

Nanocomposite mullite/mullite powders by spray pyrolysis

Daniel M. Dabbs^{1,2}, Nan Yao² and Ilhan A. Aksay^{1,2}

¹Department of Chemical Engineering and ²Princeton Materials Institute, Princeton University, Princeton, NJ 08544, USA

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Abstract

A mullite/mullite nanocomposite powder has been synthesized, composed of nanometer-size $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ('3:2') mullite precipitates within a matrix of the high alumina $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ('2:1') mullite. Historically, the transition from the metastable high-alumina phase to the thermodynamically stable '3:2' phase of mullite has been thought to be a continuous process, involving a continuous solid solution between the two forms of mullite. In contradiction to this widely held view, our high resolution transmission electron microscopic characterization confirms that a first order phase transition between two distinct mullites occurs. The high degree of interface coherence between the precipitates and the matrix allows us to speculate that the mechanical properties of the matrix could be enhanced by a process similar to the precipitation hardening of metals.

Introduction

The use of precipitation hardening in the strengthening of metal alloys and the importance of coherent interfaces in the expression of this phenomenon are well known [1,2]. A comparable mechanism for improving the mechanical properties of ceramics may exist for ceramic matrices, utilizing coherent, nanometer-sized inclusions within the ceramic matrix. This expectation is supported by studies on ceramic nanocomposites, for which significant increases in strength are observed in samples containing nano-sized inclusions within the grains or at the grain boundaries of the matrix phase [3,4].

The traditional method for making precipitation-hardened metals is to heat treat an alloy in a single-phase region at elevated temperatures, then thermally quench it to a two-phase region to induce the formation of nano-sized inclusions within the matrix [1,2]. Thermal quenching methods are not suitable for ceramics due to their weak thermal shock resistance. In contrast to this high temperature approach, recent

work on self-organized quantum dots uses comparatively low temperature ($\sim 625^\circ\text{C}$) processes to form patterned arrays of coherent quantum dots on GaAs substrates [5]. In a similar manner, we create a homogeneous, single-phase precursor powder of an aluminum silicate at low temperature ($\sim 350^\circ\text{C}$), then raise the temperature of the powder to induce nucleation and growth of nanosize precipitates within the powder grains. An expected outcome of this decomposition reaction, as predicted by the equilibrium phase diagram [6], is to form alumina precipitates within the mullite matrix. Contrary to this expectation, we show that the precipitates and the matrix phases are two distinct phases of mullite: the precipitates composed of the $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ('3:2') phase and the matrix composed of the $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ('2:1') phase.

Mullite is an economically important material as a structural ceramic given that it retains a significant fraction of its room temperature strength at high temperatures, and strongly resists thermal shock, corrosion, and creep [6–10]. Its low dielectric and thermal expansion coefficients suggest its use in electronic

packaging applications [8]. From the combination of mullite properties, mullite/alumina composites have been long regarded as a composite system of high promise for high-performance, high temperature structural materials [11].

The elemental structure of mullite can be expressed as $\text{Al}_2^{\text{VI}}(\text{Al}_{2+2x}^{\text{IV}}\text{Si}_{2-2x}^{\text{IV}})\text{O}_{10-x}$ where x represents the missing oxygen and lies within the limits $0.17 \leq x \leq 0.6$ [6,7,11–16]. The roman numerals VI and IV represent octahedral and tetrahedral sites respectively within the unit cell. It is generally accepted that mullite can be found in one of two forms: (i) the stable $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ phase (3 : 2 or the orthorhombic phase); and (ii) a high-alumina, metastable phase given the nominal composition of $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (2 : 1 (77.24 wt% Al_2O_3) or the tetragonal or pseudotetragonal phase) [11,14–16]. (For 2 : 1 mullite, $x = 0.4$; for 3 : 2 mullite, $x = 0.2$).

As a result of the apparently small differences between the structures of the two mullites, past studies on the transition from one form of mullite to the other have interpreted the results of ^{27}Al NMR [17], X-ray diffraction (XRD) [15,18], and Fourier transform infrared spectroscopy (FTIR) [19] characterization to suggest that a so-called transitional mullite exists, as a product of a continuous solid solution that spans the 3 : 2 and 2 : 1 phases. In direct contradiction to this conventional view, the present study shows that annealing spray pyrolyzed powders corresponding to a 2 : 1 composition ($2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) at high temperature for short intervals results in 3 : 2 nuclei within a 2 : 1 matrix. We believe this is the first demonstration that the two forms of mullite are indeed discrete phases and negates the view that they are merely the respective edges of a continuous solid solution phase.

Experimental

The precursor powder used in the synthesis of mullite/mullite composites was derived from a solution of aluminum nitrate nonahydrate and tetraethoxysilane (TEOS) in absolute ethanol and subsequently spray pyrolyzed. The metals content of the solution contained sufficient salt and alkoxide to (theoretically) yield a composite powder composed of 20% alumina and 80% mullite by weight when fully converted to the constituent oxides. This composition is equivalent to an overall alumina mole fraction of 0.67, equivalent to the stoichiometry of 2 : 1 mullite. The clear solution was sprayed onto a hot metal surface ($T \sim 350^\circ\text{C}$) to

rapidly remove the solvent. The resulting brown powder was calcined at 600°C for 8 h in air, which reduced but did not eliminate the off-white appearance of the powder. High temperature heat treatment at 1400°C (in air) for 1 h resulted in a fine white powder of loose agglomerates.

Samples for high-resolution transmission electron microscopy (HRTEM) were prepared from slices cut from pellets of powders embedded in epoxy resin. Thin slices were prepared using the standard techniques of mechanical grinding followed by argon ion-milling at 4 kV with liquid nitrogen cooling. Imaging and elemental analysis were performed using a Philips CM 200 Field-emission TEM equipped with an EDAX MX-10 and PGT-IMIX energy dispersive X-ray spectroscopy system. FTIR spectroscopy was used to follow the chemical changes in the precursor powder during heat treatment. Transmitted-light samples for FTIR were prepared by mixing ~ 3 mg of the sample powder with 300 mg spectra-grade KBr powder, grinding to mix, and then pressing to form a semi-transparent disk of KBr containing the suspended sample powder. All FTIR runs were transmitted energy experiments, performed on an IBM IR/44 spectrophotometer.

Results and discussion

Phase separation was observed in samples heat treated at 1400°C (Figure 1). The nano-inclusions were composed of a lower Al : Si ratio within an almost perfect crystalline matrix of higher Al : Si ratio. As shown in Figure 1(a), the nano-inclusions appear randomly distributed with domain sizes ranging from a few up to 20 nm in diameter. Each domain is clearly observed to share a common crystalline orientation with the matrix. Figure 1(b) is an example of a typical HRTEM image of the matrix when viewed along the (100) zone axis. The interface between two mullite phases is quite coherent.

This process can be compared with the controlled positioning of self-organized quantum dots on GaAs facets, also performed at low processing temperatures [5]. In these systems, the phase that forms the quantum dot selectively grows on high-surface energy facet surfaces on the GaAs surface. The coherence between the substrate and the quantum dot induces high strain at the interface.

The transformation of one mullite to the other can be viewed as decomposition of the 2 : 1 phase to 3 : 2 phase, exsolving α -alumina [20]: $2(2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2) \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \alpha\text{-Al}_2\text{O}_3$. In this

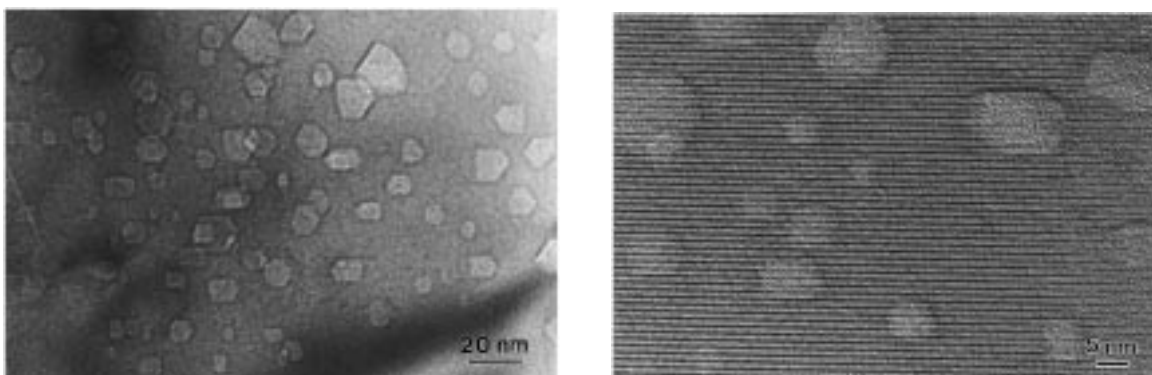


Figure 1. (a) Low-magnification TEM image and (b) high-resolution TEM image of mullite sample annealed at 1400°C for 1 h, when viewed along the (100) zone axis at 200 keV.

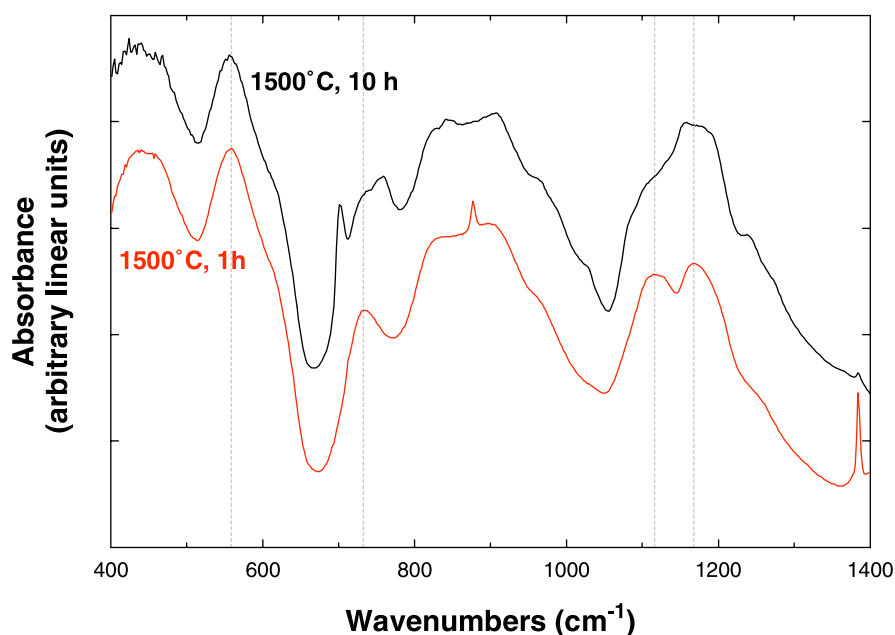


Figure 2. FTIR of the transition of 2 : 1 mullite to 3 : 2 mullite with respect to annealing time. The chemical shifts observed in the Al–O–Si region of the spectra (1120 , 1167 cm^{-1}) reveal the transformation of 2 : 1 to 3 : 2 phase. Similar studies in the past have interpreted the gradual shifts as indicative of a transitional solid solution. However, in conjunction with TEM observations, the changes in band structure and position can also be explained as the combined absorption from distinct phases.

model, the 2 : 1 mullite phase can be regarded as a supersaturated phase; metastable with respect to a composite of the 3 : 2 and alumina phases. We would then expect that the 2 : 1 phase would completely convert to 3 : 2 with exsolved α -alumina providing the included phase. However, for reasons not yet fully understood, the included phase did not consist of alumina but instead were particles composed of the 3 : 2 phase.

FTIR observations (Figure 2) of powder held at anneal temperature for different times show the transformation of one phase to the other. The gradual nature of the transformation has led past researchers to the conclusion that the mullite/mullite transformation passes through a continuous solid solution range, with the alumina precipitating out of solution as the transformation proceeds. In our case, the precipitating phase within the

matrix is mullite not alumina. Mass balance requires that the alumina rejected by the precipitation of the 3 : 2 phase be incorporated within the matrix phase making it richer in alumina content than the starting 2 : 1 composition.

The shape of the nuclei is constrained by considerations of total surface energy and the coherence between the matrix phase and the daughter nuclei [21]. As the volume change caused by the 2 : 1 to 3 : 2 transition is small and the concomitant coherence between the two phases large, it is expected that the nuclei will be anisotropic and resemble twinned regions in the low degree of disregistry between the two phases (Figure 1). Eventually, an alumina phase is expected to precipitate as predicted by the equilibrium phase diagram [6]. During this transition stage, alumina appears to be retained within the 2 : 1 solid solution matrix. Such behavior resembles the transitional mullite model, but the different degrees of alumina solubility in the respective phases do not affect the over-all conclusion: that a mullite/mullite nanocomposite powder has been made, composed of nano-sized 3 : 2 inclusions within a 2 : 1 matrix.

Conclusions

We have observed a discrete phase separation within a metastable, high-alumina mullite matrix using high resolution transmission electron microscopy. The formation of 3 : 2 nuclei within the 2 : 1 matrix supports the view that two distinct mullite solid solutions exist. The interfaces between the nanoinclusions and the ordered matrix are seen to be highly coherent, implying that the matrix may be strengthened by a process similar to the precipitation hardening of metal alloys.

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