Application Note

Fusion 500™

Simultaneous Electrical and Heating Using Fusion: Electric-Field Assisted Sintering of ZrO_2 Nanoparticles

Introduction

Sintering is the phenomenon of densification and consolidation of powders into desired shapes and geometries. Examples include the firing of pottery and densification of powder metals or ceramics into desired shapes and to increase material strength. The sintering process occurs at temperatures below the material's melting point, so it saves material and energy. Other advantages include high precision fabrication of complex geometries and minimization of post-processing requirements, so parts are ready to use. However, voids and pores often remain in the material from the original powder, which can lead to undesired behavior and poor performance.

Sintering, using heat alone, occurs at high temperatures (~80% of melting point) and can take several hours. During the sintering process, metal or ceramic powders undergo a three-stage evolution: the particles make contact, then neck and finally the porosity reduces significantly. The dominant driving mechanism for sintering is diffusion. To lower the sintering temperature, required time, and enhance the properties of the final product, electrical current is often used in addition to temperature. However, the role of electrical current — whether sintering enhancement is due to the current passing through the particles or the applied electric field surrounding the particles — is not well understood.

The transmission electron microscope (TEM) enables researchers to image and analyze materials at the atomic scale. New, advanced tools used to apply stimuli *in situ*, such as heat and electrical bias, expand the capabilities of the TEM so scientists can better understand dynamic mechanisms in their samples. The Protochips Fusion system is capable of heating from room temperature to 1200 °C and taking electrical measurements down to the picoAmp level. Fusion is controlled with easy-to-use, advanced workflow-based software called Clarity. Semiconductor MEMS devices, called E-chips, enable ultra-stable heating experiments with best in class temperature uniformity and accuracy, and low noise electrical measurements. A new generation of electrothermal E-chip now combines heating and electrical biasing to allow simultaneous heating and electrical stimuli. Fusion is the only *in situ* solution on the market today that offers such a unique and useful feature. The electrical contacts on the new electrothermal E-chips are patterned over a high-quality, insulating silicon nitride membrane, directly on a silicon carbide membrane, which serves as the sample support and heater. Fusion E-chips are available in a variety of geometries that suit many types of experiments and enable scientists to perform studies that were previously unfeasible.

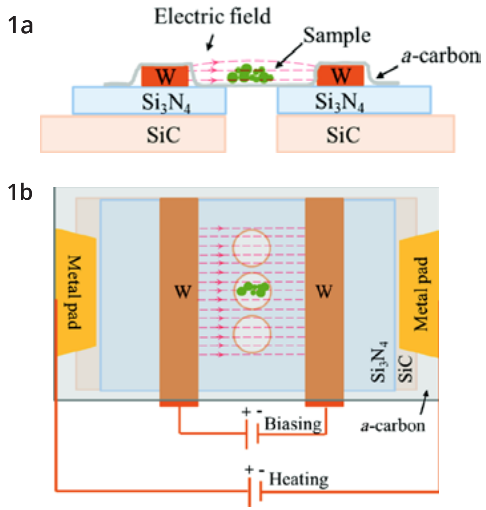

Figure 1: (**a**) Side-view and (**b**) top-view schematics of the Protochips electrothermal E-chips. Sample is heated by SiC heating membrane. Electric field is applied via two parallel W electrodes to generate a homogenous noncontacting electric field.

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Experiment

Researchers in the van Benthem group at University of California, Davis, studied sintering mechanisms in 3 mol% yttria-stablized ZrO_2 (3YSZ) nanoparticles using an aberration-corrected JEOL JEM 2100F/Cs operating in STEM mode. The experiments were carried out with thermal E-chips at temperatures up to 1200 °C, and with electrothermal E-chips to 900 °C and under an electric field of 500V/cm. *In situ* TEM and STEM images were used to monitor the microstructural evolution of the agglomerates during densification in both studies. MATLAB was used to generate densification curves to quantify pore shrinkage as a function of time and applied electric field strength.

Discussion

Fig. 2 shows the consolidation process of 3YSZ particles upon heating, with and without the application of an electric field. Using heating chips, the particles remain structurally unchanged when heated at 900 °C for 106 minutes, Fig. 2 (a-c), and the pores shrink after increasing the temperature to 1200 °C, as indicated by arrows in Fig. 2d and 2e. To compare sintering effects under an electric field, a fresh 3YSZ sample was heated with electrothermal chips to 900 °C and a homogeneous 500 V/cm noncontacting electric field was applied. After just 4 minutes pore shrinkage and particle coalescence occurred. The insets in Fig. 2f-h show a close up view of the interparticle neck growth and particle coalescence observed in the presence of the electric field. Image analysis using MATLAB indicated the projected area of the agglomerate

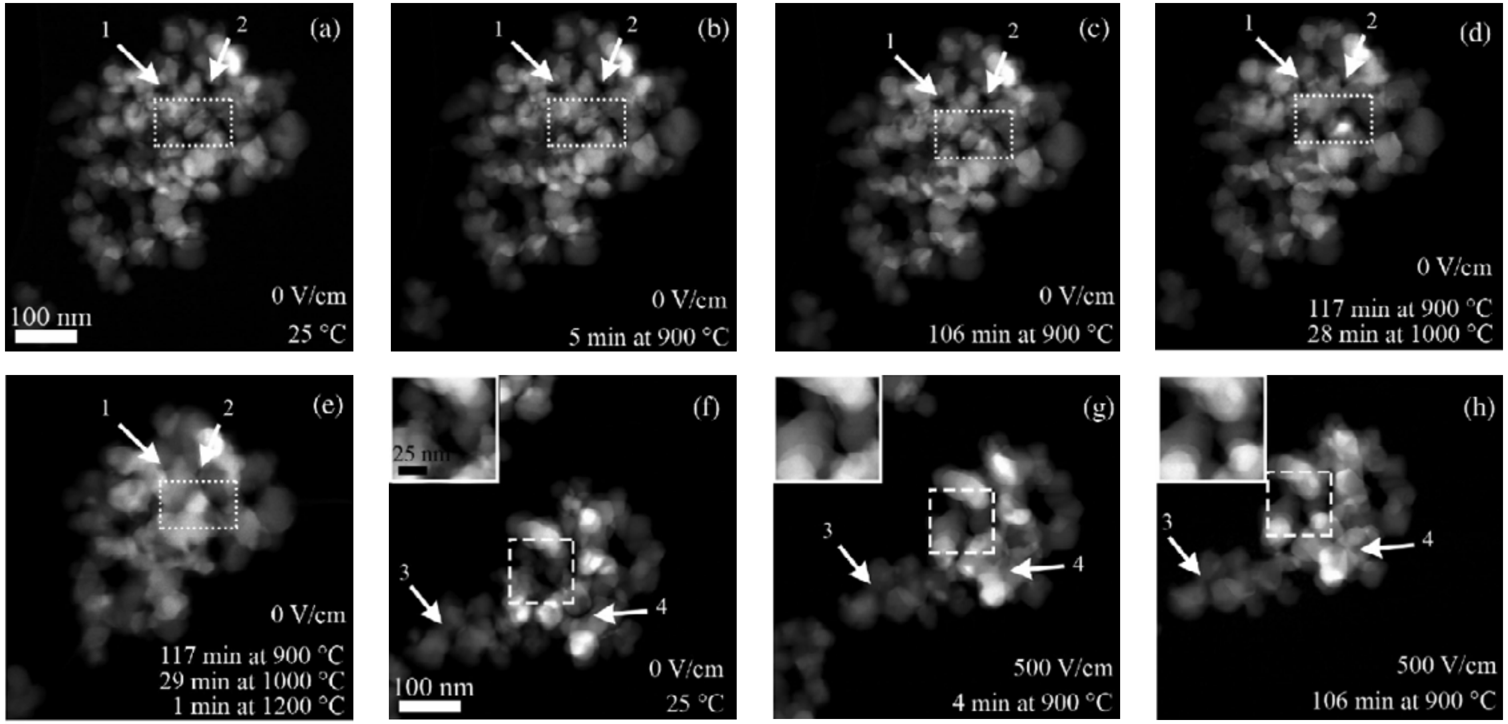

Figure 2: Under no external electrical field: (a-c) Heating to 900 °C does not show significant structural changes after 106 min. (d) and (e) represent pores annihilation upon heating to 1200 °C. Upon application of electrical field: (f-h) show significant morphological changes at 900 °C after only 4 minutes.

was reduced by 3% after 106 minutes when heating to 900 °C in the absence of electric field, while upon application of electric field only after 4 minutes the projected area was reduced by 7%. The authors postulate that enhanced mass transport is a result of defect formation between two adjacent powder particles, which facilitates diffusion. This results in an increase in electrical conductivity and promotes neck formation and consolidation at lower temperatures. However, current-assisted processes have shown faster densification rates compared to noncontacting electrical field assisted processes, likely due to additional Joule heating caused by electrical current passing through the sample.

Applications

Simultaneous temperature and electrical current stimuli are necessary in various fields such as studying domain switching at high temperatures, diffusion rates and directions dependence upon heating, aging and degradation of electronics, etc. For instance, fuel cells and lithium-ion batteries studies at high temperature can reveal the role of diffusion paths that are not activated at room temperature. The Fusion system offers an innovative and unique approach via E-chip devices that are suitable for a wide variety of experiments and work with nearly all microscopes from JEOL, FEI and Hitachi. Contact us to discuss the full range of capabilities of the Fusion platform with the thermal and electrical biasing E-chip sample supports. We can be reached at (919) 377-0800 or contact@protochips.com.

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