This, however, would interfere with deposit accumulation on the cathode. Coating weight of nickel hydroxide was reported (13) to be unaffected by moderate agitation of the concentrated solution. In this regard, coating weight is expected to be influenced when low-concentration solutions and severe stirring conditions are used.

The time pattern of the pH level of the solution is shown in Fig. 8. Below 40 mA/cm<sup>2</sup>, the pH varied little, but at higher c.d.'s significant decreases were observed already from the outset. It should be mentioned that the pH was measured in the bulk of the unstirred solution; local readings at the cathode may show an increase in pH due to the OH<sup>-</sup> ions. The explanation may be that the pH as measured was governed by the H<sup>+</sup> ions generated at the anode, since the OH<sup>-</sup> ions formed at the cathode were used up in deposit formation without contributing to the resultant pH of the bulk solution.

The present work demonstrated the potentialities of the electrolytic method for producing ZrO<sub>2</sub> coatings, with relatively easy control of their thickness. However, it is necessary to control the drying stage in order to achieve sound and crack-free coatings. Optimal conditions for the formation of ZrO<sub>2</sub> coatings are low current densities and short coating times, in view of the nonconductive nature of this oxide.

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# Electrolytic ZrO<sub>2</sub> Coatings

## II. Microstructural Aspects

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#### ABSTRACT

Zirconia coatings were formed on graphite and titanium substrates by electrodeposition. The as-deposited coatings were amorphous and cracked during the drying stage. Sintering of the coatings on the graphite substrates caused crystallization, with formation of a variety of mixtures of the tetragonal and monoclinic ZrO<sub>2</sub> polymorphs having nanosize crystallites. Oxidation of the Ti substrate and reaction with zirconia during the heat-treatment resulted in addition to a microstructure resembling ceramic composite coatings.

Ceramic functional coatings on metallic and ceramic substrates are currently under extensive investigations. An electrochemical route based on an electrophoretic process has been applied largely for ceramic coatings (1-4). Since this technique makes use of a ceramic powder suspension, the final microstructure of the coating is strongly influenced by the powder characteristics. The thin-film Sol-Gel technique (5) and electrolytic deposition of ceramic coatings directly from an aqueous solution, developed recently (6-10), enable control of coating composition and microstructure through the chemical, electrochemical, and firing process parameters.

The present paper deals with microstructural evolution of the electrolytically formed zirconia coatings on two types of substrates: graphite and titanium. Although from the technological point of view these substrates were considered to be equally important, their chemical reactions with the zirconia coating are expected to differ significantly, and thus evolve various microstructures within the fired coating.

### **Experimental Procedure**

The details of the substrate materials, chemical solution, and the electrochemical coating parameters were described in Part I of this series (11).

The deposits formed on the substrates were dried in air at room temperature. Firing was carried out at 400 and 600°C in air, and at 900°C in argon for 1 h for the graphite substrates. The coated titanium substrates were fired at 780°C for 1 h in air.

The microstructure and composition of the zirconia coatings were characterized after the different stages of the process, using optical and scanning electron microscopy (SEM) (Model JSM-840), equipped with energy-dispersive spectroscopy (EDS). The phase content and the crystallite size were determined by x-ray diffraction (XRD) with a diffractometer (Model PW-1820) operated at 40 kV and 40 mA, using monochromatized Cu k-alpha radiation, at a scanning speed of 0.4 [degree/min].

#### **Results and Discussion**

The as-deposited coatings appeared as a transparent viscous fluid, especially at high current densities and long coating durations, where thick deposits were visually observable. In situ microscopical observations showed development of cracks within the coating layer on graphite during the drying process. The wet deposit contained many bubbles. During drying some of the bubbles coalesced to form larger ones, while others were expelled from the deposit and migrated to its surface. The bubbles

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Fig. 1. SEM images of dried zirconia coatings on graphite resemble a "cracked-mud" morphology both for (a) thin coating (25 mA/cm<sup>2</sup> for 15 min) and (b) thick coating (25 mA/cm<sup>2</sup> for 75 min). Thick coatings are often composed of two layers. (c) Cross section shows penetration of the coating into pores of the graphite.

resulting from the drying process were observed only for graphite substrates and presumably result from entrapped gases within pores, which are not present in Ti substrates. During the drying process discontinuities formed within the coating, which became deep cracks toward the end of the process. The resultant coating layer had a "crackedmud" appearance (as shown in Fig. 1 and 2), irrespective of the substrate material. In both systems, the nonuniform contraction of the wet coating was attributed to these surface microcracks.

The coating weight and thus its thickness was found to increase with increase (up to certain values) of the current density and the coating duration. Thicker coatings showed larger islands in the cracked-mud morphology.

Thick coatings (over  $\sim 20 \ \mu m$ ) on the graphite substrates often consisted of two layers, the upper layer being thicker and composed of coarser islands (Fig. 1b). These layers are believed to form during different stages of the coating pro-



Fig. 2. SEM images of dried zirconia coatings on Ti showing the "cracked-mud" morphology. This featureless surface morphology is characteristic of the amorphous nature of the coating. (b) At higher magnifications, no drying pools are visible in coatings on Ti.

cess, as discussed in Ref. (11). SEM observation of the coating cross sections have clearly shown the coating build-up at the surface porosity (Fig. 1c).

X-ray diffraction patterns of the dry as-deposited coatings and of the fired coatings are shown in Fig. 3 and 4 for the graphite and titanium substrates, respectively. The coating layers before firing have the typical pattern of



Fig. 3. X-ray diffraction pattern of zirconia coatings on graphite. (a) Amorphous-type broadened peak from the as-deposited coating and the sharp peak from the graphite (gr) substrate. (b) Reflections from the tetragonal (t) and monoclinic (m) polymorphs are characteristic of the  $ZrO_2$  coatings, sintered at 600°C for 1 h.



Fig. 4. X-ray diffraction pattern of zirconia coatings on Ti. (a) Absence of sharp reflections from a deposited coating indicates on its amorphous nature. (b) Typical reflections from alpha-Ti,  $TiO_2$  (rutile-R),  $ZrO_2$  (tetragonal-t and monoclinic-m) and various zirconium titanates (ZT) are seen for coatings sintered at 780°C for 1 h.

amorphous zirconia, in which a broadened amorphoustype peak appears around the angle  $2\theta \sim 30$  degrees (Fig. 3a and 4a), irrespective of the substrate material. This finding is consistent with the relatively smooth and featureless morphology of the as-deposited coating surfaces (Fig. 1 and 2).

Firing induced a different phase evolution and morphology in these substrate/coating systems as was expected, and the resulting fired coatings were opaque. The microstructure of the coating on the graphite substrate was characterized by fine equiaxed submicron particles (Fig. 5). These particles were identified as a mixture of tetragonal (t) and monoclinic (m) polymorphs of zirconia (Fig. 3b), based on the  $\{111\}$  and  $\{400\}$ -type reflections. The line broadening of the {111}-type reflections was used to calculate the crystallite size of the polymorphs with the aid of the Scherrer equation (12), assuming no strain effects due to the substrates. (This assumption was based on the similar line broadenings in XRD, which have resulted from the same zirconia coating before and after spallation from the graphite substrates.) The volume fractions of the two phases (t and m) were determined through the "polymorph" equation as corrected by Porter and Heuer (13).

The crystallite size was found to be 2 and 12 nm for the 400 and 600°C treatments, respectively, with the polymorphs indistinguishable. By contrast, treatment at 900°C for 1 h in argon resulted in crystallite sizes of 25 and 20 nm for the tetragonal and monoclinic phases, with volume fractions of 15 and 85%, respectively. These size data indicate that the SEM image (Fig. 5) represents zirconia aggregates.

Firing of the zirconia coatings on graphite substrates at the various temperatures led only to crystallization of the amorphous coating. According to the Ellingham diagram (14), graphite oxidizes under the present firing conditions to form CO gas, but no reaction with the zirconia is expected to occur. Formation of undoped zirconia via solution by different techniques and crystallization of the lowtemperature polymorphs of zirconia by firing at the relatively low temperature are well documented in the literature (15-17). The presence of the t polymorph is related primarily to the crystallite size effect (18, 19), by which the tetragonal phase may be retained metastably at room temperature. The crystallite sizes of the tetragonal phase pres-



Fig. 5. SEM image of sintered (600°C/1 h) zirconia coating on graphite. The submicron particles represent aggregates constituting a mixture of tetragonal and monoclinic polymorphs of zirconia.

ent within the coating (12-25 nm) matched well with the reported particle sizes for similar calcination treatments (14-28 nm) (16), the range within which this polymorph exists.

The zirconia coating on the Ti substrates exhibited a totally different inner microstructure after firing. Oxidation of the metallic titanium during firing resulted in the original spaces between the cracks in the coating layer being filled by the growing titanium oxide (Fig. 6). Microchemical EDS analyses of the various features of the coating (see Table I), and elemental mapping for Ti (Fig. 6d) confirmed the Ti-rich nature of the polycrystalline phase between the zirconia islands. An appropriate x-ray diffraction pattern from this specimen (Fig. 4b) contained reflections of TiO<sub>2</sub> in the form of rutile, ZrO<sub>2</sub> with the tetragonal and monoclinic phases, and additional reflections coincident with those of the  $Zr_{0.5}Ti_{0.5}O_{0.19}$ ,  $Zr_{0.72}Ti_{0.28}O_{0.28}$ , and  $Zr_{0.5}Ti_{0.5}O_{0.33}$  hexagonal phases (20). In this case at a firing temperature of 780°C, stable titanium oxide grows due to oxidation of a parabolic type (21, 22). Furthermore, oxidation of Ti at this temperature occurs mainly by diffusion of Ti rather than that of oxygen through the growing oxide layer, a circumstance which favors formation of the low-oxygen titanium zirconate phases. The volume fractions of the tetragonal and monoclinic phases in these coatings were calculated to be 37 and 63%, and their crystallite sizes 26 and 25 nm, respectively.

Although the pH of the mother solution was intentionally adjusted for work in the cathodic regime, it also affects the relative stability of the zirconia polymorphs. In this regard, the ratio of the t/m phase content after calcination at 400-600°C was reported (23) to increase at pH values above 10 and below 6 for the zirconyl nitrate solution from which the zirconia gel was precipitated. Again,

Table I. EDS composition results for ceramic coating on Ti substrates.<sup>a</sup>

Microstructural feature	Chemical composition (mole percent)		
	Zr	Ti	$\operatorname{Remarks}^{\mathrm{b}}$
Zirconia island center (reacted regions)	48.0 59.0 65.0 69.0 76.0	$52.0 \\ 41.0 \\ 35.0 \\ 31.0 \\ 24.0$	Pl in Fig. 6e
Zirconia island periphery (nonreacted regions)	73.0 85.0 87.0	$27.0 \\ 15.0 \\ 13.0$	P2 in Fig. 6e
Oxidized regions between zirconia islands	9.0 0.0 0.0	91.0 100.0 100.0	P3 in Fig. 6e

<sup>a</sup> Fired at 780°C for 1 h in air.

<sup>b</sup> Examples for the analyzed regions.

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Fig. 6. SEM images of sintered zirconia coatings on Ti, showing formation of  $TiO_2$  at the cracks between the zirconia islands. (a) At low and (b) higher magnifications, the topography of the machining grooves is visible. (c) At the bottom of grooves "BG," the  $TiO_2$  crystals grew only between the zirconia islands. (d) Ti elemental mapping of (c). (e) At the top of grooves "TG,"  $TiO_2$  crystals grow and bury the zirconia islands (see text for further details).

where comparison is possible, the measured *t* crystallite size (26 nm) and the *t/m* phase ratio (37/63) have showed good match to the reported values [22 nm and 40/60, respectively (24)] in a similar solution (pH ~ 3.0) and calcination condition (850°C). The effect of pH on stabilization of the zirconia polymorphs was speculated to be both by replacement of the incorporated anions by either OH<sup>-</sup> or O<sup>-2</sup>, and pH-dependent transformations of hydroxyl ligands to bridging hydroxyl groups to bridging oxide ions (17).

The surface microstructure of the coating layer on Ti substrates was dependent on the coating thickness prior to firing. At locations with greater coating thicknesses (*i.e.*, at the bottom of the machining grooves), titanium oxide growth was confined to the gaps between the zirconia islands (Fig. 6c). However, at locations with smaller coating thicknesses (*i.e.*, top of the machining grooves), the oxide grew to the extent that it partially buried the zirconia islands (Fig. 6e). In both cases, the centers of the islands appeared to have reacted with the titanium substrate (see also Fig. 9), and were most probably converted into the titanium zirconate phases. EDS results from such regions (Table I) have revealed compositions similar to those of titanium zirconate phases, which were identified by XRD (Fig. 4b). Thus, direct oxidation of the crack surfaces together with crystallization and chemical reaction of the coating with the metallic matrix at the island/substrate in-



Fig. 7. SEM image showing the line traces of the zirconia island contours prior to (single arrows) and after sintering, from which the sintering shrinkage may be deduced.



Fig. 8. SEM image of the scratch trace, showing high density of microcracks at the smeared regions, perpendicular to the scratch direction.



Fig. 9. SEM images showing: (a) Typical coating cross section where fine TiO<sub>2</sub> crystals grew around the zirconia islands, accompanied by shrinkage and bending. (b) Debonding at the coating/substrate interface results in dimpled fracture surfaces.

terfaces, form the composite morphology of the zirconia islands embedded in the TiO<sub>2</sub> matrix.

In many cases, traces parallel to the periphery of the zirconia islands were observed on the titanium oxide layer, as shown by the single arrows in Fig. 7. [These traces could be identified as the original contours of the zirconia islands prior to firing, since some broken pieces from the edges of the original islands were buried and left at these locations (double arrows in Fig. 7).] By this means, the firing shrinkage of the coating was estimated to be of the order of  $\sim$ 20%, assuming a similar percent shrinkage for the third dimension of the coating thickness.

The diamond Vickers microhardness of the coating on the Ti substrates has an average value of 520 kg/mm<sup>2</sup>. Scratches were applied manually to the coating surface with a diamond indentor in order to qualitatively characterize the adherence and brittleness of the composite coating layer. A typical trace of one of these scratches is shown in Fig. 8; it exhibits a high density of microcracks perpendicular to the scratch direction. The presence of these microcracks in the smeared region indicates heavy deformation of the material by the indentor. Moreover, some regions of the coating near the scratch trace were debonded from the substrate (Fig. 9). This debonding occurred by crack propagation either through the coating or at the substrate/coating interface. In the latter case, the fractured surface was composed of very fine dimples, indicating some ductility at the interface.

Finally, the qualitative scratch test of the coating and its debonding behavior indicate relatively good adhesion to the Ti substrate. In this regard, the chemical reactions between substrate, coating, and atmosphere determine the microstructural evolution within the coating. The characteristic microstructure which resulted from these reactions is similar to those of transformation toughened zirconia composites, and may be considered for design of wear-resistant, oxidation-resistant and thermal barrier coating applications.

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