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CRADA Final Report
for
CRADA Number ORNL 92-0115

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IMPROVED CATALYST MATERIALS AND EMISSION CONTROL SYSTEMS

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Prepared by the Oak Ridge National Laboratory
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Managed by
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ORNL-27 (3-96)

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ABSTRACT

CRADA No. ORNL92-0115
Delphi Automotive Systems

IMPROVED CATALYST MATERIALS AND EMISSION CONTROL SYSTEMS

The overall goal of this CRADA was the improvement of performance and/or development of alternate systems for conventional fuel, flex-fuel, and alternate fuel vehicles in order to meet stringent future emission standards. The objectives had three major thrusts; 1) the characterization of the structural and chemical evolution of the precious metals and washcoat during ageing under bench flow reactor, engine dynamometer, and vehicle conditions, 2) the correlation of measured catalyst performance and degradation over time with details of microstructural changes under bench flow reactor and engine dynamometer conditions, and 3) the simulation and testing of an in-cylinder catalyst system to determine the effect on emissions of a single-cylinder engine. Catalyst formulations for both gasoline and natural gas applications were studied. The emission testing and structural characterization were performed on alternate formulations and processing variables in order to evaluate the relative conversion efficiency, lifetime, and stability. The ageing parameters were correlated with the evolving structure and properties of the tested catalytic convertors. A major portion of the second thrust area was the construction and validation of both the bench flow reactor and engine dynamometer test facility and the identification of deactivation/regeneration mechanisms associated with alternative fuels relative to those for conventional fuel.

A number of microstructural changes were identified that could contribute to the deactivation of the catalyst during ageing, including sintering of the oxide and precious metals components of the washcoat, $\gamma \rightarrow \alpha$ transformation and growth of α-alumina, the encapsulation of both precious metal clusters and other washcoat components, the redistribution of the precious metals, and the general or preferential surface deposition of poisons on the washcoat. The stability of several catalyst formulations and alternate processing procedures relative to these microstructural changes and changes in conversion efficiency and lifetime were studied.

IMPROVED CATALYST MATERIALS AND EMISSION CONTROL SYSTEMS

BACKGROUND

A CRADA between Delphi Automotive Systems (Delphi; formerly General Motors - AC Delco Systems) and Lockheed Marietta Energy Research (LMER) was aimed at improved performance and lifetime of noble metal based three-way-catalysts (TWC), which are the primary catalytic system for automotive emission control systems. While these TWC can meet currently required emission standards, higher than optimum noble metal loadings are required to meet lifetime requirements. In addition, more stringent emission standards will be mandated in the future, demanding improved performance and service life from these catalysts. Understanding the origin of convertor performance and changes in TWC conversion efficiency with ageing are critical needs in improving these catalysts. Initially in a fresh catalyst, the active material is often distributed on a very fine scale, approaching single atoms or small atomic clusters. As such, a wide range of analytical techniques have been employed to provide high spatial resolution characterization of the evolving state of the catalytic material. During the second half of CY 1995, a no-cost extension of the CRADA was requested by both Delphi and Lockheed Marietta Energy Systems and approved for all of FY 1996.

CRADA OBJECTIVES

The overall goal of this CRADA was the improvement of performance and/or development of alternate systems for conventional fuel, flex-fuel, and alternate fuel vehicles in order to meet stringent future emission standards. The research covered under this CRADA was divided into three projects; Project 1 - Improved Catalyst System Materials for Use with Conventional Fuels, Project 2 - Catalyst Materials for Alternate Fuel Engines, and Project 3 - In-Cylinder Catalysis and Thermal Barriers. The associated objectives for each Project of the CRADA are summarized below.

The objective under Project 1 was to evaluate, develop, and apply analytical techniques to characterize the structural and chemical evolution of the precious metals and washcoat during ageing under bench flow reactor, engine dynamometer, and vehicle conditions. Based on these observations, alternate materials and processing variables were evaluated. The ageing parameters were correlated with the structure and properties of the tested catalytic convertors.

The objective under Project 2 was to seek correlations of measured catalyst performance and degradation over time with details of microstructural changes. The intent was to relate catalyst conversion efficiency and deactivation mechanisms obtained from the bench flow reactor and engine dynamometer tests to catalyst formulation and surface characteristics and to identify deactivation/regeneration mechanisms peculiar to alternative fuels.

The objective under Project 3 was to conduct simulations and experiments on a single-cylinder engine using an in-cylinder catalyst system to determine the effect on emissions.

DISCUSSION OF TECHNICAL PROGRESS

In Project 1 the LMER role concentrated on the structural and elemental characterization of the catalyst and washcoat of different advanced and model catalyst systems in both the as-prepared and as-aged conditions. Delphi produced or supplied the catalysts, aged the catalyst monoliths and measured the emission performance of the monoliths before and after ageing. Project 2 dealt with the development and application of the LMER engine test stand and bench flow reactor facilities. The test stand facility included four gasoline engines and a natural gas engine. Project 3 studied the application in-cylinder catalysis in order to reduce emissions and several in-situ measurement techniques.

Progress-to-date for all three projects was presented to Delphi and LMER participants at quarterly review meetings which alternated between the Flint and Oak Ridge sites. In the last 1.5 years, these meetings also served as program planning and analysis meetings. Three quarterly reports and one annual report were prepared each year for the Advanced Industrial Concepts Program which funded the Project 1 portion of the CRADA. These reports contained only non-sensitive information about the CRADA and were approved by Delphi for release.

TECHNICAL PROGRAM RESULTS

1. Project 1 - Improved Catalyst System Materials for Use with Conventional Fuel

1.A. Tech-III Monoliths

The first materials supplied by Delphi were as-prepared catalytic convertors of their advanced Tech-III formulation along with the starting materials (e.g.; washcoat powders (γ-Al_2O_3 and CeO_2) and mixed slurry, the precious metal loading solution, and cordierite honeycomb monoliths ranging from the bare brick, with washcoat added, and with precious metals loaded. The structure of the washcoat was characterized with scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS), electron probe microanalyzer (EPMA), both high resolution and analytical electron microscopy (HREM and AEM), X-ray diffraction and the X-ray fluorescence microprobe (XFM). Though the precious metals could be detected by the elementally-sensitive techniques (EDS, EPMA, AEM, and XFM), no precious metal clusters were observed with any of the above techniques in the as-prepared Tech-III washcoat. Apparently the precious metals are present as near-atomic clusters or fine, non-crystalline material below the resolution limit of the techniques (~1 nm). Mercury porosimetry was utilized to characterize the pore structure of the blank, washcoated, and washcoated and precious-metal-loaded monoliths.

One of the major ORNL technical accomplishments of the CRADA was the development of reliable techniques for the preparation of electron transparent, transverse section specimens for both high resolution imaging and analytical electron microscopy. Such specimens preserve the spatial correlation of different areas of the washcoat relative to the original free surface and the substrate. The variation of washcoat and precious metal cluster (PMC) structure and chemistry was studied as a function of depth in the washcoat. In addition, the segregation of catalyst poisons at the free surface, the formation of glazes, and the reaction or interdiffusion of the washcoat and the substrate could be examined directly. The development of this technique has generated interest from a number of external researchers and catalyst companies and has contributed to research under both the Lean Burn Technology CRADA (Y12-93-0166) and several collaborations under the HTML User Program. Several open literature publications and both invited and contributed presentations at international scientific meetings have resulted from work performed under this CRADA, which are listed later in this report.

Bulk surface analytical techniques such as X-ray photoelectron spectrometry (XPS), Auger electron spectrometry (AES), and secondary ion mass spectrometry (SIMS) in general did not provide significant additional information to that obtained by the previous analytical techniques, as the result of the low loading of precious metals, the distribution of the precious metals through the thickness of the washcoat, or overlap between analytical signals for the precious metals and elements present in the washcoat. Further work with these bulk surface analytical techniques was curtailed in favor of the other techniques which provided the needed information.

Various microscopy techniques revealed the coarse, multi-phase nature and significant porosity of the washcoat. Several of the analytical techniques (AEM, SEM/EDS, EPMA, and XRM) indicated a strong association of precious metals with specific oxides in the as-prepared washcoat. Variations of precious metal concentration with local washcoat thickness, depth in the washcoat, and position along the length of the monolith were observed. These variations and the association with specific washcoat oxides resulted in an inhomogeneous distribution of the precious metals on both the microscopic and macroscopic scales. The measured Pt/Rh ratio for the as-prepared washcoat was significantly higher than the nominal Pt/Rh loading ratio, suggesting that the as-deposited distribution of platinum and rhodium in the washcoat differed to some degree.

Delphi initially supplied three types of dynamometer-aged monoliths: (D1 and D2) two moderate ages with slightly different temperatures equivalent to 50,000-100,000 miles, depending on the model of the automobile, and D3 which simulates exposure to significant over-temperature relative to D1 and D2. As the washcoat initially experiences the highest temperatures near the inlet surface, the microstructural evolution of the aged monoliths was characterized at ~1 inch from both the inlet and outlet surfaces and in some cases at the mid-plane of the monolith. There was microstructural evidence for sintering of the washcoat that increased from D1 to D3; including coarsening and consolidation of the ceria (especially the fibrous variant) and the formation of large (>1 μm), secondary grains in regions of finely-mixed ceria and γ-alumina. These grains were identified by both AEM and XRD as α-alumina. These alumina grains exhibited low dislocation density and contained fine embedded ceria particles. The degree of $\gamma \rightarrow \alpha$ alumina transformation was quantitatively measured with XRD. The sintering of the ceria decreased the available ceria surface area, while the $\gamma \rightarrow \alpha$ transformation and growth of the alumina encapsulates nearby ceria particles, isolating them from the exhaust gas stream. As such, both of these processes have negative impacts on the oxygen storage capacity and conversion efficiency of the washcoat. This is especially true for the D3 aged material where higher temperatures produced more sintering and $\gamma \rightarrow \alpha$ transformation and growth.

All the aged Tech-III washcoats exhibited precious metal clusters (PMCs) which varied in both cluster size and Pt/Rh ratio. As observed in the as-prepared washcoat, the PMCs exhibited a strong association with certain oxides in the washcoat and certain positions in the monolith. The Pt/Rh was found to increase with cluster size. Though there was a significant variation of Pt/Rh for a given size, this variation was shown to correlate with spatial variations of the inhomogeneously deposited Pt and Rh. There was also indication of redistribution of the precious metals throughout the monolith as a function of ageing, especially at higher temperature exposures.

As catalytic convertors experience cyclic exposure to oxidizing and reducing exhaust gas streams, as-prepared monoliths were bulk annealed in both air and reducing atmospheres in order to simulate the changes possible in PMCs during each period. PMCs formed under oxidizing conditions were similar in size, but 3-5 times higher in Pt/Rh than those formed under reducing conditions for the same time and temperature. This behavior is consistent with rhodium being in an oxidized state and relatively immobile as compared to platinum under oxidizing atmospheres, whereas the mobilities of the two precious metals are more similar under reducing conditions.

The structural evolution determined for the dynamometer-aged washcoat was compared to that of a convertor vehicle-aged for 110,000 km. Significant sintering of the entrance washcoat was consistent with over-temperature exposure; whereas the mid-plane and exit washcoats exhibited little washcoat sintering and a relatively fine PMC size distribution. A discontinuous glaze enriched in P, Zn, and Ca was observed on the entrant washcoat surface, but only slight poison deposition was present on the exit washcoat. All of these observations were consistent with the service history of the test vehicle, which included an initial engine with high oil consumption. The observed poisons on the washcoat surface could be derived from oil additives used in the test vehicle. The high conversion efficiencies observed during post-ageing dynamometer testing are in agreement with the performance predicted for the washcoat and PMC structures observed in most of the monolith.

The correlation of the PMC structure (i.e.; PMC size or Pt/Rh) with the conversion efficiencies measured for the monolith is, unfortunately, not a simple function. There are a number of changes in the washcoat structure which impact the conversion efficiencies that are not reflected in such fundamental parameters. The variation in washcoat structure along the length of the monolith determines both the lifetime and the overall performance of the convertor. The sintering of the washcoat component powders and the $\gamma \rightarrow \alpha$ alumina transformation and growth can degrade both rapid access to the catalytic surfaces and the oxygen storage capability of the washcoat. Poisons and the associated formation of glazes can also hamper access to both the catalytic and oxygen-active materials by physically sealing either the washcoat free surface or active materials themselves. In addition, poisons can chemically react with the washcoat or PMCs and inhibit the conversion process.

1.B. Ceria Variation Study

Delphi supplied a series of dynamometer-aged and emission tested monoliths which were identical, except for the amount of ceria present in the washcoat. These monoliths were aged to test the long term stability of the washcoat and PMCs and the influence of poisoning on the conversion efficiency at long exposures. The final washcoat and PMC structures were characterized and compared to the post-ageing conversion efficiency measured by Delphi. Similar to the aged Tech-III monoliths, the PMCs exhibited an association with a specific oxide in the washcoat. The Pt/Rh of the PMCs was size dependent and that dependence varied as a function of the washcoat ceria level.

Significant sintering of ceria and transformation/growth of α-alumina were observed in these materials as a result of the prolonged high temperature exposure. X-ray diffraction was utilized to quantify the amount of α-alumina present as a function of ceria in the washcoat. However, there were also variations observed in the blending of the washcoat powders that resulted in different levels of spatial inhomogeneity of the component oxides, which complicated the explanation of the optimum ceria level observed in dynamometer-based performance testing.

1.C. Process Variation Study

In order to identify process steps which produced improved loading and distribution of the precious metals, Delphi produced a series of both as-prepared and dynamometer-aged monoliths for which specific processing variables were varied. These variables included precious metal loading solution chemistry and procedures, washcoat oxides and drying/calcining sequences. Different processing parameters were identified which permitted significant differences in precious metal loading and uniformity of distribution. These results were compared to the conversion efficiencies for dynamometer-aged duplicate monoliths to determine what process variations and associated precious metal distributions resulted in improved catalytic performance.

1.D. Poisoning of Stabilized Washcoats

Based on the sintering, α-alumina formation and growth, and the related detrimental changes in the

PMCs structure, the performance of stabilized washcoat monoliths was investigated. Delphi supplied both as-prepared and dynamometer-aged monoliths. The dynamometer-ageing was performed under accelerated poisoning conditions via elevated levels of zinc dialkyl phosphate (ZDP) in order to test the resistance of these advanced formulations to poison degradation. Both single and dual layer washcoat formulations were studied.

The association of specific washcoat additions with specific phases and a specific layer was identified in both single and dual layer washcoats. The single layer washcoat was loaded with palladium and Pd-based PMCs were observed on all of the oxide phases present in the dynamometer-aged material. Two types of PMCs were observed in the aged dual layer washcoat; one was a single pure metal cluster, which tended to be larger in size, and the other, smaller clusters which were tri-metallic in nature and tended to be rhodium-enriched. The alloy PMCs in the dual layer washcoat exhibited a size dependent Pt/Rh, which increased with cluster size. The palladium level in the tri-metal PMCs appeared to increase as the Pt/Rh increased. Rhodium appeared to be surface loaded on the second layer; whereas palladium and platinum were more uniformly distributed in their respective washcoat layers. Near the washcoat layer interface, relatively large Pd-Pt PMCs were observed in the dual layer washcoat.

A region enriched with Al-P was observed on the free surface of the aged washcoat, often engulfing the Rh-enriched PMCs. Similar enrichment of both P and Zn was observed in association with localized concentration of certain washcoat stabilizing additions. Small regions of α-alumina were observed in association with ceria; whereas most of the alumina remained untransformed.

1.E. Ancillary Studies

Several sets of as-prepared and aged convertors were supplied by Delphi in order to investigate specific questions which developed from the above studies. Included among these specimens were dynamometer-aged convertors with higher Rh levels and single metal model catalysts (Rh/CeO_2 and Rh/ Al_2O_3) which had undergone ageing under cyclic oxidation/reduction conditions.

For the dynamometer-aged material, both alloy and essential pure Rh PMCs were observed, which exhibited similar preferential association to a specific oxide in the washcoat as observed for the Tech-III washcoats. The aged Rh/CeO_2 material was heavily sintered and exhibited a ~100 fold increase in grain size relative to the fresh material. The majority of the Rh PMCs were oriented with respect to the ceria lattice and at least some were internal to the large ceria grains. Such PMCs which were associated with ceria would contribute to a loss in catalytic activity, as observed in the absorption testing. The aged Rh/Al_2O_3 material there was localized formation and growth of α-alumina. No PMCs were observed in the fine-grained γ-alumina regions; however, coarse PMCs were observed in the transformed α-alumina regions.

2. Project 2 - Catalyst Materials for Alternative Fuel Engines

2.1. Bench Flow Reactor and Engine Test Facility Set Up.

A computer controlled bench flow reactor was designed and fabricated to evaluate and screen the performance of catalyst materials at ORNL under well-controlled, simulated engine exhaust conditions that are difficult to achieve in engine dynamometer tests. This bench flow reactor also simulated the oscillations in exhaust gas composition from an internal combustion engine that occurs about the stoichiometric point during closed-loop operation as well as departures from the stoichiometric point during engine cold starts and acceleration. Mass flow meters and pressure transducers were interfaced with a computer to allow control and reading of individual gas flows and pressures at various points in the gas stream. Typical gases used in the bench-flow reactor for simulating engine exhaust feed stream included CO, CO_2, NO, H_2, SO_2, N_2, H_2O, and defined hydrocarbons like propylene, propane, or methane. State-of-the-art emission analyzers were utilized to measure the gas chemical composition upstream and downstream of a catalyst sample. Catalyst light-off and temperature sweep tests were performed under varying degree of net oxygen or air-fuel ratio bias by controlling the gas temperature entering the catalyst bed.

2.2. Engine Test Facility

An engine dynamometer test facility was designed and built at ORNL to support the catalyst testing phase for gasoline and natural gas automotive engines. Two engines, provided by GM Delphi Automotive Systems, were set up to support this CRADA. A natural gas fueled, eight cylinder, 5.7L engine was coupled to a 400 hp eddy current dynamometer. Engine speed and load were digitally controlled. A second engine, a gasoline fueled, four cylinder 2.5L, was set up on a portable engine dolly and coupled to a water brake. A sophisticated exhaust system was designed for catalytic converter evaluation that allowed regulation of exhaust space velocity and converter temperature control independent of engine operating conditions. Production engine electronics provided closed-loop fuel system control to maintain air-fuel ratio stoichiometry. An electronic heads-up module was coupled to the engine computer to allow display of selected engine operating parameters as well as some regulation of air/fuel ratio and spark advance. Tests with the 5.7L natural gas engine were made using high purity (99.995%) methane from a six bottle fuel manifold system. This was done to ensure that fuel composition remained the same throughout the catalyst evaluation tests. The engine test facility was equipped with state-of-the-art engine and emissions instrumentation. Engine pressures, temperatures, flows, and emissions data were monitored, logged, and analyzed using a data acquisition system.

2.3. Test Facility Validation

Shakedown tests were conducted on the newly built bench flow reactor and engine/dynamometer test facility. Their operating performance was benchmarked with well-defined GM catalyst materials and converters of known conversion efficiencies. The results obtained were in agreement with data found by GM, thus providing a high level of confidence in the operating accuracy of both facilities.

2.4. Catalyst Evaluations

ORNL bench flow reactor tests were conducted on two GM Delphi supplied Tech-III catalyst monoliths that contained 20% and 40% ceria in the washcoat. These monoliths were exposed to a 600° C, 200 hour, rapid ageing test schedule by GM Delphi prior to delivery to ORNL. Cyclic lightoff tests were conducted on three 20% ceria monolith samples and three 40% ceria monolith samples taken from the inlet, midplane, and outlet flow position of a larger monolith. Bench flow reactor results showed that the mid-plane section of the 20% ceria monolith exhibited lower NO_X and CO conversion efficiency and higher light-off temperatures for peak NO_X, CO, and HC conversion than observed for either end. For the 40% ceria monolith, there were no major differences found in NO_X and HC conversion efficiency or light-off temperatures between the three samples tested. However, peak CO conversion efficiency was slightly higher for the outlet sample. Tests were also conducted on a 40% ceria sample to study the effect of water content in the exhaust gas stream. It was found that light-off temperatures increased and conversion efficiencies decreased as the water content of the exhaust gas increased. Differences in lightoff temperatures and conversion efficiencies obtained from bench flow reactor tests were correlated with microstructure analysis results obtained from the same samples to help identify the mechanisms responsible for changes in catalyst performance.

ORNL obtained eight catalytic converters from natural-gas-powered GMC Sierra pickup trucks for evaluation at our engine dynamometer facility. While other investigators have addressed emissions from natural-gas-powered vehicles, we are not aware of any that have examined the emissions from field-aged catalytic converters. The catalytic converters were a beaded Pt-type with a volume of 4916 cm^3 (300 in^3) and were from trucks with 3,500 to 78,000 miles of use. Evaluation of the field-aged converters were performed on a production natural-gas-fueled, 5.7L GM V-8 engine (same engine used on the natural gas powered GMC Sierra pickups) that had been set up in the ORNL engine dynamometer test facility. Engine speed and load were set to achieve exhaust flows that would yield a space velocity through the catalyst of 50,000 hr^{-1}. Air-fuel ratios were maintained at stoichiometric conditions throughout the tests. A temperature sweep (high to low) was performed for each catalytic converter while maintaining a space velocity of 50,000 hr^{-1} for each temperature point.

Conversion efficiencies for NO_X, CO, and HC were measured as a function of temperature for all eight field-aged catalysts. The catalysts were identified by the mileage of the vehicle. Though the mileage ranged from 3,500 to 78,000, catalyst performance did not correlate well with prior mileage, especially on the high mileage end. Catalysts with 3,500 and 13,000 miles had best performance. On the other hand, a catalyst with only 34,300 miles was worst than catalysts with higher mileage. While driving logs were unavailable for these vehicles, we speculate that the worst performers had more frequent, shorter trips than the worst performer. Another important factor could be the composition of the local natural gas. Variations in the composition of natural gas will affect the air-fuel ratio of the engine and could significantly affect emissions and vehicle driveability. Certain natural gas blends, such as during "peak shaving" periods in winter months, when additional air and propane is added, affect both the density and energy content of the mixture. Higher concentrations of non-methane hydrocarbons tend to produce a rich mixture and reduce the octane number of the fuel. This can lead to engine knock and high emissions. High concentrations of inert gases will result in lean mixture that reduces engine power and yields rough engine idle operation.

Surface area and porosity measurements were made of samples taken from five of the beaded catalysts tested, in an effort to correlate measured catalyst performance with details of microstructural changes. The worst-performing catalysts appeared to have suffered losses in surface area and porosity, indicating the loss of active sites. It was found that the surface area of the worst performer was 43% lower than the surface area of the low mileage catalyst. The reduction in surface area implies a loss of active sites for catalytic activity. Because CH_4 is the most difficult HC species to oxidize in the catalyst and pure CH_4 was used in the dynamometer evaluation of the catalytic converters, the lack of active sites was most obvious in HC conversions (i.e., significant decrease in efficiency, some after only 30,000 miles. This is consistent with other studies on aged catalytic converters from gasoline vehicles.

A paper entitled "Laboratory Evaluation of Field-Aged Catalytic Converters from Natural Gas Vehicles" was written and presented at the 89th Annual Meeting and Exhibition of the Air & Waste Management Association in June 1996.

2.5 Catalyst Brick Temperature Measurement

In a technological first, a laser-fluorescence thermometry technique was employed to measure in-situ the temperature of a catalyst brick in a converter during engine operation. The technique involves the pulsed activation of a thin layer of a chemically stable, rare-earth-doped phosphor material that exhibits a strong fluorescence behavior with absolute temperature. The surface painted phosphor is activated by using a laser system which produces nanosecond-duration pulses in a variety of ultraviolet (UV) wavelengths. A calibration curve is generated for the phosphor by recording the characteristic decay of fluorescent emission bands during its activation by pulsed UV wavelengths as a function of absolute temperature. A measure of component surface temperature is obtained from the calibration curve by measuring the decay time of fluorescence intensity of the phosphor at the surface. This laser-induced fluorescence of thermographic phosphors provides a technique for making remote, non-contact temperature measurements of objects without interference from background thermal radiation or surface emissivity.

A small portion (~4 mm) of a natural gas catalytic converter brick was coated with a phosphor material. The converter was coupled to the natural gas engine test stand where steady state and transient temperature tests were made at various engine loads. The phosphor temperature data was checked against thermocouple data obtained at the same brick location. It was found that phosphor temperature data agreed within 0.5-1% of the thermocouple data.

3. Project 3 - Control of Engine-Out Emissions by In-Cylinder Catalysts and Thermal Barriers

In order to facilitate catalyst selection, temperature measurements were made on a metallic piston bowl surface of a methanol-fueled, single cylinder, direct injected stratified charged (DISC) engine. Surface temperatures ranged from 550 to 650° C. Measurements of engine-out emissions were also made with this piston configuration.

After extended discussions with GM about near and long term goals for this project, it was decided to use a homogeneous-charged Kohler gasoline engine for coating and washcoat durability testing and in-cylinder catalysis evaluation. Aluminum coupons, machined from an aluminum Kohler piston, were plasma sprayed at ORNL with zirconia. Unfortunately, within one month of deposition, some of the coatings had debonded and large regions of the coating had flaked off the coupons. Though similar coatings had remained adherent on steel parts, it was determined that ORNL's plasma spray capability would not be able to produce adherent zirconia coatings on aluminum. Based on this setback, GM recommended that the in-cylinder catalysis study be dropped and that manpower and funding resources for Project 3 be applied to Project 2 efforts. After several discussions, all parties agreed to the program change.

PUBLICATIONS/PRESENTATIONS AT INTERNATIONAL MEETINGS

1. K.L. More, D.W. Coffey, and T.S. Geer, *Microbeam Analysis - 1995* (Proc. 29th Ann. Conf. of Microbeam Analysis Soc., ed. E.S. Etz, VCH Publishers, New York, pp. 137-138 (1995).
2. E.A. Kenik, K.L. More, W. LaBarge, and R. Beckmeyer, *Proc. Microscopy and Microanalysis 1995* (Proc. 53rd Ann. Mtg. Microscopy Soc. of Amer., eds. G.W. Bailey et al., Jones and Begell Publishing, New York, pp. 430-431 (1995).
3. K.L. More, D.W. Coffey, and T.S. Geer, *Proc. Microscopy and Microanalysis 1995* (Proc. 53rd Ann. Mtg. Microscopy Soc. of Amer., eds. G.W. Bailey et al., Jones and Begell Publishing, New York, pp. 412-413 (1995).
4. J.M. Storey, N. Domingo, R.N. McGill, and E.A. Kenik, *Proc. 89th Annual Meeting and Exhibition of the Air & Waste Management Association*, Volume 89, Pittsburgh, PA, pp. 89.04-1-13 (1996).

INVENTIONS

A patent application has been submitted by Delphi in December 1995 which utilized microstructural characterization from this CRADA in support of the application.

SUMMARY OF INDUSTRIAL SUPPORT

Delphi Automotive Systems provided all the starting materials and as-prepared catalytic convertors, performed all the engine dynamometer testing/ageing of the convertors, and performed all conversion efficiency and FTP testing of both the as-prepared and aged convertors. In addition, Delphi Automotive Systems and other General Motors divisions provided both gasoline and natural gas engines and limited hardware for the ORNL engine test stand facility. Delphi also provided technical support and information during the construction and operation of the engine test facility and the bench flow reactor.

BENEFITS TO THE DEPARTMENT OF ENERGY

The work performed at ORNL under this CRADA was funded by the U.S. Department of Energy (DOE), Office of Industrial Technology (OIT), Advanced Industrial Materials (AIM) Division, and the Office of Transportation Technologies (OTT), Alternative Fuel Compatible Materials (AFCM) Program and the Alternative Fuels Utilization Program (AFUP), under contract DE-05-96OR22464 with Lockheed Martin Energy Research Corp. The mission of the AIM Program under OIT is to support development and commercialization of new or improved materials to improve productivity, product quality, and energy efficiency in partnership with industry. The mission of OTT is to work in partnership with the domestic transportation industry, energy supply industry, and research and development organizations to develop and promote user acceptance of advanced transportation vehicles and alternative fuel technologies which will reduce oil import requirements, reduce criteria pollutant emissions and greenhouse gases. By developing a strong transportation technology base, OTT enables the transportation industry to assure strong competition in the domestic and world markets.

This CRADA project has benefitted the aim of DOE Office of Industrial Technology and the Office of Transportation Technologies by collaborating with General Motors, one of the largest U.S. suppliers and end-user of transportation vehicles and emission reduction components. Work under this CRADA has enabled General Motors to better understand catalyst degradation mechanisms and improve their catalyst processing methodology. Facilities, techniques, and expertise developed under this catalyst program are now being utilized in another CRADA program that addresses reduction of NO_x emission for lean burn engine technology, as well as other High Temperature Materials Laboratory collaborations. The current CRADA helps to meet goals of the National Energy Strategy through improved energy efficiency, decreased industrial process waste, and improved competitiveness of U.S. industry.

PLANS FOR THE FUTURE

Delphi Automotive Systems and General Motors will utilize the information and insight on the evolution of catalyst structure developed under this CRADA in their Joint Venture with Allied Signal EC aimed at commercializing advanced catalyst systems.

BUDGET SUMMARY

Project 1 AIM Materials (B&R ED 22 04 00 0)
Budget: FY93 = $300K FY94 = $190K FY95 = $200K FY96 = $200K Total = $890K
Actual: Total = $779K (as of 8/25/96)

Projects 2 and 3
OTT-AFCM (B&R EE 51 02 00 0 and EE 51 06 00 0), OTT-AFUP (B&R EE 50 01 00 0)
Budget: FY93 = $675K FY94 = $375K FY95 = $500K Total = $1,550K

Overall Budget: $2,440K Overall Actual: $2,329K

ACKNOWLEDGEMENT

Successful completion of this CRADA involved significant levels of effort from a relatively large group of participants.

From ORNL, the support, encouragement, and overall management provided by P. A. Angelini, R. L. Graves, R.N. McGill, and P.S. Sklad are gratefully acknowledged. N. Domingo and E. A. Kenik provided overall coordination of the technical aspects of the CRADA, especially communications and planning with the industrial participants. N. Domingo, E. A. Kenik, K. L. More, and J. M. Storey directed and performed for the majority of the CRADA technical research efforts. D. W. Coffey, E. L. Fuller, Jr., D. L. Joslin, S. T. Misture, and B. H. West contributed their specific technical expertise to the CRADA as was needed; including SEM, porosimetry and infrared techniques, EPMA, X-ray diffraction, and testing for the engine test stand and the in-cylinder catalysis project.

From General Motors, the support, encouragement, and overall management provided by L. A. Carol, C. E. Miller, and D. B. Quinn are gratefully acknowledged. R. F. Beckmeyer provided overall coordination of the technical aspects of the CRADA, especially communications, approval of information released from the CRADA, and planning with the ORNL participants. R. F. Beckmeyer, W. LaBarge, and J. R. Theis directed and performed for the majority of the CRADA technical research efforts. W. LaBarge coordinated the preparation and testing our the majority of the convertors provided to ORNL for characterization. D. Monroe (GM NAO RD) and R. Wiltse (GM Power Train) contributed their specific technical expertise and efforts to the CRADA as was needed; information on bench flow reactor construction/operation/testing and providing the natural gas engine and limited hardware for the engine test stand, respectively.

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