

ADVANCED CERAMICS RESEARCH

SEMI-ANNUAL REPORT #2

FIBROUS MONOLITH WEAR RESISTANT COMPONENTS FOR THE MINING INDUSTRY

2ND TECHNICAL SEMI-ANNUAL REPORT

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ABSTRACT

During this reporting period, work continued on development of formulations using the materials identified as contenders for the fibrous monolith wear resistant components. The FM structures fabricated were: diamond/WC-Co, B₄C/WC-Co, TiB₂/WC-Co, WC-Co/Co, WC-Co/WC-Co. Results of our consolidation 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. Prototype component fabrication focused on the fabrication of WC-Co/WC-Co FM conical tools, diamond/WC-Co coated drill bit insert prototypes. Fabrication of WC-Co/WC-Co FM insert prototypes for a grader blade is also underway. ACR plans to initiate field-testing of the drill bit insert prototypes and the grader blade insert this summer (2002). The first WC-Co/WC-Co FM conical tool prototypes were sent to Kennametal for evaluation towards the end of the current reporting period.

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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.

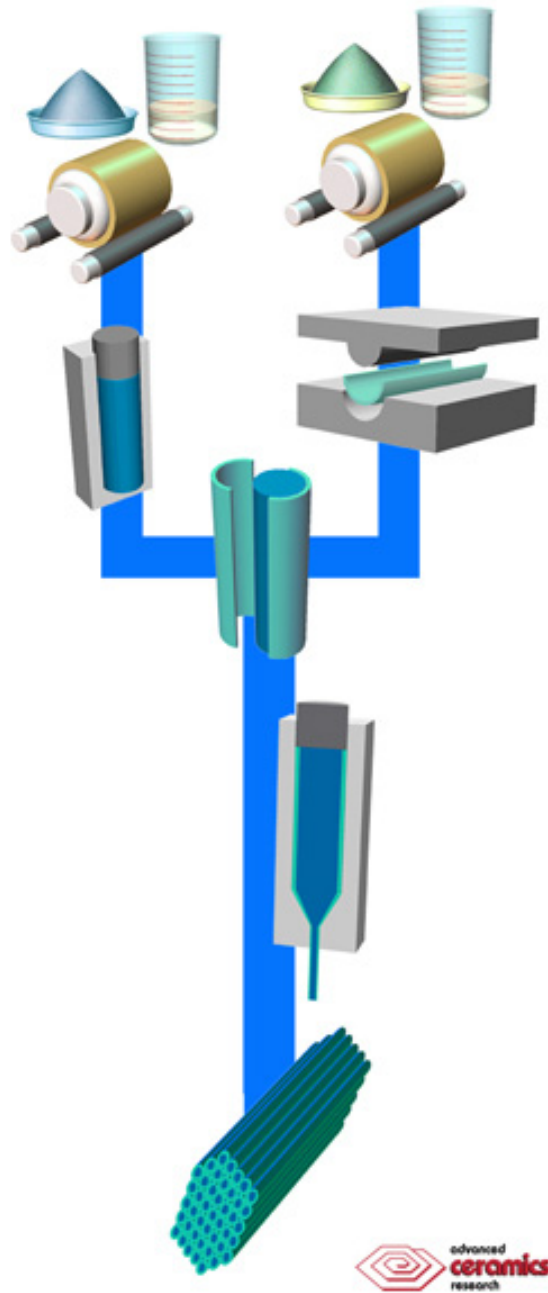


Figure 1. Illustration of the Fibrous Monolith co-extrusion process. Ceramic and/or metal powders are blended separately with thermoplastics and plasticizers. The resulting mixtures are pressed into shells and rods. The shells and rods laminated to form a composite feedrod that is then placed in a heated 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 and wear resistance of the Fibrous Monolith composite. For example, a Diamond-based FM composite with a relatively ductile WC-Co interface forms a very wear resistant and damage tolerant composite that can be applied as a coating to drill bit inserts for use in rock drilling applications for oil, gas, and ore deposit exploration and production (**Figure 4**).

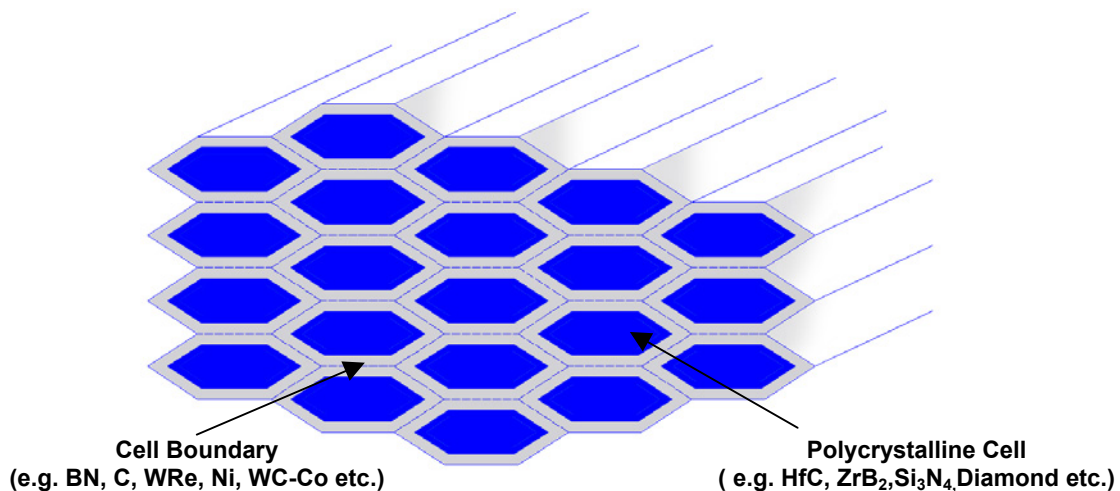


Figure 2. Schematic of a typical uniaxial Fibrous Monolith microstructure shown perpendicular to principal fiber direction.

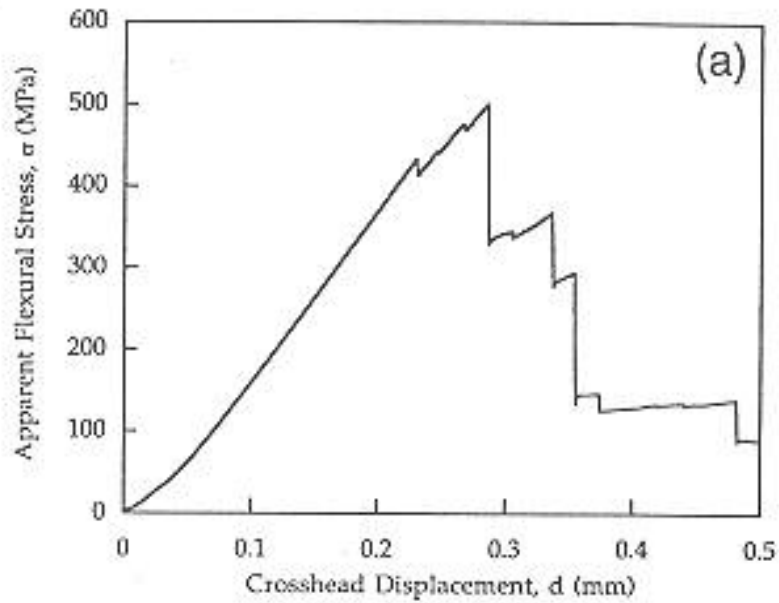


Figure 3. Typical flexural stress-strain curve for a silicon nitride/BN FM material.

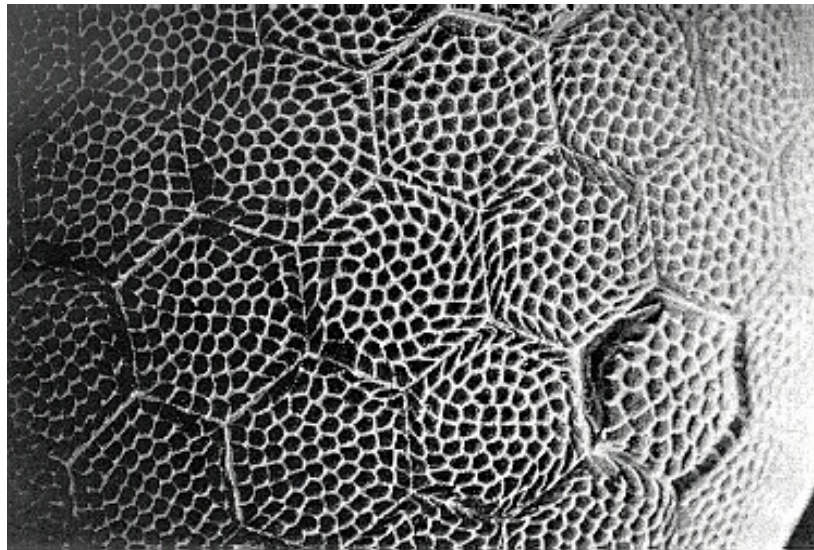


Figure 4. ACR's Diamond/ WC-Co FM composite applied as a coating on the surface of a WC drill bit insert (100x). Note the isolation of the darker material (Diamond) into discrete cells by the lighter contrast phase (WC-Co).

EXECUTIVE SUMMARY

During the reporting period, work continued on development of formulations using the materials identified as contenders for the fibrous monolith wear resistant component. The FM structures fabricated were: diamond/WC-Co, B₄C/WC-Co, TiB₂/WC-Co, WC-Co/WC-Co. Results of our consolidation 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 is 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 are being fabricated using the WC-Co/WC-Co FM system. Kennametal is also interested in Diamond /WC-Co coated roof bit inserts and has provided ACR with WC substrates for the development of coated inserts. The drill bit insert prototypes are being fabricated using diamond/WC-Co coatings and the grader blade insert plates are being fabricated using the WC-Co/WC-Co FM system. ACR expects to begin field-testing of drill bit insert prototypes and the grader blade inserts this summer (2002). Testing of the conical tool inserts is expected to take place in the fall of 2002.

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 that we can press 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. We expect to have results of the results of insert fabrication and begin laboratory testing over the next 2 months.

Meetings with Kyocera Corporation took place November 5 and 6, 2001, at the Kyocera Sendai plant and at the Kyocera Kokubu plant. ACR participants included Randy Cook, (Product Development Engineer); program PI Dr. Mark J. Rigali (Manager of Composite Ceramics), and Ken Knittel, (Research Engineer). On the Kyocera side the participants were Hiromi Fujioka Materials Development, Junichi Imada Manager, Yoshio Nagato Vice-department Manager, Tatsuyuki Nakaoka Materials Development, Kenji Noda Materials Development, Daisuke Shibata Materials Development. Both Kyocera and ACR personnel presented results of materials development for 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 TiB₂ fibrous monolith composite systems fabricated by ACR (presented in detail in the Fabrication of Test Samples section later in this report).

PROGRAM MANAGEMENT

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

Dennis Tool Company

A meeting with Dennis Tool Company took place on October 24, 2001. ACR participants included Randy Cook, (Product Development Engineer); program PI Dr. Mark J. Rigali (Manager of Composite Ceramics), and Matthew Pobloske (Vice President of Marketing and Product Development). Dennis Tool participants included Dr. Mahlon Dennis (President), Thomas M. Dennis (Vice President of Engineering), Roger McEachron (Market Development Engineer), William B. Hampshire (Chief Metallurgist). 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 on February 7th. 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. In addition Phoenix has agreed to contribute the costs of high-pressure consolidation as cost share to this program.

Kyocera Corporation

Meetings with Kyocera Corporation took place November 5 and 6, 2001, at the Kyocera Sendai plant and at the Kyocera Kokubu plant. ACR participants included Randy Cook, (Product Development Engineer); program PI Dr. Mark J. Rigali (Manager of Composite Ceramics), and Ken Knittel, (Research Engineer).

Those present from the Kyocera Sendai plant visit were Hiromi Fujioka Materials Development, Junichi Imada Manager, Yoshio Nagato Vice-department Manager, Tatsuyuki Nakaoka Materials Development, Kenji Noda Materials Development, Daisuke Shibata Materials Development. Yoshio Nagato, Vice-department Manager, presented a general overview of ceramic products. A tour of the cutting tools Production facility was conducted. Significant equipment available at the facility included a belt press for diamond consolidation and a machining center and CNC lathe for customer tooling evaluations. Additional presentations by Kyocera Sendai personnel included: Materials development for Diamond

formulation grain size effects with respect to hardness and fracture toughness (Kenji Noda), Materials development for CERMET – Cemented carbide fibrous monolith composite sintering, diffusion and partial characterization (Diasuke Shibata).

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

EXPERIMENTAL

Task 2. Develop Compositions of Fibrous Monoliths

During the previous reporting period, a trade study was carried out to select the most promising materials for both the core and shell components of the FM systems to be developed and evaluated for this program. Core materials were selected by considering hardness, toughness, thermal conductivity and cost. Interface materials were selected by considering hardness, elastic modulus, ultimate tensile strength and thermal conductivity. The trade study was completed and discussed during the previous reporting period. A detailed discussion of the trade studied was presented in the previous semi-annual report. Based on the results of the trade study, the materials listed in Table 1 were selected for development into FM systems and evaluation.

Table 1 – 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

Task 3. Develop Fabrication Process Parameters of Fibrous Monoliths

Work to develop suitable thermoplastic blends of the materials listed in **Table 1** has been completed, and was discussed in the previous report. Currently, all steps of green processing are under scrutiny to identify areas where improvements can be made. These areas include thermoplastic blending, core and shell molding, core and shell co-extrusion, coupon fabrication, and binder removal. The development of optimized binder burnout conditions is focused on understanding into the breakdown and removal of materials under vacuum conditions using thermal gravimetric analysis (TGA). Preliminary vacuum TGA measurements have given an indication of the need for further analytical work required for the combination of materials, binders, plasticizers and modifiers. The removal of binders with no distortion to the unconsolidated blank prior to firing is a critical step if high levels of density are to be achieved during firing. Any potential improvements identified in these areas will be thoroughly investigated, both theoretically and experimentally, prior to being implemented into the FM fabrication process.

Task 4. Densification Process Development

Densification process development was carried out for each of the four FM core material systems listed in **Table 1**. Results from this development work are presented below.

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 2**.

Table 2 - 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.

Photographs of the B₄C-based powder test coupons are presented in **Appendix B**. 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, as 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 the consolidation by hot pressing, one test coupon (B₄C/W) was consolidated by isostatic hot pressing (HIP) for comparison. A list of the FM test coupons prepared, and their measured Archimedes densities, is given in **Table 3**.

Photographs of the B₄C-based FM test coupons are presented in **Appendix B**. Despite the relatively high consolidation temperature (~2000 °C), none of the test coupons fabricated have densities high enough to be considered as usable materials for our target applications. In addition, 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 have been excluded from further investigation as of this reporting period. Investigation of this material may be pursued at a later date if applications and/or suitable interface materials are identified, and if cost considerations make this a desired material for use in mining applications.

Table 3 - 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 enhancing additives. Additives used (in both monolithic and FM coupons), which were reported in the literature to enhance the sintering of TiB₂, included Al₂O₃, Ni, Co, and Si₃N₄ [6]. Sintering additives were expected to be necessary based on the high melting point of TiB₂ (2980 °C). A list of the powder coupons prepared, and their measured Archimedes densities, is given in **Table 4**.

Table 4 - TiB₂ – 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.

Photographs of the TiB₂-based powder test coupons are presented in **Appendix B**. 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, TiB₂-based FM test coupons were fabricated, using TiB₂ (with and without additives) as the core phase, and W, WC-Co(3%), or WC-Co(6%) as the interface phase. As was the case for the B₄C-based FM systems, experience suggested that the use of a lower melting point interface phase would reduce the consolidation temperature required for the TiB₂-based FM systems. A list of the FM test coupons prepared, and their measured Archimedes densities, is given in **Table 5**.

Table 5 – 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.

Photographs of the TiB₂-based FM test coupons are presented in **Appendix C**. 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 of this reporting period. Investigation of this material may be pursued at a later date if high temperature applications interface materials are identified, and if cost considerations make this a desired material for use in mining applications.

WC-Co-based Systems

As was done for the B₄C and TiB₂ FM systems, monolithic WC-Co test coupons were first prepared using WC-Co powder with varying Co percentage, 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 6**.

Table 6 – 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.

Photographs of the WC-Co powder test coupons are presented in **Appendix D**. For the monolithic WC-Co powders, containing from 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 vol% cobalt) 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, is given in **Table 7**.

Photographs of the WC-Co-based FM test coupons are presented in **Appendix D**. 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 consolidation 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. It is expected that with further optimization of the binder removal and densification processes, densities approaching full theoretical can be achieved on a consistent basis. The relatively low consolidation temperature, compared to the B₄C and TiB₂-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 will now be focused on the development of WC-Co-based FMs for mining applications. Promising alternative systems, such as diamond/WC-Co, will continue to be investigated, at a lower priority, as time and resources permit.

Table 7 – 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).

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 as 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. These disks were then applied to WC-Co blanks, canned and the binders removed. The coated blanks were then consolidated at Phoenix Crystal. Microphotographs of the surface of one of the consolidated inserts are presented in **Figure 5**.

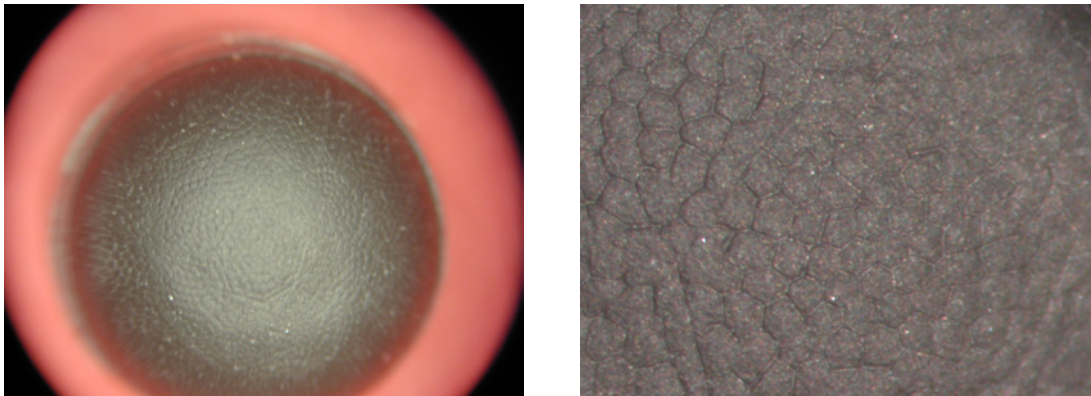


Figure 5 – Surface of Diamond/WCCoFM coated drill bit insert at 10X (left) and 50X(right).

Optimization of the coating formulation and consolidation conditions will continue during the next reporting period. Additional samples, for drill bit and roof bit inserts, will also be fabricated and consolidated during this time.

Task 5. Fabrication of Test Samples

Testing underway

Samples of WC-Co 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 presented in **Table 8 – Kyocera Test Sample Physical Properties**.

Table 8 – Kyocera WC-Co Test Sample Physical Properties

Formulation Shell/Core	Hardness HV	Fracture toughness MPa(m) ^{1/2}	% Full Theoretical Density
WC-Co(3-4%) monolithic	In testing	In testing	95.4
WC-Co(6%) monolithic	1700	9.3	100.3
WC-Co(14%) monolithic	1650	14.9	101.0
WC-Co(16%) monolithic	1090	22.0	101.7
WC-Co(3-4%)/WFeNi	1480	11.9	96.9
WC-Co(3-4%)/WC-Co(6%)	1040	18.2	91.5
WC-Co(3-4%)/WC-Co(6%)	1160	15.2	90.8
WC-Co(3-4%)/WC-Co(6%)	1010	nd	92.1
WC-Co(6%)/WC-Co(14%)	1380	11.5	93.7
WC-Co(6%)/Co	800	nd	91.0
WC-Co(6%)/Co	600	17.9	84.4

Photographs of the prepared sample coupons appear in the **Appendix A**. The hardness of the monolithic samples compares very favorably with data on the WC-Co powder reported in the literature (6% Co – 1700, 14% Co – 1000-1100, and 16% Co – 900-1000 HV). In the case of the FM samples, the hardness of all samples is 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. The lower than expected hardness values are most likely not representative of the overall composite hardness, since the hardness test uses an indentation method that produces an indent significantly larger than the average cell core size. For that same reason, the toughness values are also most likely not representative of the overall composite toughness. Until a test can be found that can adequately measure the overall hardness and toughness of the composites being studied, work to develop compositions will proceed using the hardness values of the core phase, which is the bulk wear phase, and using the toughness value of the interface phase, which is the toughening phase of the composite.

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. All of the images obtained appear at the end of this report in the **Appendix A, Section 2**. Elemental analysis through SEM showed various levels of Co diffusion in all of the samples evaluated. Limiting cobalt diffusion and migration across the core/interface boundary, in order to preserve the desired FM structure, has been identified as an area of focus for consolidation optimization work during the upcoming reporting period.

Task 6. Fabrication of Drill Bit Inserts

Six bit inserts drill bit inserts were fabricated during the reporting period. Photographs of the inserts are presented in **Figures 6 and 7**. The inserts were made using an FM composite with an 82.5 vol% WC-Co(6%) core and a 17.5 vol% WC-Co(16%) shell. All inserts were sintered at 1300°C in a nitrogen atmosphere, and had smooth surfaces and minor cracking in the base or the sides thought to be attributed to the binder removal step and/or the lamination pressure used during green processing. Archimedes densities for the inserts are listed in **Table 9**. Work is continuing to improve the binder removal for the fabricated inserts. Efforts during the next reporting period will be focused on the use of vacuum burnout for the fabricated inserts. As discussed in Task 5, limiting the migration of cobalt by reducing the sintering temperature and/or soak time will also be a focus for the upcoming period.

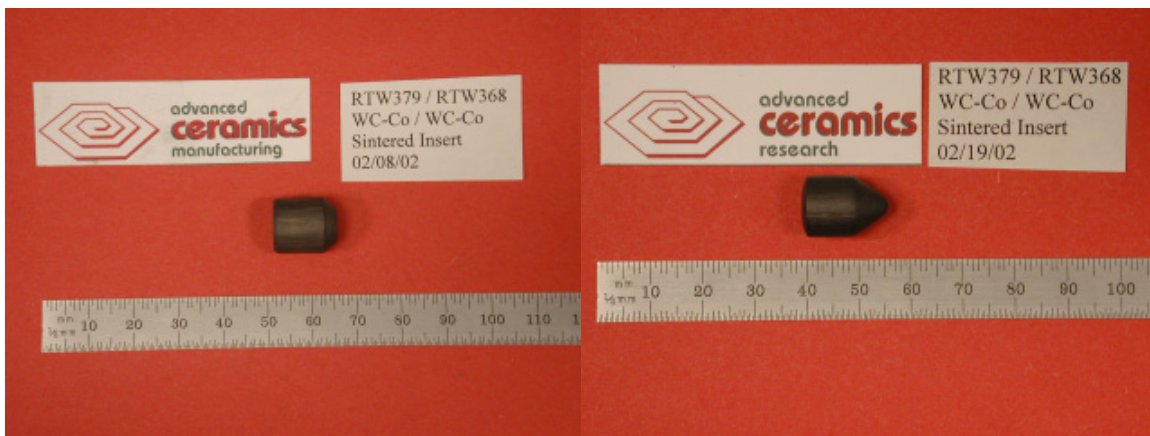


Figure 6 - WC-Co(6%)/ WC-Co(16%) prototype drill bit inserts.

Table 9 – 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.

PLANS FOR THE NEXT REPORTING PERIOD

1. Complete the development of fabrication process parameters of Fibrous Monolith compositions selected for the drill bit insert application (Task 3).
2. Continue densification process optimization of Fibrous Monolith compositions selected for the mining drill bit insert application (Task 4).
3. Complete analysis of preliminary drill bit design using materials properties (Task 6).
4. Design Fibrous Monolith drill bit inserts (Task 6).
5. Continue fabrication of Fibrous Monolith drill bit inserts for evaluation of green properties and sintered inserts for field testing (Task 6).

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5. June-Ho Park, Yong-Ho Lee, Young-Hag Koh and Hyoun-Ee Kim, "Effect of Hot-Pressing Temperature on Densification and Mechanical Properties of Titanium Diboride with Silicon Nitride as a Sintering Aid" *J. Am. Ceram. Soc.*, **83**, [6], (2000).
6. June-Ho Park, Yong-Ho Lee, Young-Hag Koh and Hyoun-Ee Kim, "Effect of Hot-Pressing Temperature on Densification and Mechanical Properties of Titanium Diboride with Silicon Nitride as a Sintering Aid" *J. Am. Ceram. Soc.*, **83**, [6], (2000).
7. Z. Zak Fang, et al., "Fracture Resistant Super Hard Materials and Hardmetals Composite With Functionally Designed Microstructure" *Int. J. Refractory Metals & Hard Materials*, **19**, 453-459, (2001).

Appendix A

Section 1

Hardness and fracture toughness testing samples

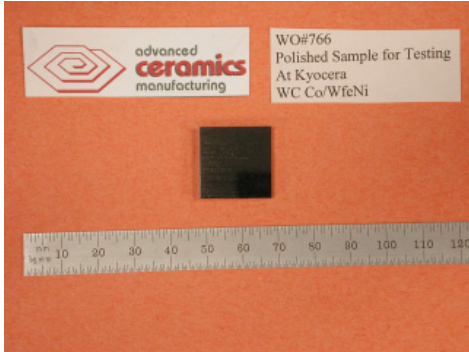


Figure A1A1
WCCo(3%)/WFeNi WO766(693B)

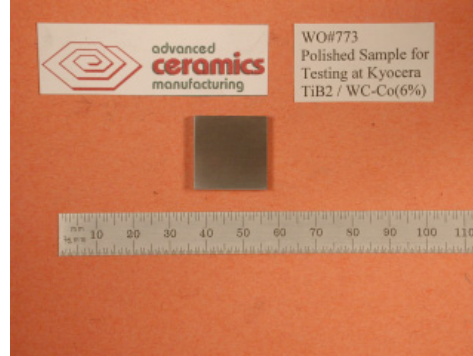


Figure A1A2
TiB₂/WCCo(6%) WO773(708B)



Figure A1B1
WCCo(3%)/WCCo(6%) WO851(719T)

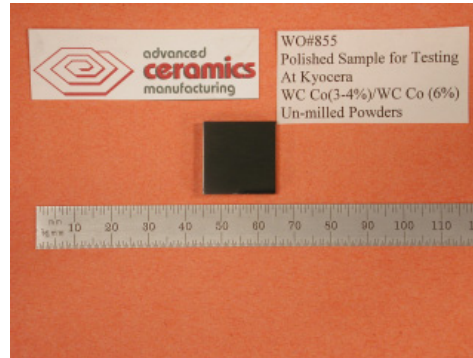


Figure A1B2
WCCo(3%)/WCCo(6%) WO855(719B)

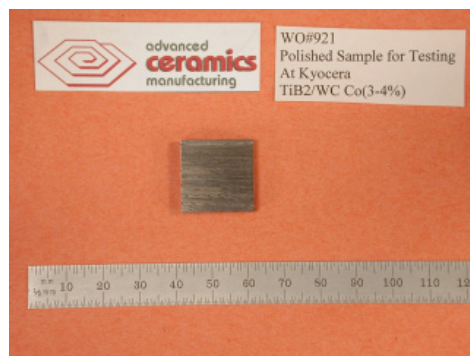


Figure A1C1
TiB₂/WCCo(3%) WO921(789B)

Section 2

Scanning electron microscope (SEM) analysis images WCCo samples

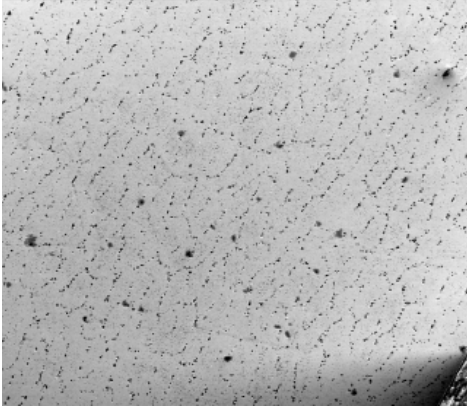


Figure A2A1
693B 50X SE

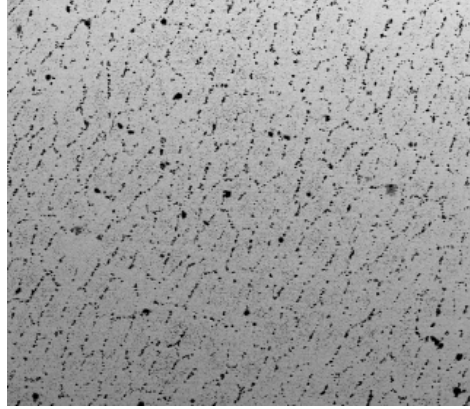


Figure A2A2
693B 50X BSE

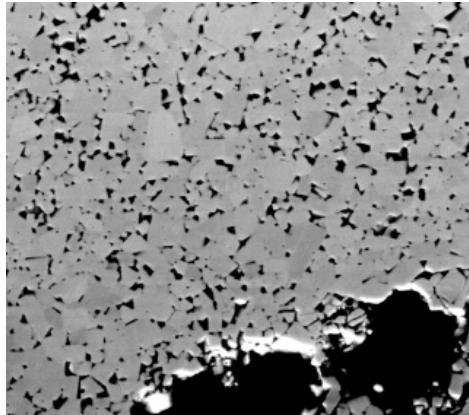


Figure A2B1
693B 2500X BSE

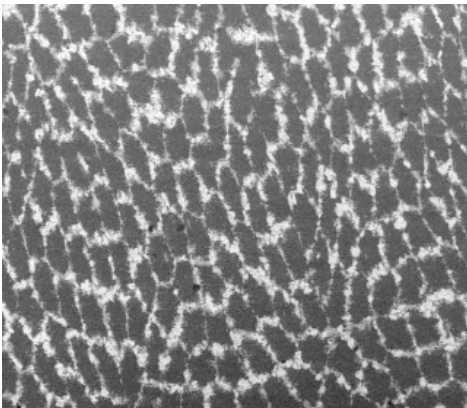


Figure A2C1
702T 50X BSE

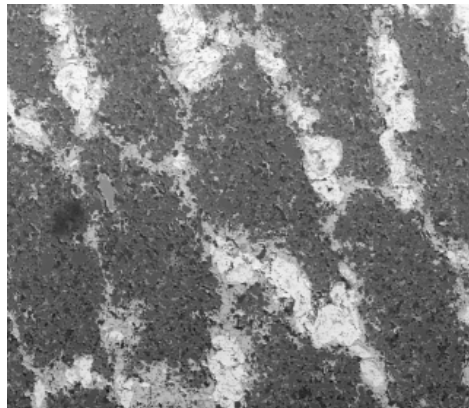


Figure A2C2
702T 250X BSE

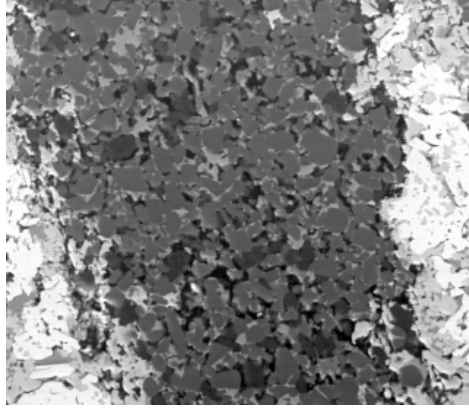


Figure A2D1
702T 1000X BSE

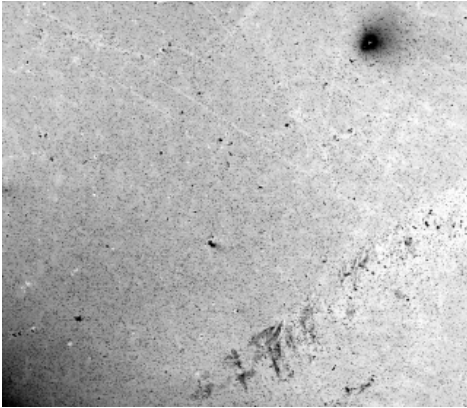


Figure A2E1
719T 50X SE

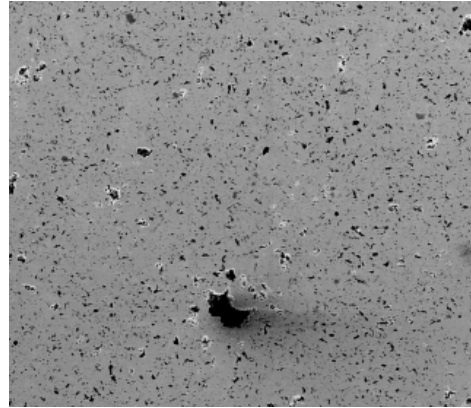


Figure A2E2
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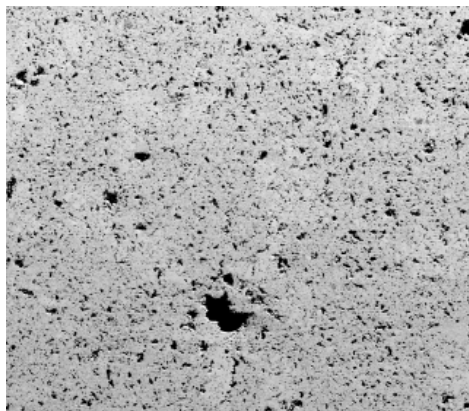


Figure A2F1
719T 250X BSE

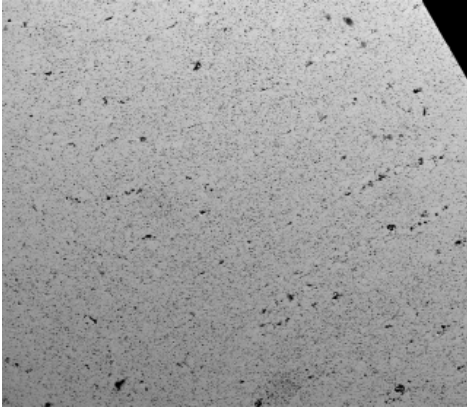


Figure A2G1
719B 50X BSE

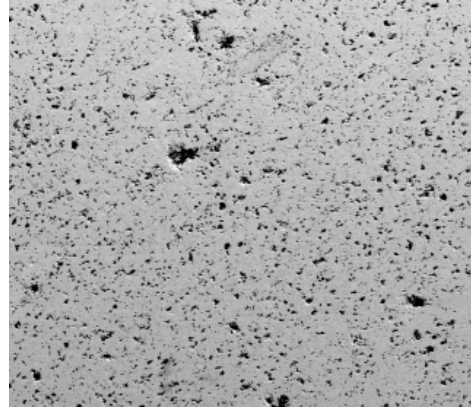


Figure A2G2
719B 250X BSE

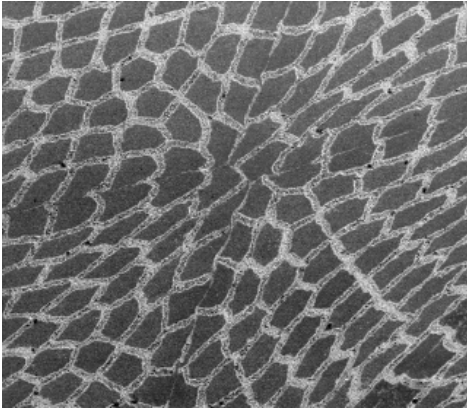


Figure A2H1
757T 50X SE

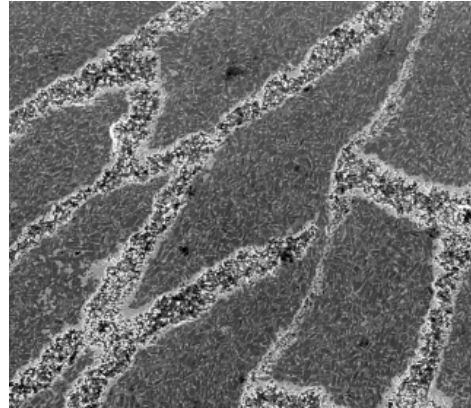


Figure A2H2
757T 250X SE

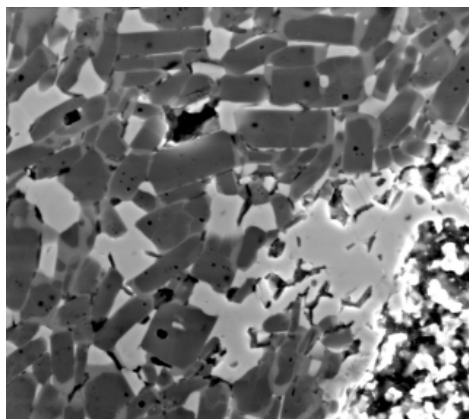


Figure A2I1
757T 2000X SE

Appendix B

Section 1 - B₄C based samples

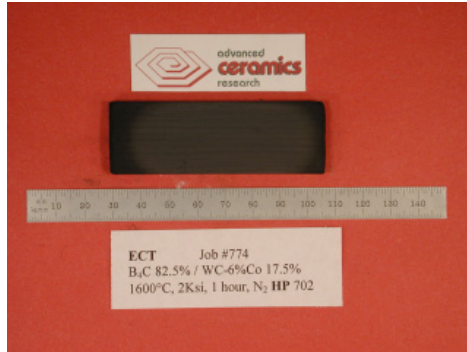


Figure B1A
82.5%B₄C/17.5%WC-(6%)Co



Figure B1B1
82.5%B₄C/17.5%WC-(6%)Co

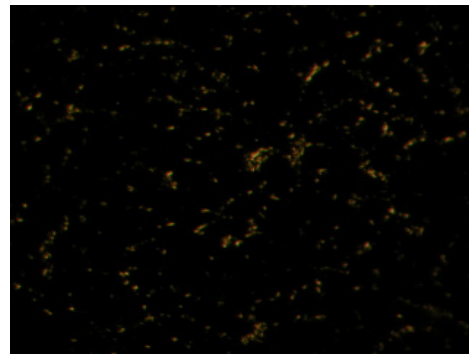


Figure B1B2
82.5%B₄C/17.5%WC-(6%)Co



Figure B1C1
B₄C



Figure B1C2
B₄C-Co(6%)



Figure B1D1
B₄C

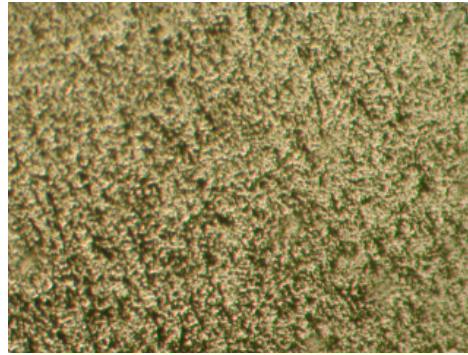


Figure B1D2
B₄C



Figure B1E1
B₄C-(5%)SiB₆

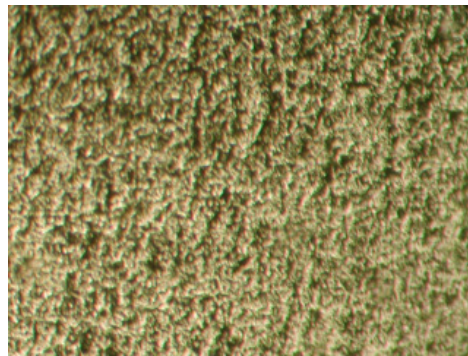


Figure B1E2
B₄C-(5%)SiB₆



Figure B1F1
B₄C



Figure B1F2
B₄C



Figure B1G
 B_4C -(5%) SiB_6



Figure B1H1
 $82.5\%B_4C$ -(6%) SiB_6 /17.5% WC -(6%) Co

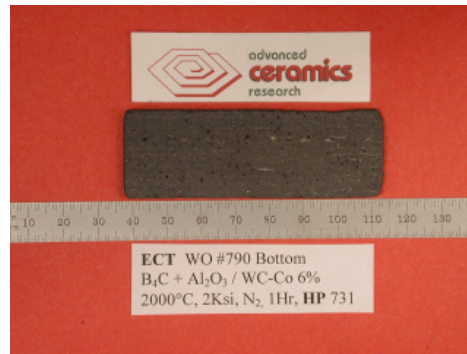


Figure B1H2
 $82.5\%B_4C$ -(5%) Al_2O_3 /17.5% WC -(6%) Co



Figure B1I1
 $82.5\%B_4C$ /17.5% W

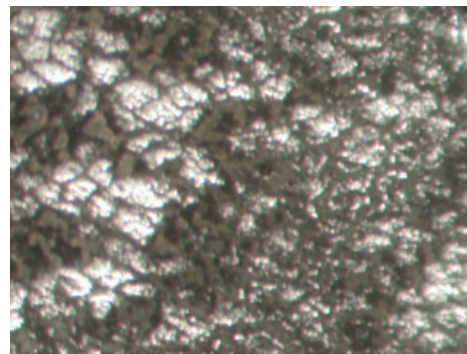


Figure B1I2
 $82.5\%B_4C$ /17.5% W



Figure B1J1
82.5%B₄C/17.5%W

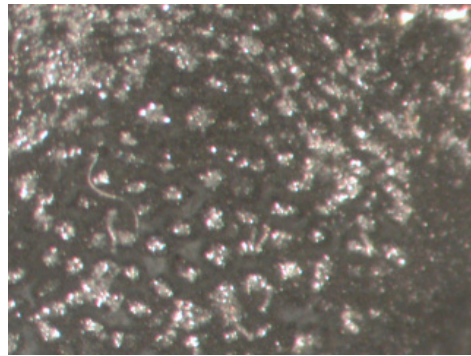


Figure B1J2
82.5%B₄C/17.5%W

Appendix C

Section 1 - TiB₂ based samples

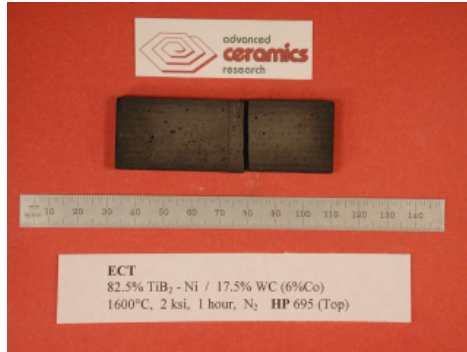


Figure C1A
82.5% TiB₂-(10%)Ni/17.5%WC-(6%)Co

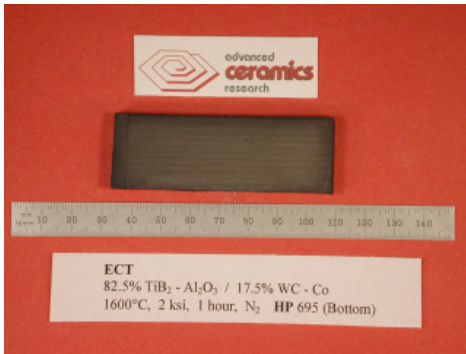


Figure C1B1
82.5% TiB₂-(5%)Al₂O₃/17.5%WC-(6%)Co

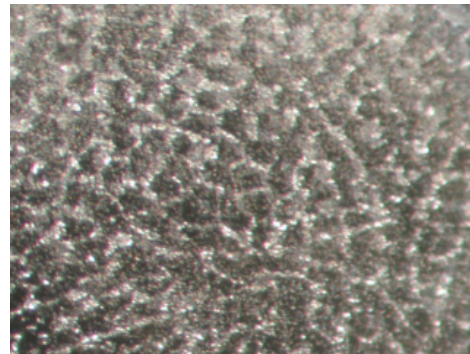


Figure C1B2
82.5% TiB₂-(5%)Al₂O₃/17.5%WC-(6%)Co



Figure C1C1
82.5% TiB₂/17.5%WC-(6%)Co

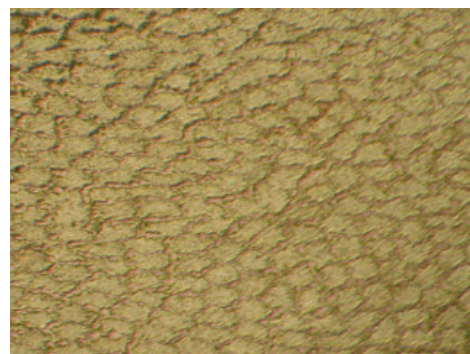


Figure C1C2
82.5% TiB₂/17.5%WC-(6%)Co



Figure C1D1
82.5% TiB_2 /17.5%WC-(6%)Co

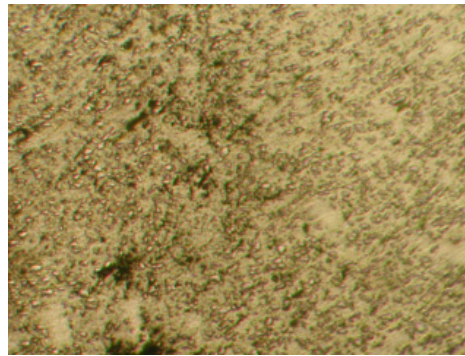


Figure C1D2
82.5% TiB_2 /17.5%WC-(6%)Co



Figure C1E1
 TiB_2

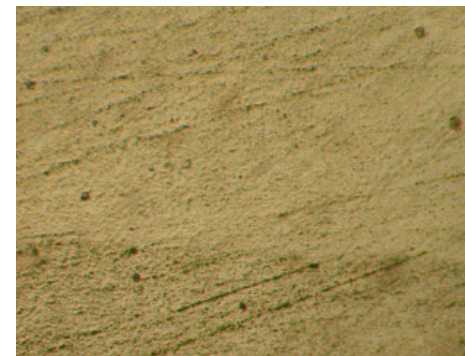


Figure C1E2
 TiB_2

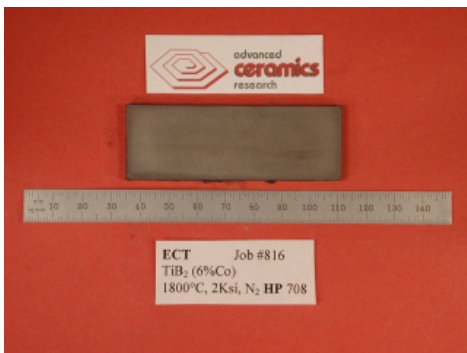


Figure C1F1
 TiB_2 -(6%)Co

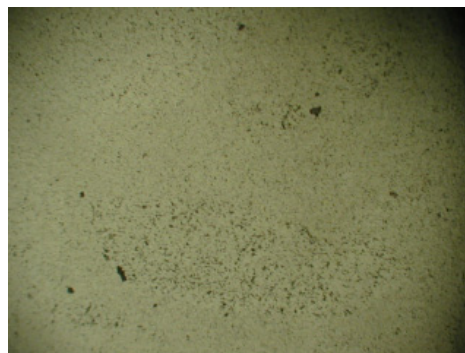


Figure C1F2
 TiB_2 -(6%)Co



Figure C1G1
 82.5% TiB₂-(5%)Ni/17.5%WC-(6%)Co

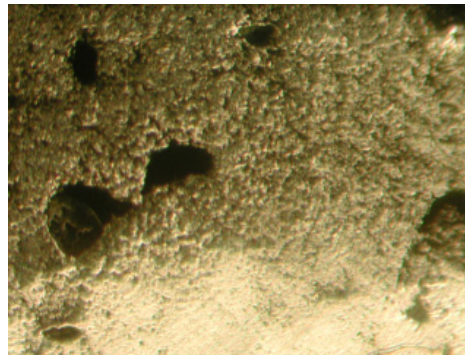


Figure C1G2
 82.5% TiB₂-(5%)Ni/17.5%WC-(6%)Co



Figure C1H1
 82.5% TiB₂-(5%)Al₂O₃/17.5%WC-(6%)Co



Figure C1H2
 82.5% TiB₂-(5%)Al₂O₃/17.5%WC-(6%)Co



Figure C1I1
 82.5% TiB₂/17.5%WC-(3-4%)Co

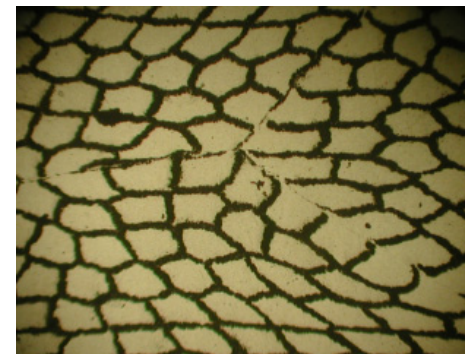


Figure C1I2
 82.5% TiB₂/17.5%WC-(3-4%)Co



Figure C1J1
82.5% TiB₂/17.5%W



Figure C1K1
82.5% TiB₂-(2.5%)Si₃N₄/17.5%WC-(3%)Co

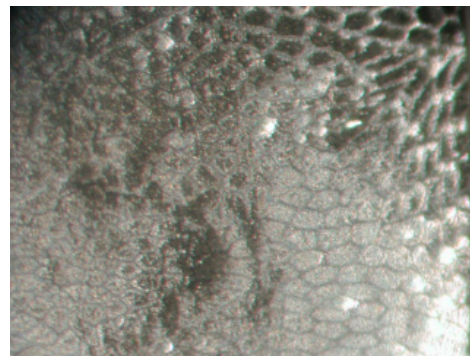


Figure C1K2
82.5% TiB₂-(2.5%)Si₃N₄/17.5%WC-(3%)Co



Figure C1L1
82.5% TiB₂-(2.5%)Si₃N₄/17.5%WC-(6%)Co



Figure C1M1
82.5% TiB₂/17.5%WC-(3-4%)Co

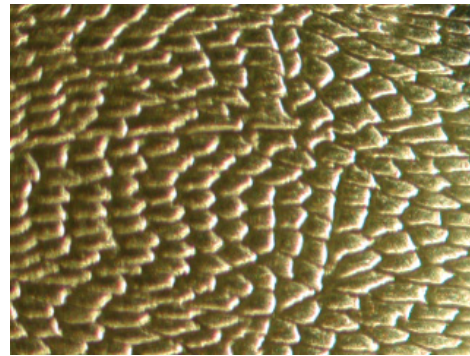


Figure C1M2
82.5% TiB₂-/17.5%WC-(3-4%)Co



Figure C1N1
82.5% TiB₂-(2.5%)Si₃N₄/17.5%WC-(6%)Co



Figure C1N2
82.5% TiB₂-(2.5%)Si₃N₄/17.5%WC-(6%)Co



Figure C1O1
82.5% TiB₂-(2.5%)Si₃N₄/17.5%WC-(6%)Co



Figure C1O2
82.5% TiB₂-(2.5%)Si₃N₄/17.5%WC-(6%)Co



Figure C1P1
82.5% TiB₂-Si₃N₄/17.5%WC-(3%)Co

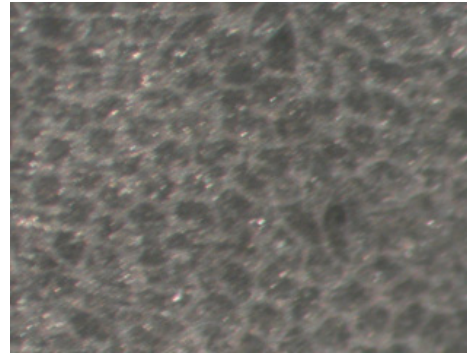


Figure C1P2
82.5% TiB₂-Si₃N₄/17.5%WC-(3%)Co



Figure C1Q1
82.5% TiB₂ / 17.5% WC-(6%)Co

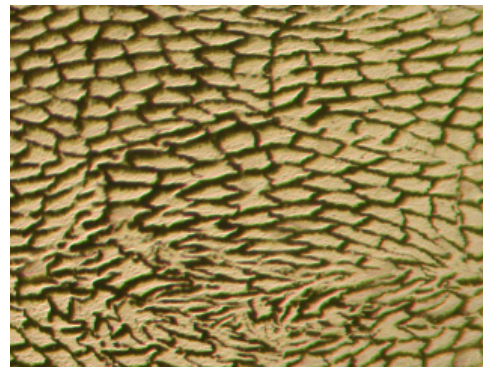


Figure C1Q2
82.5% TiB₂ / 17.5% WC-(6%)Co



Figure C1R1
82.5% TiB₂/17.5%Co(66%)(33%)

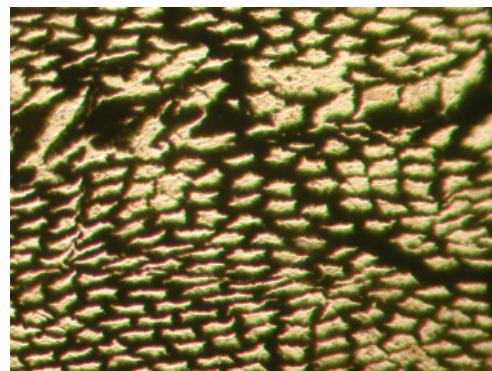


Figure C1R2
82.5% TiB₂/17.5%Co(66%)(33%)



Figure C1S1
82.5% TiB₂-(5%)Al₂O₃/17.5%WC-(6%)Co

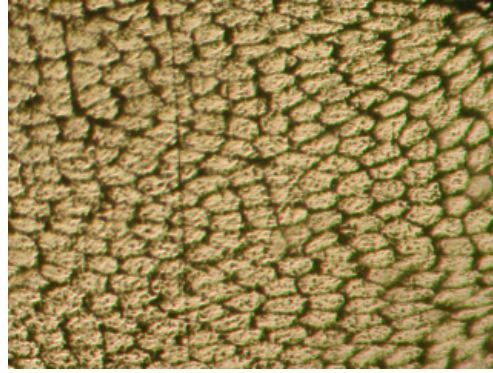


Figure C1S2
82.5% TiB₂-(5%)Al₂O₃/17.5%WC-(6%)Co

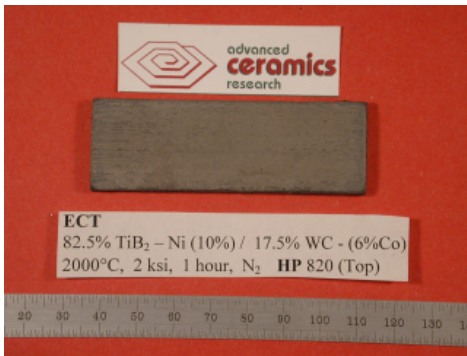


Figure C1T1
82.5% TiB₂-(10%)Ni/17.5%WC-(6%)Co

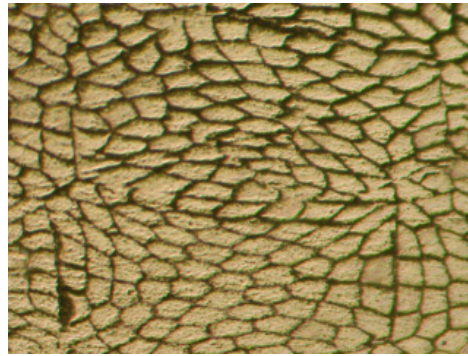


Figure C1T2
82.5% TiB₂-(10%)Ni/17.5%WC-(6%)Co

Appendix D

Section 1 – WCCo-based FM micrographs

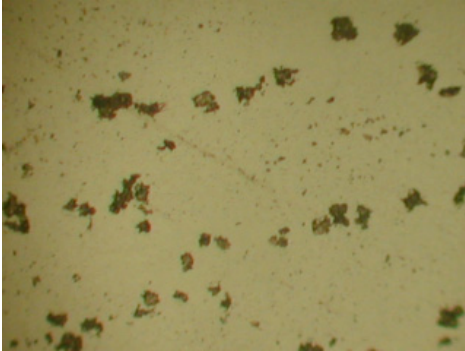


Figure D1A1
WCCo(6%) / WFeNi (693T) 200x



Figure D1A2
WCCo(6%) / WFeNi (693T) 50x

Section 2 – WCCo-based FM systems

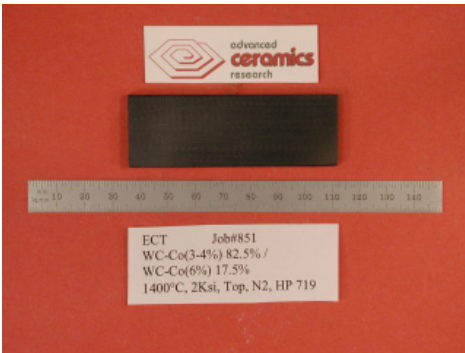


Figure D2A1
82.5% WC- (3-4%)Co / 17.5% WC-(6%)Co

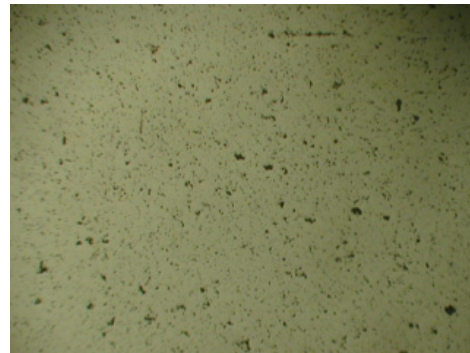


Figure D2A2
82.5% WC- (3-4%)Co / 17.5% WC-(6%)Co

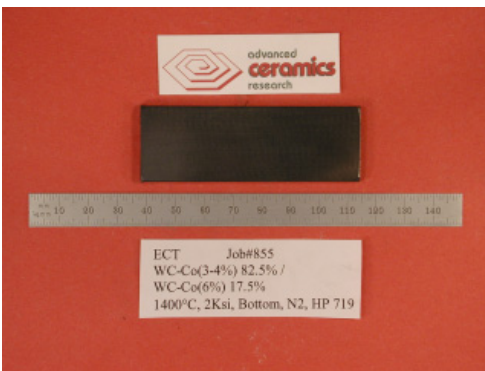


Figure D2B1
82.5% WC- (3-4%)Co / 17.5% WC-(6%)Co

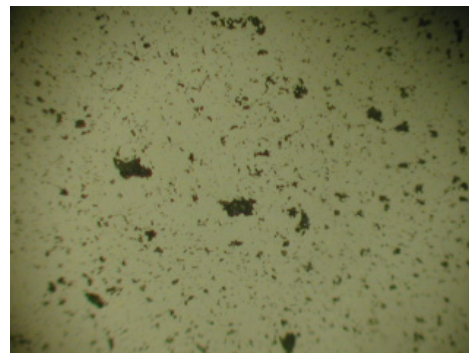


Figure D2B2
82.5% WC- (3-4%)Co / 17.5% WC-(6%)Co

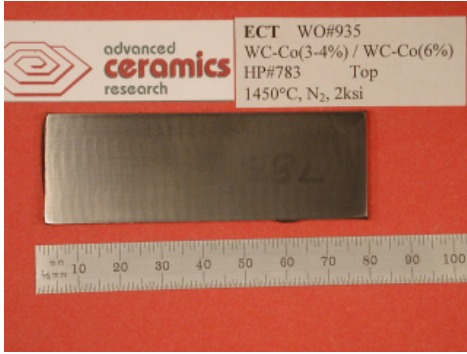


Figure D2C1

82.5% WC- (3-4%)Co / 17.5% WC-(6%)Co

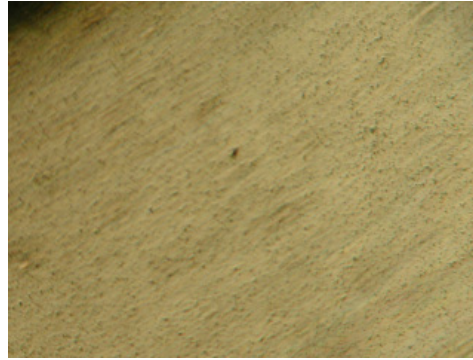


Figure D2C2

82.5% WC- (3-4%)Co / 17.5% WC-(6%)Co



Figure D2D1

82.5% WC- (6%)Co / 17.5% Co (unground)

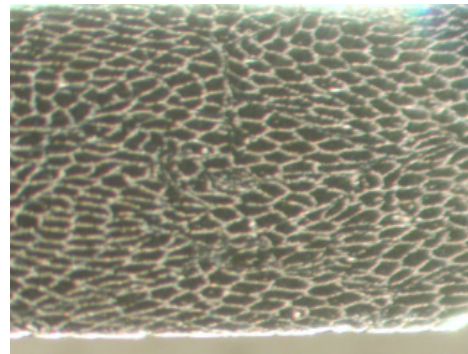


Figure D2D2

82.5% WC- (6%)Co / 17.5% Co



Figure D2E1

82.5% WC- (6%)Co / 17.5% Co

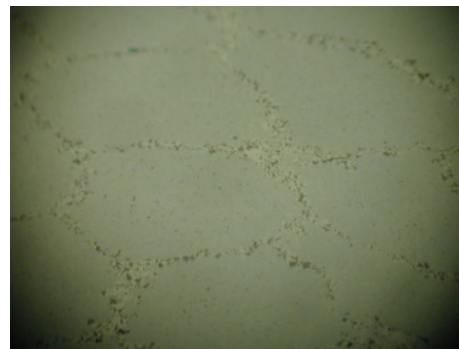


Figure D2E2

82.5% WC- (6%)Co / 17.5% Co



Figure D2F1
WC-(16%)Co powder billet top,
WC-(16%)Co powder billet bottom



Figure D2G1
82.5%WC- (6%)Co / 17.5%WC-(16%)Co



Figure D2G2
82.5%WC- (3%)Co / 17.5%WC-(6%)Co



Figure D2H1
WC-(14%)Co powder billet



Figure D2H2
WC-(14%)Co powder billet