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In Situ Grain Growth of Nanograined Magnetite under Ion Irradiation at Room Temperature and 500 ℃

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Grain growth studies of nanograined metals under both thermal and ion irradiation conditions has been studied extensively [1-2]. Oxides, on the other hand, have not been studied as extensively, especially under irradiation. Some studies have focused on nanograined oxide grain growth on ZnO under thermal conditions [3] only and on SnO_2 and CeO_2 using 250 keV Ar^{2+} and 3 MeV Au^{+} ions at 300 K [4-5], respectively. There does not appear to be any studies on grain growth of nanosized oxides which are commonly found to form under light water reactor conditions. Oxides such as magnetite (Fe_3O_4), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and wustite (FeO) are examples of common oxides which have not been studied. This study focused on the grain growth of nanograined Fe_3O_4 under both thermal and ion irradiation conditions in situ inside a Transmission Electron Microscope (TEM) to better understand the kinetics of grain growth of oxides.

A 100 nm thin film of Fe_3O_4 was grown on a substrate of KCl (001) using Pulsed Laser Deposition (PLD) at Pacific Northwest National Laboratory (PNNL). The deposition was conducted at room temperature. Sample suitable for TEM observations were obtained by dissolving the substrate in distilled water followed by placing the floating film onto a copper grid. Initial TEM characterization of the thin film revealed small equiaxed grains with an average size of ~14 nm. For the experiments, a 1 MeV ion beam was used to irradiate the samples in-situ at a flux of 6.25×10^{15} ions/m^2, which corresponded to a dpa rate of ~7.5×10^{-4} dpa/s, based on simulations done using SRIM-2008 in the Kinchin-Pease (Quick) mode with displacement energies for Fe and O set to 40 eV and 28 eV, respectively.

Two experiments were performed using a Gatan double tilt heating holder at Room Temperature (RT) and 500℃. During the irradiation, a series of Bright Field (BF) images were captured at successive doses of 0.5 dpa, 1 dpa, 1.5 dpa, 2.5 dpa, and 5 dpa. The average grain size was measured for each dose point. **Figure 1a** shows the series of BF images which show the progression of grain growth under irradiation at RT. The grains were found to grow from an initial size of ~14.3 nm to a size of ~17.9 nm after 5 dpa. A graph of the average size of the grain as a function of irradiation dose is shown in **Figure 2a**. The graph shows an initial rapid growth between 0 to 0.5 dpa followed by a deceleration of growth up to 5 dpa. The series of BF images corresponding to the 500℃ experiment is shown in **Figure 1b**. The grain size was found to increase from temperature alone from ~14.3 nm to ~25.3 nm after 34 min at 500℃ . After irradiation to 5 dpa, the average grain size was found to be around ~31.1 nm, showing that grain growth continued with irradiation. **Figure 2a** depicts the progression of average oxide grain growth as a function of irradiation dose at 500℃. It should be emphasized that since a significant amount of growth already occurred thermally before the irradiation started, the driving force for grain growth was already less at the beginning of the irradiation compared to the irradiation at RT, which can explain the apparent difference in kinetics trend (grain growth exponent) and corresponding activation energies. At 500℃, grain growth is expected to be due to both thermal and irradiation effects. To separate the two effects, average grain sizes were measured in a "shadowed" area of the sample where the copper grid shielded the samples from ion irradiation while remaining at 500℃. **Figure 2b** shows the effects of the sample being at 500 ℃ on

grain size as a function of time. As is evident from **Figure 2b**, there is a sharp increase in the average grain size initially from ~14.3 nm at RT to ~25.7 nm within the first 60 min of heating and then the growth slows down with an average size of about ~27.8 nm after 220 min (coinciding with the end of the irradiation experiment). Clearly, the process of irradiation enhanced the grain growth since the average grain size in the irradiated region was ~31.1 nm compared to the non-irradiated region at ~27.8 nm, however thermal grain growth alone, even before the irradiation started was extremely effective. Such fast thermal grain growth was reported for some other nanocrystalline oxides such as nanocrystalline Yttria Stabilized Zirconia [6] and nanocrystalline SnO_2 [7]. Irradiation induced was also reported to be extensive in CeO_2 and ZrO_2[5,8] under 3 MeV and 2 MeV Au^+ at 160 K [5,9]. Conventional mechanisms of grain growth proposed for metals such as (1) the curvature driven grain boundary mechanism and (2) grain rotation mechanism do not seem adequate to describe the fast kinetics of grain growth observed in ceramic oxides including our own study. A third mechanism has been proposed based on the assumption that the ordering of the interface regions in nanocrystalline oxides (SnO_2) occurs simultaneously with grain growth by structural relaxation [7]. This implies that the as processed state of ceramic oxide films already has some level of atomic disorder (maybe due to intrinsic high vacancy concentrations to begin with). Under irradiation, the results would have to be put in perspective with the thermal-spike model proposed based on experiments done in metals [1,2,10] considering now a different initial state (i.e. with pre-existing atomic disorder in the initial film). Molecular dynamic simulations done for ion-irradiated CeO_2 seem to confirm the role of the thermal spikes (i.e. point defect cascades) and the influence of their size, which is embedded in the thermal spike model of grain growth under irradiation [1,10].

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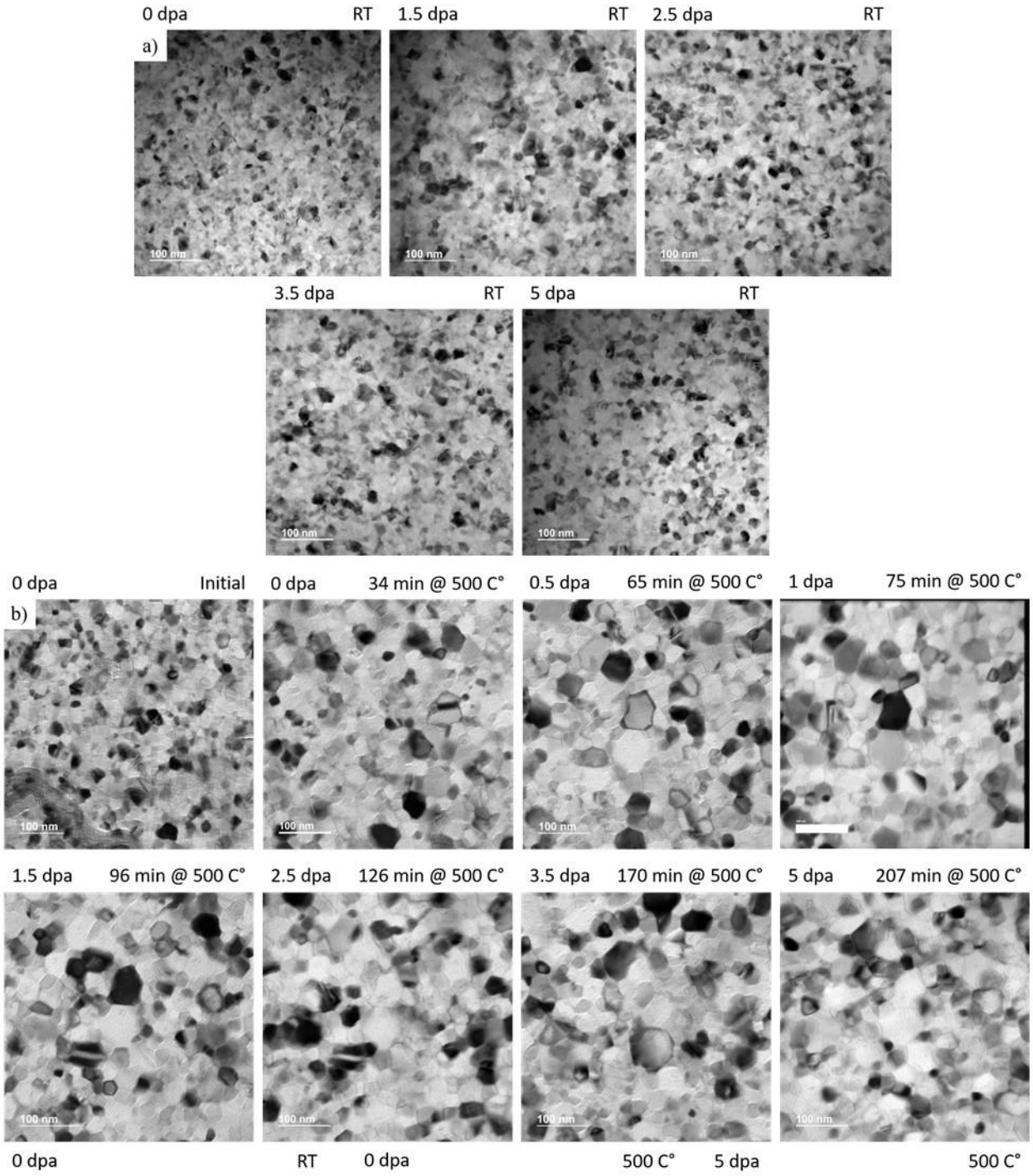

Figure 1. Figure 1: a) Bright Field Micrographs at Room Temperature for varying Irradiation Doses Showing Grain Growth with Dose b) Bright Field Micrographs at Room Temperature and 500 °C for varying Irradiation Doses and Increasing Time Showing Grain Growth with Dose and Time

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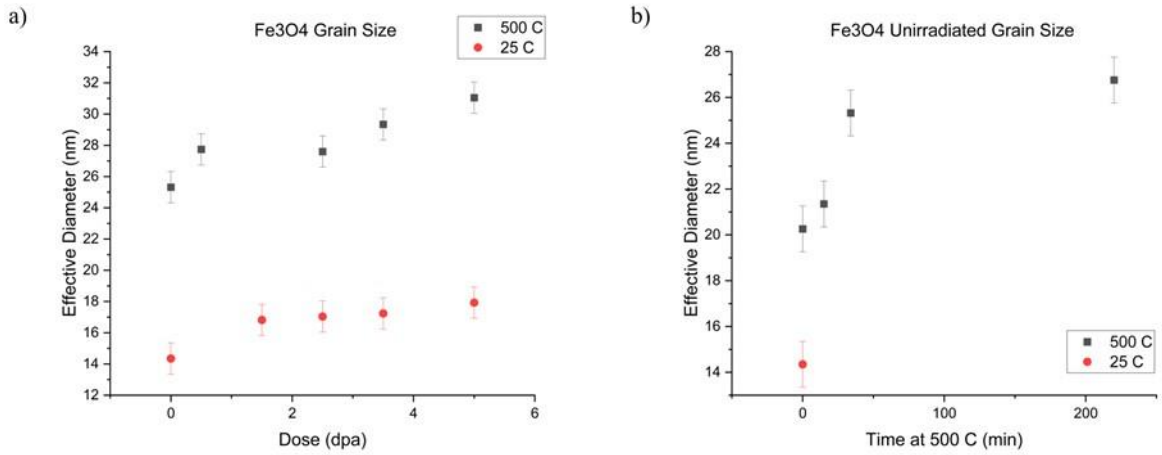

Figure 2. Figure 2: a) Irradiation assisted grain growth: Grain Size at Room Temperature (25 °C) and at 500 °C as a Function of Dose b) Thermal grain growth: Grain Size of Unirradiated Material as a Function of Time Spent at Various Temperatures

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