Densification and Grain Growth for Powder-Derived Ta$_2$O$_5$–TiO$_2$ Ceramics

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Thermal processing of powder-derived Ta$_2$O$_5$-based ceramics reveals that rapid grain growth associated with a high temperature phase transformation hinders densification, necessitating the development of a reduced-temperature processing methodology. Data are reported for the densification behavior with emphasis on microstructural changes associated with the phase transformation between a stable low-temperature phase (L-Ta$_2$O$_5$) and a phase which is stable at high temperatures (H-Ta$_2$O$_5$). The H-Ta$_2$O$_5$ phase is metastable at room temperature and reverts back to the L-Ta$_2$O$_5$ phase with thermal or mechanical treatment. TiO$_2$ additions stabilize the H-Ta$_2$O$_5$ phase and result in enhanced dielectric properties. Because TiO$_2$ additions decrease the temperature of the densification-hindering phase transformation, an alternate reduced-temperature processing route is necessary. A simple solution-coated powder method was used to produce the first-ever dense and chemically homogeneous TiO$_2$-modified Ta$_2$O$_5$ ceramics in both the L- and H-Ta$_2$O$_5$ forms. Thus, this work represents the first comprehensive study of the effects of composition and the L$\Rightarrow$H-Ta$_2$O$_5$ phase transformation on microstructural development. The results indicate that the effect of TiO$_2$ additions on the sintering behavior of Ta$_2$O$_5$ ceramics was largely limited to a reduction in the temperature for the densification-hindering phase transformation.

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1. Introduction

Interest in tantalum pentoxide (Ta$_2$O$_5$) has been driven by dielectric applications. For example, electrolytic capacitors based on Ta$_2$O$_5$ have been available for nearly 60 years, and the past decade has seen the integration of Ta$_2$O$_5$ into dynamic random access memory (DRAM) technology. Published results have suggested that Ta$_2$O$_5$ might also be used as a piezoelectric. In addition, Ta$_2$O$_5$ has been studied as a possible electrolyte for solid oxide fuel cells (SOFCs) and is also a strong candidate for thermal and environmental barrier coatings (TBCs and EBCs).

In spite of such widespread interest, further development of Ta$_2$O$_5$-based ceramics is hindered by a lack of a basic understanding of the structure-processing-property relationships. Of particular concern is a phase transformation that occurs at 1360°C ± 10°C upon heating unmodified Ta$_2$O$_5$ (and at lower temperatures in the presence of certain additives), transforming the material from an orthorhombic (L-Ta$_2$O$_5$) structure to an apparently monoclinic structure (H-Ta$_2$O$_5$). Unusual microstructural changes associated with this transformation often lead to severe cracking of specimens, and must be controlled if, for example, these ceramics are to be used as high temperature barrier coatings, or if applications are to take advantage of the enhanced dielectric properties of the high-temperature phase stabilized at room temperature.

Surprisingly, little has been reported on the powder processing of Ta$_2$O$_5$ ceramics. Heintz et al. showed that grain growth in L-Ta$_2$O$_5$ obeyed normal Arrhenius-type behavior, controlled by grain boundary diffusion at temperatures $\leq$ 1200°C and lattice diffusion at higher temperatures. The rate of grain growth was found to be controlled by the curvature of the grains, and was uninhibited by the presence of porosity. No mention was made of the L$\Rightarrow$H-Ta$_2$O$_5$ transformation. Moldovan et al. reported on thick Ta$_2$O$_5$ films for EBCs deposited by a thermal-spray method. The films were a mixture of H- and L-Ta$_2$O$_5$ phases when initially deposited, but appeared to be single-phase L-Ta$_2$O$_5$ after annealing for 72 h at 1200°C. They also noted that grain growth in dense L-Ta$_2$O$_5$ proceeded normally, though at a relatively slow rate. Wu et al. reported that pellets of pure Ta$_2$O$_5$ transformed into H-Ta$_2$O$_5$ when sintered at 1400°C for 5 h, then crumbled upon cooling. Addition of 2–4 mol% Al$_2$O$_3$ improved mechanical integrity but presented densification difficulties. Higher dopant levels (~12%) resulted in the precipitation of a second phase (AlTaO$_4$) and enabled production of dense specimens.

Earlier work on the electrical properties of doped H-Ta$_2$O$_5$ ceramics used traditional mixed-oxide processing and produced porous specimens. Early studies on defect compensation by Kofstad and coworkers, and Tuller and coworkers, commented on difficulties in densifying doped Ta$_2$O$_5$, and showed that a wide range of dopant cations, including Ti$^{4+}$, had minimal effect on the electrical properties of Ta$_2$O$_5$, suggesting a structural rather than a vacancy defect compensation mechanism. Pavlovic, Cava et al., and Wang et al. all reported relative densities of ~85–90% for specimens heated directly to sintering temperatures of ~1400°C, but none commented on the microstructures of their ceramics. Cava et al. were the first to show enhanced dielectric properties for TiO$_2$-modified Ta$_2$O$_5$ ceramics, reporting a dielectric constant ($K$) of 128 for a porous 92Ta$_2$O$_5$–8TiO$_2$ (92-8) specimen. Guo et al. followed with a study on 92-8 ceramics, producing >90% dense specimens with $K$ values as high as 230, and reporting unusual microstructures with large and oriented grains for specimens sintered at 1600°C. Ji et al. showed that undoped H-Ta$_2$O$_5$ (H-100) specimens treated by a CO$_2$ laser had microstructures similar to those of Guo et al. with dielectric constant ($K$) values >70, approximately twice that of annealed specimens prior to laser treatment.

Thus, previous studies have experienced difficulty in producing dense Ta$_2$O$_5$-based ceramics when sintered at temperatures above the L$\Rightarrow$H-Ta$_2$O$_5$ phase transformation, but observed normal grain growth and densification below the phase transformation temperature. In addition, published
microstructures of ceramics prepared above the $L \Rightarrow H$-Ta$_2$O$_5$ transformation are similar and unusual, exhibiting plate-like grains with a significant amount of trapped porosity. Our current work, reported here, reveals that the $L \Rightarrow H$-Ta$_2$O$_5$ phase transformation is accompanied by a drastic change in microstructure that traps porosity and halts densification. Thus, in order to produce dense specimens of H-Ta$_2$O$_5$, full densification must occur prior to the phase transformation. Since TiO$_2$ additions decrease the temperature of the $L \Rightarrow H$-Ta$_2$O$_5$ phase transformation, the coated powder method used here is the only approach yet demonstrated to achieve full densification of 8TiO$_2$/92Ta$_2$O$_5$ specimens in either the L- or H-Ta$_2$O$_5$ phase.

2. Experimental procedures

Particle sizes of as-received H. C. Starck Ta$_2$O$_5$ and Aldrich TiO$_2$ powders were ~50–100 nm and 100–200 nm, respectively, as determined by dynamic light scattering (Zetasizer 3000HS, Malvern Instruments) and verified by scanning electron microscopy (SEM, Hitachi S-4700 and JEOL 6060LV) and transmission electron microscopy (TEM, JEOL 4000EX and JEOL 2010F). For standard mixed oxide processing of the 92-8 composition, a stoichiometric mixture of Ta$_2$O$_5$ and TiO$_2$ was calcined twice at 1100°C for 12 h, with each calcination followed by ball milling in methanol for 6 h using stabilized ZrO$_2$ media. The calcined powders were identified to be single phase L-Ta$_2$O$_5$ by X-ray diffraction (XRD, Rigaku D-Max, CuK$_\alpha$ radiation) with a broad distribution of particle sizes ranging from ~500–900 nm. A coated powder method which we reported previously was also used to fabricate specimens with the 92-8 composition.\textsuperscript{22} Titanium (IV) isopropoxide ($\text{Ti}($ $\text{OPr})_4$, Aldrich) was first chelated with glacial acetic acid ($\text{CH}_3\text{COOH}$), then diluted with methanol ($\text{CH}_3\text{OH}$). A stoichiometric amount of Ta$_2$O$_5$ powder was then added to the solution and stirred vigorously. After several hours, distilled H$_2$O was introduced drop wise into the alcohol solution to hydrolyze the Ti-species, followed by further stirring and then drying at 140°C. The chemical compositions of both coated and calcined powders were verified by inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer OES Optima 2000DV).

Pellet specimens of both unmodified (100Ta$_2$O$_5$) and 92-8 powders were prepared by uniaxial compaction. Pressed pellets were surrounded by powders of their own composition in covered Al$_2$O$_3$ crucibles and heated at 5°C/min to a predetermined sintering temperature at which they were held for 24 h, before cooling in the furnace with a maximum rate of 5°C/min. Consistent with early work by Waring and Roth,\textsuperscript{23} differential thermal analysis (DTA, Netzsch STA 409) showed that the temperature of the $L \Rightarrow H$-Ta$_2$O$_5$ phase transformation was lowered by ~200°C through the addition of 8% TiO$_2$, so two sintering temperatures were chosen for direct comparison of the densification and grain growth behaviors: one below (1150°C) and one above (1400°C) the phase transformation temperature for both compositions.

3. Results

Specimens of 100Ta$_2$O$_5$ held at 1150°C for 24 h remained in the L-Ta$_2$O$_5$ phase and sintered to near theoretical density with an average grain size of ~2–3 $\mu$m. Mixed oxide 8-28 pellets held at 1150°C for 24 h remained in the L-Ta$_2$O$_5$ phase but sintered to only ~85–90% relative density, which increased only slightly—~92%—for specimens sintered for one week. The sintered microstructures of specimens prepared from coated 92-8 powder and heated to 1150°C for 24 h were indistinguishable from specimens prepared from unmodified Ta$_2$O$_5$ under the same conditions; doped specimens were >98% dense with an average grain size of ~2–3 $\mu$m (Fig. 1). There was no evidence of Ti localization at the grain boundaries of sintered L-92-8 specimens as examined by SEM and TEM EDS. Incomplete densification in mixed oxide 92-8 specimens was attributed to the larger particle size for the calcined powder.

Specimens of each composition heated directly to 1400°C and held for 24 h transformed into the H-Ta$_2$O$_5$ phase and were relatively porous (~90–93% dense for unmodified or coated-powder-derived specimens, and ~85–90% dense for mixed-oxide specimens, Fig. 2). An accurate determination of grain size was not possible for H-Ta$_2$O$_5$ specimens, as distinct grain boundaries were not observed. Fracture surfaces under low magnification revealed large regions of homogeneous orientation of features similar to those reported by Guo et al. and Ji et al.\textsuperscript{19–21}

100Ta$_2$O$_5$ powders heated to $\leq 1330°C$ remained in the L-Ta$_2$O$_5$ phase according to XRD, while those heated to 1400°C were in the H-Ta$_2$O$_5$ structure after cooling. The reversibility of the H-Ta$_2$O$_5$ transformation was confirmed by extended annealing of H-Ta$_2$O$_5$ powders at temperatures
below the L⇒H-Ta₂O₅ phase transformation temperature, resulting in H⇒L-Ta₂O₅ reversion. In addition, powders that were in the metastable H-Ta₂O₅ phase at room temperature and were then crushed were observed to gradually revert to the L-Ta₂O₅ phase. Thus, both thermal and mechanical treatments aided the H⇒L-Ta₂O₅ phase reversion (Fig. 3). Further phase transformation studies were therefore carried out on uncrushed powders and sintered specimens rather than crushed powders. Similar results were observed for 92-8 powders, though longer annealing and/or crushing times were required to revert TiO₂-modified materials, supporting earlier reports of TiO₂-stabilization for H-Ta₂O₅.

Powders transformed into H-Ta₂O₅ consisted almost entirely of large (≥ 5 μm) and porous hard agglomerates, making densification of specimens prepared from such powders impossible. Because such powders reverted to the L-Ta₂O₅ phase when crushed, transformation-induced grain growth occurred again upon heating. Thus, sintering pre-transformed powders offered no advantage over sintering as-received powders.

In order to better understand the microstructural evolution during the L⇒H-Ta₂O₅ transformation, unmodified specimens were first densified at 1300°C, then heated further for various times at temperatures at and above the phase transformation temperature. Full transformation into the H-Ta₂O₅ phase was complete after 12 h at 1400°C, with specimens heated for lesser times exhibiting a mixture of L- and H-Ta₂O₅ phases. The L⇒H-Ta₂O₅ phase transformation appeared to take place by a nucleation and growth process, whereby a small number of very large H-Ta₂O₅ grains grew through a matrix of fine L-Ta₂O₅ grains. The identification of the large grains as H-Ta₂O₅ and the fine grain matrix as L-Ta₂O₅ was accomplished by micro-Raman spectroscopy. Spectra collected from individual large grains and from the fine grain matrix were consistent with spectra collected from single-phase H- and L-Ta₂O₅ specimens, respectively.

Fracture surfaces of partially-transformed specimens showed a significant difference in grain morphology between the fine L-Ta₂O₅ grains and the large H-Ta₂O₅ grains. The same plate-like features observed previously in H-Ta₂O₅ materials are shown in Fig. 4, suggesting that the plates are features within individual H-Ta₂O₅ grains, rather than elongated and oriented grains themselves. Observation of partially-transformed specimens in cross section revealed no significant preference for surface nucleation by the large H-Ta₂O₅ grains, but it was found that such grains could be seeded by packing previously unheated powder around a single grain of H-Ta₂O₅ powder (Fig. 5). The exact cause of the rapid and expansive grain growth is currently unknown, but it is intimately linked to the reconstructive L⇒H-Ta₂O₅ phase transformation.

4. Discussion

Lagergren and Magneli first reported the existence of a reversible L⇒H-Ta₂O₅ phase transformation in 1952, and several subsequent studies—most notably by Roth and co-workers—have reported the effects of dopants on crystal structure and phase transformation behavior. However, no studies have reported the effects of composition or phase transformation on microstructure development. Due to simi-
lar post-transformation microstructures for H-100 and H-92-8 specimens observed in preliminary study, experiments were first carried out on 100TaO5 specimens, followed by verification with 92-8 specimens. The behavior of 92-8 specimens was similar to that of 100TaO5 specimens except where differences are explicitly stated.

As mentioned earlier, distinct grain boundaries were not observed in the sintered surfaces of H-TaO5 specimens. In an attempt to thermally groove the grain boundaries, H-100 specimens were polished to a 0.03 μm finish and then thermally etched for 30 min at 1000°C. Polished and thermally etched H-100 specimen surfaces exhibited no apparent grain boundaries, but close inspection revealed features that had grown out of the previously flat surface during thermal etching.22 XRD of etched H-100 specimens revealed trace amounts of L-TaO5, suggesting that the surface features were related to the H⇒L-TaO5 reversion.

Phase transformation studies confirmed that porosity found in traditionally-processed Ta2O5-based materials resulted from residual porosity trapped by rapid and expansive grain growth associated with the L⇒H-TaO5 phase transformation. Thus, in order to produce dense H-TaO5 specimens, it was essential to sinter the specimens to full density prior to the phase transformation. Use of fine, high-surface-area powders, such as the starting Ta2O5 and TiO2 powders with an average particle diameter of ~100 nm, is known to promote reduced-temperature sintering. However, after the calcination steps required to achieve chemical homogeneity, the average particle size grew to ≥500 nm—even larger than the powder Heintz et al. used when they reported that temperatures ≥1300°C were required to densify L-Ta2O514—and the TiO2 additions decreased the phase transformation temperature to ~1175°C. The microstructural evolution and associated constraints imposed by the L⇒H-TaO5 phase transformation highlight the limitations of traditional mixed-oxide processing. These limitations inspired the development of a hybrid solution-coated powder method that enabled the production of the first-ever dense and homogeneous specimens of TiO2-modified Ta2O5 in both the L- and H-Ta2O5 phases.

Energy dispersive spectrometry (EDS) analysis from scanning transmission electron microscopy (STEM, JEOL 2010F) revealed that particles of the coated powder were initially covered by a discontinuous layer of Ti-containing gel, and were compositionally homogeneous after 12 h at 1100°C. Further, TEM analysis also revealed the plate-like features of the H-TaO5 phase to be crystallographic twins, presumably resulting from a displacive phase transformation during cooling.22 Extensive STEM EDS studies were carried out on thinned disks to probe any compositional variations that might occur in dense specimens produced from coated powders. No significant variation in the Ti:Ta ratio was observed across twin boundaries (Fig. 6a) or around trapped pores (Fig. 6b). Thus, the hybrid solution-coated powder method was found to be an alternative processing method which can lead to both chemical homogeneity and reduced-temperature densification. This method combines the increased reactivity of solution processes and fine powders with the simplicity of powder processing, requiring less time and fewer steps than traditional mixed-oxide processing. Most importantly, development of this hybrid approach has enabled the production of the first ever reported dense and chemically homogeneous ceramics in the TiO2–Ta2O5 system.

Combining the coated-powder approach with a two-step sintering process produced dense specimens of H-92-8. The initial heat treatment (1150°C 12 h) resulted in both chemical homogenization and densification while remaining below the temperature of the L⇒H-TaO5 phase transformation, with the second heating step (>1200°C, >3 h) serving to transform the dense specimen into the H-Ta2O5 phase. All dense specimens prepared from unmodified or coated Ta2O5 powders had large-grain (~300–500 μm) microstructures after transformation into the H-Ta2O5 phase. The effect of TiO2 additions on the processing of Ta2O5-based materials was negligible, outside of the decrease in the L⇒H-Ta2O5 temperature. However, the impact of the H-Ta2O5 stabilization should not be overlooked, as it reduced the allowable densification temperature by ~200°C.

TEM studies confirmed that the plate-like features within H-Ta2O5 grains were actually crystallographic twins.29 These twins lead to unusual mechanical behavior in H-Ta2O5 grains, as shown in the fracture surface in Fig. 7. The grains absorb compressive stress via buckling and delamination of the twinned layers, leading to regions within the grain that bend 90° or more without fracture—highly unusual behavior for oxide materials! The origin of this nanoscale plasticity is currently under study, and preliminary results indicate the mechanism appears similar to incipient kink bands observed in Ti3SiC2 and related materials.30,31

5. Conclusion

Investigations of the sintering behavior of Ta2O5-based ceramics have concluded that extremely rapid and expansive grain growth accompanies the L⇒H-TaO5 phase transforma-
tion. The exact mechanism for the exaggerated grain growth is under investigation, but full densification requires that sintering temperatures remain below the temperature of the L→H-Ta$_2$O$_5$ transformation since the rapidly-growing H-Ta$_2$O$_5$ grains trap residual porosity. Sintered densities >98% are possible at temperatures as low as 1150°C by choosing fine (50–100 nm) powders, but are not practical for larger ≥500 nm powders prepared by calcinations of mixed oxides. A solution-coated powder processing method was used that enabled the first reported fabrication of dense and chemically-homogeneous TiO$_2$-modified Ta$_2$O$_5$ ceramics in the L-Ta$_2$O$_5$ phase. These dense L-Ta$_2$O$_5$ ceramics could then be transformed into the H-Ta$_2$O$_5$ phase by a second heat treatment. Beyond the decrease in the temperature of the L→H-Ta$_2$O$_5$ phase transformation, the effect of TiO$_2$ content on the sintering of polycrystalline Ta$_2$O$_5$ was negligible.

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