

## A Review on the Sintering and Microstructure Development of Transparent Spinel (MgAl<sub>2</sub>O<sub>4</sub>)

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A review of the densification mechanisms and the microstructural development for transparent spinel made by free sintering and by hot pressing is given. The paper is divided into two main parts. The first part considers spinel without any sintering additives because there still is some controversy concerning the role of cation stoichiometry on sintering and grain growth. The second part discusses the role of the classic sintering aid, LiF, in processing transparent spinel. LiF is shown to have multiple behaviors: (1) it initially wets spinel and forms a liquid phase at relatively low temperatures, which affects early-stage densification and also grain growth; (2) upon cooling from intermediate temperatures, or even from higher temperatures if microstructure evolution (e.g., formation of closed porosity) prevents volatization, the LiF-containing liquid dewets and resides in isolated pockets; (3) LiF alters the cation stoichiometry, thereby enhancing diffusion via an increase in the concentration of oxygen vacancies; this affects both the densification rate and grain growth; and (4) it reacts with impurities in the system, thereby acting as a cleanser. For the production of transparent spinel, it is critical that LiF or associated reaction products not be retained as a secondary phase.

#### I. Introduction

NUMEROUS studies have been performed to understand the densification and microstructure evolution mechanisms of magnesium aluminate spinel, MgAl<sub>2</sub>O<sub>4</sub> (hereafter termed "spinel").<sup>1-28</sup> Some of these are generic and focus on fundamental mechanisms that have broad applications as refractories, fusion reactor components, and electronic ceramics. Others are driven by the desire to make transparent spinel. Applications for transparent spinel include infrared domes and windows for missiles, transparent armor for air and ground vehicles, optical lenses, laser host materials, windows for lasers, optical heat exchangers, windows for radio frequency powder injectors, plasma diagnostic devices, watch crystals, sight glass for high pressure or temperature vessels, high pressure arc lamps, and chomatographs. Much of the research has been motivated by the need to obtain transparency across the visible and/or infrared electromagnetic radiation spectrum.<sup>29–31</sup> The latter need implies that a residual porosity of less than about 0.1% and pore dimensions not greater than about a tenth of the wavelength of the light of in-

Manuscript No. 25570. Received November 30, 2008; approved March 21, 2009. Presented at the International Conference Sintering 2008, November 16-20, 2008, San Diego, USA. terest are required; for infrared applications, this means that pore diameters should not exceed about 20 nm.<sup>29</sup> This stringent requirement on the allowable level of porosity has provided considerable challenges for reliable manufacturing, and has driven up the cost by mandating that parts be hot-isostatically pressed. The fabrication of large parts has been particularly difficult. Recent efforts have been focused on minimizing final grain size for mechanical strength improvement.<sup>3</sup> A focus on *late-stage* sintering has occupied significant research that the present paper attempts to summarize. In addition to the removal of porosity, microstructure evolution is also governed by processes during late-stage sintering, namely dopant-grain-boundary and pore-grain-boundary interactions.<sup>19</sup>

Some consideration must also be given to the source of the spinel powder, because different methods used to synthesize spinel lead to variations in powder characteristics that may govern the densification behavior, microstructure development, and final properties, as with other ceramics. In particular, the particle size, size distribution, morphology, purity, and stoichiome-try are known to be important.<sup>7,8,30,32,33</sup> Spinel starting powder may be synthesized by several chemical routes, typically using solutions of Mg and Al nitrates or sulfates, followed by coprecipitation and calcination. The most commonly used commercial powder, made by Baikowski Incorporated, is synthesized through the coprecipitation of Mg and Al salts. This is followed by desulfurization, further calcining, and, finally, jet milling to adjust the particle size and surface area. Typically, small amounts of sulfur remain in the commercially available powder. Other techniques used to synthesize spinel powders include modified Bayer-type processes, metal alkoxide hydrolysis, various sol-gel-type procedures, and a chemical technique that was shown to have tremendous versatility in terms of controlling stoichiometry, particle size, size distribution, and shape, as well as being able to achieve high levels of purity.<sup>34</sup>

Like in many ceramics, astoichiometry typically leads to an increase in the concentration of vacancies and, hence, and increase in diffusion rates,<sup>35</sup> as discussed in more detail below. While the presence of impurities (i.e., not including intentional additives such as sintering aids) may influence the stoichiometry, its main effect appears to be that impurities act as direct light scattering sites in the final part<sup>7,8</sup>; in any case, their influence on stoichiometry has not been systematically studied. Chiang and Kingery<sup>32</sup> report that changes in purity in their investigation had no measurable influence on diffusion kinetics during graingrowth studies, and it would seem the same should be true for sintering. On the other hand, it is possible that impurities segregated at grain boundaries alter the grain-boundary structure, which in turn could significantly impact grain-boundary mobility. Indeed, for alumina, it has been well documented that relatively small amounts of impurity (hundreds of ppm) may lead to the formation of a grain-boundary liquid phase that then dramatically increases the boundary mobility.<sup>36–38</sup> Clearly, care-

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ful and systematic electron microscopy studies on grain boundaries in spinel must be performed in conjunction with grainboundary mobility measurements.

This paper is organized as follows. Section II reviews densification and grain growth in spinel without sintering additives; while the studies discussed here were not motivated to produce transparent spinel, the issues they cover are nonetheless germaine. In the absence of sintering additives and impurities, it is assumed no liquid phase is present, and one needs to consider the competition between grain-boundary mobility and pore mobility under a solid-state diffusion mechanism. The grain-boundary structure may have an important role in governing late-stage densification and microstructure evolution, as shown for alumina,<sup>39-41</sup> but it has not been studied in spinel and thus is not covered here. Section III is devoted to the sintering and microstructure evolution of spinel containing the most commonly used sintering aid, LiF. It is generally agreed that in the presence of LiF, a liquid phase develops, but the precise role of this phase and its subsequent evolution at elevated temperatures, have not been well established. The final section describes a phenomenon not covered in the spinel literature, swelling, which typically results in opaque components with a white appearance.

# II. Densification and Grain-Growth Mechanisms in Spinel without Densification Aids

#### (1) Densification

Mass transport mechanisms during the late stages of densification *and* during the microstructure development of spinel are not fully understood, although there is agreement about certain features. There is a general consensus that late-stage sintering of spinel, similar to many other oxides, is dominated by solid-state diffusion and that the rate limiting species is the oxygen ion.<sup>14,20,21,27,28,32,35,42</sup> As seen in Table I, the diffusion coefficient of oxygen is typically several orders of magnitude smaller than those of the cations. Not surprisingly, the same trend is observed for the constituent oxides, Al<sub>2</sub>O<sub>3</sub> and MgO.<sup>33,43–49</sup>

The importance of oxygen diffusion derives from the fact that it ultimately controls the ratio of the densification rate to the coarsening rate. Coarsening is undesired because in early-stage sintering it reduces the driving force for densification,<sup>19,50</sup> and in late-stage sintering it leads to a coarse final grain size that is generally not desired in applications for transparent spinel.<sup>3,5,31</sup> The challenge in developing a densification model for any ceramic lies in specifying the mechanism for densification and for coarsening. These mechanisms are not established, and are probably not constant over a wide range of processing conditions for spinel. For late-stage sintering in many ceramics, the key variables for achieving nearly theoretical density while minimizing grain size are the grain-boundary mobility,  $M_{\rm b}$ , and the pore mobility,  $M_{\rm p}$ . In particular, as pore removal proceeds, the influence of pores on the grain-boundary drag will decrease, and one would expect an increase in grain growth. However, unlike in some other oxide systems, as for example, MgO and  $Al_2O_3$ ,<sup>19,33,51</sup> pore entrapment within grains has not been reported as a major problem in the manufacturing of transparent spinel; this implies that the general conditions for densification must be such that the ratio  $M_{\rm b}/M_{\rm p}$  is small enough to allow pore removal before pore entrapment. On the other hand, pore entrapment has been reported in model studies of spinel in association with abnormal grain growth,<sup>28</sup> and thus, the consideration of  $M_p$  is relevant in the present discussion. As in alumina, the  $M_{\rm p}$  for spinel is expected to be controlled by either surface diffusion or vapor transport, which would be characterized by the surface diffusion coefficient,  $D_{\rm s}$ , or the vapor transport diffusion coefficient, Dg, respectively. In contrast, the intrinsic  $M_{\rm b}$  (i.e., the grain-boundary mobility is not influenced by the drag effects from impurities or second phases) is related directly to the grain-boundary diffusion coefficient,  $D_{\rm b}$ ,<sup>19</sup> and thus is expected to be strongly influenced by the presence of a liquid phase.<sup>37,38</sup> However, the possibility of a liquid phase has not been considered in densification or microstructure evolution studies on spinel without sintering aids.  $M_{\rm p}$  and  $M_{\rm b}$  are of course typically coupled, because pores may pin grain boundaries; furthermore,  $M_{\rm b}/M_{\rm p}$  is expected to change in the presence of additives that alter the diffusion rates for the various mass transport mechanisms. Because in the kinetic studies discussed below, the spinel powders were obtained from different sources (i.e., different purity levels), and because quantitative microstructural characterization was typically not performed, a direct comparison of all the data is challenging. However, several studies report on experiments where the influence of cation stoichiometry on densification and grain growth was examined, and these are discussed in the next several paragraphs.

Thermodynamic calculations have shown that MgAl<sub>2</sub>O<sub>4</sub> at low oxygen partial pressures (e.g., reducing environments), above  $1650^{\circ}$ C will lead to a decomposition reaction in which elemental Mg gas is formed,<sup>44</sup> and which is also accompanied by the creation of oxygen vacancies. Indeed, experimental studies have indicated that the removal of MgO during densification has a profound influence on the resulting microstructure.<sup>14,29,33</sup> Ting and Lu<sup>28</sup> investigated the effect of low oxygen partial pressure on the sintering of  $MgO_nAl_2O_3$  where *n* varies between about 0.9 and 1.2. They observed enhanced densification at sample surfaces due to the evaporation of MgO during densification, and they inferred that predominantly the oxygen vacancies, which would be created in addition to the Al vacancies, enhance diffusion. A similar mechanism was suggested by Bratton<sup>14</sup> earlier, although grain-boundary diffusion could not be ruled out completely. Ting and Lu's results showed that sintering under vacuum (or reducing atmosphere) creates a sandwich-like microstructure with three regions of different grain size. In their study, the sample interior exhibited grains containing voids, characteristic for high stresses arising during differential sintering. A large grain area was observed in the near-surface region. Similar abnormal grain-growth behavior was observed by Matsui et al.,<sup>52</sup> who sintered n = 1.07 spinel at 1800°C under hydrogen. The exterior of Ting and Lu's samples consisted of excess Al<sub>2</sub>O<sub>3</sub> spinel, and the [Al<sub>2</sub>O<sub>3</sub>/MgO] ratio decreased to the interior of the samples considerably. A similar result has been reported for the grain-boundary chemistry of spinel with varying overall stoichiometry: for all compositions, a strong local stoichiometry deviation exists at the grain boundary, with the Al/Mg ratio increasing sharply across the boundary; Chiang and King $ery^{33}$  deduced that such a deviation governs  $M_b$ .

Table I. Experimental Diffusion Coefficients ( $D = D_0 \exp(-Q/k_BT)$ ) for Ions in MgAl<sub>2</sub>O<sub>4</sub>

Diffusing element	$D_0 ({ m m}^2/{ m s})$	Q (kJ/mol)	Temperature range (K)	References and comments
Al	$2.2 \times 10^{-2}$	292	1703-2013	Stubican, et al.43 (S)EM
Al	$1.63 \times 10^{-2}$	250	NA	Chiang <sup>44</sup> (S)EC
<sup>28</sup> Mg	$2 \times 10^{-2}$	360.5	1173–1673	Lindner and Aakerstrom <sup>45</sup> (P)RT
<sup>18</sup> O	$8.9 \times 10^{-5}$	440	1703-2013	Oishi and Ando <sup>46</sup> (S)GS
<sup>18</sup> O	$3.8 \times 10^{-6}$	384.1	1583–1967	Oishi and Ando <sup>46</sup> (P)GS
<sup>18</sup> O	$1.06 \times 10^{-6}$	415	1625–1925	Reddy and Cooper <sup>47</sup> (S)RT
0	NA	489-505	1773–1898	Ting and Lu <sup>27</sup> (P)PS

S, single crystal; P, polycrystal; EM, electron-microprobe analysis; RT, radio tracer experiment; GS, gas-solid isotope exchange; EC, electronic conductivity; PS, pressureless sintering.

Perhaps the most comprehensive and recent study connecting stoichiometry with densification and microstructure development is that by Ting and Lu, who reported in a series of papers on the examination of hot pressed and pressureless sintered samples.<sup>20,21,27,28</sup> They studied the defect reactions and the controlling sintering mechanisms during the densification of excess MgO, stoichiometric, and excess Al<sub>2</sub>O<sub>3</sub> spinel compositions at 1500°-1625°C. Excess MgO compositions revealed the highest densification rates<sup>27</sup>; interestingly, excess MgO compositions were not associated with excessive grain growth, which they observed during microstructure evolution experiments.<sup>28</sup> Ting and Lu constructed the Brouwer defect equilibrium diagram for MgAl<sub>2</sub>O<sub>4</sub> based on intrinsic Schottky defects, which are energetically more favorable than Frenkel defects (Chiang and Kingery<sup>33</sup>), and concluded that oxygen vacancies are the principal charge-compensating defects for excess MgO spinel. By considering the classical expression for the densification rate,<sup>53</sup> the grain size exponent, p = 3, and the determined activation enthalpies of 489-505 kJ/mol, it is also suggested that densification proceeds via a lattice diffusion mechanism (oxygen self-diffusion) in the solid state. In this case, the densification of spinel would be dependent on the concentration of oxygen vacancies, and this has been shown experimentally, albeit indirectly.<sup>27,28</sup> A recent study on the sintering kinetics of spinel showed that the effective activation energy, as determined by the master sintering curve theory approach, is essentially equal to the activation energy for oxygen diffusion (Table I),<sup>26</sup> giving support to the notion that densification is controlled by oxygen vacancies. During hot pressing, dislocations dominate mass flow under critical pressures (~30 MPa in uniaxial hot pressing, depending on the stoichiometry),<sup>20,21</sup> as discussed briefly below.

Because the formation energies for intrinsic defects in spinel are relatively low,<sup>54</sup> one would expect a relative ease in forming defects that enhance diffusion, particularly at processing temperatures.<sup>55,56</sup> The concentration of oxygen vacancies is therefore a function of spinel stoichiometry. Spinel exhibits a wide range of stoichiometry at elevated temperatures (e.g., >1400°C),<sup>57</sup> and because of sluggish kinetics at lower temperatures, the wide range of compositions can be preserved at room temperature. Thus, substantial tailoring of the sintering kinetics is possible simply through stoichiometric change, although the open literature indicates that this potential method has not yet been explored in the fabrication of transparent spinel.

In addition to diffusion, dislocation kinetics, which probably play a role during pressure-assisted densification,<sup>20,21</sup> are altered with changes in overall stoichiometry. Ting and Lu have considered climb-controlled dislocation creep as a rate limiting mechanism for hot-pressed spinel, when the applied pressure exceeds a critical level.<sup>20</sup> The critical pressure at which dislocation creep dominates over diffusion decreases as n increases for  $MgOnAl_2O_3$ . Consistent with this, the critical resolved shear stress of MgOnAl<sub>2</sub>O<sub>3</sub> has been observed to decrease by nearly two orders of magnitude when n is increased from 1 to 3.5. Interestingly, the windows and dome fabrication community has used the stoichiometric sensitivity of the yield stress of spinel in the processing of fusion-cast spinel,  $^{6,30}$  before the above-mentioned studies. Thus, it is concluded that stoichiometry is important in governing the densification of spinel without the addition of sintering aids, because it influences the concentration of oxygen vacancies and also the critical resolved shear stress for plastic flow. It is likely that within a given set of processing conditions, only one of these mechanisms dominates. Because of the wide range in possible spinel stoichiometry, finding the optimum for particular densification conditions may be challenging but needs to be considered by transparent spinel manufacturers. Specifically, it should be possible to fabricate transparent spinel without sintering additives.

#### (2) Grain Growth

Grain-boundary mobility measurements in spinel have focused on the influence of stoichiometry, but are in disagreement. Chiang and Kingery infer that solid solution drag, due to astoichiometry, is the rate limiting process in grain growth, and their inference is supported by the fact that grain-boundary mobility measurements do not vary with changes in purity,<sup>32,33</sup> leaving astoichiometry as the only explanation. They found that the grain-boundary mobility is  $10^2 - 10^3$  times greater in excess MgO spinel than in excess Al<sub>2</sub>O<sub>3</sub> spinel. On the other hand, Ting et al.<sup>27</sup> have examined the relevant defect reactions in detail, and have used those reactions to explain their observations that increased densification and grain growth occur as a result of MgO deficiency. In contrast to that, the earlier work of Uemastu et al.<sup>19</sup> showed that the highest grain-boundary mobilities occur at or very near perfect spinel stoichiometry  $(n \sim 1)$ . Currently, no reconciliation between these extreme viewpoints exists, unless certain characteristics of the spinel were unintentionally varied between the different experiments. Chiang and Kingery<sup>33</sup> rule out the possibility that small amounts of impurity could alter  $M_{\rm b}$ , but there may be other characteristics. For example, in addition to the variation in stoichiometry, the cation disorder, a parameter not measured in any of those experiments, may have varied between the studies. Synthetic spinel always contains some degree of cation disorder,56 and this would be expected to shift the various defect reactions. One can certainly conclude, however, that the above studies have shown that nonstoichiometry in spinel is very important for densification and the corresponding microstructure development.

#### III. Densification Mechanisms in Spinel with LiF

Studies have shown that relatively small variations in amounts and types of sintering additives may have large effects on the densification of spinel.  $^{2-4,59-61}$  A number of additives have been used in attempts to obtain dense components, including LiF,  $CaB_4O_7$ ,  $B_2O_3$ , NaF,  $CaF_2$ ,  $ZnF_2$ ,  $BaF_2$ ,  $CaCl_2$ ,  $CaCO_3$ , and  $TiO_2$ .<sup>50-53,62</sup> However, except for the case of LiF, there have been no studies that have revealed their specific role in densification and microstructure development. Although not widely reported in the early literature, presumably due to proprietary issues, it is now generally accepted by American transparent spinel manufacturers that even small amounts of additives (typically 0.5–2.0 mass% of LiF) are needed to produce dense transparent spinel.<sup>2–5,11,13,63–66</sup> Somewhat surprisingly, the specific role of LiF is still not well established. However, it is generally agreed that LiF must be removed before final densification, because its presence defeats transparency.<sup>12,13,15</sup> The kinetics of LiF removal must be governed by the part size, shape, and nature of porosity as well as by the vapor pressure of LiF and the relevant chemical gradient that drives gaseous diffusion. Pure LiF melts at  $845^{\circ}$ C, but the vapor pressure is substantial just above this temperature<sup>10,24,67</sup>; therefore it is expected that vapor transport also plays a dominant role in the removal of LiF from the system.

## (1) Uniformity of LiF Distribution

Apart from the overall removal of LiF in the late stages of densification, the manner by which LiF is added to spinel powder before sintering has been shown to be important in governing the densification and microstructure development.<sup>7,15,68</sup> In particular, if LiF is not spread uniformly, it may not escape from the concentrated areas in the subsequent firing, and it is reported to react locally with spinel, leading to MgO or Mgrich regions that do not sinter well.<sup>15</sup> It is noted that grain-boundary mobility has been observed to increase for spinel in which the stoichiometry is excess MgO,<sup>32,33</sup> as discussed in Section II; however, MgO precipitates would be expected to impede grain growth and likely sintering.<sup>19,33</sup> A complete systematic study on the relative importance of LiF distribution within the spinel powder has not been performed, but the present authors have observed that ultrasonic mixing with a solvent such as ethyl alcohol before forming and/or firing facilitates the production of more uniform and transparent microstructures. Different homogenization methods, for example, utilizing fluoride salts to coat spinel particles, have also been shown to be successful in producing a uniform LiF distribution that leads to transparent material.<sup>68–70</sup>

#### (2) Sensitivity of Microstructure Evolution

LiF has been observed to play a direct role on the grain size in spinel. This has been reported in recent work.<sup>26,71</sup> For example, (I. E. Reimanis, unpublished data) performed a statistically designed model experiment with 32 hot press runs in which variables included the various processing conditions such as heating rates, soak times, soak temperatures, and pressure, as well as the composition (0, 0.5, and 1.0 mass% LiF), in which the grain size for specimens containing no LiF was 2.7  $\mu$ m (±0.2  $\mu$ m), and the grain size for specimens containing either 0.5 or 1.0 mass% LiF was 7.3  $\mu$ m ( $\pm$ 0.8  $\mu$ m). This somewhat contradicts the results of Reimanis and Kleebe,<sup>26</sup> in which it was shown that specimens hot pressed with 1 mass% LiF showed a finer grain size than those hot pressed with no LiF. The only reconciliation between these two reports is that some notable differences exist that may have impacted how LiF alters the microstructure: (1) the latter study used powder synthesized by Baikowski Incorporated (Baikowski International Corporation, Charlotte, NC), whereas the former study (I. E. Reimanis, unpublished data) used powder synthesized by Corning Incorporated; in particular, the specimens pressed with the Corning powder contained small amounts of MgO, which is assumed to have dominated microstructure development. (2) The latter study utilized ultrasonic mixing, whereas the former study used ball milling to mix LiF with spinel before densification. As stated earlier, methods of mixing are very important in the densification and microstructure development of transparent spinel. These differences illustrate the extreme sensitivity of microstructure development to the processing conditions for spinel.

It is not discussed in the literature, but different studies reveal that the effect of LiF on grain size may also depend on how much is present (I. E. Reimanis, unpublished data).<sup>71</sup> Such a concentration effect may in fact impact the influence of inhomogeneous mixing discussed in Section III(I), because inhomogeneously mixed powder means that the concentration of LiF varies locally. Earlier reports show that specimens hot pressed with 1 mass% LiF exhibited a finer grain size (grain diameters  $\sim 20 \ \mu m$ ) than specimens prepared identically but without LiF (grain diameters  $\sim 50 \ \mu m$ ).<sup>26</sup> This result is surprising because it would be expected that the presence of LiF leads to a liquid phase, which enhances mass transport and grain-boundary mobility, but in this case there must have been a mechanism that suppressed grain-boundary motion even in the presence of LiF. It is assumed that in this particular case, LiF reacted with Al<sub>2</sub>O<sub>3</sub>, leading to Mg-enriched regions with poor sinterability, similar to the process suggested by Villalobos et al.<sup>15</sup> Because the powders were mixed by ball milling, it is likely that there were inhomogeneously mixed regions. It should be noted that there have been other ceramic systems where LiF has led to a runaway coarsening (of grains and porosity) at temperatures above about 1000°C, in which LiF begins to vaporize.72,73 Other reports by transparent spinel manufacturers, who likely use LiF as a sintering aid, although this is not confirmed, indicate that a bimodal grain-size distribution is a rather common feature.<sup>30</sup> An attempt to rationalize such observations is given in the following section.

### (3) Chemical Reaction with LiF

It is likely that when spinel with LiF addition is continuously heated to temperatures exceeding about  $1500^{\circ}$ C, first a transient liquid phase is formed the wets the spinel grains<sup>10,71</sup> and, with ongoing sintering/densification, leaves the system. There is a great deal of evidence that LiF also chemically reacts with spinel and possibly with other constituents. It has been shown that the presence of LiF leads to a decrease in the effective activation energy for sintering.<sup>26</sup> The first published systematic study that

targeted possible reactions between LiF and spinel in the context of sintering was performed by Villalobos *et al.*,<sup>15,16</sup> who reported that LiAlO<sub>2</sub> forms and leaves behind regions of a phase rich in either Mg or MgO in the microstructure, both of which may subsequently defeat transparency. More recent studies by Rozenburg and colleagues also confirmed that LiAlO<sub>2</sub> forms when large quantities of LiF (e.g., 40 mass%) are reacted with spinel. It was further shown in their study that a transient liquid phase, likely LiF:MgF<sub>2</sub>, is present parallel to the formation of LiAlO<sub>2</sub>. When the temperature is further raised, MgF<sub>2</sub> vapor forms and subsequently reacts with LiAlO<sub>2</sub> to nucleate spinel crystals and LiF vapor according to the following equation:

$$MgF_{2(v)} + 2LiAlO_{2(s)} \Rightarrow MgAl_2O_4(s) + 2LiF_{(v)}$$
(1)

From the results of these model experiments with 40% by mass LiF in spinel, Rozenburg and colleagues proposed a transient liquid phase sintering mechanism for spinel with smaller quantities of LiF (up to 5 mass%), and they suggested a mechanism for the final removal of LiF from the system. As with the study by Villalobos, the proposed mechanism for sintering in the presence of LiF involves the presence of LiAlO<sub>2</sub>, and thus a study that could confirm the presence of an intermediate phase would give confidence to the mechanism proposed by Rozenburg and colleagues. Furthermore, a key part of this transient liquid phase sintering mechanism included the reprecipitation of spinel grains. A liquid-assisted reprecipitation process is interface-reaction controlled and should lead to faceted grain-boundary morphologies.<sup>74</sup> In an attempt to validate the above proposed mechanism, Reimanis and Kleebe<sup>26</sup> performed a study on spinel specimens containing from 0 to 5 mass% LiF, cooled quickly from  $800^\circ$ ,  $900^\circ$ , and  $1000^\circ$ C, the temperatures where an intermediate phase is expected. An extensive investigation showed that only spinel and a glassy phase were present; no residue of crystalline LiAlO<sub>2</sub> was detected, contradicting the conclusions of Villalobos *et al.*<sup>15</sup> as well as those by Rozenburg et al.<sup>24</sup> Furthermore, the glassy phase persisted in pockets and was not observed as a thin grain-boundary layer, as might be expected for a liquid phase sintering process. However, all of the boundaries observed in the TEM were facetted, indicating that a transient liquid phase may have formed; only quench studies could confirm the presence of a transient liquid phase along grain boundaries, but such studies have not yet been performed.

#### (4) Oxygen Vacancy Formation

The observation by Reimanis and Kleebe<sup>26</sup> that the grain boundaries of spinel partially sintered with LiF contain no continuous intergranular grain-boundary phase is significant in that it would imply that during densification and grain growth at intermediate temperatures, the kinetically controlled mechanism involves either (1) solid-state diffusion or (2) a transient liquid phase. For the latter case, once the liquid phase disappears (during late-stage sintering), it must be that a solid-state diffusion mechanism takes over. It is noted that HRTEM imaging of



**Fig. 1.** HRTEM images ((a) and (b)) of a spinel sample doped with 1 mass% fraction LiF hot pressed at 1550°C for 2 h in air. No continuous residual amorphous phase was detected along internal interfaces. The insets at the right upper corner represent the corresponding Fourier-filtered images of the interface area, indicated by the dotted line.



**Fig. 2.** Scanning electron micrograph showing (a) the fracture surface of a tri-layer specimen created by hot pressing pure LiF powder between pure spinel powder. The hot pressing direction is vertical in the figure. The central region where LiF was placed led to coarse grains of spinel. Upon chemically etching a polished surface, (b) it is apparent that the large grain spinel reacts differently to the chemical etch than the finer grain material adjacent, likely because the large grain material contains defects.

interfaces in transparent spinel indicates that no secondary phases are present at neither triple junctions nor grain boundaries, as shown in Fig. 1 for a dense sample hot pressed at 1550°C. Thus, in either case, one needs to consider the role of defect chemistry in the sintering of spinel, even when it is densified in the presence of LiF. The possibility exists that LiF itself might be soluble to some extent in the spinel structure. As shown by Belov,<sup>75</sup> Li ions can take the place of Mg in spinel, with F ions taking O lattice sites, producing  $LiAl_2(O_{0.75}, F_{0.25})_4$ . In both cases, some Mg or Li moves to Al sites, creating an inverted spinel structure along with oxygen vacancies. A similar defect reaction was proposed by Reimanis and Kleebe to describe their TEM results that revealed a bimodal distribution of grains during fast-cooling studies. In those studies, the large spinel grains contained F ions within the grain interiors whereas small grains did not, suggesting that LiF dissolves into spinel, enhancing grain growth as a result of increased oxygen vacancies. Note that it is not possible to detect the Li via energy-dispersive X-ray spectroscopy (EDS); hence, the incorporation of LiF into MgAl<sub>2</sub>O<sub>4</sub> was concluded because of the detection of F in those large grains only. The corresponding defect reaction proposed is given in Kröger-Vink notation as

$$3\text{LiF} \xrightarrow{\text{MgAl}_2\text{O}_4} \text{Li}_{\text{Mg}'} + 2\text{Li}_{\text{Al}}'' + 3\text{F}_{\text{O}}^{\bullet} + \text{V}_{\text{O}}^{\bullet\bullet}$$
(2)

Meir *et al.*<sup>10</sup> proposed a similar reaction, modified by the presence of the impurity C, which reacts with F and leaves the

system as a gaseous carbon-fluorine compound before the above reaction. The solubility of  $\text{Li}^+$  and  $\text{F}^-$  within the spinel is not surprising, considering that they are soluble in MgO<sup>76</sup> and other oxides.<sup>24,72,73</sup>

A model experiment performed by the present authors involved a sandwich sample with a large quantity of LiF at the center of the specimen, which led to enhanced grain size due to the presence of LiF.7 The results of this study are shown in Fig. 2. The experiment was performed by fabricating a tri-layer specimen, comprised of spinel powder, LiF powder, and spinel powder. The LiF powder was added in a quantity corresponding to a theoretical dense LiF thickness of 100 µm after sintering. This was hot pressed under typical spinel sintering conditions for transparent spinel (35 MPa, vacuum, 1550°C for 2 h). Observation of the cross-sectional fracture surface (Fig. 2(a)) reveals large grains that were determined by X-ray diffraction to be spinel. However, EDS within the scanning electron microscope showed that the Mg/Al ratio varied substantially in this region of large grains. When the specimen was polished and then etched with HF, the etch preferentially attacked the large grains (Fig. 2(b)). A likely explanation is that the large grains are highly defected and hence more sensitive to the chemical etch, which is seen as indirect evidence that Li and F ions were incorporated into the lattice of the large grains (cf. Eq. (2)). Moreover, these observations support the notion that LiF can dissolve into spinel and enhance volume diffusion.

It is worth noting that a reaction between LiF and spinel may also lead to astoichiometry. In fact, there are experimental data suggesting that the presence of LiF results in an excess  $Al_2O_3$  spinel (n > 1),<sup>15,63,77</sup> which implies an increase in the oxygen vacancy concentration and hence an increase in either the densification rate, the grain-boundary mobility, or both.

## (5) LiF as a Cleanser

LiF has been reported to influence densification behavior by the removal of specific impurites.<sup>10</sup> A systematic study with LiF in spinel fabricated by spark plasma sintering (SPS) led Meir *et al.*<sup>10</sup> to conclude that LiF reacts with C to form  $CF_x$  (where *x* represents F stoichiometry), which leaves as a vapor. C is abundantly present in SPS because high electrical currents lead to sputtering of C from the chamber fixtures. If C were left at the grain boundaries in spinel, it would tend to prohibit sintering between grains, likely by a swelling-type mechanism, as discussed below. The removal of impurities by LiF during hot pressing has been reported for MgO<sup>73</sup>; in this case, hydroxyl groups were removed. If LiF removes C through the formation of  $CF_x$  (where *x* represents F stoichiometry), then the remaining



**Fig. 3.** HRTEM images from spinel samples doped with 5 mass% fraction LiF cooled from intermediate temperatures: (a) from 900°C and (b) from 1000°C. Note that in both cases no continuous intergranular amorphous film was observed, which led to the hypothesis that a wetting-dewetting mechanism is acting in this system, which, however, could only be verified via additional quench experiments. The insets at the right upper corner represent the corresponding Fourier-filtered images of the boxed areas.



Fig. 4. Optical photographs of hot-pressed spinel specimens that are 25.4 mm in diameter. The labels provide the specimen processing conditions (amount of LiF as a mass%, and the time duration of the heat treatment in air at  $1550^{\circ}$ C).

Li ions may diffuse through the spinel structure, for example by substituting for Mg ions, similar to the reaction presented in Eq. (2). In addition, it may be possible that LiF removes transition metal elements by a similar process.

## (6) Wetting/Dewetting Mechanism

Earlier studies have shown that, at intermediate temperatures, LiF exists as a segregant in isolated regions, rather than as a continuous amorphous film, which would be expected for a liquid-assisted sintering process.<sup>22</sup> This rather unexpected result, in particular, when considering the grain coarsening observed in samples containing LiF, can be explained by a wetting-dewetting mechanism upon cooling from such temperatures. A similar behavior has been observed for liquid-phase-sintered SiAlON (composition z = 1),<sup>78</sup> where the room temperature microstructure did not reveal the presence of a residual liquid phase at grain boundaries; however, quench experiments from temperatures up to 1380°C clearly showed the presence of an amorphous secondary phase wetting the SiAlON interfaces. Although a similar quench experiment has not been performed for polycrystalline spinel, the experimental results on LiF-containing spinel given above strongly suggest such a mechanism, because HRTEM analysis of spinel polycrystals cooled from 900° to 1000°C showed no evidence of grain-boundary wetting, as illustrated in Fig. 3. On the other hand, isolated pockets filled with glass residue (enriched in fluorine) were detected in both samples. Therefore, it is concluded that the densification of LiFdoped transparent spinel proceeds as follows:

(1) at the early stage of sintering, a homogeneous liquid is formed that wets the spinel grains and promotes the rearrangement of grains and grain-boundary mobility,  $M_{\rm b}$ ;

(2) MgAl<sub>2</sub>O<sub>4</sub> continues to dissolve in the transient liquid phase, leading to the precipitation of spinel particles (with incorporated Li and F); those grains are prone to coarsening due to a high concentration of oxygen vacancies (cf. Eqs. (1) and (2));

(3) at higher sintering temperatures, the LiF vapor pressure is sufficiently high for evaporation;

(4) upon cooling to room temperature, no LiF remains in the component, with the exception of  $Li^+$  and  $F^-$  ions incorporated into the spinel host lattice.

Note that the above-mentioned wetting-dewetting mechanism only applies when samples are cooled to RT from intermediate temperatures between 800° and 1000°C. When sintered bodies are held at a high temperature such as 1550°C for an extended time, no residual glass phase is expected to be present in the densified ceramic. Moreover, the densification steps listed above rationalize why a bimodal grain size is commonly observed (the precipitation of Li and F ions containing spinel) instead of a more homogeneous coarsening of the microstructure. In addition, this mechanism is in agreement with the model experiment (sandwich sample; cf. Fig. 2), where only the inner layer revealed an enhanced grain growth and pronounced etching attack.

#### IV. Swelling Due to Impurities

It has been previously reported that upon extended heat treatments, transparent spinel turns opaque and acquires a white appearance, which reflects an increase in either the number, size, or total volume of porosity.<sup>79</sup> Figure 4 illustrates the change in color for a specimen fabricated without LiF (0% LiF) and one with 1 mass% LiF (1% LiF). Both specimens were made by a conventional hot press technique, as described elsewhere.<sup>79</sup> Each specimen was then heated in air to 1550°C for 50 h. The corresponding fracture surfaces for the specimen containing 1 mass% LiF (as processed and heat treated for 50 h) are shown in Fig. 5. A similar result was obtained for the specimen without LiF, except that an increase in pore coalescence was observed.

as-processed heat-treated beat-treated b

Fig. 5. Scanning electron micrographs showing the fracture surfaces of a 1 mass% LiF specimen corresponding to Fig. 2. (a) As-fabricated and (b) heat treated for 50 h at  $1550^{\circ}$ C in air.



Fig. 6. Scanning electron micrographs images of fracture surfaces of undoped spinel hot pressed and postannealed for 50 h at 1550°C in air. Note the pronounced coalescence of pores located at spinel interfaces upon long-term annealing.

It is suggested that the appearance and growth of pores arising from an elevated temperature heat treatment are caused by the formation of gaseous species from small amounts of impurities present in the spinel. Specifically, C and S, present in small quantities (tens of parts per million), would form gaseous oxides in the presence of oxygen, and under elevated temperatures and extended times, these gaseous oxides would form pores at spinel grain boundaries. This mechanism of pore growth has previously been reported for hot-pressed Al<sub>2</sub>O<sub>3</sub> heat treated at 1600°C.80 Bennison and Harmer showed in Al<sub>2</sub>O<sub>3</sub> that pressures over 1 GPa may be generated with relatively small amounts of oxidized C or S, and that without the confining pressure present during hot pressing, the part increases in volume (i.e., it swells).<sup>80</sup> For the case of spinel, powders synthesized by Baikowski Incorporated are known to contain sulfur, as they are synthesized from sulfates<sup>30</sup>; carbon is ubiquitous in oxide processing. The issue of swelling is not only relevant to heattreatment studies, but also to processing, because it is clear that the same pore growth process counters the effects of sintering. Meir et al.<sup>10</sup> point out that C present due to field-assisted hot pressing (SPS) inhibits sintering; indeed, they showed a microstructure of a pressureless spark plasma sintered spinel that exhibits the classic characteristics of the formation of gaseous species (substantial porosity located along grain boundaries), similar to Fig. 5(b). They conclude that one of the roles of LiF is that it may react with C and ameliorate this problem. Experiments to confirm the above description include an extensive heat treatment of the powders before hot pressing, similar to what Bennison and Harmer discuss for hot-pressed  $Al_2O_3$ . It is worth noting that prolonged heat-treatment times can lead to pore coalescence along spinel grain boundaries, as illustrated in Fig. 6, strongly diminishing transparency. On the other hand, using an ultra-pure starting powder in addition to a powder heat treatment to eliminate even small amounts of impurities before densification will ultimately suppress swelling, as depicted in Fig. 7, and result in a highly transparent spinel sample.

#### V. Conclusion

The final-stage sintering of transparent spinel is complex and proceeds by a number of mechanisms, in which the stoichiometry and concentration of oxygen vacancies play an important role. The sintering environment and also the specific action of



**Fig.7.** Scanning electron micrographs showing the fracture surfaces of a 1 mass% LiF specimen hot pressed for 2 h at 1550°C in air. The elimination of pores at spinel interfaces was achieved by using an ultra-pure starting powder in addition to a powder heat treatment before densification, resulting in high transparency.

the sintering aid LiF alter the stoichiometry and concentration of oxygen vacancies during densification. However, more importantly, the addition of LiF leads to a liquid phase formation at lower temperatures (up to  $\sim 1000^{\circ}$ C), strongly promoting grain-boundary mobility and densification. Although the presence of a liquid phase along grain boundaries could not be unambiguously determined-this is assumed to be the result of a wetting-dewetting mechanism upon cooling from intermediate temperatures-all experimental results indicate that the densification of spinel is governed by a transient liquid-assisted sintering process. It is proposed that at elevated temperatures, a solid-state diffusion mechanism takes over when the liquid phase disappears.

In addition, LiF may react with impurities trapped at grain boundaries such as C and S to form volatile fluoride species. The ultimate removal of excess LiF or of any fluoride gas before pore closure is an important prerequisite for obtaining high transparency. If excess C or S remains, it leads to swelling during subsequent heat treatment, which in turn results in a milky opaque ceramic part.

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