TEM investigation of defects in ceria

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Cerium oxide is an important material for energy applications due to its high oxygen diffusivity, which makes ceria an attractive candidate for intermediate temperature fuel-cell electrolytes [1], and the ease with which the cerium ion is reduced, which is useful in catalytic applications and hydrogen production [2]. More generally, fluorite-structured oxides have a variety of applications from nuclear fuels (uranium oxide) to structural ceramics (zirconia). Relatively few structural investigations of line and planar defects in ceria have been performed. Grain boundaries are known to play an important role in oxygen transport in ceria [3] while the possible effects of dislocations have been ignored. This paper reports observations of dislocation loops introduced via electron beam damage, dislocation networks and grain boundaries in polycrystalline ceria.

Samples were prepared from powder from Alfa Aesar that was originally 99.99% pure. The powder was pressed in a uniaxial press and sintered for 10 hours at 1400 °C. The samples contain porosity as revealed by light microscopy and TEM. Specimens were prepared for TEM by ultrasonic coring, grinding, dimpling and ion milling. A JEOL 2010 operated at 200 kV and an FEI Tecnai T12 operated at 120 kV were used for imaging.

During imaging beam damage produces dislocation loops. Yasunaga *et al* [4] previously observed this phenomenon and suggested the loops were oxygen interstitial loops based on comparison with results in zirconia. Figure 1 shows a set of images acquired *in situ* over time. The circled defects move, interact and eventually disappear. Not clear from the images is the fact that the loops move short distances (a few nm) back and forth. Previously, beam damage in ceria nanoparticles and abrasive powders was observed to reduce the cerium ion to the 3+ oxidation state as revealed by electron energy loss spectroscopy [5, 6]. Loops formed during imaging using both 200 kV and 120 kV accelerating voltages, but damage appeared to occur more rapidly at 200 kV. Annealing the specimen in air at 500 °C for 1 hour removes the loops.

Only dislocations with Burgers vector 1/2[110] were identified with **g.b** analysis. Dislocation nodes were also observed; figure 2 is a weak-beam dark field image of dislocation nodes.

Grain boundaries appear to be primarily random high-angle grain boundaries with some low-angle boundaries composed of dislocation arrays observed within a larger grain. Figure 3 is a TEM image of a low-angle boundary. No twins or special orientations have been identified.

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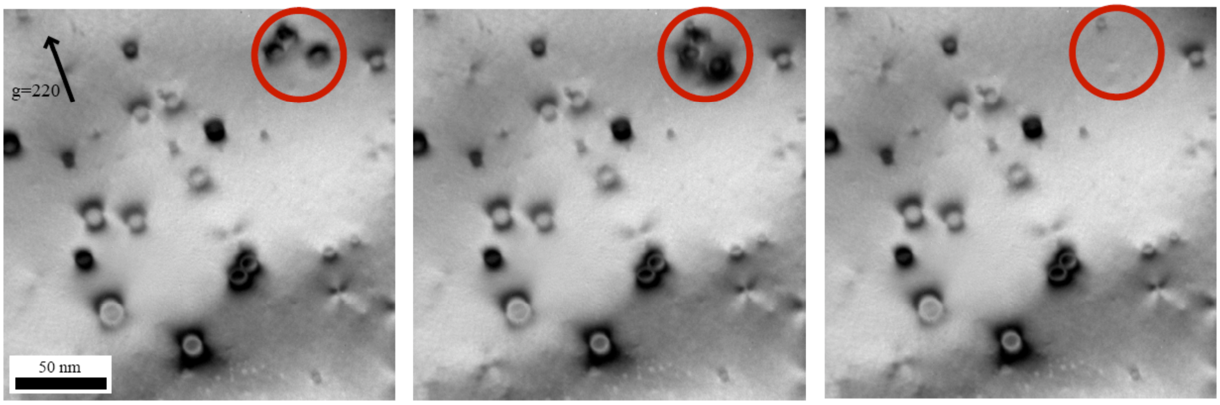

Figure 1. Strong-beam TEM BF images from an *in situ* series showing the movement and disappearance of what are believed to be interstitial loops in ceria. Approximately five seconds separates each image.

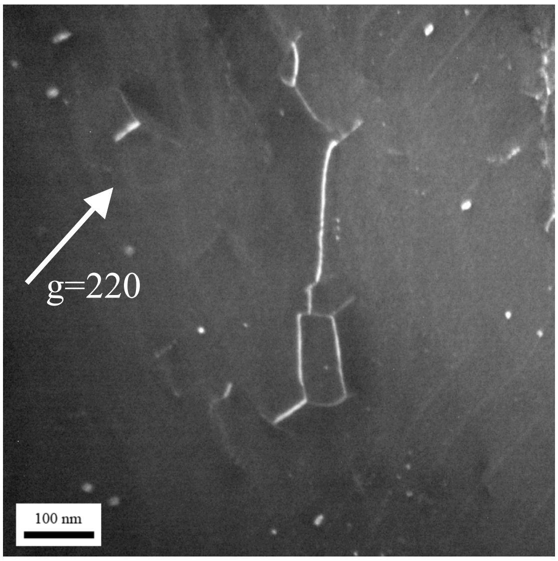

Figure 2. Weak-beam dark field image of dislocation nodes in ceria.

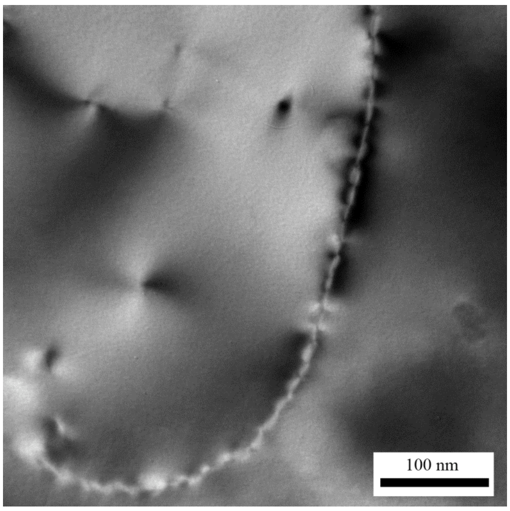

Figure 3. TEM image of a low-angle grain boundary in ceria.

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