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Evidence of surface cleaning during electric field assisted sintering

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The cleaning of nanoparticles from surface oxides or contaminants is critical during the initial stages of spark plasma sintering (SPS). However, so far only indirect evidence has suggested the occurrence of surface cleaning. In situ transmission electron microscopy was used to replicate the processing conditions during SPS to directly observe surface cleaning. Dielectric breakdown was discovered to lead to surface cleaning. Electrothermal depletion of surface oxides is obtained through defect formation, electron trapping and local field enhancement.

Keywords: Sintering; SPS; TEM; Dielectric breakdown

Dense ceramic microstructures are typically formed by sintering green-pressed powder compacts at high temperatures. Compared to conventional densification methods, electric field assisted sintering (EFAS), also termed spark plasma sintering (SPS) or field assisted sintering technology, represents sintering techniques that have shown the potential to increase densification rates, lower sintering temperatures, shorten holding times and suppress grain growth while achieving full density [1–6]. However, the atomic-scale mechanisms for enhanced densification in the presence of an externally applied electrical field remain mostly unexplored [1].

Various EFAS studies [7–14] have demonstrated the densification of metallic nanoparticles that were initially covered by insulating surface oxides or other contaminants. Surface effects during EFAS have been suggested to have a significant influence on inter-particle neck formation during the initial stage of sintering, and can thus contribute to enhanced densification [15]. Munir [16] has shown that the presence of surface oxide films can cause retardation of densification. Such an effect is correlated to the thickness of the surface oxide relative to the particle diameter, and is caused by the stability of some oxide materials at high temperature and limited oxide solubility in the metal particles. Using in situ transmission electron microscopy (TEM), however, Matsuno et al. [17] observed a lowering of sintering temperatures for oxide-covered nickel nanoparticles due to reduction–oxidation reactions in the presence of carbon. Risbud and co-workers [18] used high-resolution TEM imaging conditions to demonstrate the formation of "clean", i.e., contaminant-free, grain boundaries after SPS of AlN powders. The cleaning of particle surfaces from oxide layers or contaminants and entrapped gases at the contact points of nanometric powders must occur during the initial stage of sintering. Several potential mechanisms for surface cleaning effects are discussed in the literature. Tokita [19] described the removal of impurities and adsorptive gases on the surface of powder particles during SPS by a high-temperature sputtering phenomenon generated by plasma formation. However, plasma formation under conventional SPS conditions remains to be verified experimentally. Hulbert et al. [20,21] found no evidence of plasma formation during SPS conditions using in situ atomic emission spectroscopy, direct visual observation and ultrafast in situ voltage measurements. Groza et al. [22] reported in situ removal of surface oxides during plasma-assisted sintering of AlN caused by a combination of electrical discharge, resistive local heating and externally applied pressure. Subsequently, another study suggested that electrical discharge was associated with the thermal and electrical breakdown of insulating films [9]. Bonifacio and van Benthem [23] recently employed in situ TEM experiments for the repeated application of electrical stress to individual nanoparticles and directly observed surface oxide migration away from inter-particle contact areas. Furthermore, the application of constant voltage on nanometric powders during in situ TEM experiments has shown a

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stepwise current increase [24]. The latter observation therefore contradicts spark formation, for which an abrupt but temporary current increase is expected.

With this study we provide for the first time direct experimental evidence for dynamic surface cleaning during EFAS of metallic nanoparticles that are initially covered with ultrathin native oxide layers. We have found that the "cleaning" of ultrathin NiO layers from the surfaces of nickel nanoparticles occurs through electric field-induced dielectric breakdown. Dielectric breakdown describes the loss of capacitance in insulating thin films and is commonly studied in the framework of reliability physics [25]. The configuration of metallic nanoparticles in contact covered with an ultrathin insulating layer is similar to the metal–oxide semiconductor interface in semiconductor devices. Previous studies have suggested dielectric breakdown as a mechanism for surface cleaning [9,17,26], while others suggested that local field intensification at inter-particle contact areas may contribute significantly during the initial stage of EFAS [15,17]. However, there is still no direct experimental evidence for oxide migration stimulated by an applied electrical field combined with a comprehensive mechanistic description.

EFAS studies carried out by in situ TEM [24,26] have demonstrated that dielectric breakdown of surface oxide films occurs at the onset of sintering and hence supports the premise of surface cleaning discussed above. An initially constant and progressively increasing leakage current was observed for individual agglomerates of nanometric nickel particles that were in electrical contact with a scanning tunneling microscopy tip during in situ TEM observation [24]. Figure 1 shows a sketch of the experimental setup. The results from a time-dependent dielectric breakdown study revealed electrical signatures similar to those representing soft breakdown events for single planar oxide interfaces in a semiconductor device structure [23]. However, for the nanoparticle agglomerate, additional initial current spikes were observed followed by subsequent intervals of constant leakage current [24]. Hence, in a particle agglomerate with several oxide interfaces, the gradually improving electrical conductivity results from dielectric breakdown and subsequent neck formation at individual inter-particle contacts [24,27]. For a single inter-particle contact, i.e., the case of only two adjacent nickel particles, each covered with surface oxides, dielectric breakdown will occur at a faster rate compared to a planar dielectric layer in a semiconductor device structure due to particle shapes and respective surface curvature (cf. [23,26]). At inter-particle contact areas, therefore, it is suggested that the local field strength due to accumulated surface charges is at or above the breakdown strength for ultrathin oxide dielectric layers. Such a hypothesis can be explained by a time-dependent charge accumulation up to maximal attainable surface charge density [15,28].

In situ scanning transmission electron microscopy (STEM) observations show the removal of the ultrathin NiO film with the application of an electrical stress of roughly 10^6 V cm^{-1}. The high-angle annular dark field (HAADF) images in Figure 2 reveal that the surface oxide layer with a thickness of ~2 nm observed before electrical biasing (stage I) is depleted at the inter-particle contact and forms a 3 nm wide neck (stage III). Grain boundary formation was initiated by dielectric breakdown, with subsequent oxygen migration due to Joule heating. Oxygen migration accommodates an increase in neck size at the inter-particle contact (stage IV). Electron energy loss spectroscopy (EELS) analysis

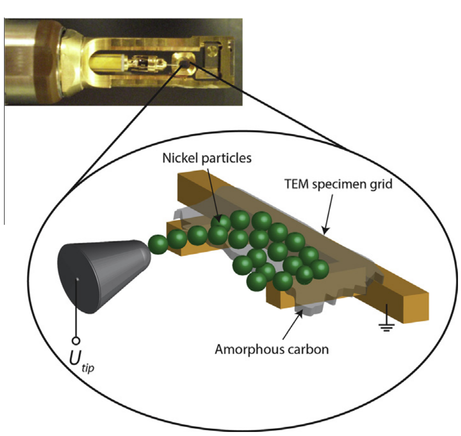

Figure 1. Picture of the utilized TEM specimen holder and sketch of the experimental geometry. Ni nanoparticles were deposited on a TEM specimen grit that supports an amorphous carbon film. A tungsten scanning tunneling microscopy tip mounted on a TEM specimen holder was used to electrically contact the nanoparticles and apply an electrical bias U_{tip}.

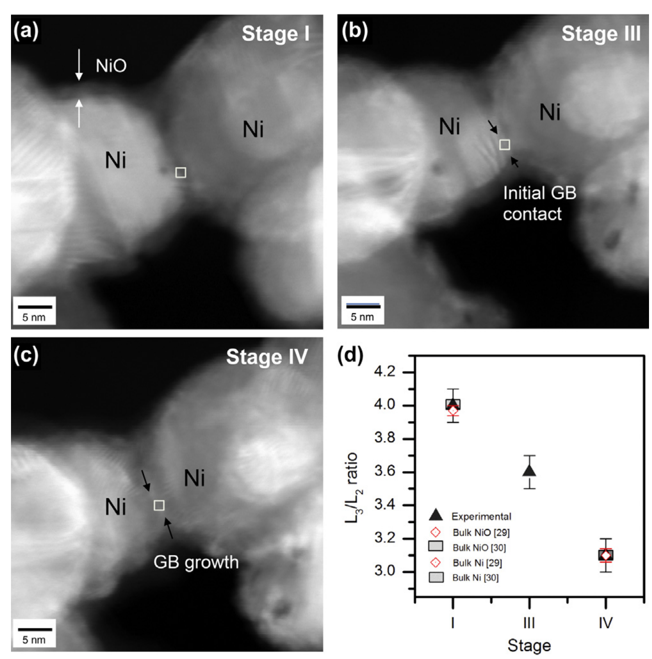

Figure 2. HAADF STEM images of two contacting particles before (a) the application of an electrical bias (stage I). The particles are covered with continuous NiO layers. (b) and (c) show the progression of surface oxide removal and the subsequent neck formation. EELS spectra of the Ni $L_{2,3}$ absorption edges were recorded while the electron beam across the inter-particle contact area (box in (a)–(c)) was scanned. The L_3/L_2 EELS intensity ratio were calculated from experimental EELS data of the Ni $L_{2,3}$ edges and plotted in (d). Reference spectra for bulk NiO and Ni are plotted for comparison.