Electric Field Induced Texture in Titania during Experiments Related to Flash Sintering

S. K. Jha¹, J. M. Lebrun¹, K. C. Seymour², W. M. Kriven² and R. Raj¹

¹Department of Mechanical Engineering
University of Colorado at Boulder
Boulder, CO 80309

²Department of Materials Science and Engineering
University of Illinois Champaign Urbana
Urbana, IL 61801

Abstract

We show that (110) and (111) peaks weaken while the (211) X-ray diffraction peak gains in intensity in titanium dioxide under the influence of the electric field, during *in-situ* experiments of flash sintering, carried out at the Advanced Photon Source (APS). The effect is reversible, appearing and vanishing when the field is turned on and off. The changes in the peak intensities are immediate, but they fluctuate with time even though the electric field remains constant. Similar experiments with 3 mol% yttria stabilized zirconia have shown time dependent emergence of new peaks signaling the formation of a different phase, apparently by a diffusion controlled process. In contrast, in titania the existing peaks change intensity under the electric field. We attribute the events in titania to short range movement of atoms and defects in the lattice.

Keywords: Flash sintering, in-situ, X-ray diffraction, texture

Corresponding author: Shikhar K. Jha, Fnu.Shikhar@Colorado.EDU

1. Introduction

The recently discovered phenomenon of flash sintering [1] where sintering occurs at unusually low furnace temperatures in mere seconds is evolving into additional unexpected physical properties. The surge in conductivity which accompanies sintering is a signature of the flash event [2]. When the experiments are carried out at a constant furnace temperature, and the field is applied as a step function, the flash occurs after an incubation time [3]. The stage related to this time delay has been called Stage I. The non-linear increase in conductivity is controlled by limiting the current through the specimen, known as Stage II. The specimen may then be held in a constant state of flash under current control, which is Stage III of the flash experiment. The sample sinters during Stage II. Therefore the sample is often dense and stable during the Stage III experiments.

Recent experiments in Stage III with yttria stabilized zirconia have revealed a new physical phenomenon: the oxide exhibits intense electroluminescence [4]. In these experiments, the specimen temperature was measured from lattice expansion during *in-situ* experiments to account for Joule heating. The luminescence was compared with the radiation spectrum that would be expected from black body radiation. The shape and nature of the radiation spectrum was consistent with electroluminescence rather than black body radiation. The spectrum showed two distinct peaks that remained at the same wavelengths when the specimen temperature was increased, consistent with recombination of electron-hole pairs or excitons [5]. Furthermore, the emission peaks were at shorter wavelengths than would have been expected from black body radiation. Measurements of optical luminescence have been confirmed in another laboratory as well [6].

In a different set of experiments, also conducted at the synchrotron, we have observed the emergence of a new phase in 3mol% yttria stabilized zirconia (3YSZ) [7]. The phase emerged and then dissolved when the field was turned on and then off. The experiments could be repeated in several on-off cycles, and therefore were attributed to a thermodynamic force induced by the electric field. There was, however, a time lag between the appearance and the dissolution of the new phase relative to the moment that the field was switched, showing that the phase transformation was diffusion controlled.

In this article, we present results of field induced change in the intensity of the diffraction peaks in titania during flash experiments. As was the case of 3YSZ, these experiments were also carried out in Stage III. However, we discover that in this instance the change in structure is very rapid, appearing and disappearing nearly instantaneously when the field is turned on and off. These experiments build on earlier results on flash sintering and measurements of electrical conductivity of titania in the state of flash [8].

2. Experimental methods

The schematic of experimental methods are shown in Fig. 1. The specimens were prepared from titania (rutile) powders of purity 99.995% and particle size 20 nm (NP-TiO₂-R-20 MTI Corporation Material Ltd. USA, Richmond CA). Powders were pressed into rectangular bars under a pressure of 130 MPa, leading to specimens having a green density of ~ 48%. They were then conventionally sintered to 1200 °C for 3 hours which yielded dense samples with a grain size of 3-5 μm. The effective gage length of sintered specimens was measured to be 3.72 mm with a cross-section area of 1.33 mm x 0.55 mm.

Electric field was applied to the specimens through platinum wires that were wrapped around the ends of the specimens, with a DC power supply (Sorensen 300-2, Sorensen San Diego, CA). The power supply was switch to current control after the onset of the flash. The switching time is specified to be 50 ms. The current flowing through the specimen was measured with a digital multimeter (Keithly 2000, Keithley Instruments, Cleveland, OH).

The *in-situ* experiments were carried out at the Advanced Photon Source (APS) at the Argonne National Laboratory. The experiments were carried out on beamline 33BMC, at a wavelength of 0.59 Å. The diffraction spectra were measured with a Pilatus 100K 2D image plate detector (DECTRIS Ltd, Villigen, Switzerland). Diffraction data were obtained by two methods: in the full scan mode, and the local scan mode. In the full scan mode the detector moved from $2\theta = 7^\circ$ to 22° in 75 steps with an exposure time of 1 sec at every step; thus the full scan took ~~75 sec~~ 4:15 min. For the local scan mode experiments, the detector remained stationary covering the range $2\theta = 18.5^\circ \pm 1.5^\circ$, within which the (211) peak of rutile resides for the given wavelength of X-ray. These XRD data sets were acquired once every of 0.5 s.

A quadrupole Lamp Furnace [9] was used for the *in-situ* experiments. All experiments were carried out at a constant furnace temperature of 800 °C. In all instances a field of 100 V cm⁻¹ was applied as a step function. The current limit for the experiments was set at 25 mAmm⁻². The field was turned on and off at 100 s intervals for several cycles. The electric field, the current density, and the power density, calculated as their product, normalized for the specimen volume, are shown in Fig. 2. At this value of the applied field, the incubation time for the onset of the flash is negligible; the specimen flashes immediately upon the application of the field.

The specimen temperature was measured with a platinum standard. A thin narrow strip of platinum paste was applied to the surface of the specimen. The procedure has been described in greater detail in [4]. The shift in the (111) peak from platinum was used to estimate the specimen temperature. Standard handbook value for the thermal expansion of platinum [10] was used for this purpose. Under the conditions of Stage III flash, described in Fig. 2, the specimen temperature is measured to be 925 °C, at $2\theta = 14.775^\circ$ for the platinum peak. The application of the black body radiation model [11] to the conditions of power dissipation and specimen surface-to-volume ration, and assuming the emissivity to be equal to 0.9, yields the estimate of the specimen temperature to be 917 °C, in good agreement with the measurement using the platinum standard.

3. Results

The results from the full scan measurements while the specimen is held under the constant state of flash in Stage III are shown in Fig. 3. Two on-off cycles are given. Note that (211) peak gains in strength while the (110) and (111) peaks weaken when the field is turned on. The sample recovers essentially to its original state when the off condition. The response reproduces over several cycles. The change in the strength of the peaks coincides with the change in the applied field.

The change in the relative strength of the peaks from different planes may be quantified in terms of a texture coefficient, TC , as described in Barret and Massalski [12], which is the ratio of relative peak intensity of a certain plane with respect to intensity of same plane without electric field,

$$TC = \frac{I^*}{I_o^*} \quad (i)$$

where,

$$I^*(hkl) = \frac{I(hkl)}{\sum_{n=1}^4 I(hkl)_n} \quad \text{(ii), and}$$

$$I_o^*(hkl) = \frac{I_o(hkl)}{\sum_{n=1}^4 I_o(hkl)_n} \quad \text{(iii)}$$

Here, $I^*(hkl)$ is the relative peak intensity of a particular (hkl) peak, given by the area integral of that peak divided by the summation of all the peak intensities. $I_o^*(hkl)$ is the relative peak intensity of (hkl) plane with no applied electric field. Therefore, the value for TC is equal to unity in the absence of the applied field since $I = I_o$. However, in the presence of the electric field, the peak intensities change and the numerator in Eq. (1) fluctuates relative to the denominator. The value for TC deviates from unity for different planes in different ways. The data from four diffraction peaks, $n=1$ to 4, *i.e.* for the planes (110), (101), (111) and (211), were considered. The results from the application of Eq. (1) to the data are shown in Fig. 4, for two cycles. In both cases the denominator in Eq. (1) was set equal to the intensities obtained during the first cycle. Thus we see that there is some residual effect in the second cycle when the field is turned off. However, the apparent texture persists when the field is on. Keep in mind that these data were obtained from full scans which required a time of 75 s ~~4:15 min~~. Therefore, fluctuations over this period are implicit in these data.

We have noted that the strength of the peaks fluctuated with time even though the specimen is held at a constant current. For example as seen in Fig. 3, the strengthening of the (101) peak is sporadic. This point is further clarified in the results from the local scan mode experiments where the detector was kept at the fixed position to record the strength of the (211) peak. These data, measured at the rate of 2 Hz, are shown in Fig. 5. Note that the peak strength fluctuates even though the power expended in specimen remains steady and the peaks are stronger during the power surges when the field is switched on, meaning that the strength of the peaks may be related to power dissipation.

The sporadic fluctuation in peak strength can be seen in the video, attached as supplementary material (S1). A systematic response is observed for the peak at $2\theta = 19.95$ (corresponds to (211) peak of rutile) with electrical power dissipation. Three ON-OFF experiments were performed. In every case, the intensity reverted to its original value when the field was switched off. The peak

shapes, including the (211) peak, appear to become non-Gaussian. Such behavior has been seen in rutile; it is attributed to the formation of higher order oxides ($\text{Ti}_n\text{O}_{2n-1}$) [13] and preferential growth of defects on shear planes [14].

Since flash experiments involve Joule heating, it springs to mind as the first explanation for the change in structure. Recall that the specimen temperature with the applied field was measured to be 925 °C with the platinum standard. The diffraction patterns obtained at furnace temperatures of 1000 °C, 900 °C and 800 °C, without the applied field, have been compared with the specimen flashed at 800 °C in Fig.6, proving that the change in the diffraction pattern is not a result of Joule heating.

The peaks from the texture fluctuated with time suggesting some type of stochastic events within the polycrystal. Our measurements do not provide information regarding the rate of these stochastic fluctuations but given that our measurements were made at the rate of 2 Hz, we can say that they occurred at least at this rate. Experiments with AC fields may provide further insights into the frequency of these fluctuations.

4. Discussion

In the earlier work on 3YSZ [7] we have shown the emergence of new peaks which were attributed to a pseudo-cubic phase. However, this phase transformation was time dependent. The peaks for the field induced phase developed gradually, and also extinguished gradually when the field was turned off, implying a diffusion controlled mechanism of phase transformation.

In the present results with titania, we show that the diffraction changes immediately (the data were acquired at 2 Hz) when the field is on, and dissolves as soon as the field is turned off. In contrast to 3YSZ, we do not see new peaks but instead strengthening of the intensity diffracted from (211) and weakening of intensity from the (110) and (111) planes, under the applied field. It is reasonable to assume that the field-induced change in titania is produced by small-scale displacement of atoms from their ideal positions, rather than by diffusion. Since we do not see the emergence of a new phase it may not be characterized as a martensitic transformation. Instead it seems that the crystal suffers some distortion under the electric field in such a way that the (211) planes become more reflective, and other planes less so. If indeed, as has been proposed [11], defect formation is an

underlying cause of flash sintering then the defects may align in a specific manner within the unit cell to produce the distortion. Certainly a very high concentration of defects aligned in specific way will influence the reflectivity of the specific lattice planes. This hypothesis has been discussed in the literature. Blumenthal *et. al.* [15] suggest formation of defects such oxygen vacancies and titanium interstitials (Ti^{3+} , Ti^{4+}) which are held responsible for the higher conductivity. As the concentration of these defects increases, they form ordered clusters on crystallographic shear planes [14,16,17]. However, the difference with the present work is in the concentration of defects. Without the electric field, the rise conductivity with temperature, for a given partial pressure of oxygen, follows Arrhenius behavior. However, under electric field we observe an abrupt jump in conductivity [8], which lies above the equilibrium defect concentration for that temperature.

The stochastic nature of the intensity of the diffraction peaks is another notable feature of the present results. They are seen in the movie that is attached as supplementary material. This behavior is not consistent with the response of titania as a oxygen sensor which requires a steadfast change in defect concentration with oxygen partial pressure. We hypothesize that the fluctuations, which occur at about 2 Hz, may be due to the back and forth jumps of defects in the crystal. The defects cluster on specific crystallographic planes which affects that reflectivity and hence the intensity of the diffraction peaks.

The effect reported in this work is different from the piezoelectricity, where very high electrical fields are used to pole the crystals. In poling experiments dipoles, which exist in the structure, are forced into alignment under the electric fields. In present experiments the fields are several orders of magnitude weaker and the structure is not intrinsically polar.

5. Summary

This article is a second report on the change in the structure of polycrystals induced by the electric field in flash sintering experiments. Earlier, we have shown the emergence and extinction of a new phase in 3YSZ [7] where peaks from the new phase developed and dissolved gradually with time. This phase evolution was diffusion controlled and therefore probably occurred by a nucleation and growth process.

In the present experiments with TiO_2 , the structure change apparently occurs by distortion of the unit cell under an electric field such that the diffraction peak from (211) planes gains, and those from the (110) and (111) planes weaken in intensity. This effect is distinct from the 3YSZ [7] experiment in two ways:

(i) The change in the intensity of the peaks occurs immediately, and is restored in about one second, when the field is switched on and off.

(ii) We do not see the emergence of a new phase but rather a change in the reflectivity of the planes in the crystal. The (211) planes begin to reflect more intensely while the (110) and (111) become less reflective to X-rays.

One possible explanation of the above results is a distortion of the unit cell from the development of defects, which are induced by the electric field. We hypothesize that the defects, being charged, could segregate preferentially to certain crystal planes, which may change their reflectivity.

Acknowledgements

We are pleased to acknowledge assistance and discussion with Evguenia Karapetrova, physicist at the beam line 33BMC at the Argonne Photon Source, where these experiments have been performed. Jean-Marie Lebrun is pleased to acknowledge support from the Office of Naval Research under the direction of Dr. Lawrence Kabacoff, under grant number N00014-12-1-0710. Jha and Raj, as well as the development of the facilities used in these experiments have been supported by the Basic Energy Sciences Division of the Department of Energy under grant number DE-FG02-07ER46403. Waltraud M. Kriven acknowledges the support of the Air Force Office of Scientific Research under Grant FA9550-09-1-0322. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357

List of Figures

1. Figure 1. The configuration of the set-up for *in-situ* experiments of X-ray diffraction at the APS. The experiments were carried out in the transmission mode.
2. Figure 2. The electrical field, the current and the power expended in the sample in ON and OFF cycles. The power spike is associated with a change from voltage to current control. Under current control the specimen resides in a steady state of flash described as Stage III.
3. Figure 3. The change in the peak intensities in Stage III during two ON-OFF cycles. Note the strengthening of the (211) peak and weakening of the (110) and (111) peaks under the influence of the electric field.
4. Figure 4. Change in the intensities of four peaks when the field is turned on. The data show some degree of hysteresis since the peak intensities are not completely restored when the field is turned off in the second cycle.
5. Figure 5. Stochastic fluctuations in the intensity of the (211) peak. The fluctuations can be seen in real time in the movie, which is attached as supplementary material (S1).
6. Figure 6. Full X-ray diffraction scan under flash, compared with the patterns at different temperatures with no electric field.

References

- [1] Cologna M, Rashkova B, Raj R. Flash sintering of nanograin zirconia in <5 s at 850 C. J Am Ceram Soc 2010;93:3556–9.
- [2] Cologna M, Francis JSC, Raj R. Field assisted and flash sintering of alumina and its relationship to conductivity and MgO-doping. J Eur Ceram Soc 2011;31:2827–37.
- [3] Naik KS, Sglavo VM, Raj R. Flash sintering as a nucleation phenomenon and a model thereof. J Eur Ceram Soc 2014;34:4063–7.

- [4] Terauds K, Lebrun J-M, Lee HH, Jeon TY, Lee SH, Je JH, Raj R. Electroluminescence and the measurement of temperature during Stage III of flash sintering experiments. *J Eur Ceram Soc* 2015;35:3195–9.
- [5] Lebrun J-M, Raj R. A first report of Photoemission in Experiments related to Flash Sintering. *J Am Ceram Soc* 2014;97:2427–30.
- [6] Muccillo R, Muccillo ENS. Light emission during electric field-assisted sintering of electroceramics. *J Eur Ceram Soc* 2015;35:1653–6.
- [7] Lebrun J-M, Morrissey TG, Francis JSC, Seymour KC, Kriven WM, Raj R. Emergence and Extinction of a New Phase During On-Off Experiments Related to Flash Sintering of 3YSZ. *J Am Ceram Soc* 2015;98:1493–7.
- [8] Jha SK, Raj R. The Effect of Electric Field on Sintering and Electrical Conductivity of Titania. *J Am Ceram Soc* 2014;97:527–34.
- [9] Sarin P, Yoon W, Jurkschat K, Zschack P, Kriven WM. Quadruple Lamp Furnace for High Temperature (up to 2050 K) Synchrotron Powder X-ray Diffraction studies in Air in Reflection Geometry. *Rev Sci Instrum*, 2006;77:093906.
- [10] Hahn TA., Kirby RK, Wolfe HC, Graham MG, Hagy HE. Thermal Expansion of Platinum from 293 to 1900 K 1972;87:87–95.
- [11] Raj R. Joule heating during flash-sintering. *J Eur Ceram Soc* 2012;32:2293–301.
- [12] Barret C, Massalki TB. *Structure of Metals*. Pergamon Oxford; 1980.
- [13] Page YL, Strobel, Structure Chemistry of the Magneli Phases Ti_nO_{2n-1} , $4 \leq n \leq 9$. *J. Sol. St. Chem.* 1982; 44; 273-281.
- [14] Bursill LA, Hyde BG. Crystallographic shear in the higher titanium oxides: Structure, texture, mechanisms and thermodynamics. *Prog. Sol. St. Chem.* 1972, 7; 177-253.

- [15] Blumenthal RN, baukus J, Hirthe WM. Studies of the defect structure of Nonstoichiometric Rutile, TiO_{2-x} . J. Electrochem. Soc.: Sol. St. Sc.; 1967; 114, 172-176.
- [16] Fergus JW. Doping and efect association in oxides for use in oxygen sensors, J. Mater. Sc., 2003;38; 4259-4270.
- [17] Ganduglia-Pirovano MY, Hofmann A, Sauer J. Oxygen vacancies in transition metal and rare earthe oxides: Current state of understnading and remaining challenges. Surface Science reports. 2007;62; 219-270.

Figure1

Figure 1. The configuration of the set-up for in-situ experiments of X-ray diffraction at the APS. The experiments were carried out in the transmission mode.

Figure2

Figure 2. The electric field, the current and the power expended in the sample in ON and OFF cycles. The power spike is associated with a change from voltage to current control. Under current control the specimen resides in a steady state of flash described as Stage III.

Figure3

Figure 3. The change in the peak intensities in Stage III during ON-OFF cycles. Note the strengthening of the (211) peak and weakening of the (110) and (111) peaks under the influence of the electric field.

Figure4

Figure 4. Change in the intensities of four peaks when the field is turned on. The data show some degree of hysteresis since the peak intensities are not completely restored when the field is turned off in the second cycle.

Figure5

Figure 5. Stochastic fluctuation in the intensity of the (211) peak. The fluctuations can be seen in real time in the movie, attached as supplementary material.

Figure6

Figure 6. Full X-ray diffraction scan under flash, compared with the pattern with no electric field at different temperatures.