Effect of LiF and CaO Additions on $MgAl_2O_4$ Dynamic Behavior

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Abstract. Lithium fluoride as well as calcium oxide were used, isolated and combined, as sintering additives to magnesium aluminate ceramic in order to provide both better densification and transparency. This work assessed the dynamic behavior of $MgAl_2O_4$ by performing split Hopkinson bar dynamic tests, since they provide the material strength, strain rate, and strain measurements. The total amount of additives was 1.5 wt% in which the percentage of LiF and CaO varied from 0 to 100 wt% with an increment of 25 wt%. The obtained results indicated that CaO low concentrations weakened the ceramic. By increasing the amount of CaO, the $MgAl_2O_4$ samples were dynamically strengthened. The strain rate was reduced as the amount of CaO increased, indicating a higher trend of energy absorption corroborated by K_{Ic} measured values. On the other hand, the ceramic strain was increased with increasing CaO additions. These obtained dynamic properties are very useful to predict the expected ceramic armor ballistic performance.

Introduction

The ballistic armor systems are made up of many layers of different materials, each one designed to play a specific role [1]. The first one, which first receives the projectile is, usually, a hard ceramic material, that breaks the projectile tip reducing significantly the bullet penetration power. Besides, the penetration resistance transparency has been required in multiple applications. Therefore ceramics were developed to be used as transparent armor such as sapphire, AlON, magnesium aluminate, among others. The transparency is achieved preventing light scattering. As a result, an almost pore free microstructure and large grain sizes are desired for good light transmittance. The proper choice of sintering additives arises as an important variable to fit the microstructural features. The literature has reported LiF and CaO, each one separately, as effective sintering additives to $MgAl_2O_4$. LiF activates liquid phase sintering due to its relatively low melting point. On the other hand CaO, which possesses higher melting point, triggers solid state sintering on magnesium aluminate. The objective of this work was to investigate the dynamic behavior of $MgAl_2O_4$, with additions of the referred additives simultaneously, throughout split Hopkinson bar tests.

Experimental Procedures

Magnesium aluminate spinel ($MgAl_2O_4$) powders, provided by American Elements, were mixed with LiF and CaO as sintering additives. The total amount of additives was maintained constant and equal to 1.5 wt% in the powder mixture for all the studied samples. LiF has low melting point and provides liquid phase sintering while CaO with higher melting point triggers solid state sintering. This work investigated these additives together and separately. Fig. 1 presents the investigated additive compositions.

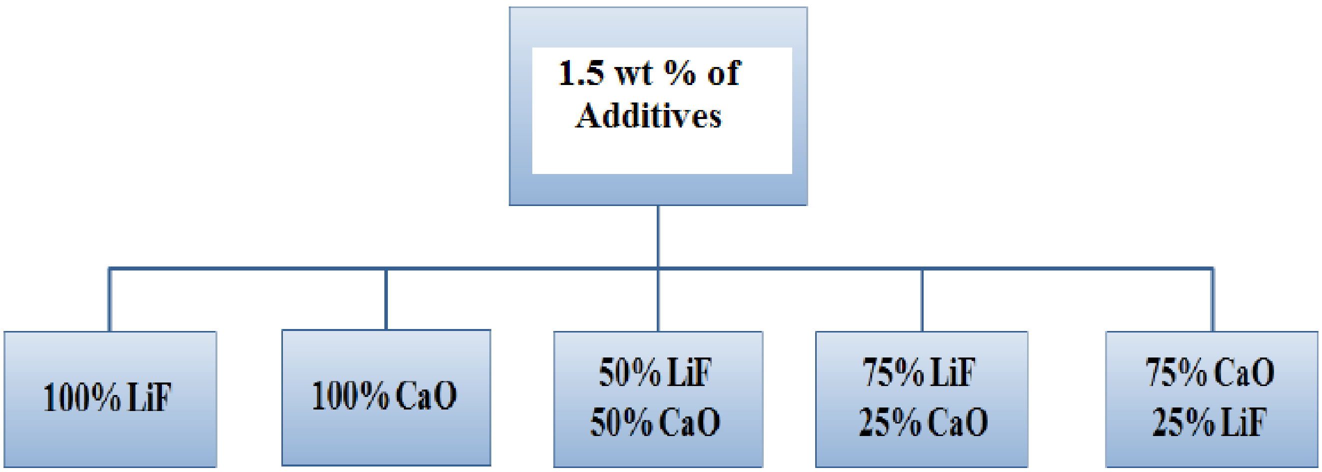

Fig. 1: Investigated additive compositions

The powder mixtures were initially cold pressed into discs of 10 mm diameter and 6 mm thick pellets. The discs were then hot pressed at 35 MPa and sintered at 1550^{o}C for 1 hour. The sintered samples densities were determined by Archimedes' method, Vickers microhardnesses by indentation, grain size by the line intercept technique, fracture toughness by indentation, and phases by XRD. The samples dynamic behavior was assessed by performing Hopkinson bar tests, as shown schematically in Fig. 2, by measuring the stress, strain, and strain rate behavior under impact [4]. The tests were accomplished on $MgAl_2O_4$ samples using copper as pulse shaper to prevent samples from collapsing below their dynamic strength limit. The pulse shaper was placed between the striker bar and the incident bar. The striker bar velocity was 13.5 m/s, and the pressure required to trigger the striker bar was 10 atm provided by compressed air. The strain gages generated signals registered in a oscilloscope regarding the incident, transmitted, and reflected pulses on the incident and transmitter bars. These pulses were able to provide stress, strain, and strain rate values acting on the $MgAl_2O_4$ sintered samples. Fig. 3 shows the Hopkinson bar apparatus setup carried on in this investigation.

Results and Discussions

Table 1 shows results from the hot pressed sintered samples. The density results indicated that LiF as sintering additive on $MgAl_2O_4$ was less effective in densification in comparison with LiF + CaO. LiF has a lower melting point than CaO. Therefore, the sintering mechanism activated by LiF is that of LPS (liquid phase sintering), and, in the case of CaO, the expected mechanism is that of SSS (solid state sintering) [5]. Therefore, the investigated additive mixture was able to improve density to higher values. Microhardness values were approximately constant around 13.5 GPa, with low value without LiF. In this condition the K_{Ic} value was probably higher due to better plasticity. CaO-rich additive compositions yielded low grain size and it agreed with the role of CaO, which holds grain boundaries, favoring densification. Many phases were detected by XRD where the major among them was spinel as expected. The sample with 25% of CaO was the only one where CaF_2 was observed, and this phase probably affected the dynamic properties, as it will be pointed out. Figures 4, 5, and 6, show the dynamic behavior of sintered $MgAl_2O_4$ by hot pressing, obtained by Hopkinson bar tests.

Table 1: Properties of doped $MgAl_2O_4$ after sintering by hot pressing

Additive Composition [%CaO]	Average Density [g/cm^3]	Average Microhardness [GPa]	K_{Ic} [MPa.m$^{1/2}$]	Grain Size [µm]	Phases by XRD
0	3.47	13.1	2.17	152	Spinel; BN
25	3.52	13.4	2.26	161	Spinel; BN; CaF_2
50	3.54	14.1	2.79	Not available	Spinel; BN
75	3.55	14.2	2.86	123	Spinel; BN; $Ca_3Al_2O_6$
100	3.55	12.9	2.95	133	Spinel; BN; Ca_3N_2

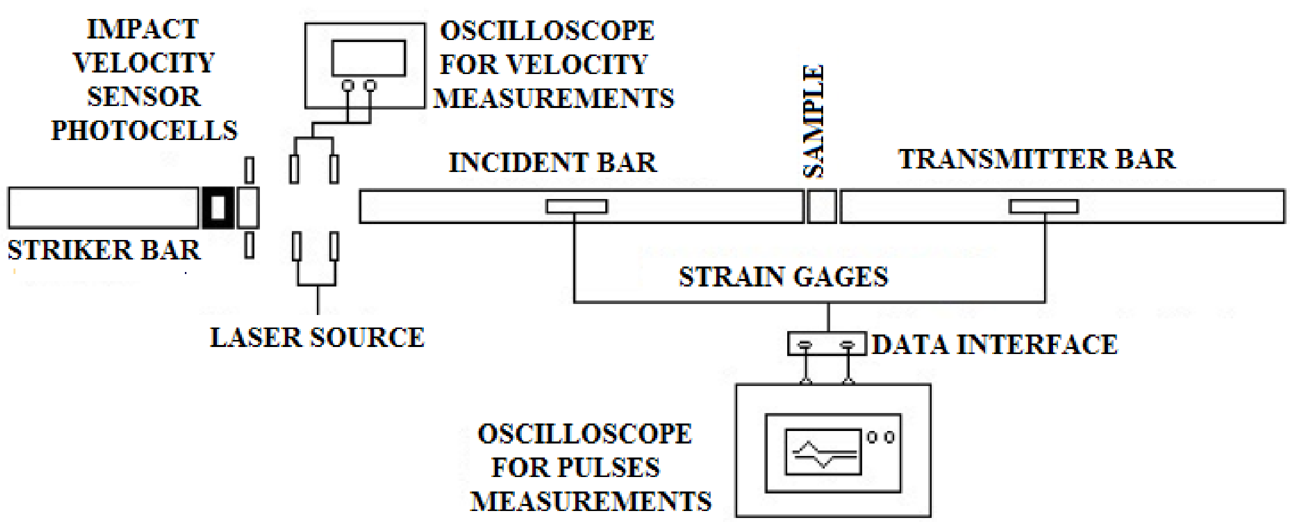

Fig. 2: Schematic representation of Hopkinson Bar tests performed on $MgAl_2O_4$ sintered samples.

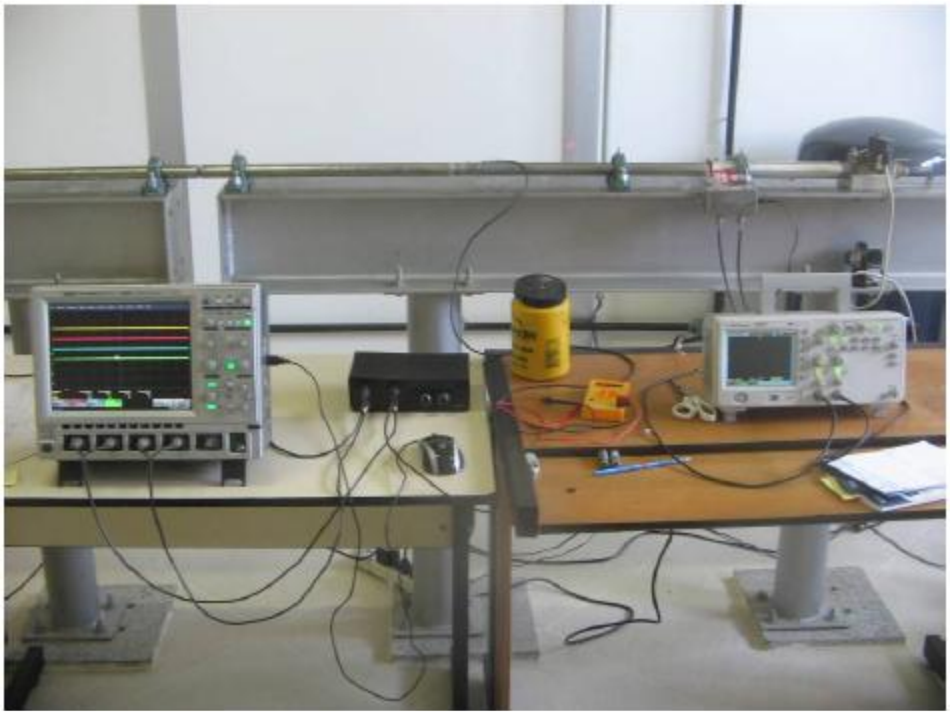

Fig. 3: Setup of Hopkinson bar and oscilloscopes

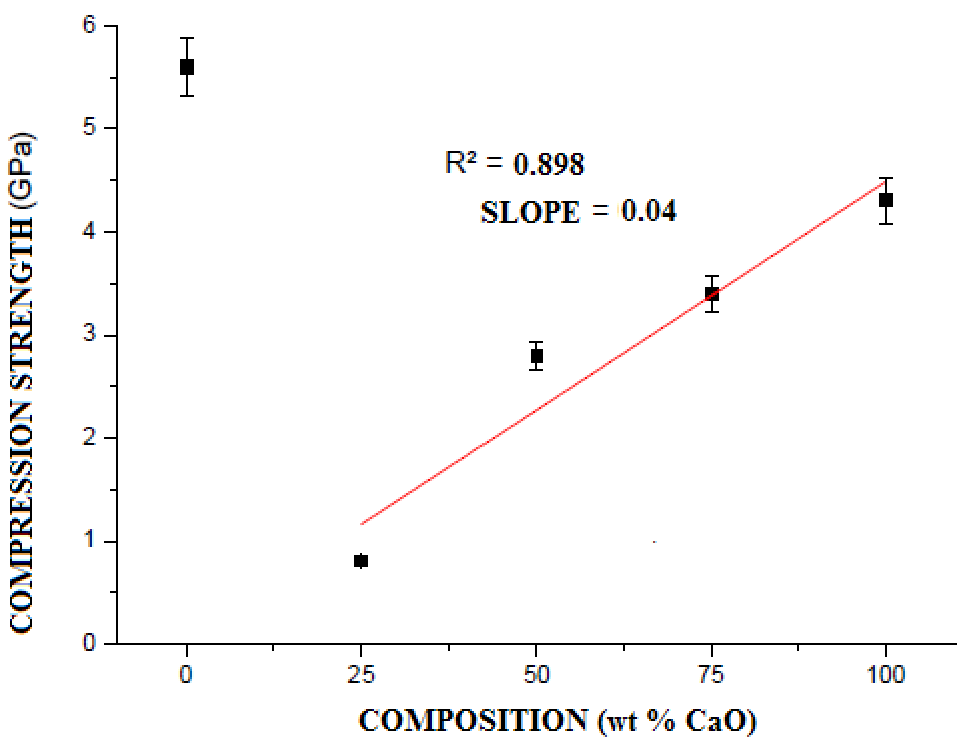

Fig. 4: $MgAl_2O_4$ compressive strength as a function of CaO in the additive composition.

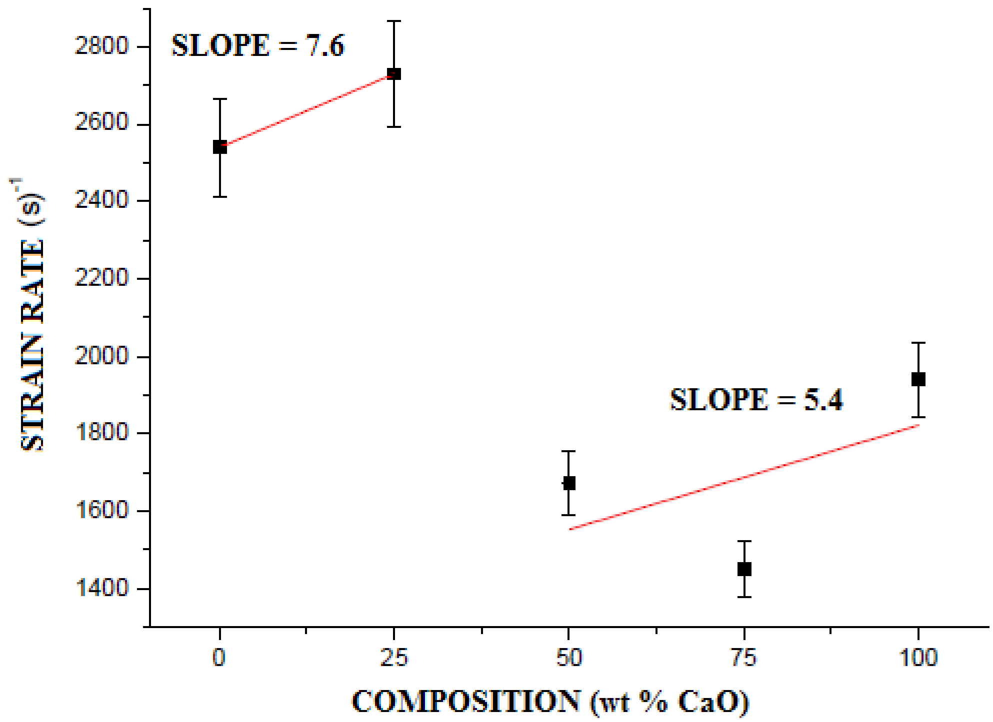

Fig. 5: $MgAl_2O_4$ strain rate as a function of CaO in the additive composition.

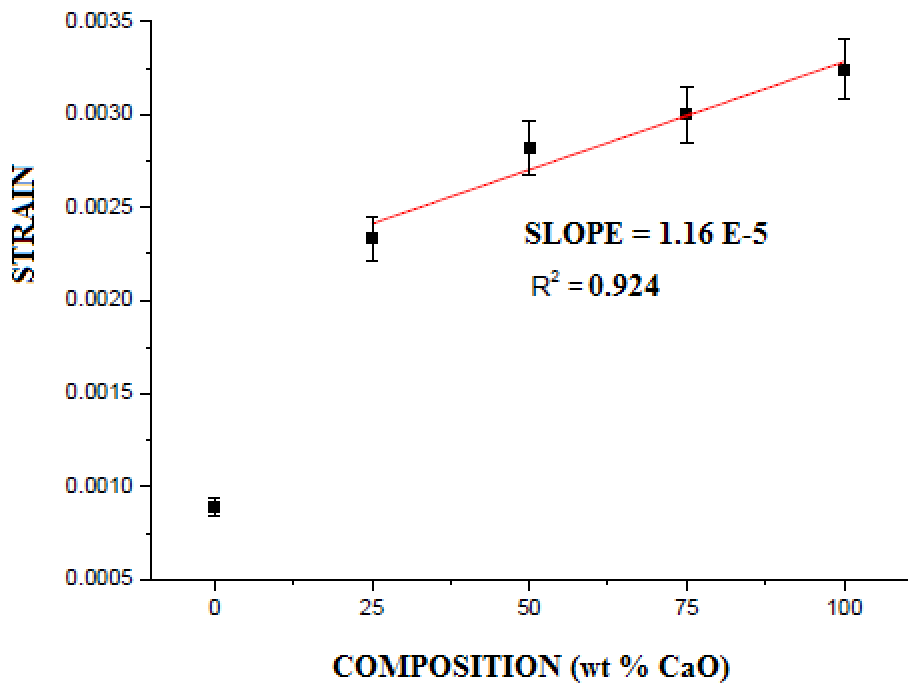

Fig. 6: $MgAl_2O_4$ strain as a function of CaO in the additive composition.

The results of compression dynamic strength tests given in Fig. 4 revealed the highest value for spinel without CaO addition. By adding 25% of CaO, in the additive composition, a significant reduction in the material dynamic strength was observed. This may be due to the CaF_2 brittle phase precipitated at spinel grain boundaries weakening the ceramic. However, additional increases of CaO strengthened the ceramic to a value of 70% of that obtained for the sample without CaO (only with LiF). Smaller grain sizes were observed by increasing CaO additions. According to the Hall Petch relation [6], it could be responsible for the observed strength recovery. Also, calcium nitrate precipitated in the CaO-rich samples, which could be associated to the referred strength recovery. Fig. 5 exhibits the strain rate behavior, showing that low CaO concentrations leaded to higher rates as compared to CaO higher concentrations. Since the strain rate modulus is inversely proportional to time, then lower rates means more time for deformation before fracture. Therefore, the time increase favored additional energy absorption which agreed to the higher values of K_{Ic} in the samples containing higher concentrations of CaO. Fig. 6 showed the dynamic strain behavior, where the strains increased with increasing CaO concentrations. Since the fracture toughness is represented by the area below the stress vs strain curve, then increasing strain together with longer strain times for lower strain rates before fracture resulted in larger fracture toughness, as measured.

Conclusions

1. $MgAl_2O_4$ with only LiF showed the highest compression dynamic strength, and with 25% of CaO in the additive composition this property presented the lowest value. Increasing CaO in the additive composition the dynamic strength also increased up to 70% of the highest value for spinel doped only with CaO.
2. CaO additions caused smaller strain rates but larger strains. This combination led to higher fracture toughness, as obtained.
3. The weaker sample was that containing 25% of CaO in the additive composition.

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