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# In situ Nanoindentation of Nanocrystalline $MgAl_2O_4$ Agglomerates and Their Effect on Densification Behavior

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Many variables, such as temperature, time, and heating rate affect the consolidation behavior and final densities during sintering. One critical aspect is the resultant microstructure from green pressing prior to sintering. Ultrafine magnesium aluminate, $MgAl_2O_4$, was synthesized via the co-precipitation and Pechini/polymeric precursor methods [1,2]. The Pechini method of powder synthesis utilizes metal ion chelates by the polymerization of citric acid and ethylene glycol with stoichiometric amounts of metal nitrate salts dissolved in water that are then calcined in a highly oxidative environment. The co-precipitation method drops dissolved metal nitrates into an ammonia solution where the presence of a large pH gradient drives the creation of metal hydroxides that can be subsequently washed and calcined. The average particle size of each respective nanopowder ranged between 5nm and 16nm.

The two types of powder were simultaneously and isothermally sintered at 1300°C for various times. Drastic differences in the densification behavior between the two nanopowders were observed with the co-precipitated powder reaching relative densities upwards of 90% whereas the Pechini powder only achieved a maximum density of 55% (Figure 1a and 1b, respectively). After a thorough investigation, including infrared spectroscopy, thermal gravimetry, differential scanning calorimetry, and transmission (TEM) and scanning (SEM) electron microscopy it was discovered that the major contributing factor, for the difference in densification behavior between the two powders, was the degree of agglomeration in one versus the other. SEM imaging of sintered co-precipitated fracture surfaces showed dense microstructures with very little porosity whereas the sintered Pechini fracture surfaces contained areas of dense, well sintered grains with large pores spread throughout the microstructure (Figure 1c and 1d, respectively). The pores are what produced the low density sintered pellets, however, the pores themselves were due to the presence of strong agglomerates within the pellet green body [4].

The agglomerates were observed to be qualitatively “strong” due to the inability to destroy them during initial green pressing. In this case, “strong” hypothesizes the presence of primary bonding between particles in the form of necks or pre-sintered bonds. In situ nanoindentation experiments of individual agglomerates were carried out using a JEOL-JEM 2500 SE TEM with a flat 1 micron canonical tip mounted on a Hysitron PI-95 Picoindenter. By performing displacement controlled indentations with nanometer resolution, load data (μN) was generated that directly represents agglomerate strength and mechanical property information. Quantitative indentation data was acquired in real time inside a TEM allowing imaging and other microscopic analysis techniques during deformation of the agglomerate (Figure 2a). Pressures at the tip upwards of 350 MPa were observed during compression of individual agglomerates. Linear regions were extracted from the load vs. displacement data (Figure 2b) that represent elastic deformation because of the primary bonding mentioned above. Advancements in sample holders used for this work allowed mechanical analysis of agglomerate properties at length scales previously unattainable. In situ TEM experiments will be discussed and correlated to data obtained by macroscopic pressing of green bodies. Preliminary results reveal that the agglomerates of the Pechini powder were exceedingly strong, which has limited its densification [5].

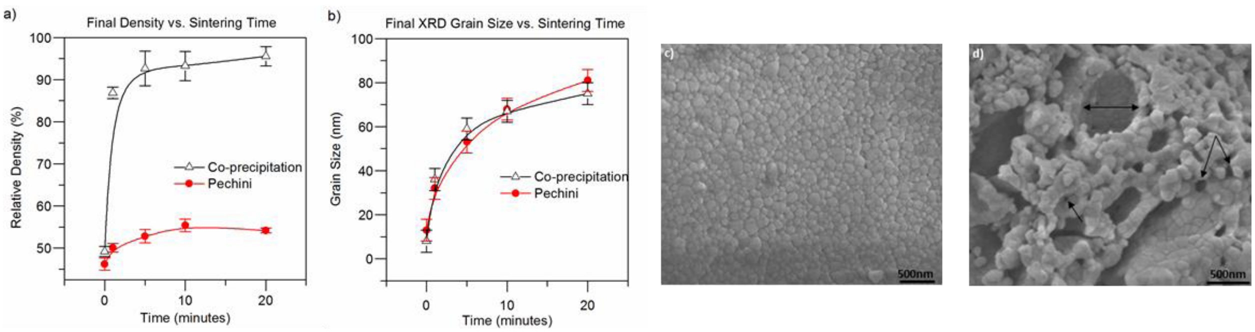


**Figure 1.** (a) The final sintered density of the Co-precipitated powder was much higher than the Pechini powder for every amount of time even though the (b) crystallite size was comparable between the two. SEM micrographs of fracture surfaces show dense, low porosity microstructures of the (c) co-precipitated powder but large pores are present limiting density of the (d) Pechini powder *(figure reproduced from [1])*.

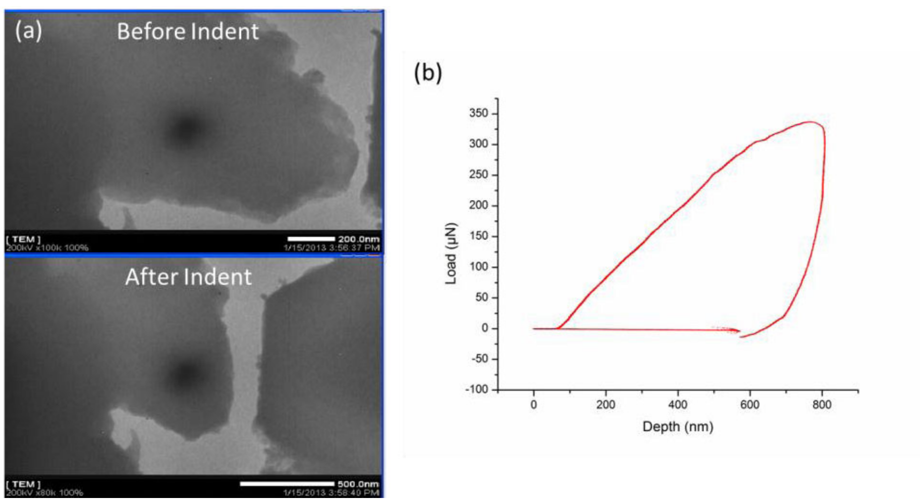


**Figure 2.** (a) Screen shots from TEM in-situ nanoindentation of an approximately 1 μm diameter agglomerate before and after indenting along with the corresponding (b) real-time load vs. displacement curve.

References:

[1] M. P. Pechini, "Method of Preparing lead and alkaline earth titanates and biobates and coating method using the same to form a capacitor.", U. S. Pattent, no. 3,330,697, 1967
[2] J. G. Li, T. Ikegami, J.-H. Lee, T. Mori, andY. Yajima, "Synthesis of Mg–Al spinel powder via precipitation using ammonium bicarbonate as the precipitant," J. Eur. Ceram. Soc., 21[2] 139-48 (2001)
[3] Jorgen Rufner et al, presented at Material Science and Technology Conference 2012, Pittsburgh, PA
[4] Jorgen Rufner et al, *Synthesis and sintering behavior of ultrafine (< 10 nm) magnesium aluminate spinel nanoparticles*, Journal of the American Ceramic Society, *(submitted Dec. 2012)*
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