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Al_2O_3/CeO_2 Washcoats for Three-Way Automotive Emission Catalysts

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Platinum-rhodium based three-way-catalysts (TWC) are the primary catalytic system for control of hydrocarbon, CO, and NO_x automotive emissions. Mixed Al_2O_3/CeO_2 oxides are often dispersed on a cordierite honeycomb monolith as a washcoat and act as a high-surface-area carrier for the heavy metal catalyst clusters. There are both regulatory and marketplace demands for improved performance, lifetime, cost and reliability of these catalytic convertors. The conversion efficiency and lifetime of a convertor is determined by the microstructure of the washcoat/monolith and its evolution during high temperature exposure to the exhaust gas stream. Scanning electron microscopy (SEM), electron microprobe analysis, and analytical electron microscopy (AEM) were utilized to characterize these catalysts. Some AEM was performed on crushed washcoat specimens dispersed on holey carbon films. In addition, an innovative technique was developed for the preparation of transverse section specimens from the monolith,[1] which preserves the spatial correlation of microstructure and elemental distribution with respect to position in the washcoat/cordierite.

Engine dynamometer tests can simulate the ageing a convertor would experience under different driving conditions and mileage. Test 1 simulates 50,000-100,000 miles, depending on the engine/exhaust system; whereas Test 2 simulate exposure to significant over-temperature relative to Test 2. For a new convertor, maximum temperatures are observed near (within ~25 mm) the inlet surface of the monolith. The maximum monolith temperatures typically measured for Tests 1 and 2 are ~1000°C and ~1150°C. Figure 1a shows the general microstructure of the as-prepared washcoat; ceria particles are distributed inhomogeneously as both clumps and individual particles throughout a γ-alumina matrix. Large clumps of the fine-grained (~10 nm) alumina surrounded by a mixture of fine alumina and ceria indicate insufficient blending of the powders. Figures 1b and 1c show the microstructure of the ceria clumps in washcoats as-prepared and after Test 2 ageing, respectively. There is obvious sintering of the ceria phase in the aged washcoat. Sintering was also evident, though less pronounced, after Test 1 ageing. Figure 2a shows a coarse-grained particle (~1 μm) of alumina from the same Test 2 washcoat. Though regions of fine-grained alumina were found in this specimen, a number of large alumina grains were observed that exhibited low dislocation density and fine embedded ceria particles. Electron diffraction indicated that these grains were α-alumina (e.g., Fig. 2b). Similar large α-alumina grains also were observed in the Test 1 aged washcoat, though less frequently. These observations indicate that phase transformation of the alumina matrix and sintering and grain growth of both the alumina and ceria occurred during dynamometer ageing under Tests 1 and 2. These microstructural changes were confirmed by X-ray diffraction on powder samples scraped from the aged washcoats.

The microstructure of the aged washcoats varies with both position along the monolith and depth in the washcoat. Near the inlet surface of the Test 2 aged monolith, the washcoat near the exhaust gas interface exhibited some sintering and grain growth, though both the alumina and ceria had grain sizes <0.1 μm. However, more grain growth was observed in the washcoat close to the cordierite (Fig. 3), with both alumina and ceria exhibiting grain sizes >0.3 μm. In addition, many ceria particles appeared to wet the alumina grain boundaries and some boundaries exhibited a line of bright contrast (arrowed). High spatial resolution X-ray microanalysis with a <2 nm probe (Fig. 4) indicated a marked segregation of cerium (~16 at.%) to such boundaries along with lesser amounts of both silicon (~8 at.%) and titanium (~4 at.%). The slight cerium level (1.4 at.%) indicated in the matrix arises, at least in part, from the excitation of the ceria by both direct (i.e., hole count) and indirect (secondary excitation) routes. The cordierite is an abundant source of silicon. Titanium is an impurity element in both the cordierite and the alumina matrix. The impurity atoms observed at α-alumina boundaries in the washcoat may have diffused long distances. Interphase boundaries can provide fast-diffusion paths for such impurity atoms. In addition, impurity atoms in the matrix may be swept along with the transformation zone and concentrated at the boundary as the alumina transforms from $\gamma \rightarrow \alpha$. The presence of silicon at the grain boundaries of the washcoat may indicate the presence of a glassy, silica phase at the boundaries at elevated temperatures. Such an intergranular phase could promote rapid atom

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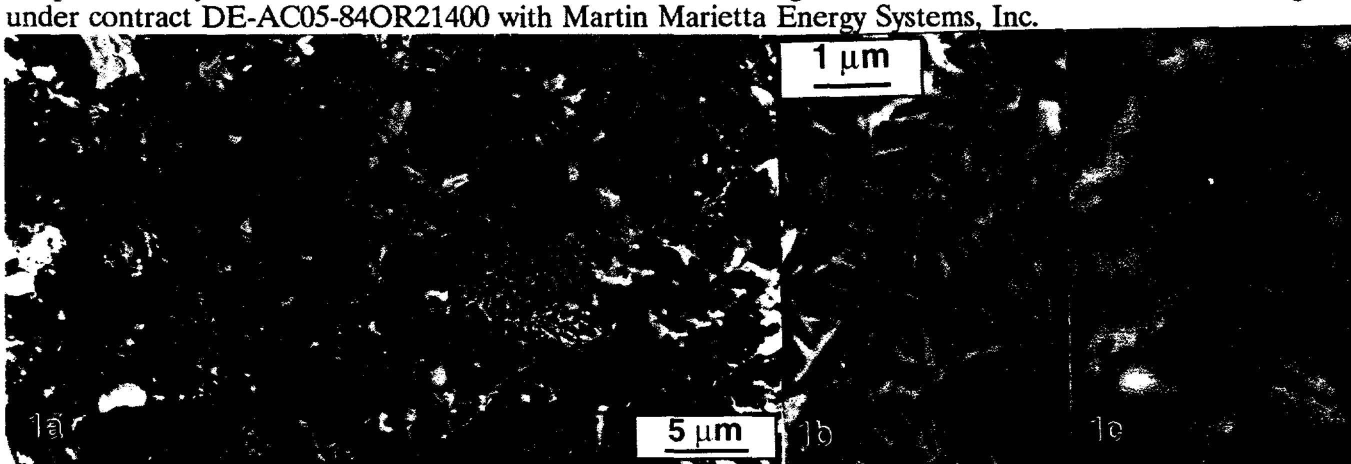
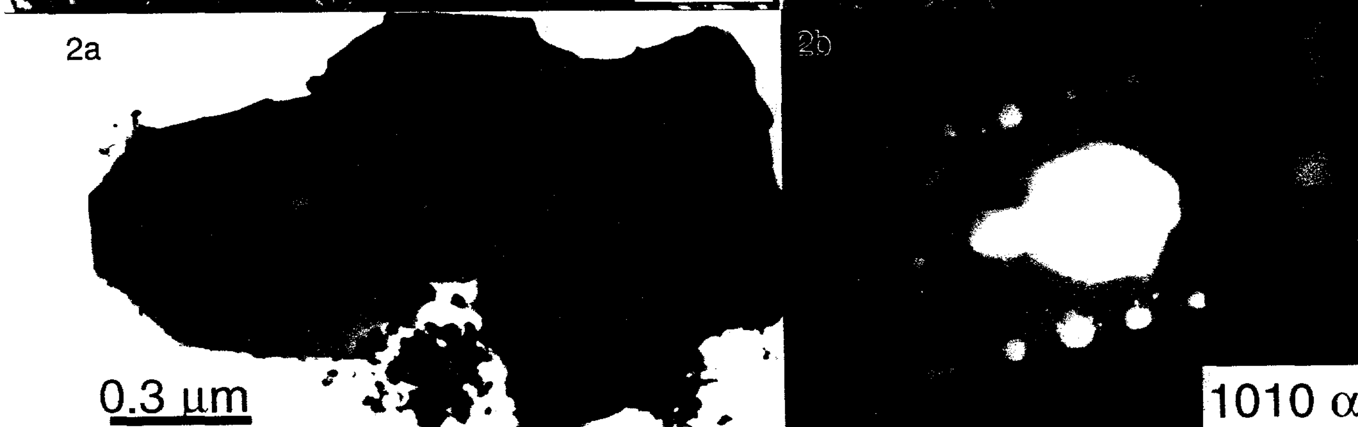
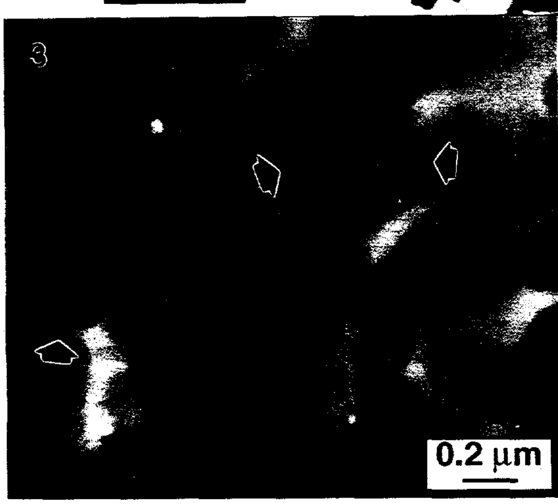
transport between crystalline phases, which in turn would favor sintering and the $\gamma \rightarrow \alpha$ transformation of the alumina matrix.[2]

References

1. K.L. More, T.S. Geer, and D.W. Coffey, submitted to the 29th Microbeam Analysis Society Meeting.
2. Sponsored by the U.S. DOE, Office of Industrial Technologies, Advanced Industrial Materials Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.







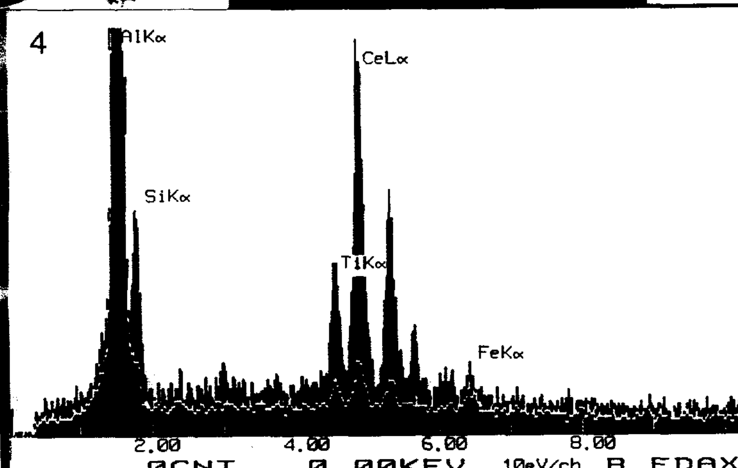


FIG. 1.--SEM micrographs of as-prepared washcoat (a,b) and Test 2 aged washcoat respectively (c).
FIG. 2.--(a) TEM micrograph and (b) convergent beam electron diffraction pattern from large α-alumina particle in Test 2 aged washcoat. FIG. 3.--SEM micrograph of Test 2 aged washcoat near cordierite.
FIG. 4.--EDS spectra for boundary (solid curve) and α-alumina matrix (line curve) of Test 2 aged convertor.

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