INTEROFFICE CORRESPONDENCE

Date: September 6, 1994
To: P. Erickson, MS 3810
From: K. M. McHugh, MS 2050
Subject: COMPLETION OF CRADA 93-ST-9 - KMM-28-94

With regard to the inquiry of D. E. Hage (see enclosed letter), Cooperative Research and Development Agreement 93-ST-9 with Exxon Research and Engineering Company has been successfully completed. A letter to the participant confirming completion of the CRADA, and a final report, are provided in the enclosed letter to Dr. Robert Schucker. There were no Subject Inventions filed as a result of this work. In addition, CRADA stamps were never provided for this project.

The following is suitable as a nonproprietary abstract for this CRADA:
A study was conducted to assess the feasibility of spray depositing a metal ring on the end of ceramic tubes using a low temperature spray forming process developed at the INEL. 1/16"-1/8" thick x 1/2" wide tin, zinc, and aluminum alloy rings were spray formed using a bench-scale nozzle without damaging the ceramic. Analysis of the deposits indicated they were suitably dense and exhibited good adherence to the ceramic material.

If you have any questions, please give me a call at 525-5713.

kmm

Enclosure:
As Stated

cc: J. F. Key, MS 2050
     K. M. McHugh file

DISCLAIMER

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OSTI BENEFITS CHECKLIST

CRADA NO.: 93-ST-9

PARTNER: Exxon

PRINCIPAL INVESTIGATOR: Kevin D. McHugh

ACCOUNT EXECUTIVE: Dennis Cheney

MARK “X” in the appropriate response.

BENEFITS REALIZED? YES NO
LIST: Researchers learned how to spray form liquid metal using on a Coordinate Type

CONSTRAINTS/EXTERNAL INFLUENCES:

- Technical or manufacturing problems
- Funding Availability
- Personnel Changes
- Work Scope Changes
- Other:

FOLLOW-ON ACTIVITIES

- CRADAS
- Cost-shared Contracts
- Invention Disclosures
- Technical Assistance
- Patent Applications
- Other: None

Licenses
Copyrights
Reimbursable WFO
Use of Facilities
Non US

Were Any Awards Given? YES NO
List:

Completion Date: 9/15/94
February 10, 1994

Dr. Robert C. Schucker
Exxon Research and Development Laboratories
P. O. Box 2226
Baton Rouge, LA 70821-2226

SUMMARY OF CRADA NO. 93-ST-9 RESULTS - KMM-9-94

Dear Bob:

Results from Phase I of the INEL/Exxon cooperative research program (CRADA No. 93-ST-9) are summarized below. The study involved assessing the feasibility of spray depositing a metal ring on the end of a cordierite tube using a low temperature spray forming process developed at the INEL. Tin, zinc and two aluminum alloys were deposited during Phase I. Phase II will involve optimization of the process using one of these metals or a higher melting point metal, and technology transfer to Exxon or a designated vendor.

Rings were spray formed by injecting a liquid metal, heated about 200°C above its melting point, into a converging/diverging nozzle. There, the metal contacted a high temperature, high velocity (~ Mach 1.5) inert gas that atomized the melt into very fine droplets (~ 10 µm), entrained the droplets in a directed flow, and deposited them onto a cordierite tube supplied by Exxon. After exiting the nozzle, the droplets were quenched rapidly, resulting in high solidification rates (normally > 10^3 K/s) at the substrate.

Prior to deposition, the tubes were masked to allow the spray to form a deposit 1/2" wide from one end of the tube, while preventing the spray from coating the honeycomb features at the ends of the tube. Deposit thickness was approximately 1/16"-1/8". No surface preparation to the cordierite tubes was performed prior to coating because the surface texture was rough enough to produce an adequate mechanical bond between the deposit and ceramic. For all experiments, the rotational speed of the ceramic tube was 38 rpm, which corresponds to a surface speed of 2.2 in/s. While an exhaustive experimental matrix was not possible due to the scope of the program, three spray parameters were found to strongly influence the quality of metal deposits: liquid metal temperature, nozzle-to-substrate distance, and nozzle pressure.

Tin was deposited, using a bench-scale apparatus, at mass flow rates of 40, 50, and 60 lb/h per inch of nozzle width transverse to the flow direction, and at gas-to-metal mass flow ratio of 3.8 to 4.7. The metal was superheated to 470°C and atomized with argon heated to the same temperature. Nitrogen could be used as a more cost effective alternative with comparable results. A nozzle inlet pressure of 27 psia was found to give good results with tin.
Tin deposits were close to 100% dense, as measured by water displacement using Archimedes’ Principle. Sectioned samples were examined with a metallograph for porosity, microstructure, and conformality of the deposit to the substrate. Polished samples revealed very low porosity in all deposits with no interconnected porosity; an example is given in Figure 1a. Grain structure of etched samples was equiaxed for most spray conditions, with an average grain size of about 9 μm, i.e., much more refined than the cast microstructure of the starting material, due to rapid solidification (Figure 1b and 1c). Figure 2 is an example of columnar growth that was found in deposits formed at high mass flow rates. Deposit conformality to grooves and other features on surface of the tubes was excellent under all conditions; examples are given in Figure 3 and Figure 4 for polished and etched deposits. One tin coated tube was provided during your visit to INEL. Another tin coated tube, sample 1E2563A, was prepared during your visit and is enclosed. The honeycomb portion of that tube had been treated at Exxon with a ceramic wash.

Zinc was also found to exhibit excellent adhesion and surface conformality to the cordierite tubes. As-deposited densities were typically 90 to 95% of theoretical with no evidence of interconnected porosity. A sample was provided during your visit.

Early runs with aluminum alloy 6061 did not give satisfactory results. While the alloy sprayed well, and deposits showed good adhesion and conformality, cracks were observed in the tubes. The hairline crack in sample 3E3013A (enclosed) is typical of what we saw.

Several observations have led to the conclusion that fracture was caused by contraction of aluminum during cooling rather than thermal shock. First, fracture was not observed until after the sample cooled to room temperature. Moreover, some samples, such as 3E0134A (enclosed), had fractures that appeared to be localized at the interior of the honeycomb structure. Finally, measurements of the temperature of the spray at impact with the substrate also suggest that fracture was not caused by thermal shock. These observations are consistent with the high thermal shock resistance (500 °C), and low compressive strength (350 MPa (50 ksi)) of cordierite.

Four approaches were attempted to eliminate the problem:

1) Al alloy 390 was sprayed. This alloy has a lower thermal expansion coefficient (18.5 X 10^-6/°C) and lower melting range (510-650°C) than does 6061 alloy (23.6 X 10^-6/°C and 582-652°C, respectively) due to the addition of 17 wt% Si. This approach reduced, but didn’t eliminate, the problem. A hairline crack was still observed on part of the cordierite tube.

2) An in situ anneal was conducted on a sample that had been sprayed with Al alloy 390 in order to increase the ductility of the sprayed metal, but once again the tube cracked when cooled to room temperature.

3) Aluminum foil was folded and wrapped around the end of the tube to act as a gasket to absorb the compressive forces as the sprayed metal ring cooled to room temperature. Two runs were conducted and no cracks were found in the cordierite. Sample 3E0244A is an example. This approach looks feasible, but the correct number of foil wraps that will provide a leak tight seal as the deposited aluminum contracts around the gasket, will need to be determined.
4) The spray was intermittently started/stopped to allow the deposit to cool somewhat during the buildup of metal. Cracks were not observed in the ceramic. Sample 3E0274A is an example. The honeycomb portion of the tube also had been coated at Exxon with a ceramic wash.

In summary, Phase I results seem encouraging and demonstrate feasibility of the process for applying tin, zinc, and aluminum alloy rings onto cordierite tubes. Perhaps a good starting point for Phase II, if you decide to continue the program, would be for you, Jim Key and I to choose an alloy that best satisfies your needs, and an experimental matrix that will optimize the process and provide statistical validity for that alloy. If you have any questions, feel free to call me at (208) 525-5713.

Sincerely,

Kevin McHugh
Materials Processing

kmm

Enclosures:
As Stated
Fig. 1(a) - Spray formed tin, polished, 40X.

Fig. 1(b) - Grain structure of spray formed tin, 200X.
Fig. 1(c) - Grain structure of cast tin, 200X.

Fig. 2 - Columnar grains in tin spray formed at a high deposition rate.
Fig. 3 - Tin deposit conformality to cordierite surface.
(a) Polished, 40X.

(b) Etched, 40X.

Fig. 4 - Tin deposit conformality to cordierite surface.