Degradation of Magnesium Aluminum Spinel by Lithium Fluoride Sintering Aid

Guillermo R. Villalobos,*,[†] Jasbinder S. Sanghera, and Ishwar D. Aggarwal

U.S. Naval Research Laboratory, Washington, District of Columbia 20375-0001

The effect of LiF sintering aid on the degradation of transparent magnesium aluminate spinel during hot-pressing was studied. LiF is used to etch spinel particles during the hot pressing process. The LiF was found to react with the aluminum in the spinel structure, thereby leaving Mg-rich regions behind that do not sinter well and result in opaque white regions in the otherwise transparent matrix.

I. Introduction

MAGNESIUM aluminate spinel has great potential as a transparent armor material and as a visible-infrared window material due to its good mechanical and optical properties.¹ Its mechanical properties are comparable with polycrystalline aluminum oxide and, since it has a cubic structure (i.e. no birefringence), polycrystalline samples can transmit from 200 nm to 5.5 μ m with no optical distortion. Although magnesium aluminate spinel has been studied on and off since the 1960s,^{2.3} the literature has very little information on its sintering behavior, and the material still cannot be sintered to transparency reproducibly.^{4,5}

Spinel is generally densified with the use of sintering aids, the most common being LiF. Without LiF sintering aid the material tends to be translucent and gray. Previous researchers have proposed that the LiF etches and removes impurities from the surface of the spinel particles, thereby enhancing diffusion. It is also believed that the molten LiF can aid initial compaction by lubricating the particles and allowing better packing. The LiF must be removed from the material before complete consolidation or it will manifest itself as white precipitates.⁶

The spinel hot press schedule is designed around two successive thermal treatments that are used to first allow the LiF to react with the particle surfaces, and then a higher temperature treatment to allow the LiF to volatilize and be removed from the material before the pore structure collapses and traps the LiF sintering aid.

Although we eventually wish to form reproducibly transparent spinel shapes, in this portion of the work we were concerned with identifying the cause of the inconsistent sintering behavior and understanding the reactions involved during the course of the hot-pressing schedule. We have therefore analyzed the opaque white regions and related those to the effect of LiF concentration, interactions between the matrix and LiF, and hotpressing conditions.

II. Experimental Procedure

Spinel powder was purchased from Ceralox (Tucson, AZ). The powder was mixed using a mortar and pestle with 0.5, 2, and 10

[†]Author to whom correspondence should be addressed. e-mail: villalobos@nrl.navy.mil

wt% LiF (Sylvania, Towanda, PA) sintering aid. Ten grams of powder/sintering aid mixture was loaded into a 25 mm diameter I.D. graphite die (Poco Graphite, Decatur, TX) lined with grafoil (Polycarbon Inc., Valencia, CA) to minimize carbon diffusion and extend die life. The samples were hot pressed in a vacuum hot press (Electrofuel, Toronto, Canada) at a heating rate of 10° – 1600° C/min and held for 2 h. There were also two 30 min holds: one at 950°C and the other at 1200°C. Pressure schedule consisted of maintaining 200 psi until the end of the 1200°C hold. The pressure was then slowly increased to 4000 psi and held until the end of the 1600°C treatment. The resulting samples were 25 mm diameter × 2 mm thick.

Powder samples were mixed in a mortar at a 50/50 weight ratio of spinel/LiF, Al₂O₃/LiF, and MgO/LiF and heat treated at 950°C in a vacuum furnace to identify reactions during the initial hot press hold temperature. The 50/50 ratio was used to increase the amount of reacted material and thereby enable detection of the reaction products by X-ray diffraction (XRD). The 50/50 mixtures were also run in an SDT (TA Instruments SDT 2960, New Castle, DE) to determine the reaction temperatures and weight loss. The SDT was run in flowing argon at a 10° C/min rate to 1500°C. The powder and densified samples were also analyzed using optical microscopy, scanning electron microscopy (SEM)/energy-dispersive spectrum (EDS) (LEO 1550 LEO Electron Microscopy Inc., Thorwood, NY), and XRD (Sintag XDS 2000, Sunnyvale, CA).

III. Results and Discussion

The literature is not clear on why the two specific holds are used during the hot press schedule. It is implied that the first hold at 950°C is to allow homogenization of the LiF sintering aid, and the second hold at 1200°C to allow LiF to escape before final consolidation. SDT analysis of LiF in flowing argon was conducted to confirm the assumptions. The SDT trace shows that LiF melts at 850°C and rapid weight loss begins at 1050°C. LiF is completely gone at 1400°C. Based on these results, we followed the traditional hot press schedule.

Figure 1 shows three spinel disks that were mixed with 0.5, 2, and 10 wt% LiF. It is apparent that increasing the amount of LiF increases the amounts of opaque white regions. This effect is characteristic of a transparent material with scattering centers on the order of the wavelength of visible light. The literature suggests that the white opaque regions are a result of LiF that has not been removed and is located at the spinel grain boundaries. The results shown in Fig. 1 appear to confirm this. Figure 2 is a high-resolution SEM micrograph of an opaque area showing that it is composed of small (300-500 nm) crystals that have not sintered as well as the surrounding material. EDS analysis shows that while the transparent area has the expected 2:1 atomic ratio of Al and Mg, the small grains have a 1:1 ratio of Al and Mg. This suggests that the small grains are made up of an MgO-rich phase. MgO is considerably more refractory than spinel and would not be expected to sinter as readily at the lower sintering temperatures used for spinel.

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Attempts to modify the Czochralski growth procedure to minimize $T1^{2+}$ Ti^{4+} pair formation have been unsuccessful. Instead, annealing treatments follow a crystal have been developed to minimize the lew of T and defects [11], [14]. The postgrowth to ment is temperature annealing of as-grown merial up atmosphere of hydrogen gas to convert T. In the annealing process must be carefully controlled formation of additional scattering centers or precipitates in the

Fig. 1. Three magnesium aluminate spinel disks with (left to right) 0.5, 2.0, and 10.0% LiF additions showing that the amount of cloudiness increases with increasing amounts of LiF.

Since increasing the amount of LiF resulted in an increase in the formation of the opaque regions, it has been assumed that the white regions were due to LiF that was not removed during the course of the sintering operation. However, this effect alone cannot explain the removal of Al necessary to create Mg-rich areas. We hypothesized that LiF does react with the particle surfaces as is generally thought, but it preferentially reacts with the Al₂O₃, thereby leaving MgO-rich areas behind. This reaction likely occurs when LiF is molten and not yet vaporizing at a great extent. To test the hypothesis, 50/50 wt% mixtures of spinel/ LiF, Al₂O₃/ LiF, and MgO/LiF were prepared and heattreated in vacuum for 2 h at 950°C (the first hold temperature routinely used when hot pressing). Figure 3 shows the XRD patterns of the spinel/LiF mixture. The XRD patterns show the presence of spinel, LiAlO₂, and MgO · LiAlO₂ was also present in the Al₂O₃/LiF sample. There was no evidence of any reaction in the MgO/LiF sample.

These results match well with a thermodynamic study of the $\text{LiF}-\text{Al}_2\text{O}_3-\text{MgO}$ system that shows that while MgO does not appreciably react with LiF, Al_2O_3 can react to form various lithium–aluminum-containing compounds. Of all the Li–Al-containing compounds listed in the JANAF tables,⁷ only LiAlO₂ appears to be a solid throughout the temperature range of the hot press schedule; the other reaction products are vapors at the hot pressing temperature and help to explain the results of the 50/50 mixture experiments and also the presence of the Mg-rich regions in the hot-pressed disks. Unfortunately, it is difficult to identify LiAlO₂ regions by EDS because EDS cannot detect lithium, and it is difficult to distinguish Al that belongs to the matrix from Al that would belong to LiAlO₂ inclusions. How-



Fig.2. Small-grained, partially sintered Mg-rich phase in $\rm MgAl_2O_4$ matrix.



Fig. 3. X-ray diffraction pattern showing $MgAl_2O_4$ spinel phase (S), and the LiAlO₂ (L) and MgO (M) compounds that formed after heat-treating a 50/50 wt% mixture of $MgAl_2O_4$ and LiF at 950°C for 2 h in vacuum.

ever, it is apparent that the LiF is reacting with the spinel particle and the reaction products are adversely impacting the transparency of the hot-pressed disks made by the traditional means.

We propose that the opacity is due to the presence of the Mgrich phase and the associated porosity that it introduces. In addition, the LiAlO₂ that produces the MgO phase more than likely remains in the structure, further contributing to the opacity of the spinel. The randomness of the opacity is attributed to the random presence of LiF in the powder mixture as a direct result of the mechanical mixing process prior to hot pressing.

IV. Conclusion

Although LiF is necessary to densify spinel to transparency, it also reacts with the aluminum in the spinel matrix to create Mgrich areas that cause opacity in the densified material due to poor sintering. It is also possible that LiAlO₂ precipitates from that same reaction contribute to the formation of opaque regions. Based on these results, it is necessary to study the times required to adequately homogenize the LiF sintering aid without allowing sufficient time for it to react with the aluminum in the spinel matrix. It may also require that the LiF be more evenly distributed in the spinel powder prior to hot pressing. A more homogeneous initial distribution should decrease the total amount of LiF needed, and also reduce the hold times, thereby producing high optical quality spinel samples with high reproducibility.

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