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PROTOTYPE DEVELOPMENT AND TESTING OF ULTRAFINE GRAIN NZP CERAMICS

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Quarterly Progress Report #4

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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. Forty pounds of CMZP powder are being prepared for Caterpillar to complete the slip casting of the 90 degree elbows. The breakdown of tests is as follows:

1. 15 trials for optimizing mold and slip casting procedures (require 2 pounds of powder for each slip casting trial), and

2. 10 castings to produce the tubes for the grey iron casting trials.

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 gives 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 Sintering Studies

The objective of this task is to determine the optimum sintering aid composition and sintering cycle for the as-received CMZP powder. The as-received powder is amorphous and has passed a -400 screen with an average particle size of 3.46 ± 6.2 microns.

An experiment was run to determine the effects of:

1. Sintering cycle (0.5 to 8 hours at sintering temperature 1250 and 1300°C, and
2. Percent zinc oxide (0.5 to 3 percent).

The evaluation criteria were bulk density, MOR, elastic modulus, and coefficient of thermal expansion (CTE) of dry pressed CMZP disks. The results are listed in Table 1.

Table 1 Effect of Sintering Cycle and ZnO Additions on The Mechanical and Physical Properties of Dry Pressed CMZP

Condition	Bulk Density (g/cm^3)	MOR (MPa)	E Modulus (GPa)	CTE 700 (rt-700°C)
0.5hr/1250°C/1%ZnO	2.46	26.4	33	+1.37
4hr/1250°C/1%ZnO	2.91	13.3	11	-1.67
0.5hr/1300°C/1%ZnO	2.79	12.3	11	-0.87
4hr/1300°C/1%ZnO	2.84	15.7	14	-1.51
0.5hr/1250°C/3%ZnO	3.02	21.3	19	-1.75
4hr/1250°C/3%ZnO	3.08	17.8	16	-2.0
0.5hr/1300°C/3%ZnO	3.09	20.8	19	-1.9
4hr/1300°C/3%ZnO	3.07	17.4	16	-2.0
8hr/1300°C	2.31	19.3	20	+1.0
0.5hr/1300°C/0.5%ZnO	2.51	27.6	26	+0.6

None of the CMZP specimens in this study has acceptable mechanical properties. Based on a microstructural analysis of these samples, the reasons for poor mechanical properties were either excessive grain growth and microcracking caused by the excessive grain growth or a continuous glassy phase between the CMZP grains. Using the physical and mechanical properties and the microstructural analysis as a guide, the following conclusions were made:

1. Excessive grain growth and microcracking in CMZP compositions containing ZnO additions can be prevented by using a sintering temperature below 1250°C, and
2. The optimum ZnO addition level is between 0.5 and 2.0 weight percent. At ZnO levels above 2.0 weight percent, the glassy phase that develops at the grain boundaries controls the mechanical properties of the CMZP.

After reviewing the results of the previous sintering study, a second study was run. This study evaluated the effect of ZnO additions (1.5 and 2.0 weight percent), and sintering temperatures (1175°C and 1200°C) on the mechanical properties of CMZP specimens. The results of this study were:

1. CMZP with 1.5% ZnO, fired at 1200°C for 0.5 hours had a MOR of 96 MPa, and
2. CMZP with 2.0% ZnO, fired at 1175°C had a MOR of 111 MPa.

These results confirmed the conclusions made from the initial sintering and ZnO additive study.

B. CMZP Slip Casting Trials

The two CMZP compositions (containing 1.5 and 2.0 percent ZnO), which produced the best mechanical properties in the dry pressed sintering studies, were slip cast into six-inch long tubes with a 49 mm OD and a 6 mm wall thickness. These tubes were then fired at either 1175°C or 1200°C for between 0.5 and 0.7 hours. After sintering, modulus of rupture bars were machined from the tubes. Table 2 contains the physical and mechanical properties obtained from these tubes.

Table 2 Physical and Mechanical Properties of Slip Cast CMZP Tubes

Condition	Bulk Density (g/cm^3)	MOR (MPa)	E Modulus (GPa)	CTE 700 (rt-700°C)
0.5hr/1250°C/2%ZnO	3.22	28	24	-1.5
0.5hr/1200°C/1.5%ZnO	2.89	96	74	+1.8
0.7hr/1175°C/2%ZnO	3.06	111	81	+1.8

Slip cast CMZP containing 1.5 to 2.0 percent ZnO additive produced sintered samples with a high MOR and a positive CTE. The microstructure of these samples did not contain the glassy phase at the grain boundaries, microcracking, or large grains observed in the specimens sintered at temperatures above 1200°C. In addition, fracture surfaces of these specimens were smooth and almost glass-like compared to the rough, jagged surfaces of the samples sintered at the higher temperatures.

It should also be noted that increasing the sintering temperature of the CMZP composition containing the 2.0 weight percent ZnO addition to 1200°C produced specimens with a flexure strength of 28 MPa that is 70 percent lower than the strength of specimens from this composition sintered at 1175°C.

The mechanical properties of the 0.5hr/1200°C/1.5%ZnO combination were duplicated in a separate slip casting trial. The verified properties measured were a 109 MPa MOR, and 80 GPa elastic modulus.

Next, the composition will be used for slip casting of the 90-degree bend CMZP tubes. These tubes will be used for the grey iron casting trials. Initial results of these casting trials indicate further modifications of the plaster mold design need to be made to allow for the drying shrinkage.