Direct measurement of interface energies of magnesium aluminate spinel and a brief sintering analysis

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ABSTRACT

Surface and grain boundary energies are key parameters for understanding and controlling microstructural evolution. However, reliable thermodynamic data on interfaces of ceramics are relatively scarce, limiting the realization of their relevance in processes such as sintering and grain growth. In this work, the heat of sintering itself was used to quantify both surface and grain boundary energies in $MgAl_2O_4$ spinel. Nanoparticles were compacted and heated inside a Differential Scanning Calorimeter (DSC) when densification and grain growth were observed. The evolved heat signal was quantitatively attributed to the respective microstructural evolution in terms of interfacial area change, allowing determination of average surface and grain boundary energies for $MgAl_2O_4$ as $1.49\,J\,m^{-2}$ and $0.57\,J\,m^{-2}$, respectively. The data was then used to interpret the thermodynamics involved in density and grain growth during isothermal sintering of $MgAl_2O_4$.

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1. Introduction

$MgAl_2O_4$ has a combination of highly desirable properties, such as high melting point, strength at elevated temperature, high chemical inertness, low thermal expansion coefficient, and high thermal shock resistance [1,2]. This combination makes it an excellent refractory material, and enables high resistance to swelling at high temperatures and irradiation environments [3]. Recently, ultrafine nanocrystalline $MgAl_2O_4$ has been reported to show hardness that surpasses the values observed for sapphire single crystals with comparable optical properties [4]. However, these properties could only be achieved when samples were properly processed to minimize defects and porosity, which constitutes one of the greatest challenges in ceramic technology [5].

Numerous studies have focused on the sintering of $MgAl_2O_4$ to provide fundamental understanding that enables densification of compacts to full density without the need for pressure-assisted processes [2,6,7]. It is generally accepted that solid-state diffusion dominates sintering and grain growth in this material, and oxygen is the rate limiting specie due to the smaller diffusion coefficient

($\sim 10^{-6}\,m^2/s$) as compared to Al and Mg ($\sim 10^{-2}\,m^2/s$) [2,8–10]. Grain-boundary diffusion of oxygen anions thus governs the densification rates, and significant pore elimination can be observed during sintering even without additives [2]. However, truly dense ceramics are still only attainable by using pressure-assisted processes.

There is very limited data on the thermodynamics of interfaces of this system to enable calculation of sintering stresses to optimize pressureless densification from a thermodynamic perspective [11–13]. As described by Lange et al. [14–16], sintering is an interface elimination/formation process, and therefore the ratio of interfacial energies, or the dihedral angle, plays a major role in the microstructural evolution regardless of the mass transport mechanism [17,18]. In particular, the stability of pores in both early and final stages is governed by the interfacial energies themselves, and therefore these can potentially be used to understand and optimize pore elimination.

In this work, both surface and grain boundary energies of $MgAl_2O_4$ spinel nanoparticles were determined by measuring the "heat of sintering" by differential scanning calorimetry (DSC). Stoichiometric $MgAl_2O_4$ was synthesized by using coprecipitation method [19], and powder compacts subjected to sintering inside a DSC. Heat of sintering was quantified and used to determine the interfacial energies by attributing the exothermic heat effect to the

observed microstructural evolution using a previously validated procedure [20,21]. Both surface energy and grain boundary data were consistent with literature results obtained by different methods. An isothermal sintering study was then performed and the interfacial thermodynamic data used to describe the quantitative relationship between densification and grain growth.

2. Experimental procedures

2.1. Synthesis and characterization

Reverse-strike simultaneous-precipitation method was used to synthesize $MgAl_2O_4$ nanoparticles [19]. This process consists in mixing the salt precursors ($Mg(NO_3)_2 \cdot 6H_2O$, >99%; and $Al(NO_3)_3 \cdot 9H_2O$, >98%; Sigma Aldrich Inc.) in the stoichiometric ratio in deionized water until a homogeneous mixture was achieved. The mixture was then dripped into a solution of 5 M ammonia and the precipitated hydroxide powder separated from the solution using a centrifuge operated at 3000 rpm. In order to remove ammonia excess, the precipitated powder was washed with deionized (DI) water, followed by 50% DI water and 50% ethanol, and finishing with an ethanol washing. After drying overnight at 100 °C, the powder was calcined at 700, 750, 800 and 900 °C for 5 h to obtain the spinel phase with different grain sizes. Samples were named according to annealing conditions: MAS700, MAS750, MAS800 and MAS900. The water contents of the nitrates were measured using thermogravimetry before the synthesis.

Powder X-ray diffraction patterns were obtained using a Shimadzu XRD-7000 (CuKα radiation, λ = 1.5406 Å) operated at 40 kV and 30 mA. Crystallite sizes were calculated from XRD full spectra of the samples mixed with a standard silicon (JCPDS # 27–1402) powder sample. Surface area was measured using the Brunauer−Emmett−Teller (BET) method in a Micromeritics Gemini VII Surface Area Analyzer equipped with VacPrep 061 degas station (Micromeritics Instrument Corporation, Norcross, Georgia).

2.2. Surface and grain boundary energy measurements

Interfacial energies were determined by inducing sintering of powder compacts inside a DSC [20]. The method relies on the accurate measurement of the exothermic heat effect expected from the densification and grain growth of the powder, and attribution of the integral heat to the associated microstructural evolution. That is, during sintering, many mass transport mechanisms can be activated, however, from an energetic perspective, the process entails reduction of surface area and formation (followed by reduction) of grain boundary area. If all processes (and reactions) other than sintering itself, such as the desorption of water or other molecules preadsorbed on the surface of the particles, redox reaction of one or more of the elements, or evaporation of an element, are avoided to the point they have negligible energetic contribution, the total integrated heat can be singularly attributed to the interface area change, and therefore interface energies can be calculated [20,21].

$MgAl_2O_4$ nanoparticles were compacted into pellets using 200 MPa of pressure. Three pellets with diameter of 3 mm and about 50 mg each were subjected to a heating cycle inside a DSC/TG Setsys Evolution 18 DSC/TG, Setaram Inc. (DSC sensitivity 0.4 μW and TG resolution 0.03 μg, calibrated by fusion of known metals). The samples were first subjected to a degassing procedure in which they were heated up inside the calorimeter up to 600 °C under vacuum to eliminate adsorbed water molecules that could affect the surface energy [22,23]. Without exposing the samples to room atmosphere, the instrument was cooled down to room temperature and heated up from 25 °C up to 1350 °C using a heating rate of 20 °C/min under synthetic air flow of 20 mL/min and held in isothermal treatment

for 15 min. This condition was observed to cause pronounced sintering and grain growth as confirmed by microstructural analysis after the thermal cycle. To enable quantification of the heat signal, without removing the sintered sample from the instrument, an additional cooling and heating using the exact same cycle was conducted to be used as a baseline of the respective sample. Pronounced sintering characteristic heat effects were observed and the respective integral heat recorded.

Additional experiments following the same protocol were performed, but with the heating ramp stopped before and after the exothermic peak of sintering. This was done so that the microstructure of the sample at each of those states could be quantified and the measured heat attributed to the interface area change. One sample was quenched before the exothermic peak and identified as State #1, while another was quenched right after the peak, and identified as State #2. The total enthalpy of these respective states can be described as:

$$H_{State\#1} = A_1^S \times \gamma_S + H_B + A_1^{GB} \times \gamma_{GB} \qquad (1)$$

$$H_{State\#2} = A_2^S \times \gamma_S + H_B + A_2^{GB} \times \gamma_{GB} \qquad (2)$$

Here, H_B is the bulk enthalpy assumed unchanged during sintering; A^{GB} and A^S are the grain boundary and surface areas, with the subscripts 1 and 2 indicating the respective state. γ_S and γ_{GB} are the surface and grain boundary enthalpies, respectively. Therefore, the measured enthalpy during sintering (integral of the heat signal) represents the subtraction between equations (2) and (1). Provided the heat value, accurate measurements of the interfacial areas at the two states shall provide a quantitative relationship between the γ_S and γ_{GB}. While the surface area can be determined by gas adsorption methods (e.g. Brunauer–Emmett–Teller, BET, method), the grain boundary area can be estimated by comparing the surface area from gas adsorption and the total interface area calculated from crystallite size measured by X-ray diffraction analysis (Scherrer method) and transmission electron microscopy. The total interfacial area (surface + grain boundary) calculation assumes a tetrakaidecahedral grain shape and a grain size distribution, such that the total area is given by $\frac{S}{\bar{d}} V_m exp\left[-2.5(ln\sigma)^2\right]$, where, V_m is the molar volume, $\bar{d}$ is the average grain size, and the exponential term accounts for the grain size distribution with a standard deviation $ln\,\sigma$, and S is a shape factor (3.55). Grain size distribution and shape were assumed the same before and after sintering. Although the tetrakaidecahedral shape is consistent with microscopy observations, it is virtually impossible to certify shape and account for deviations in a real particle. Since the surface area is being directly measured, the shape assumption only influences on the grain boundary area. However, an error of +/− 10% in the grain boundary area will provide a variation below 0.06 Jm^{-2} in the calculated final grain boundary energy, speaking for the robustness of the adopted calorimetric approach.

It is important to note that equations (1) and (2) assume that surface and grain boundary energies to be independent on temperature and grain size. The authors acknowledge this is an approximation as both energies change according to the exposed planes (in the case of surface), or grain orientation (for grain boundaries), which are sensitive to sintering and grain growth behavior [24], and temperature itself. The calculated energies should be, however, an average value along the process, which is of great practical use.

The authors also note that an extension of Gibbs thermodynamics have shown that surface energy of spherical particles should decrease with decreasing radius [25]. This would imply that nanoparticles (State #1) and large particles (State #2) could have different surface energies simply because of the size difference. However, when dealing with anisotropic ceramic nanoparticles,