DESINTERING OF THORIA*

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Abstract

Sintered ThO_2 powder compacts will sometimes undergo a density loss and become more porous if held at high temperature for a sufficient time. ThO_2 sol gel sintered to 99% of theoretical density at 1200°C will undergo a steady bulk density decrease at 1800°C with the density falling below 90% T.D. after about 15 hours. Gas release measurements from desintered ThO_2 specimens annealed in air or in vacuum indicate that gases move through the material rather freely at 1800°C , suggesting that loss of density may not be a gas pressure effect. The extent of desintering was decreased by firing in argon and vacuum and by the addition of small quantities of other oxides.

Introduction

Desintering as used in this paper refers to loss of bulk density concurrent with pore growth in sintered specimens held at elevated temperatures. This is a phenomenon which is occasionally observed in ceramic materials and is usually attributed to gas pressure in the specimen pores. A recent example is desintering of ZnO observed by Gupta and Coble.¹ Francois, et al.,² observed inhibition of sintering in UO_2 and tungsten

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powders and attributed the effect to gas pressure in the pores. Another possible mechanism which has been suggested for causing porosity growth in polycrystalline aggregates is irradiation-induced preferential growth along certain axes of anisotropic crystals.³

Bronisz and Douglas⁴ have observed pore growth in thin films of vapor deposited thoria studied in the electron microscope. When deposited films with more than one crystal layer are annealed in the electron microscope beam, voids grow between the crystal layers. Vela and Russell⁵ observed pore growth on grain boundaries in irradiated copper-boron alloys raised to an elevated temperature.

We have observed desintering in ThO_2 sintered compacts. The extent of swelling varies with composition, preparative techniques and firing histories of the oxide and can range from virtually zero up to about 12%.

Material Preparation

Sol gel type thoria was used in most tests. Typically a colloidal dispersion of 70 Å crystals of thoria in dilute nitric acid was evaporated to a thick gel. Portions of the thick gel were put on glass plates and slowly dried. The dried gel had a density of 50 to 60% of the theoretical density of ThO_2 and was sintered by heating to 1000°C in a six day cycle in an oxygen atmosphere followed by a 2-hour anneal at 1200°C in air. The density would then be about 99.5% of theoretical and the grain size sub-micron. Carrying out this sintering cycle in air, argon or vacuum produced similar results. Sol gel containing calcium oxide was prepared by a similar process after $\text{Ca}(\text{NO}_3)_2$ was dissolved in the thoria sol.

Desintering tests were also made on sintered thoria specimens prepared from oxalate in which thorium was precipitated as the oxalate from a nitrate solution, filtered, dried, converted to oxide by heat treatment up to about 650°C, cold pressed, and sintered into compacts.

After the initial sintering, specimens were tested for desintering, i.e., loss of bulk density, by annealing at temperatures much greater than the initial sintering temperature, usually at 1800°C.

Experimental Observations

The course of desintering for a thoria sol gel specimen at 1800°C in air is shown in Fig. 1. The density of the thoria sol gel specimens decreased from 9.97 g/cc with time in such a manner as to approach a limiting density of 8.8 g/cc. Approximately this density decrease by an exponential decay yielded a time constant of 2.2 hours. Individual specimens repeatedly heated to 1800°C in air for 0.5 to 2-hour intervals followed by density determinations experienced a density decrease that followed a monotonic curve within a precision of ± 0.02 g/cc. Specimens taken from the same batch of sol gel thoria that were heated at 1800°C for time intervals ranging from 0.5 to 3.5 hours also experienced density decreases that followed a monotonic curve within a precision of ± 0.02 g/cc. The density achieved by various specimens annealed for 16 hours ranged from 9.00 g/cc to 8.85 g/cc. Some specimens annealed in air as long as 40 hours desintered to a density of 8.80 g/cc.

Desintering curves for ThO_2 -0.5 mole percent CaO at 1800°C in air and sol gel thoria at 1800°C in argon are also given in Fig. 1. Both desintered with the same time dependence as sol gel thoria in air. However, the final

density achieved for CaO-doped thoria was 9.4 g/cc and that for argon-fired thoria was 9.6 g/cc. Thoria specimen desintered in argon or vacuum were grey in color, probably due to a decrease in oxide stoichiometry. The effect of alternate 1800°C anneals of sol gel thoria in air and vacuum is shown in Fig. 1 as indicated by the open triangles. A specimen initially desintered in air for 1 hr at 1800°C to 9.46 g/cc densified slightly to 9.51 g/cc when fired in vacuum for 1 hr at 1800°C and continued to desinter to 9.42 g/cc when fired again in air for 1 hour at 1800°C. This sequence of air and vacuum anneals was repeated for two other sol gel thoria specimens and yielded similar results.

Figure 2 shows: (a) the metallography of a sol gel specimen which had been heated at 1400°C for 2 hours, (b) the pore structure in a similar specimen held at 1800°C for 16 hours. Figure 3 is a replica of a shallow interior pore exposed by breaking the specimen. Replicas extending into deeper pores tended to tear. Pores formed on interior grain boundaries but did not develop on grain boundaries at exposed surfaces. Figure 4 shows a scanning electron micrograph of a fractured surface of ThO₂ sol gel sintered to a high density at 1200°C and then held at 1800°C for 1 1/2 hours. Note that the grains are faceted; the pores are on grain boundaries and are also faceted.

Grains in ThO₂ sol gel which has been sintered to high density at 1000°C or even at 1200°C are sub-micron size. On annealing the sol gel at 1800°C grain growth to sizes in the range of 10 microns occurs in a few hours with slower growth into the 20 micron range. Pores in the 99+% dense sol gel are extremely small with many probably submicroscopic. The pores grow to several microns at 1800°C as can be seen in Figures 2, 3 and 4.

Although sol gel thoria shows pronounced desintering effects, the density data in Fig. 5 for a representative selection of thoria powder compacts show that desintering may or may not occur in sintered thoria powder compacts. With the exception of one sol gel specimen for comparison, all the samples used in obtaining the data shown in Fig. 5 were compacts of thoria powder made by calcining thorium oxalate at 650° to 800°C and then sintered at 1800°C. The "DT" powders are characterized by a narrow-range ($\sigma_g \sim 1.1$) log-normal distribution of relic particle sizes near an average of 2 microns. These compacts did not exhibit the desintering behavior. Laha and Das have shown that powders of this type fit Coble's bulk diffusion model for intermediate stage sintering.⁶ Samples 305 and 355 were also calcined-oxalate thoria powders, but the digestion of sample 305 eliminated submicron oxalate particles that otherwise would have been present.

Since pressure due to gases present or being generated within the thoria could be responsible for the observed desintering phenomena, the volatile gas content of the pores after desintering was investigated by fracturing the material and analyzing the gas released. Thoria sol gel specimens used in this investigation were crushed in a diffusion-pumped ultra-high-vacuum system. A single hammer-like blow of a plunger would release the gas from the crushed portion of the sample in a pulse having a duration of less than 1 second. The pumping rate constant for nitrogen was 3.0 sec^{-1} . The gas was analyzed using a quadrupole mass spectrometer (EAI QUAD 150), which had been calibrated against individual Boyles-Law expansions of methane, argon, and nitrogen, and which was also referenced against an ionization-type pressure gauge. The gas measurement technique was similar to that used by Condon, *et al.*,⁷ to determine the

hydrogen content in metals. Under these experimental conditions $\sim 1 \times 10^{-14}$ moles of gas released during a single blow was the lower limit of detection. The gases present were identified by repetitively sweeping the mass spectrometer over the mass range of 0 to 50 AMU at a rate of ten sweeps per second. Individual mass numbers were monitored relative to the ionization gauge output in order to quantitatively determine the amount of a specific gas evolved during a single blow.

Most of these gas release measurements were carried out at room temperature. A single hammer-like blow without the thoria specimen in the system produced a gas pulse containing $\sim 1 \times 10^{-11}$ moles of gas. This background gas was composed of $\sim 40\%$ H_2 , $\sim 40\%$ methane, and $\sim 20\%$ of a mixture of CO , N_2 , C_2H_6 , etc. When air desintered thoria was crushed $\sim 1 \times 10^{-10}$ moles was released by a single blow. This gas consisted of greater than 90% N_2 which was readily identified by the temporal response and relative intensities of masses 28 and 14. The background gases mentioned above and a trace of argon was also observed. After the sample had been struck several times and the gaseous products characterized, the specimen was removed from the vacuum system with less than 0.1 w/o loss. These experiments were repeated with the hammer chamber maintained at $400^\circ C$. The background gases increased by an order of magnitude, however no new gas species were observed. The results of room temperature gas release measurements carried out using sol gel thoria specimen having various desintering histories are given in Table 1.

An exact determination of the volume of pores opened during the crushing was not feasible but approximations were made by dividing the crushed material into size ranges, determining the weight fraction in each size range, and measuring the size of typical particles. One air-fired specimen weighed

0.4899 g and had a density of 94.1% T.D. After crushing 0.4854 g were recovered, of which one big piece weighed 0.3819 g and smaller pieces which could be picked up with the tweezers weighed 0.0611 g. Smaller particles varied from micron size to 100 microns with the bulk of material represented by 50 to 100 micron pieces. The particles were mostly flat slabs which were about 5 microns thick. As pores were 2-5 microns it was estimated that 50% of the pores in this fraction were opened. The small particles which could be picked up with the tweezers were estimated to have had 10% of the pores opened. This gave a volume of pores opened equivalent to 6.36% of the total pore volume. Measurement on 3 other specimens including specimens 1 and 2 of Table I gave values close to 5% and in calculating the gas pressure in pores of the first two specimens in Table I it was assumed that five per cent of the pore volume was opened. The third specimen, which was a portion of the second specimen annealed for one hour in air at 1800°C, was much more completely crushed and similar particle size measurements indicated that approximately 50% of its pores were opened.

Discussion

An explanation of the desintering of sol gel thoria at 1800°C must be consistent with the observation that the extent of desintering, but not the rate-constant of desintering, was influenced by chemical modification of the thoria. Under highly oxidizing conditions, i.e. in air, the thoria experienced a 12% density reduction. Under conditions that caused a decrease in oxygen stoichiometry, i.e. in vacuum or argon, the thoria experienced a 4% or less decrease. The presence of CaO (0.5 mole %) limited the density loss to 6%. Having desintered a specimen to some minimum density, further annealing at 1800°C in the same atmosphere did not affect the density

of the specimen. The density of an air desintered specimen could be decreased and increased by firing in air and vacuum respectively.

A possible explanation of this phenomena is that the pores are gas bubbles created by the pressure exerted by gases in the pores. These gases could have been trapped in submicroscopic pores during initial sintering to 99+% theoretical density or formed by the decomposition of a compound at 1800°C. The gas release experiments demonstrated that nitrogen could diffuse into or out of the pores in a thoria specimen sufficiently rapidly to reach equilibrium with the external atmosphere in one half hour or less at 1800°C. Observations of uniform color changes within thoria compacts fired in vacuum or air at 1800°C indicate that oxygen diffuses through thoria with facility at 1800°C. Gases that do not readily react with thoria, i.e. hydrogen, argon, etc., would probably behave in a manner similar to nitrogen; thus, it is unlikely that these gases could be contained at high pressures in a pore for time intervals as long as those observed for the desintering phenomena. The initial sintering process imposes very stringent requirements on the nature of a gas or compound that might produce a gas at 1800°C. Very slowly (six days) heating the initially 50% porous sol gel compact of 70 Å particles to 1000°C in air or vacuum should have eliminated most absorbed gases, i.e. H₂O, CO₂, hydrocarbons, and decomposed many thermally unstable compounds, i.e. nitrates, carbonates, etc. Assuming that a gas or compound could have survived the initial sintering treatment, the gas would have to be insoluble in thoria at 1800°C at elevated pressures for times exceeding two hours.

Grain growth accompanied by sweeping up or otherwise agglomeration of very small pores can be considered as a possible method by which gas in very

small pores could cause desintering. However, a one tenth micron pore would have an equilibrium pressure of about 1500 psi (based on a surface energy of 1000 ergs/cm² and using the equation $\text{pressure} = \frac{2\gamma}{r}$). Also, to obtain an appreciable rate of desintering by a gas pressure effect the resistance of the ThO₂ to deformation must be overcome. Poterat and Yust⁸ have shown that at 1800°C thoria of similar purity requires on the order of 100 atmospheres stress for appreciable deformation to be observed. Cordiner and Dean⁹ reported that when 97.3% thoria-2.6% urania sol gel oxide (previously fired in H₂ at 1050°C) was melted in vacuum using an alumina fluxing agent, the released gases were consistent in quantity and quality with the environment in which the specimens were initially sintered and no other gases, i.e. oxides of sulfur, nitrogen, etc., were observed. The observation that an oxidizing atmosphere enhances the desintering of thoria could be correlated with the production of a gas by oxidizing an impurity component, whereas under vacuum or argon this process would be less efficient. The mechanism whereby 0.5 mole percent calcia could limit the growth of bubbles is much less obvious. Although the results presented here do not absolutely preclude the existence of a gas in sol gel thoria that meets the requirements of thermal stability, insolubility in thoria and compatibility with oxygen at 1800°C, they do illustrate that the number of gas candidates are extremely limited and their detection would be very difficult.

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Figure Captions

Fig. 1. Desintering of sol gel ThO_2 and ThO_2 -0.5 M % CeO in air at 1800°C and desintering of sol gel in argon. The open triangles are sol gel sintered one hour in air, then one hour in vacuum followed by an additional hour in air.

Fig. 2. Thoria sol gel annealed at (a) 1400°C for 2 hours and (b) at 1800°C for 16 hours.

Fig. 3. Replica of a pore in sol gel ThO_2 annealed at 1800°C . $24,000\times$.

Fig. 4. Scanning electron micrograph of the fractured surface of sol gel ThO_2 annealed 1 1/2 hours at 1800°C in air. $3000\times$.

Fig. 5. Densification phenomena in several thorias annealed at 1800°C .

Table I. Gas Released by Crushing Sol Gel Thoria Specimens

Specimen Identification	Prior Anneal	Density g/cc	Estimated Fraction Pores Opened	Total Moles Evolved*	Gas* Composition	Calculated Gas Pressure atm @ 1800°C	Specimen Weight (grams)
SG 50	Air 1800°C 1 hour	9.52	5%	8×10^{-10}	N ₂ Trace Ar	0.8	0.6528
SG 26	Vacuum 1800°C 0.5 hour	9.74	5%	$< 1 \times 10^{-11}$	Trace Ar	< 0.01	0.4666
	Air 1800°C 1 hour	9.25†	50%	2×10^{-8}	N ₂	3.2	0.2616

*Corrected for background gases.

†This specimen is a piece of 56 26 which had been previously annealed in vacuum. The density measurement was only approximate since the specimen was small.

Fig 1

0.002 inches
500X

Fig 2

Fig 3

Fig 4

ORNL DWG 70-12925R

Fig 5