catalyst dots on silicon substrates: It was found that the CNTs are easily peeled off the substrates by abrasion or by pulling with adhesive tape and that the CNTs might also be pulled off the substrates by application of strong electric fields.

ALD is a previously developed vapor-phase thin-film-growth technique. The full name of the technique reflects the fact that it is possible to tailor the film thickness to a precision of the order of a single layer of deposited atoms and, thus, to form a highly uniform, conformal coating. ALD differs from conventional chemical vapor deposition, in which material is deposited continually by thermal decomposition of a precursor gas. In ALD, material is deposited one layer of atoms at a time because the deposition process is self-limiting and driven by chemical reactions between the precursor gas and the surface of the substrate or the previously deposited layer. In order to enable growth of the next layer, it is necessary to first effect an activation subprocess that imparts the needed chemical reactivity to the surface. Thus, the thickness of the deposit can be tailored by simply choosing the number of activation/growth cycles.

The use of ALD for coating CNTs to increase adhesion was demonstrated in experiments on specimens comprising multiwalled CNTs grown to lengths of hundreds of microns extending away from 2.5-nm-thick iron catalyst layers on silicon substrates. The CNTs were coated with $Al_2O_3$ by ALD using trimethoxyaluminum and water vapor as precursor gases at a growth temperature of 250 °C. The $Al_2O_3$ was deposited to a thickness of 170 nm in 1,700 activation/growth cycles. Preparation of the specimen surfaces prior to ALD was found to be necessary for the success of the ALD: Specifically, it was found to be necessary to heat the specimens in air at a temperature of 500 °C to increase the density of hydroxyl groups on the substrate and CNT surfaces that enable formation of covalent bonds with the $Al_2O_3$ deposits. In the absence of such preparation, the $Al_2O_3$ deposits separated from the substrate surfaces.

The adhesion strengths of the ALD-coated CNTs were quantified by pull tests using known weights. For example, in the case of one specimen containing an array comprising 5-μm-diameter bundles of CNTs separated by 5-μm gaps, the measured adhesion strength was 1.23 MPa. It should be noted that this measurement sets a lower bound inasmuch as the strength value was calculated by dividing the applied force by the specimen area. After accounting for the fact that the entire specimen area was not covered by CNTs, the adhesion strength was estimated to be >10 MPa.

# Alternating-Composition Layered Ceramic Barrier Coatings

**These coatings are expected to be more durable, relative to prior thermal/environmental barrier coatings.**

*John H. Glenn Research Center, Cleveland, Ohio*

Ceramic thermal and environmental barrier coatings (T/EBCs) that contain multiple layers of alternating chemical composition have been developed as improved means of protecting underlying components of gas-turbine and other heat engines against both corrosive combustion gases and high temperatures. A coating of this type (see figure) is configured using the following layers:

• An outer, or top oxide layer that has a relatively high coefficient of thermal expansion (CTE) and serves primarily to thermally protect the underlying coating layers and the low-CTE ceramic substrate structural material (the component that is ultimately meant to be protected) from damage due to exposure at the high temperatures to be experienced in the application;

• An inner, or bottom silicon-containing/silicate layer, which is in contact with the substrate, has a low CTE and
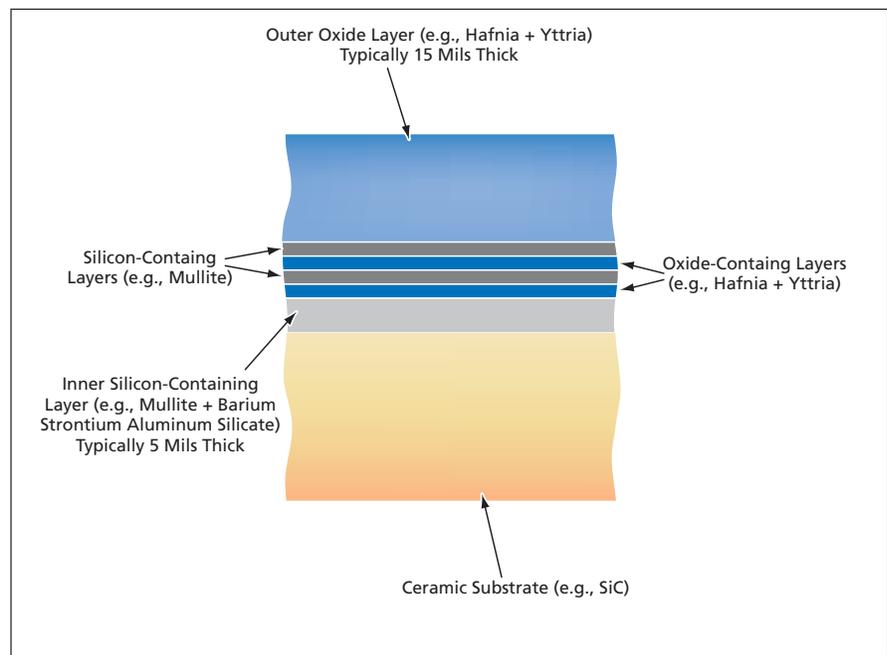


**Alternating-Composition Intermediate Layers** dissipate strain energy arising from the thermal-expansion mismatch between the inner and outer coating layers.

serves primarily to keep environmental gases away from the substrate; and

• Multiple intermediate layers of alternating chemical composition (and, hence, alternating CTE).

The intermediate alternating-composition coating layers are chemically compatible with themselves as well as with the inner and outer coating layers. These intermediate coating layers act as an energy-dissipating interlayer: they dissipate strain energy associated with the CTE mismatch between the inner and outer coating layers, thereby reducing stresses and helping to increase (relative to prior ceramic T/EBCs) coating resistance to cracking and delamination from the substrate surface.

Typically, there are between four and ten alternating-composition intermediate layers, comprising higher-CTE oxide layers interspersed with lower-CTE silicate layers, each layer having a thickness between 5 and 50 µm. The compositions of the oxide and silicate alternating layers can be the same as those of the outer and inner layers, respectively. Alternatively, different oxide and silicate compositions can be chosen to increase tolerance of strain, resistance to cracking, and/or protection against chemical attack by gases in any intended application.

During thermal cycling, the alternating layers become regions of alternating tension and compression. This stress and strain configuration facilitates microsegmentation in the oxide layers while maintaining effective compression in the silicate layers. As a consequence, the thermal expansion of the energy-dissipating interlayer is reduced, stresses are reduced, and tolerance of strain is greatly enhanced. Cracking that starts in the outer oxide layer of the coating is arrested within the alternating layers because of the compressive stress in the silicate alternating layers and the tendency toward deflection and/or bifurcation of cracks at the interfaces between the alternating layers. Moreover, during cooling, the compression in the silicate alternating layers helps to ensure the integrity of the overall coating system in its role as an environmental barrier by helping to prevent penetration of combustion gases to the surface of the substrate.

The thickness of the alternating oxide and silicate layers are quite dependent on the intended engine application. A thicker-silicate-layer/thinner-oxide-layer structure could increase the strain tolerance of the coating and protect the substrate (or engine component in application) from the hot gases in the engine environment; however, on the other hand, a slightly thinner silicate-layer next to a slightly thicker oxide-layer structure could increase the coating's resistance to stress and penetration of any damaging gas-constituents through cracks, potentially reacting with the substrate.