DOE/EE/15598--T3

**PROTOTYPE DEVELOPMENT AND TESTING
OF ULTRAFINE GRAIN NZP CERAMICS**

Project #DE-FG01-95EE15598

Quarterly Progress Report #3

for the Period

October 28, 1995 - January 27, 1996

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February 8, 1996

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Summary of Progress

Caterpillar, Inc. continues to develop a slip casting procedure for CMZP exhaust portliners for diesel engines. Appropriate tubes have been successfully cast and fired and initial properties measurements look excellent. MATVA is preparing an additional 10kg batch of CMZP with the specifications developed by Caterpillar.

Project Aim

To economically manufacture a series of manifold liners made of calcium magnesium zirconium phosphate (CMZP) and to demonstrate their energy conservation in advanced diesel engines.

Technical Objectives

To produce and test manifold liners made of CMZP in actual engines. These liners should improve the energy efficiency and performance of diesel engines.

Currently, the application of ceramics in advanced engines has been limited primarily by cost of manufacture. The economic production of CMZP lined manifolds will be established by producing powder using a solid state reaction method, forming the liners by slip casting, then having the manifolds cast around the liners. By insuring economic production using the methods mentioned along with prototype testing in engines, the potential for commercial application will be clearly demonstrated.

Details of Progress

1. Introduction

Caterpillar has been developing advanced low-heat-rejection (LHR) engine designs because by insulating the combustion chamber components for reduced heat rejection, improved fuel economy and emission reduction can be achieved. The insulation eliminates heat loss during the closed portion of the cycle and increases the combustion temperature. Increased combustion temperatures improve emissions by reducing the amount of particulate or smoke. The higher combustion temperatures also provide additional energy to drive a turbocharger that, in turn, improves the overall efficiency of the engine system and results in increased fuel economy.

Insulated exhaust portliners reduce the amount of heat rejected into the cooling system of the engine increasing the amount of energy available to drive the turbocharger. However, reducing the amount of heat rejection into the cooling system will also enable the use of smaller, less expensive, more reliable cooling

systems. New truck designs, which use aerodynamic hoods for improved fuel economy, have significantly less space available for radiators and fans and will require smaller cooling systems.

The majority of insulated portliner designs require the ceramic to be cast-in-place into the cast iron cylinder head. This process consists of pouring molten cast iron directly on the ceramic component. For this reason, the ceramic portliner must have good thermal shock resistance. In addition, the ceramic portliners must be able to function for a minimum of 30,000 hours in an engine without chemically or mechanically degrading. Finally, the ceramic portliners must have very low thermal conductivity.

Caterpillar is evaluating calcium-magnesium-zirconium-phosphate (CMZP) for insulated diesel engine intake and exhaust portliners and manifold applications. The combination of low coefficient of thermal expansion and low elastic modulus give the CMZP excellent thermal shock resistance. Casting simulations at Caterpillar have shown that CMZP has the potential to be successfully cast-in-place into grey iron without the ceramic or casting cracking. In addition, the ability to tailor the thermal expansion coefficient of CMZP by modifying its chemical composition will significantly decrease the thermomechanical stresses that develop during engine operation. This, in turn, will increase the probability that CMZP will be able to meet the commercial durability requirements of diesel engines.

2. Results

A. CMZP Powder Specification

The overall objective of this task is to determine a CMZP powder specification for slip casting diesel engine exhaust portliners.

A sintering study was completed that evaluated three variables: firing time at 1260°C, amount of ZnO oxide sintering aid addition, and CMZP powder particle size (+400 mesh vs. -400 mesh). This study showed that a -400 mesh particle size with a 2.7 weight percent ZnO addition will sinter at 1260°C. It also showed that, even with the ZnO sintering aid, none of the +400 mesh CMZP specimens sintered at 1260°C.

The effect of calcining temperature on the composition of amorphous CMZP powder was determined. The study consisted of calcining powder specimens with and without a 2.7 weight percent ZnO addition for 20 minutes at the following temperatures: 715, 780, 845, 910, 975, 1040, 1105, 1170, 1235, and 1300°C. After sintering, the specimens were water quenched. The evaluation criteria consisted of optical evaluation of microstructure, bulk density (ASTM), and sonic velocity.

The results of this study showed that the amorphous CMZP powder without the ZnO addition obtains a neutral pH when calcined between 850 to 1000°C. This change

in pH (when mixed 50/50 with distilled water) corresponds to a large decrease in zirconium phosphate peak in the powder's x-ray pattern.

The amorphous CMZP powder containing the ZnO additions formed mixtures of Zn, (Zn, Zr), and (Ca,Zr) phosphates at 1170°C. The x-ray patterns also showed evidence of phosphide formation.

B. CMZP Sintering Studies

The overall objective of this task is to determine the optimum sintering aid composition and sintering cycle (time and soak temperature) for the -400 mesh amorphous CMZP powder.

The effect of time at temperature on the x-ray patterns, bulk density (ASTM test), and sonic velocity for the following CMZP powders was determined:

1. A -400 mesh amorphous CMZP powder containing 2.7 weight percent ZnO, and
2. A crystalline CMZP powder containing 2.45 weight percent.

The results of this study showed that for both the crystalline (sintered at 1300°C) and amorphous CMZP powders (sintered at 1260°C), increasing the time at temperature above 30 minutes produced microstructures with excessive grain growth, grain boundary coarsening, and microcracking. Using the results of this study as a guide, along with the dilatometric sintering studies previously performed at Caterpillar, the following sintering schedule was specified for the -400 mesh amorphous CMZP powder: a 30-minute soak at 1260°C.

A literature review revealed that silica can be used as a grain growth inhibitor during the sintering of zirconium phosphate (*J. American Ceramic Soc.*, **70** [8] pp. 585-90, 1987). Additions of up to 3 weight percent silica to the zirconium phosphate resulted in a smaller sintered grain size and a corresponding four-fold increase in strength. For this reason, silica additions were added to the CMZP powder to determine if the silica will also inhibit the CMZP grain growth, enabling higher sintering temperatures to be used. The higher sintering temperatures should produce denser CMZP specimens with increased strength.

The 1 weight percent silica additions to a -400 mesh CMZP powder containing a 2.7 weight percent ZnO addition did act as a grain growth inhibitor producing a smaller CMZP grain size on the specimens sintered at temperatures between 1250 and 1400°C. However, for these specimens, the small grain size did not prevent the formation of microcracks. This microcracking was confirmed by measuring the sonic

velocities of the specimens after sintering. Additional studies will be performed to determine the effect of the silica additions on CMZP strength.

C. CMZP Slip Casting Trials

The overall objective of this task is the development of procedures for slip casting CMZP tubes. These tubes will be cast-in-place into a simulated cast iron diesel engine cylinder head.

Wet milling procedures were developed for the CMZP powder. Since the as-received CMZP powder is highly agglomerated, wet milling is required to achieve good slip properties. Wet milling will also reduce the particle size and enable the powder to be sintered at lower temperatures. Wet milling was selected over dry milling because the primary goal of the program is to slip cast tubes.

Particle size analyses were used to determine the effect of the wet milling time and the size of the spherical media used during milling. The analyses showed that a good distribution of submicron particles was achieved by wet milling for 24 hours using 3/16" spherical media.

Straight CMZP tubes have been successfully slip cast, dried, and fired to relative densities greater than 98 percent. The optima firing time and temperature for these slip cast tubes was determined to be 30 minutes at 1200°C. Specimens fired using these conditions exhibited smooth, shiny fracture surfaces, which are typically associated with dense brittle materials.