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Reacting oxide nanoparticles with a substrate

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Solid-state reactions are frequently encountered in ceramic processing. Titanate electronic ceramics [1] and oxide superconductors [2] are among the many materials synthesized via solid-state reaction. Solid-state reactions may also occur as an unwanted side effect of high-temperature operation of ceramic-containing devices, e.g. pyrochlore-forming reactions in solid oxide fuel cells [3]. The spinel-forming reaction between a periclase-structured oxide and a sesquioxide (sapphire is a favorite) has been studied for many years (see [4, 5]). A variety of reaction geometries have been studied including mixed powders [6], thin films [7] and powders on single crystals [8]. A new geometry using small cubes of magnesium oxide on single-crystal sapphire substrates is investigated here using the TEM. In addition to providing a novel reaction geometry this method permits analysis of particle-substrate interactions that may have broader implications for nanoparticle technology.

Nanocubes of magnesium oxide were produced as smoke particles by burning magnesium metal in air [9, 10]. Some of the smoke particles were collected on a sapphire substrate pre-thinned to electron transparency. The substrate had a surface orientation of [0001] and the smoke cubes have {001} faces so that the initial orientation relationship is limited to $\{001\}_{MgO}//(0001)_{sapphire}$. It is assumed that the particles are free to rotate in-plane until strong bonds are formed at the interface. The reaction heat treatment is performed *ex situ* in an air atmosphere. A JEOL 2010 and FEI T12 were used for microscopy.

TEM observations suggest that the particles have some preferred in-plane crystallographic orientations relative to the substrate with low-index planes being nearly aligned. Figure 1 is a BF TEM image of several particles with an in-plane orientation close to $\langle 011\rangle_{MgO}//\langle 10\bar{1}0\rangle_{sapphire}$.

After reaction at ~1100 °C spinel particles form on the sapphire substrate. The orientation relationship (OR) is predominantly $(111)_{spinel}//(0001)_{sapphire}$ and $[110]_{spinel}//[10\bar{1}0]_{sapphire}$. This OR requires crystallographic rotation of the spinel relative to the original MgO during the reaction. This suggests the OR is determined by the sapphire and the starting MgO cube orientation is irrelevant for these particular reaction conditions. Figure 2 is a diffraction pattern of a specimen after reaction showing the OR. Figure 3 shows the morphology of some particles after the reaction. Many of them form as thin triangular platelets.

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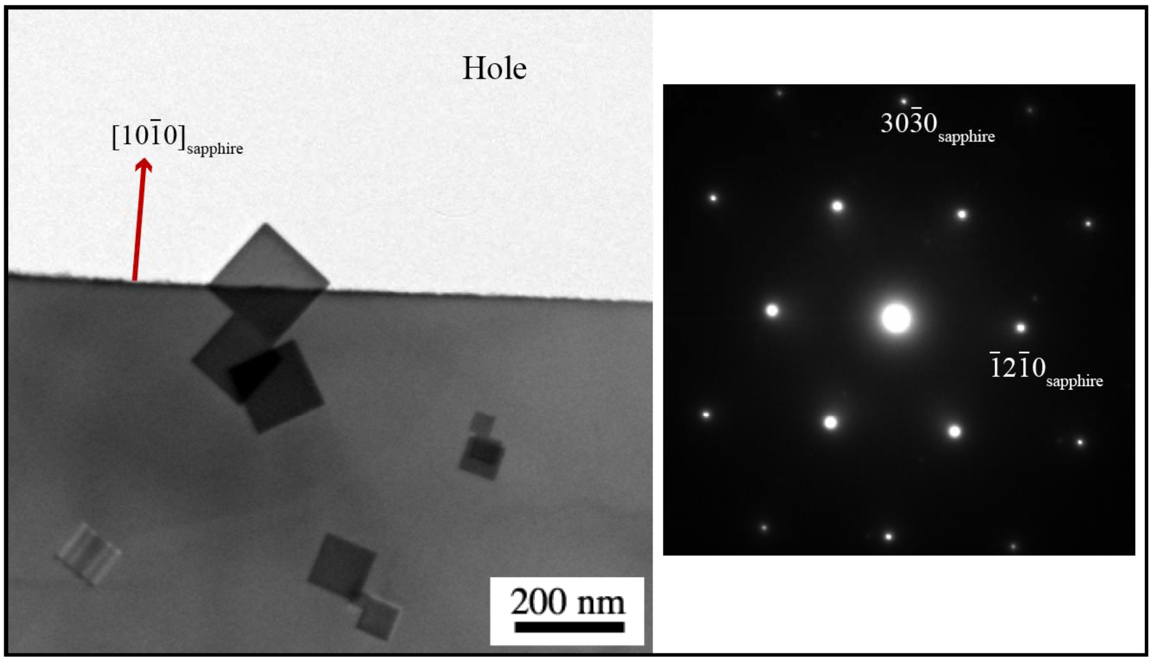

Figure 1: BF TEM image of MgO nanoparticles on a sapphire substrate with SADP indicating the orientation of the sapphire.

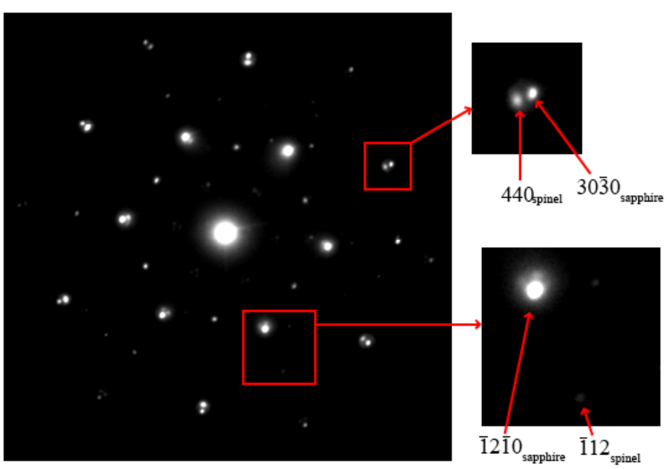

Figure 2: SADP showing the orientation relationship between the spinel phase and the sapphire.

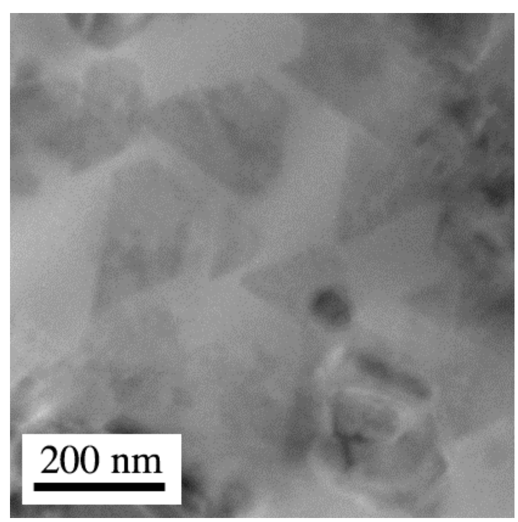

Figure 3: BF TEM image of spinel reaction products as triangular platelets.

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