2600
doi:10.1017/S1431927622009886
Microsc. Microanal. 28 (Suppl 1), 2022

Effect of Ca Doping on the Microstructure and Mechanical Properties of Magnesium Aluminate Spinel

Alexander Campos-Quiros[1*], Animesh Kundu[1] and Masashi Watanabe[1]

[1.] Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA, USA.
* Corresponding author: ajc420@lehigh.edu

Magnesium aluminate spinel (MAS, $MgAl_2O_4$) is a unique ceramic material that is transparent over a wide range of the electro-magnetic spectrum (from UV to mid-IR) and presents enhanced toughness in polycrystalline form. This combination of properties makes MAS an optimal material for various applications such as spacecraft windows, armor domes and high-temperature furnace windows [1]. One of the requirements for obtaining such high transparency is achieving a high density near to the theoretical-limit level, for which sintering aids such as LiF have been conventionally used. However, Li segregation to the grain boundaries produces a detrimental effect on fracture toughness. One alternative is the utilization of rare-earth elements which have been reported to segregate to the grain boundaries and variously affect the microstructure evolution as well as mechanical properties. Nonetheless, the rare-earth elements are expensive, scarce and undesirable for any large-scale applications. Therefore, in this study, more abundant Ca was used as an alternative sintering aid and the effect of Ca doping was evaluated focusing on the fracture toughness and grain boundary segregation behavior in MAS.

High-purity MAS powder (Baikowski, S25CR) and $Ca(NO_3)_2 \bullet 4H_2O$ (99.98%) were used to fabricate cylindrical samples of pure spinel and Ca-doped spinel (500 ppm). Samples with 25.4 mm in diameter and 10 mm in height were hot-pressed to near the theoretical density at 1250 °C and 40 MPa for 1 h. Subsequently, the samples were sectioned, leaving one pure spinel and one Ca-doped spinel sample in the as-hot-pressed condition, and other pieces of both pure and Ca-doped spinel samples were heat-treated at 1400 °C for 48 h in an air atmosphere. The samples were then polished down to 50 nm and micro-indentation hardness measurements were performed following the ASTM-C1327-15 standard (an applied force of 1 kgf, a dwell time of 10 s and 30 indentations) [2] using a LECO LM 248AT microhardness tester. Fracture toughness of each sample hwas determined by the Vickers indentation fracture method. Microstructural observations before and after heat treatment, as well as crack propagation around the indentation area, were conducted using scanning electron microscopy (SEM) coupled with electron backscattered diffraction (EBSD) analysis. The SEM images were acquired at an acceleration voltage of 7 kV and a probe current of 0.8 nA with an in-lens backscattered electron detector. The EBSD analysis was performed at an acceleration voltage of 10 kV and a probe current of 13 nA with a step size of 50 nm. Electron transparent thin specimens for transmission electron microscopy (TEM) were prepared by a focused-ion beam instrument FEI Scios operated at 30 kV. Bright-field (BF) and dark-field (DF) imaging as well as selected area electron diffraction (SAED) analysis were performed at an acceleration voltage of 200 kV. More detailed characterization at atomic-scale will be performed to evaluate the segregation behavior of Ca to the grain boundaries using high-angle annular dark-field scanning transmission electron microscopy imaging in an aberration-corrected scanning TEM JEOL JEM-ARM200CF instrument.

The EBSD characterizations shown in Fig. 1 (a) and (b) revealed that the microstructure after hot pressing for pure and Ca-doped spinel samples consists of sub-micron size grains. The corresponding grain size distributions in the hot-pressed condition indicated that Ca doping had a negligible effect on the average grain size compared to pure spinel. After heat treatment, there was an increase in the grain

size in both samples as shown in Fig. 2 (a). However, evidence of abnormal grain growth was found as a consequence of the Ca addition. A similar abnormal grain-growth behavior was reported in Eu-doped spinel materials where Eu atoms preferentially segregate on the grain boundaries inducing abnormal grain growth [5, 6].

Fig. 2 (b) shows that, after hot-pressing, the microhardness values were lower in the pure spinel sample compared to the Ca-doped sample. Based on SEM observations, the lower microhardness in the pure spinel sample can be related to a high porosity of ~ 2.2%. Moreover, it was observed that the microhardness decreased after heat treatment in the pure spinel sample but slightly increased in the Ca-doped sample. Therefore, the heat treatment also contributed to the decrease in microhardness in the pure spinel sample due to pore coarsening and grain growth. Fig. 2 (c) shows that both samples presented a decrease in fracture toughness after heat treatment, which can be associated with the increase in grain size. Additionally, Fig. 2 (d) shows that the fracture behavior after Vickers indentation was ~50 % transgranular for both pure and Ca-doped spinel after hot-pressing but, after heat treatment, this value increased to around 70 and 60 % for pure and Ca-doped spinel, respectively.

These results indicate that Ca-doping and subsequent heat treatment produced samples with similar grain sizes but higher microhardness compared to pure spinel. Although the presence of abnormal grain growth in a few locations may suggest Ca segregation to the grain boundaries, the fracture toughness measurements indicate that Ca doping does not have a detrimental effect. The fracture behavior results also indicate that the cracks propagate predominantly through the grains after heat treatment in both samples which suggests that the grain boundary strength remains nearly unaltered even after Ca doping. Finally, atomic-level characterization will be crucial to determine the role of Ca, especially at grain boundaries where a tendency to segregate to preferential sites in certain boundary planes can occur. All these results when combined with micromechanical testing will provide a better understanding of the relationship between the Ca segregation behavior and the mechanical properties in spinel [7].

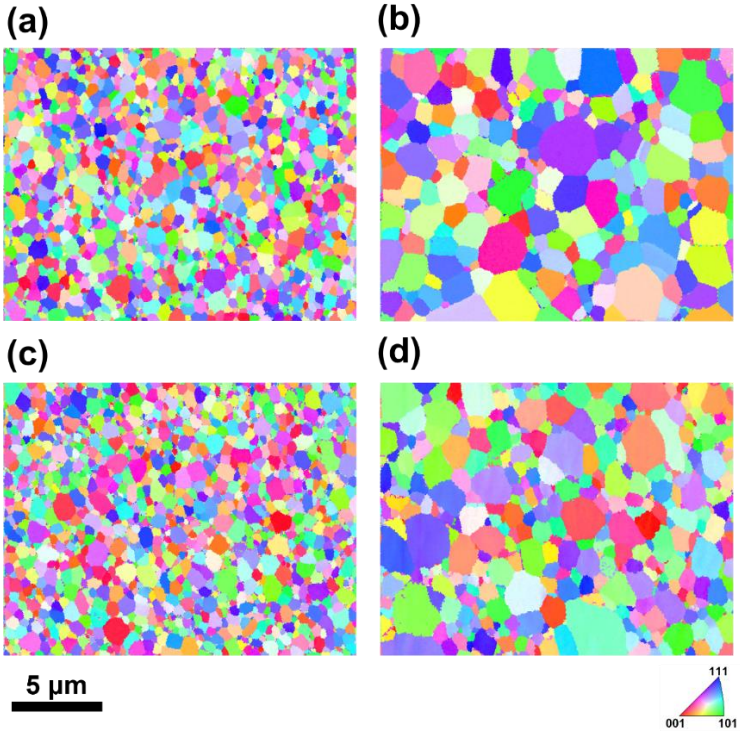

Figure 1. Electron Backscatter Diffraction (EBSD) maps of pure spinel after (a) hot pressing and (c)

heat treatment at 1400 ° C for 48 h as well as Ca-doped spinel after (c) hot pressing and (d) after heat treatment at 1400 ° C for 48 h.

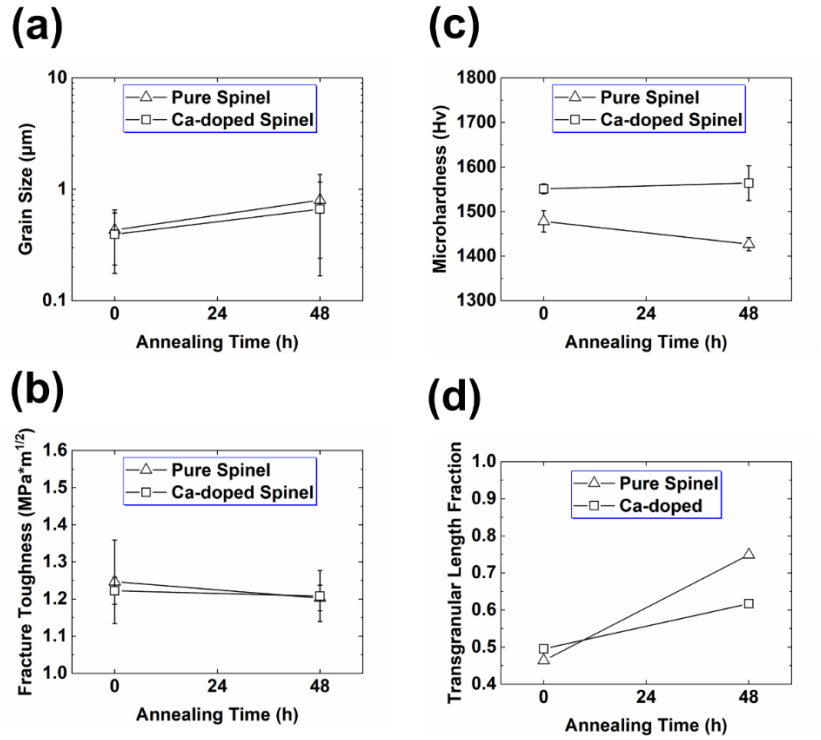

Figure 2. (a) grain size, (b) microhardness, (c) fracture toughness and (d) transgranular length fraction for pure spinel and Ca-doped spinel before and after heat treatment.

References:

[1] Z Shi et al., Mater. Des. **193** (2020), p. 108858. doi:10.1016/j.matdes.2020.108858
[2] ASTM Standard C1327-15, (ASTM International, PA). doi:10.1520/ C1327-15R19
[3] GD Quinn in “Mechanical Properties and Performance of Engineering Ceramics II: Ceramic Engineering and Science Proceedings” eds. R Tandon, A Wereszczak and E Lara-Curzio, (John Wiley & Sons, Inc., NJ) p. 45.
[4] I Ganesh, Int. Mater. Rev. **58** (2013) p. 63. doi:10.1179/1743280412Y.0000000001
[5] AR Krause et al., Scr. Mater. **178** (2020), p. 251. doi:10.1016/j.scriptamat.2019.11.041
[6] O Schumacher et al., Curr. Opin. Solid State Mater. Sci. **20** (2016), p. 316. doi:10.1016/j.cossms.2016.05.004
[7] The authors wish to acknowledge financial support from the NSF through grants DMR-2018683 and CMMI-2016279.