2. MATERIALS FOR FUEL SYSTEMS

A. Low-Cost, High-Toughness Ceramics

T. N. Tiegs, F. C. Montgomery, and J. O. Kiggans
Oak Ridge National Laboratory
P.O. Box 2008, MS-6087
Oak Ridge, TN 37831-6087
(865) 574-5173; fax: (865) 574-4357; e-mail: tiegstn@ornl.gov

DOE Technology Development Area Specialist: James J. Eberhardt
(202) 586-9837; fax: (202) 586-1600; e-mail: james.eberhardt@ee.doe.gov
ORNL Technical Advisor: D. Ray Johnson
(865) 576-6832; fax: (865) 574-6098; e-mail: johnsondr@ornl.gov

---

Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee
Prime Contract No: DE-AC05-00OR22725

Objectives

- Demonstrate that significant improvement in the reliability of structural ceramics for advanced diesel engine applications could be attained if the critical fracture toughness (K_{Ic}) were increased without strength degradation.
- Confirm that cost is a major factor in determining the applicability of new materials in engine components.
- Develop high-toughness materials that are also low cost.

Approach

- Show that TiC-Ni_3Al composites have a combination of superior physical properties and mechanical behavior using conventional powder processing methods.
- Develop TiC-based composites with 40–60 vol % Ni_3Al because they have expansion characteristics very close to those for steel.
- Collaborate development effort with CoorsTek, Inc., and Cummins Engine on processing scale-up and engine testing.
- Determine initial mechanical properties of ceramic-particulate-reinforced TiAl composites and make assessment of application in heavy vehicle systems.

Accomplishments

- Supplied large pilot-scale batch of processed powder mixtures with alternate Ni_3Al precursors to CoorsTek for injection molding of test components.
- Completed work with CoorsTek, Inc., (a parts supplier) for scale-up of the processing and to supply them with pilot plant scale quantities of powder mixtures for injection molding trials.
- Supplied sintered parts produced in conjunction with CoorsTek to Cummins Engine Co. for rig testing of machined components.

Future Direction

- End the project with the transfer of the TiC-Ni_3Al cermet technology to industry.

Introduction

TiC-Ni_3Al composites are under development for application in diesel engines because of desirable physical and mechanical properties. For these applications, the Ni_3Al volume contents are on the order of 30 to 50 vol % to match the thermal expansion of steel. Typically, flexural strengths greater than 1000 MPa up to 800°C and fracture toughnesses higher than 15 MPa $\sqrt{m}$ are obtained for the composites. The composites are densified by liquid phase sintering, and most of the early work used gas-atomized Ni_3Al particles with fine TiC powders. Later work was done using nickel and NiAl powders (along with the TiC) to form Ni_3Al by an in situ reaction during sintering. Over the last few years the in-situ reaction process was developed significantly because it produced high mechanical properties and developed a fine TiC grain size. The finer grain sizes were favored because of better wear resistance.

The fabrication techniques and equipment employed in production are very similar to those for the fabrication of WC-Co hard metals, and thus, the processing costs are well established. However, when the economics of producing the TiC-Ni_3Al composites was examined, a significant cost was associated with the use of the NiAl precursor powder (about 55% of the total raw material cost). Because the costs of the starting raw materials can be a significant fraction of the total cost of a component, alternative materials for fabricating the cermets are of interest. Part of the reason for the high cost of the NiAl is that it is produced only as a specialty powder at the present time. The development effort is being done in collaboration with CoorsTek, Inc.

Results

Alternate Precursors for Ni_3Al Formation

All previous work used a combination of nickel and NiAl for an in-situ reaction to form the Ni_3Al. A new NiAl commercial source has been identified and powder procured. Characterization of the powder by x-ray diffraction indicated that it was stoiciometric and had a pattern identical to earlier material from a different supplier. Particle size analysis showed the mean particle size was ~9.8 µm, which was similar to the previous material. However, the size distribution was broader than the earlier NiAl.

A large batch (3 kg) of TiC-50 vol % Ni_3Al powder was processed with the new NiAl powder and shipped to CoorTek for injection molding (IM) trials. Test parts were fabricated and shipped back to Oak Ridge National Laboratory (ORNL). Initial sintering results indicated the densification behavior was similar to the earlier composites, but slightly less: 6.05 g/cm^3 vs 6.11 g/cm^3.

Based on those results, new IM tooling was designed and fabricated at CoorsTek. Several large batches (>15 kg total) of TiC-50 vol % Ni_3Al powder were milled, homogeneously mixed, and shipped to CoorsTek. Parts with the new tooling have been IM and returned to ORNL. The specimens are currently awaiting sintering when the furnace is repaired.

While the initial sintering results indicated the densification behavior was similar to the earlier composites, flexural strength measurements revealed a rather low strength in comparison to the previous material from a different NiAl manufacturer. The comparison was 945 ± 150 MPa for the earlier materials and 600 ± 37 MPa for the newest batch. Scanning electron microscopy (SEM) examination of a fracture surface showed numerous agglomerates ≤100 µm in size. Energy dispersive x-ray analysis (EDAX) indicated they were NiAl particles. Evidently the new batch of NiAl powder contained larger particles (even though the powder was listed as <44 µm).

A modified milling procedure was instituted with the NiAl, and particle size analysis indicated all particles were <10 µm. Sintering of test parts with the modified powder was improved, and densities of ~6.11 g/cm^3 were obtained. This density is equal or better than the previous high-strength materials. A test batch (~3 kg) of powder with the modified milling procedure has been sent to CoorsTek for IM. Parts and test MOR bars have been sintered at ORNL and returned to CoorsTek for testing. Sintering behavior of these injection molded materials was similar to previous cermets, and the microstructure showed no unusual defects. Consequently, a large batch (>12 kg total) was fabricated and sent to CoorsTek for IM of test parts.

Assessment of Ceramic-Particulate-Reinforced TiAl Composites

TiAl offers significant improvements in weight-to-strength ratios compared to most advanced alloys. Such materials could have applications in heavy vehicle propulsion systems. Ceramic-metal composites that utilize TiAl as the bonding phase potentially could show increased fracture strength, higher elastic modulus, better creep resistance, and higher wear resistance than the base alloy. An exploratory study was initiated to fabricate ceramic-particulate-reinforced TiAl composites and determine the mechanical properties. Initial samples were fabricated by hot-pressing to readily obtain high-density specimens suitable for testing. An assessment was made to determine if the mechanical properties are suitable for further development for heavy vehicle applications.

Several compositions were fabricated including: TiC-50 vol % TiAl, TiN-50 vol % TiAl, and TiC-67 vol % TiAl. The TiAl was an alloy with the composition, Ti-48 Al-2 Cr-2 Nb, which has been shown to have excellent properties. The powder mixtures were made using similar methods to those used for the TiC-Ni_3Al cermets. Hot-pressing produced samples with closed porosity and densities of 94–95% theoretical density. Microstructural examination revealed good wetting and distribution of the TiC and TiAl particles. No obvious core-rim structure (like those observed with TiC-Ni_3Al cermets) was observed. However, the TiC did appear to have reacted with the TiAl to produce a reaction zone surrounding remnant TiC particles. EDAX showed these zones to contain Ti, Al, Nb, Cr, and C. X-ray diffraction (XRD) results indicated the formation of Ti_3AlC_2, which confirmed a reaction occurred between the TiAl and the TiC.

In contrast to the TiC, the TiAl did not appear to have wet the TiN particles very well. A reaction between the TiAl and the TiN was also evident, and EDAX indicated a metallic phase of Ti-Al-Nb-Cr and a second phase of Ti-Al-N. XRD showed the formation of $AlTi_2N$, indicating a reaction between the starting components. Indent hardness determinations showed the hardness was lower than similar ceramic particle volume loadings in Ni_3Al-based cermets. For example, the hardness of the TiC-50 vol % TiAl, TiN-50 vol % TiAl, and TiC-67 vol % TiAl composites was 4.0–4.6 GPa, 5.7–5.8 GPa, and 4.2–4.3 GPa, respectively. For comparable TiC-50 vol % Ni_3Al cermets, the hardness values would be >8 GPa.

Because of the reactions between the TiAl alloy and the TiC or TiN reinforcements, the prospects for sintering materials and obtaining good mechanical properties is not encouraging. However, other ceramic particles, such as TiB_2, ZrB_2, HfB_2, and Al_2O_3, should be compatible in the TiAl alloy matrix and provide reinforcement.

Conclusions

Pilot-scale batches of TiC-Ni_3Al composite mixtures with alternate Ni_3Al precursors were produced and supplied to CoorsTek for IM of test components. The prospects for sintering TiAl-based materials and obtaining good mechanical properties is not encouraging. However, other ceramic particles, such as TiB_2, ZrB_2, HfB_2, and Al_2O_3, should be compatible in the TiAl alloy matrix and provide reinforcement.

Presentations and Publications

T. N. Tiegs, “Aluminide Bonded Ceramic Composites,” at the American Ceramic Society Conference on Advanced Ceramics and Composites, Cocoa Beach, Florida, January 23–27, 2005.

T. N. Tiegs, F. C. Montgomery, P. A. Menchhofer, and P. F. Becher, “Aluminide Bonded Ceramic Composites,” to be published in *Ceram. Eng. Sci. Proc., Am. Ceram. Soc.*, Westerville, Ohio (2005).

T. N. Tiegs, “High Toughness Materials—TiC-Ni_3Al Cermets,” at the Heavy Vehicles Materials Peer Review, Oak Ridge, Tennessee, September 13–15, 2005.