Youngstown State University
CTME -- Center for Transportation and Materials Engineering

FINAL REPORT

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Prepared By: Tim Wagner

Project Title:

Novel Ceramic-Metallic Composites for Light Weight Vehicle Braking Systems

Principal Investigator (PI):

Dr. Timothy R. Wagner, Professor - Inorganic / Solid State Chemistry
Department of Chemistry
Youngstown State University, One University Plaza, Youngstown, Ohio 44555
330-941-1960, trwagner@ysu.edu

Co-Principal Investigators (Co-PIs):

Dr. Matthias Zeller, Instrumentation Scientist & Adjunct Professor
Department of Chemistry
Youngstown State University
Youngstown, Ohio 44555
330-941-7105, mzeller@ysu.edu

Dr. Dingqiang Li, Instrumentation Scientist, Electron Microscopy Facility
Department of Chemistry
Youngstown State University
Youngstown, Ohio 44555
330-941- 7102, dli01@ysu.edu

Industrial Collaborators:

Klaus-Markus (Mark) Peters, General Manager, TCON Division
Fireline, Inc., 300 Andrews Avenue, Youngstown, Ohio 44505
330-743-1164, mpeters@fireline-inc.com

Brian P. Hetzel, R&D Manager
Fireline, Inc., 300 Andrews Avenue, Youngstown, Ohio 44505
330-743-1164, bhetzel@fireline-inc.com

Project Overview

This project centered on a close interaction between the TCON Division of Fireline, Inc. and various individuals affiliated with the College of Science, Technology, Engineering, and Mathematics (STEM) at Youngstown State University (YSU). Fireline, a local company within 10 minutes walking distance from the YSU campus core, has developed a unique process that utilizes displacement reactions to transform ceramic preforms into ceramic-metallic co-continuous interpenetrating phase composites with enhanced properties while retaining the original shape and dimensions of the preform. Through initial development efforts, it was discovered that TCON® composite materials have extraordinary macro-, micro-, and nanoscale features that lead to their exceptional properties ideal for applications that require cost effective, lightweight materials. The unique properties of TCON composites in general are derived from the fine interlocking of ceramic and metallic phases throughout the composite microstructure. The ceramic phase provides high stiffness, low density and high strength to the composite, while the continuous network of reinforced metal gives high thermal & electrical conductivity, and high fracture toughness to the material. Such properties make these materials excellent candidates for replacing traditional materials in a number of applications, such as high wear/corrosion resistant refractory shapes for molten metal transport and/or containment in industrial processes (the major area in which Fireline currently commercializes some of its TCON products), or for new applications, including light weight, high strength components for vehicle braking systems.

This project focused on the synthesis of specific ceramic precursors (see **Table 1**) and investigations of their subsequent transformation via reactive metal displacement to produce novel ceramic-metallic interpenetrating phase composites (IPCs) for potential use in light weight braking systems in vehicles. The proposed IPCs are closely related to TCON composites currently produced by Fireline, and they are designed to yield composites with the properties required for brake rotor materials in order to expand Fireline's product line in this area even further. Specifically, the objectives for this project were to prepare novel composite materials consisting of: (1) A $MgAl_2O_4$ spinel phase combined with a light weight, high strength Ti-Al alloy and/or Al metallic phases (or other metallic phase depending on precursor), and (2) The oxynitride spinel phase, Al_3O_3N (related to so-called 'transparent spinels') combined with Al metal. The spinel phases of the proposed new composites have cubic lattices, like the predominant Al metallic component of these composites, meaning even stronger binding potential between the two phases and thus a stronger composite.

Summary of Proposed Research

The TCON process utilizes displacement chemical reactions, in which sacrificial oxides are reduced by a molten metal and subsequently form a ceramic/metal interpenetrating phase composite (IPC).[1-6] The most investigated IPC system produced via a displacement reaction is the alumina/aluminum (Al_2O_3/Al) composite.[2-6] This reaction can be carried out as follows:

$$(4+x)Al + 3SiO_2 \rightarrow 2Al_2O_3 + 3Si_{(Al)} + xAl$$

where 'xAl' is the amount of excess aluminum forming a continuous network in the composite as a result of the volumetric contraction that occurs as the silica (SiO_2) reacts to form alumina. Note also that the Si produced in the reaction is dissolved in the Al network, as represented by the '$Si_{(Al)}$' symbol. This material is extremely strong, and contains ca. 70 weight % alumina and 30 weight % aluminum. **Figure 1** represents a typical microstructure of this material.

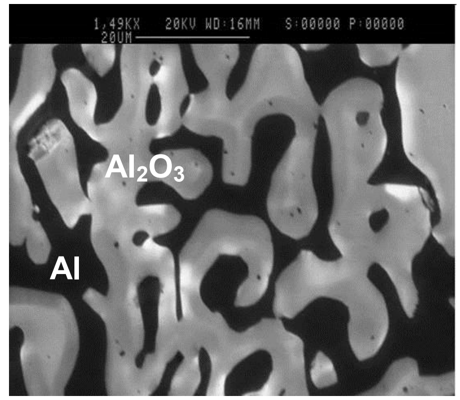

Figure 1. TCON Al_2O_3-Al matrix

In order to exploit the flexibility afforded by the TCON process in choice of precursor material, this project proposed to take advantage of synthesis capabilities in YSU laboratories to prepare novel precursors not previously transformed via the TCON process. The precursor systems and respective targeted composites originally proposed for this project are listed in **Table 1** below:

Table 1. Summary of proposed precursor materials for synthesis and TCON transformation, and their corresponding targeted composite compositions.

Targeted Novel Precursor	**Targeted Composite Phases**
MgX_2O_4 (X = Ti, Fe) spinel phases	$MgAl_2O_4$ spinel phase with X-Al Alloy
$MgTi_2O_5$	$MgAl_2O_4$ spinel and Al_2O_3 ceramic phases with Ti-Al alloy
Sialon, i.e. β-$SiAl_2O_2N_2$	Al_3O_3N spinel & AlN with Al(Si)

The overall approach for the work was to first synthesize the targeted precursors listed in Table 1 as laboratory-scale pellets (1/2 in. diameter × 1/4 in. thick) usually via standard ceramic methods. Once prepared, the precursor samples were reacted in molten Al in a laboratory kiln for potential transformation to a composite material. Transformed products were analyzed via one or more of the following techniques: optical microscopy, powder X-ray diffraction, and Scanning Electron Microscopy (SEM) methods. Also included in this project was a preliminary investigation of the preparation of precursor shapes using a 3D powder bed printer. A future goal is to utilize this technology for scale-up of precursors to be transformed to composites with desired properties.

Experimental

Precursors were sintered in a Thermolyne 59300 High Temperature Tube Furnace, usually following mixing of reactant powders in a SPEX 8000M mixer. Transformation was performed in laboratory kilns located on-site at YSU, or sometimes at Fireline. Materials characterization was a significant component of the overall project and benefitted from over $3M in NSF, state-of-Ohio, and Federal grants and contracts, utilized mainly to establish state-of-the art facilities for X-ray diffraction, electron microscopy, and mechanical properties analysis within the College of STEM at Youngstown State University. **Figure 2** summarizes the overall scheme followed.

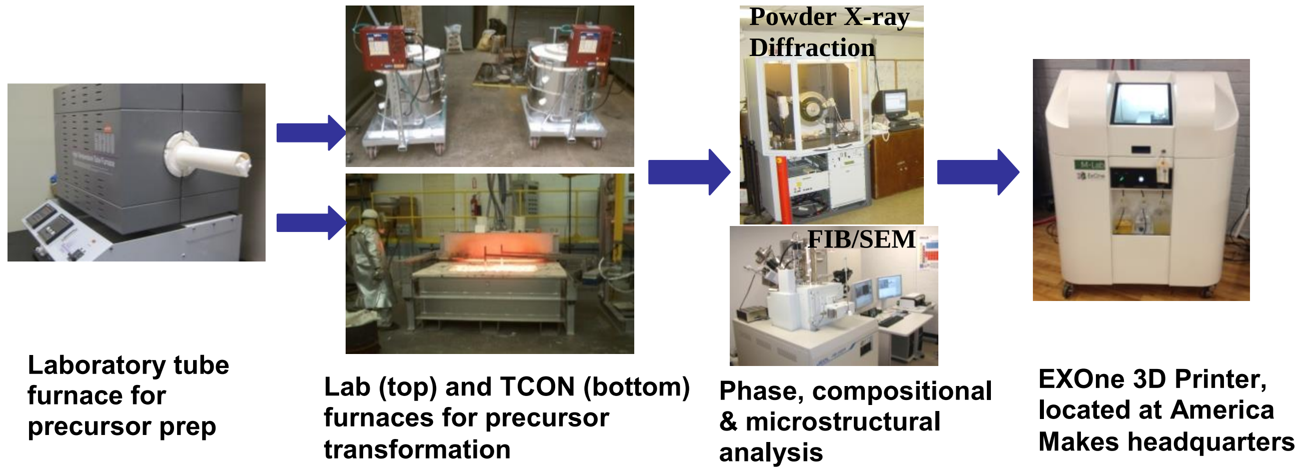

Figure 2. Sequence of steps for preparation and analysis of proposed novel composites for potential commercialization as brake rotor materials. The TCON furnace is located at Fireline, Inc.

Results

This project supported one MS graduate student (Alethea Mymo) for one summer, although a significant portion of her thesis project is related to the work proposed for this grant. Specifically, she has worked on the $MgFe_2O_4$ and $MgTi_2O_5$ systems listed in Table 1, and will graduate in Spring 2014. It should also be noted that Alethea worked as an intern at Fireline for over one year, and completed portions of several experiments on site at Fireline. A second master's level graduate student, Josh Denmeade, studied β-sialon (see Table 1) and other oxynitride systems, and completed his thesis in December 2013. Results for each of the systems studied are summarized below.

Spinel Precursors

Spinel-type precursors were targeted primarily because they offer the advantage of having the exact stoichiometry required to produce a spinel/metal-alloy composite, as indicated in the following reaction:

$$(2 + x)\ Al + MgFe_2O_4 \rightarrow MAl_2O_4 + Al_xFe_2 \ ,$$

where x = excess Al required to form a stable Al-Fe alloy. Note that we have previously observed such direct replacement reactions for the precursor material $SrFe_{12}O_{19}$, a magnetoplumbite-type phase built of stacked spinel-type blocks, in which Al displaced Fe^{3+} to give $SrAl_{12}O_{19}$.[7] In the present case however, no direct displacement was observed. The $MgFe_2O_4$ precursor was prepared and transformed in both pure Al and aluminum mixed with other (proprietary) materials. Complete transformation was typically observed, but to an Al_2O_3/Al-X composite (where 'X' depends on the melt composition). The powder X-ray diffraction (PXRD) pattern shown in **Figure 3** from a transformed $MgFe_2O_4$ composite clearly indicates the predominance of Al_2O_3 and Al phases in the system. No spinel or other Mg or Fe-containing phase was observed, suggesting that Mg and Fe diffused into the melt.

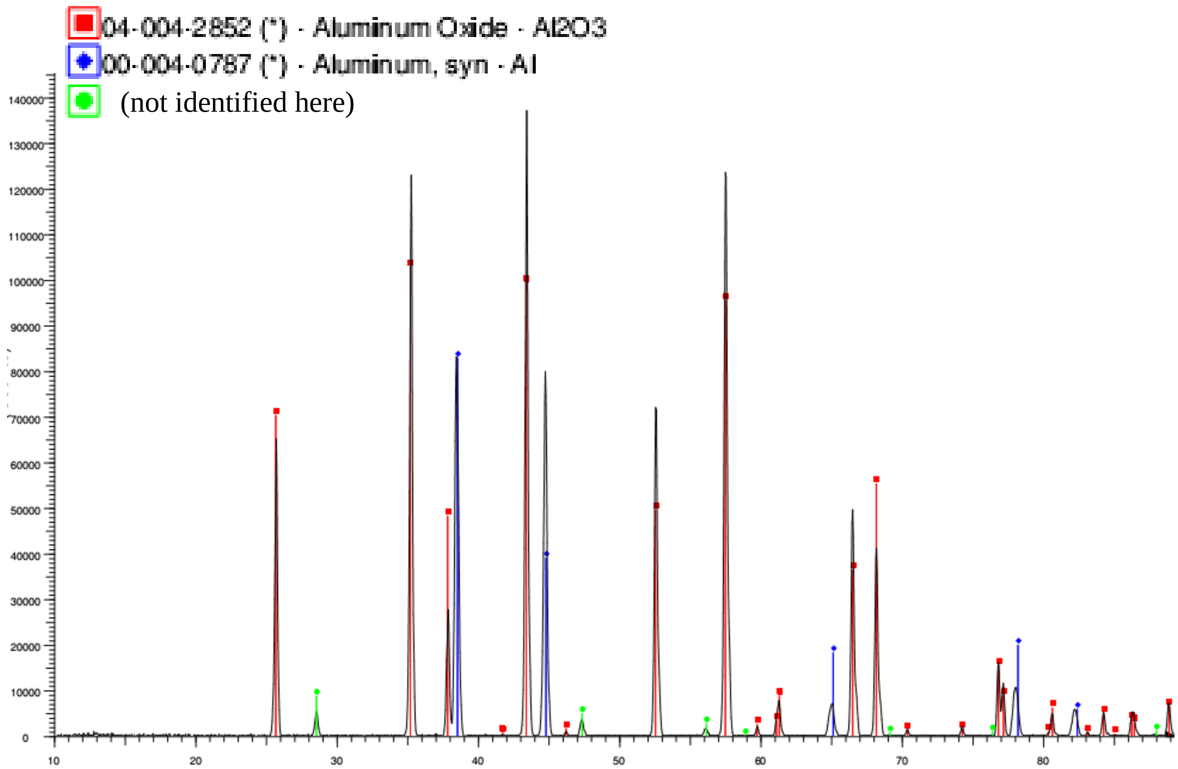

Figure 3. Powder X-ray diffraction pattern of a composite formed from transformation of an $MgFe_2O_4$ precursor in an Al-based melt.

Regarding the proposed $MgTi_2O_4$ (see Table 1) precursor, it turns out that this phase is air sensitive, and so was deemed as unsuitable for potential commercialization and thus was not further studied.

$\underline{MgTi_2O_5}$

The mechanism derived from previous studies[7] of transformation of $MgTiO_3$ in Al-based melts suggests excess MgO as a reaction byproduct, presumably due to insufficient Al_2O_3 present for further reaction to spinel. That is, in this work we hypothesized that the spinel ($MgAl_2O_4$) phase observed in the partially transformed composite was formed by secondary reaction of MgO and Al_2O_3. Thus in the present work, $MgTi_2O_5$ was selected for study as this material is predicted to supply excess alumina to use up all MgO to produce a spinel-rich composite:

$$(8+x)Al + 3MgTi_2O_5 \rightarrow 3MgAl_2O_4 + Al_2O_3 + xAl\text{-}6Ti.$$

In addition, this phase is easily prepared by stoichiometric reaction of MgO and TiO_2 at high temperature. Transformation of the $MgTi_2O_5$ precursor under TCON conditions in various Al-based melt compositions again yielded Al_2O_3/Al-based composites, as indicated in the PXRD pattern and accompanying optical micrograph shown in **Figure 4**. No Mg- or Ti-containing phases were observed.

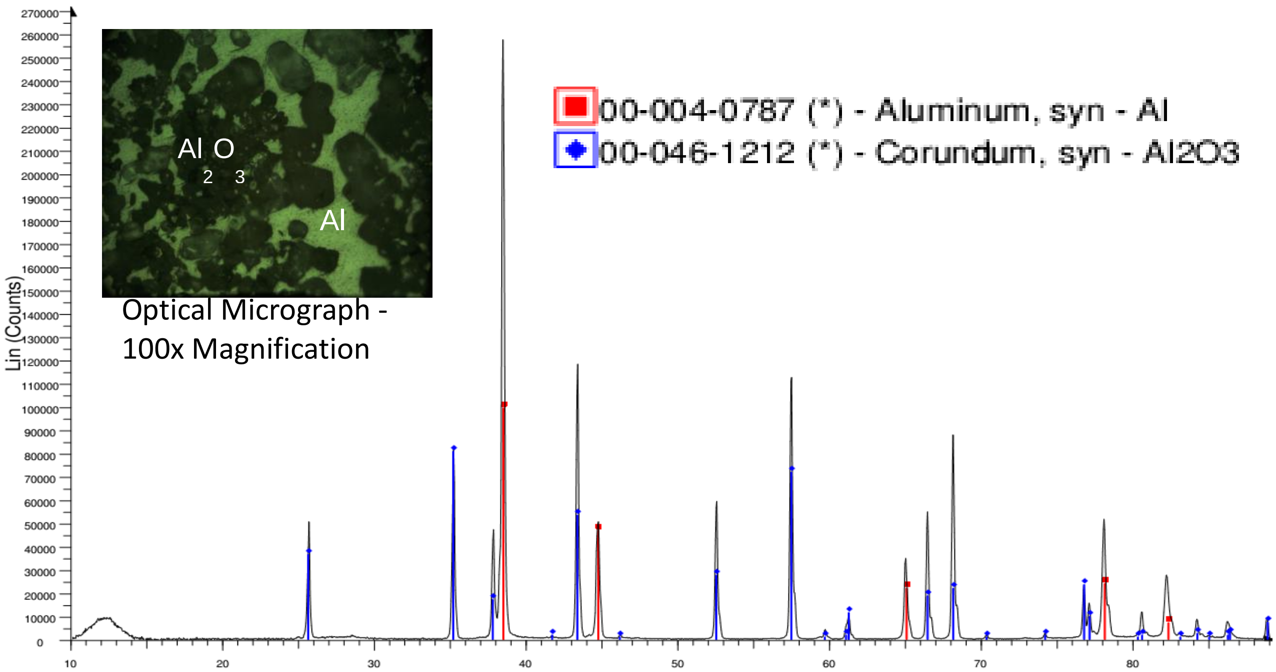

Figure 4. Powder X-ray diffraction pattern of a composite formed from transformation of an $MgTi_2O_5$ precursor in pure Al melt. The results indicate complete transformation, but to Al_2O_3/Al composite. Inset: Optical micrograph showing composite microstructure.

Oxynitride Precursor

Particularly interesting systems we have begun introducing to the TCON process via this award are oxynitride phases, an example being compounds known generally as sialons, e.g. β-$SiAl_2O_2N_2$. This precursor was targeted in the hopes of producing composites containing an aluminum oxynitride spinel phase, ideal composition Al_3O_3N, as a ceramic component. This phase is known for its use as a transparent spinel for armor applications and for its excellent optical and mechanical properties.[8-11] For example, it is over 10% harder than spinel.[12] Possible transformation routes predicted using the sialon as a precursor were:

$$4/3\ Al + SiAl_2O_2N_2 \rightarrow 2/3\ Al_2O_3 + 2\ AlN + Si$$

$$\text{or}\quad 2/3\ Al_3O_3N + 4/3\ AlN + Si$$

Although AlN is predicted as the predominant ceramic phase in these reactions, this phase is well known for its high thermal conductivity and corrosion resistance, and has flexural strength similar to Al_2O_3.[13] Furthermore, it was hypothesized that under conditions where Al_3O_3N is successfully produced, excess AlN could be removed through reaction with Al_2O_3 (in turn produced by mixing SiO_2 with the oxynitride precursor) to give additional Al_3O_3N.

After successful synthesis of the β-$SiAl_2O_2N_2$ material, we transformed it under TCON conditions and observed partial transformation to an Al_2O_3-AlN/Al composite rather than the oxynitride phase targeted.[14] The PXRD pattern taken from the transformed pellet surface shown in **Figure 5** indicates these results.

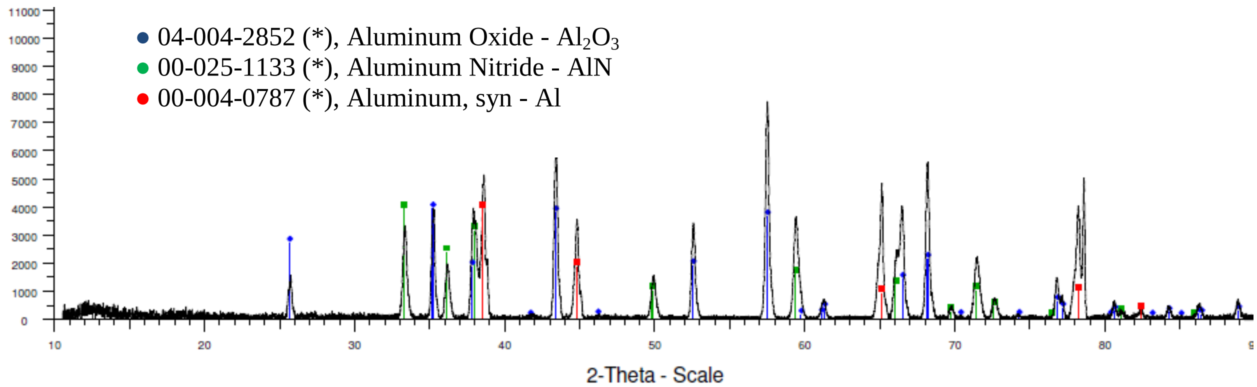

Figure 5. Powder X-ray diffraction pattern of a composite formed from transformation of β-$SiAl_2O_2N_2$ precursor in Al melt. The results reveal transformation to an Al_2O_3-AlN/Al composite.

Scale-up via 3D Printing

Very recently we have begun preparing precursor shapes of $MgTiO_3$ (well-characterized in a previous study[7]) using a 3D powder bed printer, a technique readily available onsite. **Figure 6** shows a "green shape", i.e. pre-sintered and as produced from the printer, of an $MgTiO_3$ pellet. To our knowledge, this material has not previously been printed. A major advantage of the technique is that practically any desired shape can be prepared via the software interfaced to the printer. The shape in Figure 6 was printed at the *America Makes* headquarters located in downtown Youngstown (i.e. a few blocks from the YSU campus).

Figure 6. An $MgTiO_3$ pellet as printed using an ExOne X1-Lab model powder bed printer.

Conclusions

Based on the results of transformation of all three precursor systems summarized above, it is clear that higher than TCON (proprietary) transformation temperatures are needed to produce both the spinel oxide and oxynitride phases within the composite, since Al_2O_3 is clearly the stable phase at the temperature used. A theoretical study by Barry[15] *et al*. supports this conclusion. Studies are currently in progress involving transformation using laboratory furnaces (rather than kilns) that can attain the desired temperature. It is only after the proposed spinel-containing composites are successfully prepared that mechanical properties analyses of scaled-up composite shapes can be completed, and then a “go” or “no go” decision made for further development of these materials towards potential use in commercial light weight brake rotor systems.

A positive outcome of this study is the demonstrated potential to utilize 3D printing technology for convenient production of ceramic precursor shapes for subsequent transformation. Of significance is that more complex shapes can be produced via printing technology relative to conventional methods typically used, such as slip casting.

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