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Stable Substoichiometric Cerium Oxide Formed in an Air Plasma

Abstract. *Cerium dioxide was reduced to a stable, substoichiometric monophase in an air plasma. This phase has been identified as* $CeO_{1.94}$ *by thermal gravimetric analysis. The existence of a stable, reduced phase of cerium oxide can be explained by interpretation of both theoretical and experimentally determined crystal data.*

Cerium dioxide, CeO_2, with a melting point of 2750°C, has attractive properties as a high-temperature refractory. It is stable in air but reduces to Ce_2O_3 when heated in reducing atmospheres for prolonged periods (*1*). The reduction of CeO_2 with hydrogen occurs appreciably at temperatures above 500°C (*2*).

Ceria and oxides of many other heavy metals can be reduced to oxygen-deficient compounds by heating them in inert or reducing atmospheres. For example, CeO_2 is reduced to numerous substoichiometric forms by heating in a vacuum at elevated temperatures (*3*); ZrO_2 is reduced to $ZrO_{1.96}$ by heating at 900°C at 10^{-3} torr for 1 hour (*4*); and ZrO_2 microspheres which are deficient in oxygen may be prepared in an argon plasma (*5*).

Stoichiometric CeO_2 particles were spheroidized by an inductively coupled plasma torch sustained by a 50-, 25-, and 10-kw induction heater modified to operate between 5 and 7 Mc/sec. The plasma gas employed with the 50-kw and 25-kw torches was air or O_2; the mixtures in the 10-kw system consisted of 50 percent Ar and 50 percent air or 50 percent Ar and 50 percent O_2. The operation of these plasma torches and the mechanism used to feed particles into the plasma has been described (*6*). Blue-black microspheres were obtained in the high-powered plasma systems but only ivory-colored microspheres were obtained in the 10-kw system. The spheroidized product was collected in air at room temperature.

Thermal gravimetric analyses from ambient to 1000°C were performed on representative samples of each of the cerium dioxide products. No weight increase was obtained on the ivory-colored microspheres. In duplicate samples a weight increase corresponding to an initial formula of $CeO_{1.940 \pm 0.005}$ was obtained on the blue-black microspheres. The $CeO_{1.940}$ can be oxidized by heating in air at 500°C for several hours; ivory-colored CeO_2 microspheres are produced.

Ceramographic cross sections of $CeO_{1.940}$ microspheres were optically examined at 200-power magnification. This examination showed that a homogeneous monophase was present.

X-ray diffraction powder patterns of the blue-black microspheres indicate a single face-centered cubic phase with the fluorite structure having a lattice constant of 5.4098 ± 0.0007 Å. The ivory-colored microspheres, whether from the original material or from oxidation of the blue-black microspheres, show this same face-centered cubic monophase with a lattice parameter of 5.404 ± 0.005 Å. These parameters were refined by the least-squares method (*7*) and the errors are given as standard deviations.

From x-ray diffraction studies on samples which varied between $CeO_{2.00}$ and $CeO_{1.82}$ in overall stoichiometry and which were variously quenched from 800° to 1200°C, Bevan (*3, 8*) found evidence of a face-centered cubic phase that had an unchanging lattice parameter (from a statistical viewpoint) down to an overall composition of $CeO_{1.83}$. The exact composition of this cubic phase is uncertain according to Bevan's data.

Our studies indicate that stable, monophase $CeO_{1.94}$ microspheres can be produced in an induction-coupled plasma torch under oxidizing conditions and that these microspheres will retain their nonstoichiometric nature even at 250°C. [Oxygen-deficient CeO_2 prepared in an inert or reducing atmosphere or in a vacuum contained, in general, two phases (*3*).] The absence of the $CeO_{1.94}$ prepared in the 10-kw plasma system indicates that the reduction is energy-dependent.

This detectable change of stoichiometry (CeO_2 to $CeO_{1.94}$) in the 25- and 50-kw system without notable modification of the fluorite structure or even significant alteration in lattice parameter is crystallographically favorable because the radius ratio of Ce^{4+} to O^{2-} [1.01 and 1.40 Å, respectively (*9*)] is below the ideal minimum for spherical ion contact of 0.73. Apparently, the gain from relief of anion-anion overlap by in-site reduction of a portion of Ce^{4+} ions to form larger Ce^{3+} ions (radius, 1.11 Å) and the concurrent oxidation of equivalent O^{2-} ions so nearly offsets the unfavorable energetics of Ce^{3+} relative to Ce^{4+} that in the higher-powered plasma environments, at least, a relatively stable, metastable, substoichiometric product can be obtained.

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Cholesterol: Treadmill Activity Accelerates Oxidation in Rats

Abstract. *Cholesterol-26-*^{14}C *was injected intravenously into male and female rats of two different strains. Recovery of radioactivity from the expired air was increased by treadmill activity.*

When cholesterol-26-^{14}C is injected intravenously into rats, 30 percent of the radioactivity can be recovered as $^{14}CO_2$ in the expired air within the first 24 hours (*1*). Oxidation of the side chain of cholesterol, similarly demonstrated in man (*2*), is implicated in the synthesis of bile acids (*3*), which play an important role in the elimination of cholesterol from the body (*4*). We have demonstrated that treadmill activity increases the rate of oxidation of cholesterol in rats.

Male and female rats of the Sprague-Dawley and Wistar strains were used. One milliliter of 0.9-percent solution of NaCl was added to 100 μl of methanol containing 1 mg of Tween-80 (Atlas