doi:10.1017/S1431927614009520
Microsc. Microanal. 20 (Suppl 3), 2014

In-situ TEM Investigation of Reduction-Oxidation Reactions during Densification of Iron Oxide Nanoparticles

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Sintering describes the consolidation of individual (nano) particles to form a dense microstructure through the application of heat, pressure, electric fields, etc. [1] Electric field-assisted sintering (EFAS) is a type of sintering technique with a large number of studies reported in the literature and wide application. In fact, sintering studies of various oxide materials at low temperatures has been done however not much have been devoted on consolidation of iron oxide [2]. In both cases, the atomic scale consolidation mechanisms under heating rates and electrical fields during EFAS remain mostly unclear [3].

Iron oxide (γ-Fe_2O_3) nanoparticles with size ranging from 5 to 50 nm in diameters were synthesized using a modified H2/air diffusion flame configuration [4]. Nanochains of the particles were produced by the applied magnetic field acting perpendicular to the flame direction. These particles were collected 55 mm above the visible flame by rapidly inserting the Aduro MEMS heating device. JEOL JEM 2500SE transmission electron microscope (TEM) and an aberration corrected JEOL JEM 2100F/C_s scanning transmission electron microscope (STEM) with a Gatan Tridiem parallel electron energy loss spectrometer operated at 200 KV were used for the *in situ* heating studies. With a Protochips Aduro heating holder, temperatures from 200°C to 900°C with 50°C increments for 200 s were applied. TEM/STEM images and video signals were acquired while electron energy loss spectra (EELS) were recorded in between each heating cycle. The oxidation state of iron oxide particles during annealing was quantified by calculating the Fe L_3/L_2 intensity ratio using the quantification method by Jacinski et al. [5].

Figure 1 shows the high angle annular darkfield (HAADF) images of the iron oxide nanochains at 400°C (Figure 1a) and 500 °C (Figure 1b), respectively. Neck formation between the particles and subsequent growth was observed (see Figure 1b). Further application of temperature led to rapid consolidation of the nanochains at 900°C [6]. EELS measurements and quantification of the Fe $L_{2,3}$ ionization edges (Figure 2) revealed a phase transition from γ-Fe_2O_3, Fe_3O_4, FeO and finally to Fe which was attributed to oxidation-reduction reactions during annealing [6]. In fact, the shift in Fe L_3 from 600°C- 900°C (oxide to metal in Figure 2) of 1.4 eV correlated to FeO-Fe chemical shift of EELS Fe L_3 edge by Leapman et al. [7]. In this case, the iron oxide reduction from Fe_2O_3 to Fe was driven by the increasing annealing temperature resulting to increased surface diffusion for sintering starting from 400 °C. Thus, a preferred phase of Fe_3O_4 for sintering during the *in situ* study was identified. The results from this study provided evidence for reduction-oxidation reaction mechanisms during sintering. Furthermore, the *in situ* heating experiment provided valuable information on sintering of fully oxidized nanometric material such as iron oxide [8].

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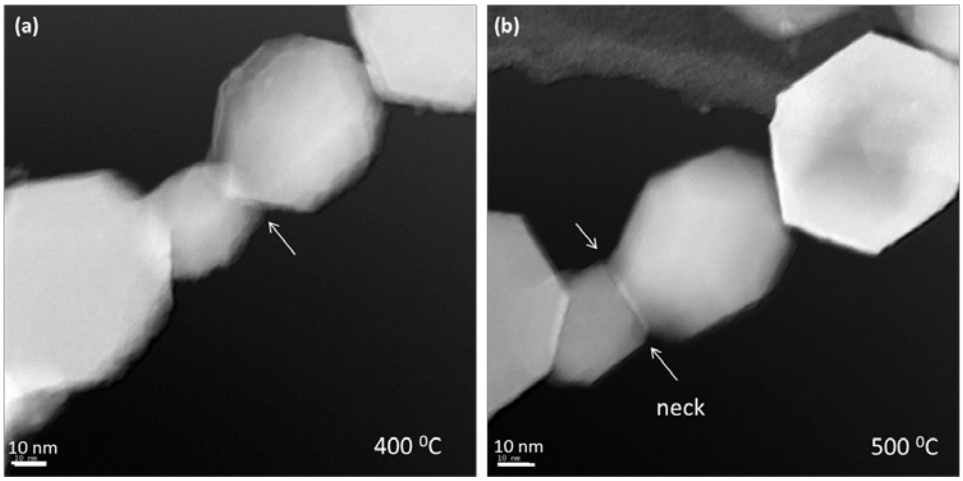

Figure 1. HAADF images of the iron oxide nanochains at 400°C (**a**) and 500°C (**b**) showing neck formation between the contact areas of the marked particle.

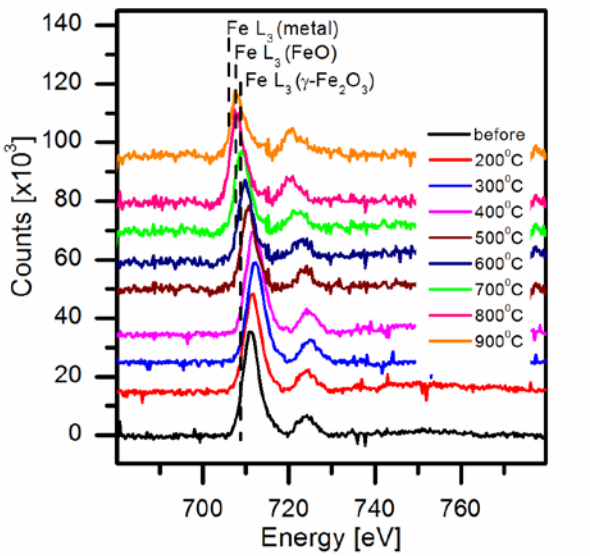

Figure 2. EELS Fe $L_{2,3}$ ionization edge across the iron oxide nanoparticles acquired during each annealing temperature from the *in situ* heating experiment.

https://doi.org/10.1017/S1431927614009520 Published online by Cambridge University Press