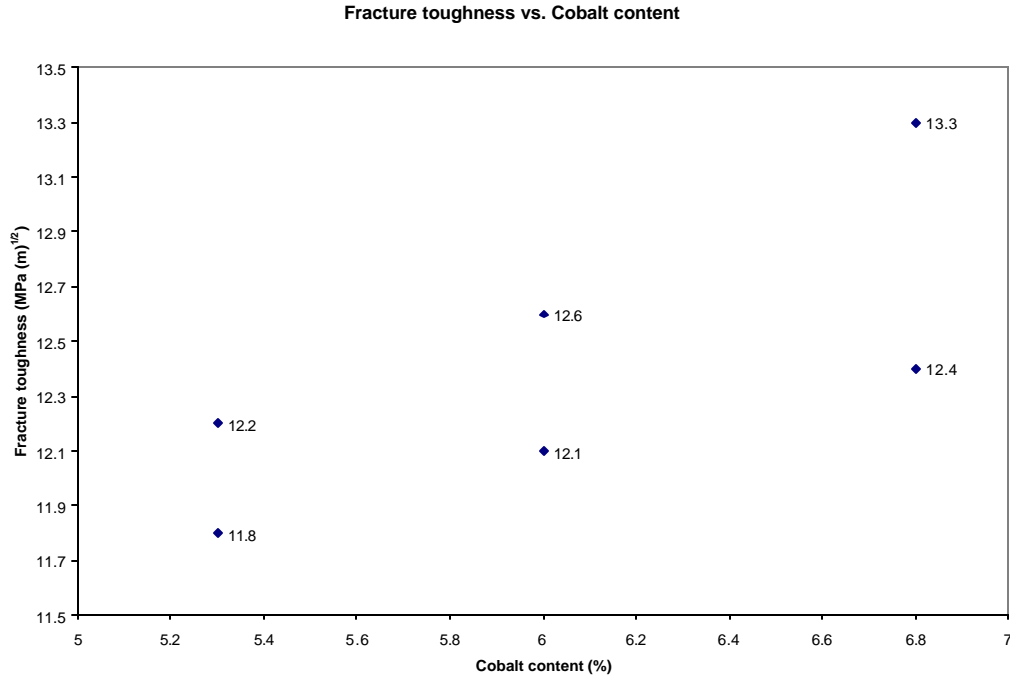


Figure 5e – Fracture toughness versus cobalt content

6% FM core results

Sample coupons were fabricated using a 6% cobalt core and the shell materials 16%, 20% and 25% Co. Wear and Rockwell A (R_A) hardness tests were performed on prepared parts. The performance of the various Co content materials suggests that the wear resistance increases with decreasing Co content. The literature and the results seen for the 3%/16%, 3%/20%, 3%/25% core materials suggest the opposite effect, that is, the wear resistance decreases with increasing Co content. Tests performed in-house for the 6% core materials demonstrated the opposite performance. Because the performance of the 6% core FM's did not meet expectations the coupons were tested a second time with the similar results. It is thought, based on results from other material systems, that the samples were mislabeled at some stage in the processing. The graph of wear number and Rockwell A versus FM composition for the 6% core materials appears as **Figure 5f** below. With the suspicion that the powders may have been mixed at some point prior to delivery, the original samples were re-made and tested to determine if the initial results are representative of these material systems. After fabrication and testing it was indeed confirmed that the materials performed the same in both groups. **Figure 5f** shows distinct differences from **Figure 5d** where the hardness and wear numbers decrease with increasing Co content in the shell. It is also possible that the particle size of the material used for the shells was indeed smaller than the particle size of the core powders. There is established evidence that the use of smaller particle sizes will significantly improve the performance of WC-Co bodies. This possibility has been investigated and, in association with the duplicated study of the wear resistance, established that the particle sizes for the WC(20%)Co was finer than that of the WC(6%)Co and WC(25%)Co.

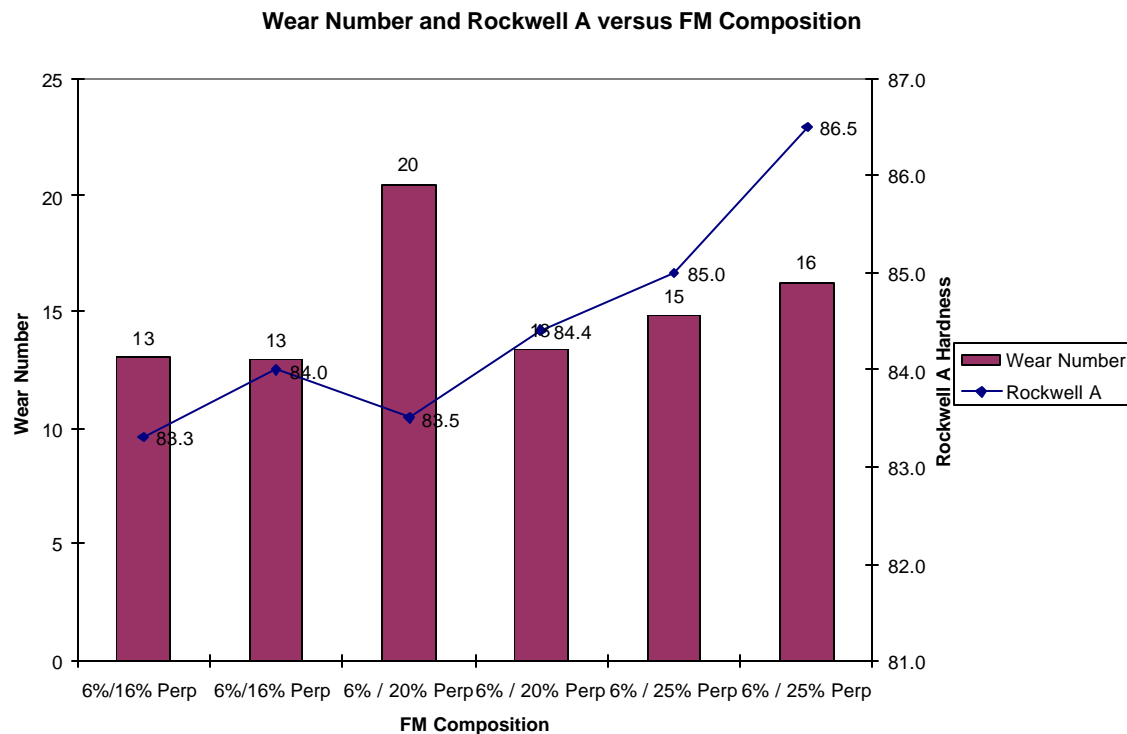


Figure 5f – Wear number and Rockwell A versus FM composition

The increased Co content is expected to improve the fracture toughness and reduce the wear resistance and macro hardness for the FM coupons. Samples to investigate the field effectiveness of these properties have been constructed. Drill bit inserts for Superior Rock Bit, wear plates for The Robbins Group, and drill bit buttons for Brady Mining and Construction Supply were fabricated for field testing.

a. Characterize fibrous monolith properties

ACR technical staff conducted material properties testing to characterize the selected candidate materials.

ACR compiled a preliminary set of tests, listed below, for mechanical and wear property evaluation for the composites developed on this program. Starting with a search of the database available at the ASTM website (www.astm.org) for ceramic wear-related testing documents specific to the testing of advanced ceramics, a list of candidate ASTM standards was generated. These standards were reviewed to determine applicability for the FM composite materials being developed on this program. In addition, the testing requirements were reviewed to determine if the testing performed by our mining industry customers is applicable. The list below includes testing requirements from both industrial and ASTM standards.

Transverse rupture strength

- Three point load similar to ASTM standard B 406-96
- Requires 5 specimens.

Modulus of elasticity

- Resonance method similar to ASTM standard C 1198-96
- Mass of at least 5 grams required.

Compressive strength

- Determined by pressing a right circular cylinder sample between two tungsten carbide blocks held in alignment by an outer sleeve assembly

Relative impact resistance

- Determined by dropping a standard weight on the free end of a test specimen held in a cantilever beam fashion. The height of fall at which the specimen breaks is recorded.

Endurance limit

- Established using the rotating beam method.

Dry abrasion resistance

- Dry sand / rubber wheel abrasion resistance similar to ASTM G65-00e1.

Tensile strength

- Thin ring specimens 2 inches O.D. X 1.9 inches I.D. X .5 inches are subjected to internal hydraulic pressure.
- Tensile strength is typically 45 to 50 % of the transverse rupture strength

Task 6. Fabrication of Drill Bit Inserts

The technical staff analyzed the material candidates for the drill bit insert application. Six bit inserts were fabricated for initial evaluation. Photographs of the inserts can be seen in **Figure 6a**. The inserts were made using an FM composite with an 82.5 volume % WC(6%)Co core and a 17.5 volume % WC(16%)Co shell. All inserts were sintered at 1300°C in a nitrogen atmosphere, and had smooth surfaces with minor cracking in the base or the sides attributed to binder removal and/or the lamination pressure during green processing. Archimedes densities for the inserts are listed in **Table 6a**. Efforts to improve binder removal with vacuum burnout and limit the migration of cobalt through reduced the sintering temperature and/or soak time were pursued throughout this program.

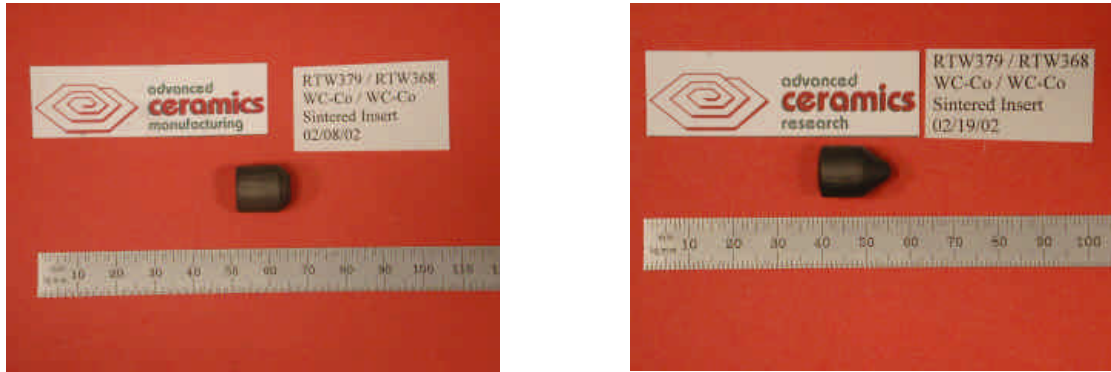


Figure 6a - WC(6%)Co / WC(16%)Co prototype drill bit inserts.

Table 6a – WCCo Drill Inserts

Composition or FM Combination 82.5% core/ 17.5% shell (volume / volume)	Temperature (° C)*	Measured Bulk Density (g/cc)	Theoretical Density (g/cc)	% Full Theoretical Density
WC(6%)Co / WC(16%)Co	1300(no press)	14.080	14.96	94.1
WC(6%)Co / WC(16%)Co	1300(no press)	14.189	14.96	94.8
WC(6%)Co / WC(16%)Co	1300(no press)	13.616	14.96	91.0
WC(6%)Co / WC(16%)Co	1300(no press)	13.645	14.96	91.2
WC(6%)Co / WC(16%)Co	1300(no press)	13.702	14.96	91.6
WC(6%)Co / WC(16%)Co	1300(no press)	14.08	14.96	94.1

* All samples were sintered in a conventional furnace with no external pressure applied.

Design fibrous monolith drill bits insert - Using the laboratory test data and the analysis results, the technical staff designed drill bit insert using fibrous monolith material systems.

With the development of improved thermoplastic blends and binder removal processes, the work to fabricate large drill bit inserts for field testing started. Fifty seven green drill bit inserts were fabricated, burned out, and consolidated. **Figure 6b** shows a typical green inserts. 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 were consolidated and sent for finish machining. Six inserts were delivered for field-testing to Superior Rock Bit Company, Virginia, MN. Frank Klima of Superior agreed to provide field-testing of inserts for no charge.



Figure 6b. WC-Co FM green drill bit insert for fabrication of hot pressed field test prototypes.

Fabricate fibrous monolith drill bit inserts - Using the best methods available the technical staff fabricated composite feedstock, “green” parts and drill bit inserts for field tests.

With the development of improved thermoplastic blends and binder removal processes, fabrication of large drill bit inserts for field-testing continued. Photographs of sample inserts before and after centerless grinding are presented in **Figure 6c**. A cross section of one of the inserts that was sectioned for abrasion testing is shown in **Figure 6d**.



Figure 6c – Hot pressed WC-Co(6%)/WC-Co(16%) FM drill bit inserts before (left) and after (right) centerless grinding.



Figure 6d – Cross section of hot pressed WC-Co(6%)/WC-Co(16%) FM drill bit insert at 5X (left) and 50X (right).

Based on the parts delivered for field testing during the previous reporting period (6 inserts to Superior Rock Bit) it was determined that the FM combination used to fabricate the inserts—82.5% WC(6%)Co/17.5% WC(16%)Co—had excellent wear resistance. Even though the wear resistance was high, the fracture toughness was not. The parts tested did not perform to the standard of the powder compacts used by Superior (**Figure 6e**). With the results of this field test the investigation of other combinations of core and shell are being pursued. We have fabricated 82.5% WC(3%)Co/17.5% WC(25%)Co inserts and forwarded them to Superior for field testing.



Figure 6e – Two of six drill bit inserts tested in the Iron Range of Minnesota shown on the roller cone to the left. The location can be identified as the two missing inserts.

With a change of materials from 6%/16% to 3%/25%, improved wear resistance and fracture toughness was seen in lab testing. It has also shown improvement over the commercial 10% powder compacts used by Superior Rock Bit. The opportunity to test FM materials on smaller diameter drills (3" and less) was offered by Brady Mining and Construction Supply of St. Louis, Missouri. They tested the drills in an underground mining application. **Figure 6f** shows the FM inserts and the drill bits after test run. Based on the brittle fracture of the bits, the fracture toughness needs to be improved for better

performance in this application. Brady has indicated a willingness perform additional tests if we are able develop a tougher FM composite.



Figure 6f – WC(3%)Co/WC(25%)Co buttons fabricated for drilling tests (left), failed drill bits with FM inserts.

Additional field test samples were fabricated to allow testing of FM materials in wear applications such as ground engagement tools. A photograph of an FM insert in a bucket lip appears below (**Figure 6g**). The bucket lip was provided by The Robbins Group of Seattle, WA. While the part was fabricated well before the close of this program, complications at The Robbins Group precluded testing before the program ended.



Figure 6g – FM wear resistant component in bucket lip for The Robbins Group—frontal view. The FM has a shiny appearance compared to the dull bucket lip.

We expected, based on material properties; that the wear resistance of the inserts to be provided would be superior to the materials used for the ground engagement tool depicted above. The tool was fabricated of ESCALLOY selected for its high fracture toughness. The FM insert is intended to improve the life expectancy of the ground engagement tools used in very demanding applications, saving money for the mine operator and reducing down time for replacement.

Additional work

Sintering

Consolidation by sintering represents a considerable cost benefit, when compared to hot pressing, and is the current practice in industry for consolidation of 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 was expected that sintered inserts suitable for field testing would be fabricated but sintering remains beyond our ability.

Extrusion die development

While pursuing a quotation on replacement extrusion die for our FM extrusion equipment one of the vendors expressed an interest in the FM materials and their application to the broader metal extrusion market. Don Ellington of Master Craft Extrusion Tools of Northport MI has provided drawings, design recommendations and finishing for extrusion dies. ACR has fabricated dies from FM ($\text{Si}_3\text{N}_4/\text{BN}/\text{Si}_3\text{N}_4$), monolithic alumina (Al_2O_3), monolithic silicon carbide (SiC) and monolithic silicon nitride (Si_3N_4). Mr. Ellington has also promoted the use of the ceramic materials to his extrusion tool customers working with brass, aluminum and plastic. Prototype extrusion dies constructed with FM have been provided to Master Craft for machining evaluation as have extrusion die prototypes of monolithic Al_2O_3 -TiCN, SiC and Si_3N_4 . The monolithic ceramic dies have been fabricated using ACR's patented non-aqueous gel casting technology. Success has been seen casting a variety of materials with the technique from structural ceramics like Si_3N_4 to dielectrics such as barium titanate (BaTiO_3). We are working to optimize sintering and to tailor the physical properties for the high compression, high wear and high temperature environment of hot metal extrusion. Typical monolithic extrusion die prototypes are shown in **Figure 6f** below:

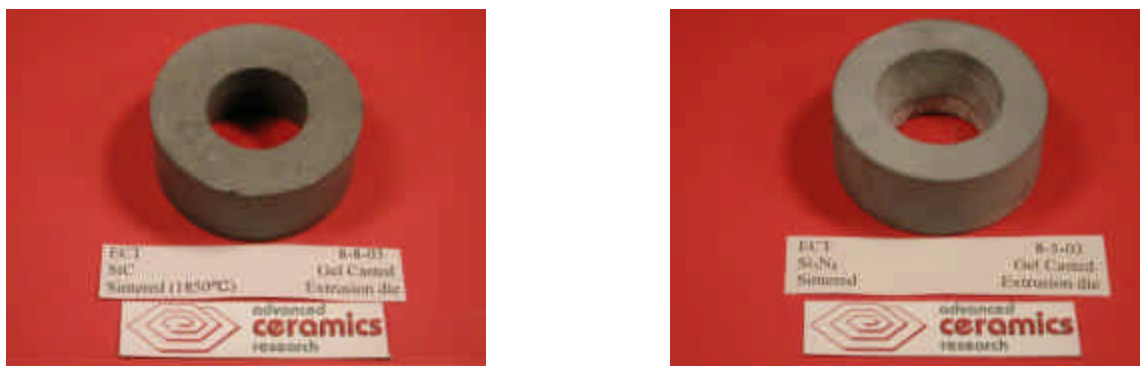


Figure 6f – Gel casted and sintered extrusion dies, with monolithic SiC on the left and monolithic Si_3N_4 on the right.

It has been discovered that the FM ($\text{Si}_3\text{N}_4/\text{BN}/\text{Si}_3\text{N}_4$) materials, after consolidation have very little strength in tension and as such cannot be used for the extrusion die application. The poor strength prevents good surface finishes which are critical for the interior of the die. The die interior forms the outer surface of the metal being extruded. Other FM systems are under consideration for fabrication—it remains to select an alternate and form additional dies for consolidation.

As a part of this program field testing has been pursued where appropriate. Since we were successful at fabricating the ceramic extrusion dies the next step was to get an extruder to test the material in an application. The opportunity for metal extrusion came with the die shape suggested by Don Allington. The drawing he provided was for extrusion of 1.00" brass rod. The drawing was converted to tooling for FM winding, hot pressing and gel casting. Extrusion dies were fabricated using both FM and monolithic Al_2O_3 -TiCN, sintered and sent to Master Craft Extrusion Tools for insertion in a die holder. The die holder was taken to Extruded Metals of Belding MI and tested against standard die materials. The ceramic extrusion die out-performed the other die (a metal die). The metal die failed by closing down after 3 shots (about 1200 feet). The ceramic die was used to form more than a mile of 1.00" diameter rod. The two engineers from Extruded Metals were so impressed they asked for additional dies. The images in **Figure 6g** below show an FM $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ -TiCN extrusion die and a sample of the roughly 6300 feet of brass extruded with it.

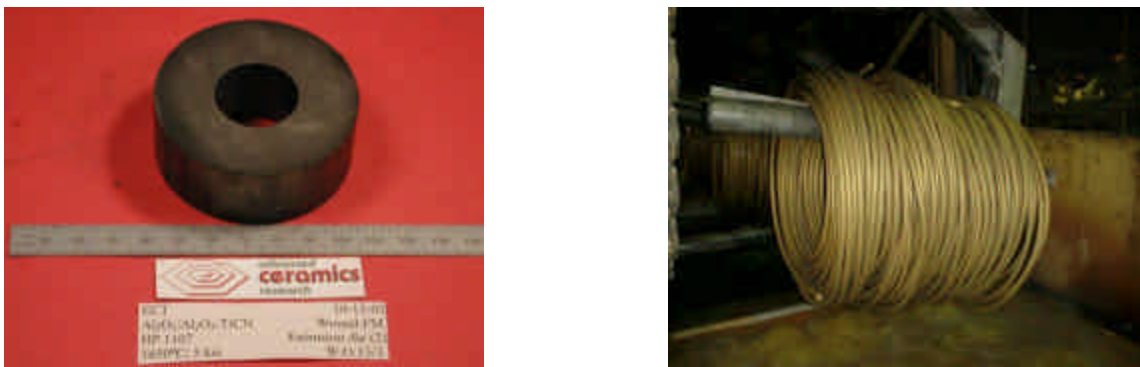


Figure 6g – Al_2O_3 / Al_2O_3 -TiCN FM extrusion die prior to machining (left) and approximately 1200 feet of 1" extruded brass rod (right).

The ceramic die clearly demonstrated the opportunity for FM materials in the cross cutting field of hot metal extrusion. We have been asked by Extruded Metals to deliver parts for additional extrusion sizes. We have also been asked to make extrusion dies for Chase Brass, the largest brass extruder in the US.

Task 7. Fabrication of Dozer teeth

The technical staff analyzed the material candidates for the drill bit insert application and by extension those of the dozer teeth. Based on the trade study performed as part of **Task 2**, the fabrication of dozer teeth using FM architecture was identified as too costly for competitive considerations.

The material of the dozer teeth, as fabricated by Caterpillar, Incorporated, Peoria IL, consists of a high toughness, work hardening, manganese steel. The forged components are sold for prices ranging from \$150 to \$250. The concept evolved at ACR was insertion of wear components into an existing dozer tooth. To this end a dozer tooth, or more accurately, a ground engagement tool (GET) made by Caterpillar was given to ACR by the Phelps Dodge Sierrita mine at Green Valley Arizona for retro-fit with wear inserts. Difficulties in obtaining standard inserts from Kennametal for comparison to the FM

inserts have prevented the completion of the GET for field testing. While the inserts have been fabricated, our partners at Kennametal had not forwarded them as of the end of January 2004.

An additional sample for use in high wear applications, a bucket lip, was provided by The Robbins Group, Seattle WA. The forging was made from Escallo, another manganese steel with work hardening properties. They were interested in wear improvement for the component. With input from the design staff at The Robbins Group, wear plates were machined from WC(3%)Co/WC(25%)Co FM plates. The wear plates were interference fit into the bucket lip. The image in **Figure 7a** shows the assembled bucket lip/wear plate.



Figure 7a — Bucket lip provided by The Robbins Group for field testing of wear plate insert. Wear plate insert appears at the broad front edge of the bucket lip.

Testing of the wear plate inserts are scheduled for a mining application in Australia in the first quarter of 2004.

Task 8. Fabrication of Cyclone apex cones

The technical staff analyzed the material candidates for the drill bit insert application and by extension those of the cyclone apex cone. Based on the trade study performed as part of **Task 2**, the fabrication of cyclone apex cones using FM architecture was identified as too costly for competitive considerations.

Krebs Engineers, a potential partner for this application of the FM technology, currently casts the cyclone apex cones from silicon carbide. Another manufacturer fabricates cyclone apex cones from fused basalt (Abresist). Casting and fusion of either of these materials requires less processing and less sophisticated tooling than the FM materials would require. The lack of economy for the FM materials along with more difficult processing eliminated this product from consideration.

Task 9. NDE of Test Samples

ACR technical staff did not work with ANL to develop non-destructive evaluation (NDE) methods for fibrous monolith materials.

Task 10. Microscopy and residual stress measurements

ACR technical staff conducted microscopy inspection of the fibrous monolith materials. Microscopy was used to determine correct macrostructural development, identification of distribution of cobalt throughout the matrix, extent of residual carbon removal from FM microstructure, and location of internal cracking defects.

Task 11. Mechanical Testing and modeling of fracture mechanics

ACR did not provide material samples for ANL and the University of California, Santa Barbara to conduct laboratory mechanical and functional testing of the materials.

Task 12. Testing of Drill bit inserts

ACR technical staff conducted drill bit insert field tests in conjunction with the mining supply partners on the program, such as Superior Rock Bits and Brady Construction and Mining Supply.

Task 13. Testing of dozer teeth

Fibrous monolith dozer teeth were not fabricated or tested.

Task 14. Testing of cyclone apex cones

Fibrous monolith apex cones were not fabricated or, as a result, tested.

Task 15. Final report

ACR PM and technical staff has written a comprehensive Final Report. ACR has submitted the final report within 90 days after the project period ends. The Final Report documented and summarized all work performed during the award period in a comprehensive manner. It also presented findings and/or conclusions produced as a consequence of this work.

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