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STATE OF THE ART IN ALUMINUM MATRIX COMPOSITES USING FLY ASH

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SUMMARY

Owing to its unique characteristics – like morphology and chemical composition-, fly ash has been identified as a potential reinforcing phase for the manufacture of metal matrix composites (MMCs). Moreover, the recent literature shows that mostly it has been used as a second reinforcement in dually reinforced aluminum matrix composites. In the case of Al/SiC$_p$ composites, essentially it offers two major benefits; namely, to protect SiC from being attacked by liquid aluminum during processing, and enhance mechanical properties. Incorporation of fly ash within aluminum matrices with proper Mg content gives place to the formation of secondary phases like magnesium aluminate spinel ($MgAl_2O_4$), which could also act as reinforcement. As for mechanical behavior, cenosphere fly ash promises to enhance the energy absorption capabilities and damage tolerance of composites subjected to impact. The aim of the current contribution is to present a critical review on the use of fly ash in aluminum-based MMCs.

Keywords: metal matrix composites; aluminum alloys; fly ash

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1. INTRODUCTION

The need for decreasing pollutant emissions to the environment and gas consumption reduction by automobiles motivated the development of light-weight materials but with similar or improved mechanical performance, specially the strength-to-weight ratio. There are of course other key aspects to take into consideration, like the corrosion and thermal behaviors. Yet long before, most of the expectations aimed at using aluminum matrix composites reinforced with ceramics (SiC, TiC, AlN, Si_3N_4, etc.) – most of which are produced with costly processing routes – to satisfy those requirements. The cost issue was indeed one of the main reasons for preventing the use of these materials in massive commercialization. Accordingly, the idea of using recycling/waste materials was received with eagerness, particularly by the automotive industry. The foremost material considered was fly ash, although more recently, rice-hull ash was also taken into account [1]. The reason behind the interest in fly ash lies in morphological, mechanical and compositional and definitely, cost aspects, though originally only the morphological/mechanical characteristics were envisioned as attractive in addition the economic subject. And, in terms of the mechanical characteristics, hardness and impact absorption behavior justified to a certain extent the first investigations. These involved then some classification/characterization tasks, including chemical analysis, particle size range and morphology studies. In composite preparation there were also some preferences in terms of the processing routes applied and aluminum alloys utilized. Commercial aluminum alloys A356, 2024, 6061 were selected for using in investigations with squeeze casting and stir casting techniques for composites with low volume fraction (10-30 v %) of the ceramic and pressure assisted infiltration for high volume fraction (50- 60 v %) of the reinforcement. Fly ash was tested originally as the only reinforcing material, though it has been proposed lately that it can be used as a co-reinforcement, specifically in Al/SiC composites [1, 2]. Then in the first investigations and even recently, the authors have tested the fly ash composites in wear abrasive, hardness and compressive testing. It should be pointed out that during processing with the liquid-alloy state route, there is always the potential for the development of reactions that give rise to products that eventually may play a positive or deleterious role. When the alloys contain sufficient amount of magnesium, evidently one of the main reaction products is magnesium aluminate spinel ($MgAl_2O_4$), followed by magnesium oxide (MgO). Associated with these events is the further consideration of the new phases as co-reinforcements, though other problems arise in terms of the corrosion behavior, because as it is generally accepted, the presence of second phases increases considerably the propensity of the composite to galvanic corrosion. And although evaluation of the corrosion behavior is paramount before launching the product to the market, the recent literature shows that this aspect has not been covered yet to an extensive degree to satisfactorily fulfill the standard requirements. The aim of this contribution is to show the current status in the development of fly ash composites by discussing some pros and cons of the processing routes, compositional alloy related aspects and mechanical as well as corrosion characteristics of materials from some prominent investigations/authors.

2. EXPERIMENTAL

The first step in order to study the potential of fly ash for aluminum matrix composite materials is to carry out of a thorough characterization.

2.1 Description and characterization of fly ash

Solid fly ash particles are generally collected in precipitators and have a density close to 2.1 g cm^{-3} and hollow fly ash particles referred to as cenospheres, are collected on the surface of ash ponds [3]. Accordingly, these two types of fly ash are referred to as *precipitator fly ash* and *cenosphere fly ash*. Figure 1a) shows the typical characteristics of fly ash.

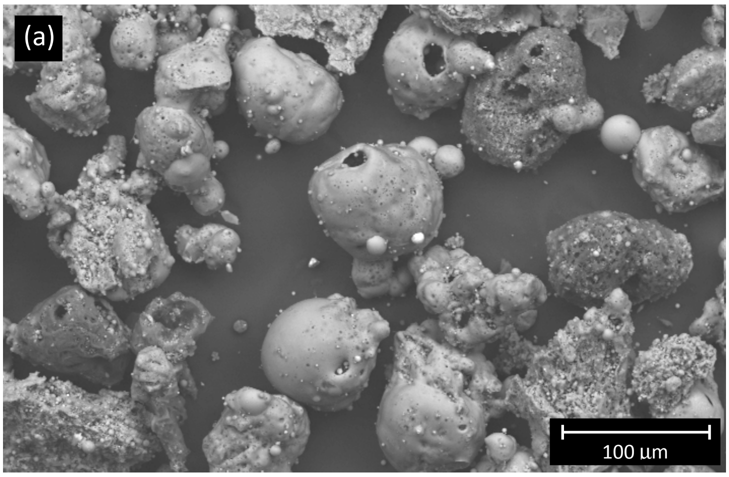

Fig. 1 Typical sample containing precipitator and cenosphere fly ash [1].

One main concern about the utilization of fly ash in a global scheme is the variation in chemical composition from one source to another (country, geographical location, plant, etc.), and consequently, a more or less wide range of compositions are found. Most of them consider some primary components and minority, in addition to an amount ascribed to loss of ignition (LOI). The following are just some examples:

Type of fly ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	K_2O	Na_2O
Precipitator	38.5	17.1	25.1	4.00	2.5	1.5	1.9	2.5	0.5
Cenosphere	60.8	25.9	4.5	0.72	1.58	1.00	0.26	3.58	0.80

Table 1 Chemical composition of fly ash particles (wt. %) [3].

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	Loss of ignition	undefined
Weight %	27.4	12.8	5.5	47	2.5	0.7	6.2	2.4	1.5

Table 2 Chemical composition of the fly ash [4].

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	K_2O	Na_2O
Weight %	30-70	15-30	10-20	1-5	0-2	0-2	6.2	1-5	0-2

Table 3 Typical chemical composition of fly ash, in weight percent [5].

This will impose a great challenging task, because for a specific application, composition will have to be standardized, in addition to the selection of the type of fly ash to be utilized (precipitator or cenosphere). It is interesting to note that precipitator fly ash has pores and its density ranges from 2.1 to 2.6 g/cm^3. The particle size of the precipitator fly ash as received from the power plants generally lies in the range from 1 to 150 µm, while cenosphere fly ash particles have sizes ranging from 10 to 250 µm, with density in the range of 0.4 to 0.6 g/cm^3.

2.2 Processing routes

Certainly, a number of pros and cons are associated to each of the processing routes available for the preparation of fly ash MMCs. For instance, using the stir casting technique, fly ash particles tend to segregate along the aluminum grain boundary due to particle pushing. They also tend to float to the top of the cast ingots due to their lower density. However, the distribution is reasonably uniform except for the top layer [6]. Using squeeze casting, a vertical pressure is applied to force molten aluminum into the fly ash preform completely. The pressure is maintained for a given time, typically 5 min, until the solidification is completed [7]. By the powder metallurgy technique, aluminum fly ash samples are compacted at different pressures (20,000 to 60,000 psi). Although the compaction operations may lead to a deformation/fracture of the fly ash particles, no significant changes in shape were observed, even when sintered at 625 ^{o} for 2.5 hours. However, when the quantity of fly ash in the composite increases above 10 % by weight, the hardness significantly decreases, and thus it can be concluded that powder metallurgy does not seem very promising for producing fly ash alloy composite parts [6].

Using the pressure infiltration technique, the aluminum alloy is poured at 840 ^{o}C, and applying pressures from 1,500 to 2,500 psi on top of the aluminum alloy for a period of 10 minutes. A significant advantage of this technique is that the distribution of fly ash particles is uniform in the pressure-infiltrated casting. The volume percentage of fly ash in the composite can be controlled by controlling the porosity in the fly ash preform, which can again be controlled by adjusting the quantity of foaming agent in the preform. It has been reported that the pressure infiltration method gave better castings than the other techniques developed earlier. We Energies and EPRI have patented a manufacturing method of ash alloy (US Patent 5, 897,973) [6]. Another potential route for the preparation of fly ash MMCs is the so-called spontaneous infiltration. This route offers attractive advantages, such as economic and simplicity, because it depends on capillary phenomena to fill up the interstices in a porous body with the liquid metal. Figure 2 is a simplified schematic representation of the pressureless infiltration technique, showing the solid metallic alloy before melting and then, the liquid metal infiltrating spontaneously.

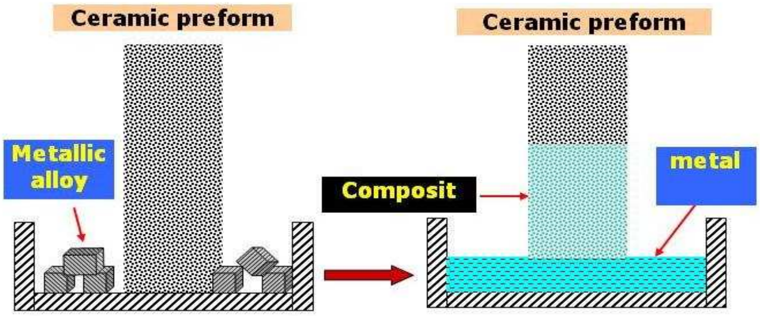

Fig. 2 Schematic representation of the pressureless infiltration method.

Accordingly the processing parameters should be optimized previously to the wetting of the solid by the specific metallic alloys, i.e., low contact angle and liquid-vapor interfacial energy. Typically the alloys (experimental) have high levels of Si and Mg to promote wetting and in the laboratory, the infiltrations are carried out between 1000 and 1150 °C, in process times that range between 50 and 70 min, using argon at pressure slightly above to that of the atmospheric pressure (total pressure ≈ 1.2 atm.).

Figure 3 shows representative photomicrographs of aluminum matrix composites produced with SiC and fly ash, via pressureless infiltration.

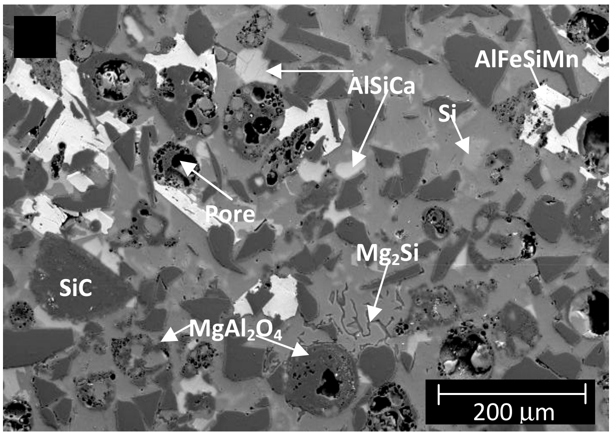

Fig. 3 Typical microstructure of Al/fly-ash composite obtained by pressureless infiltration [2].

Table 3.1 illustrates the various processing routes used for the preparation of fly ash composites. It is clear that all the differences lead to different physical, mechanical and corrosion properties.

Fabrication route	Fly ash percentage	Fly ash particle size	Al alloy	Ref.
Squeeze casting	60	20-250 µm and 200 mesh sifted particles	6061 Al	7
Squeeze casting	70	20-250 µm and 200 mesh sifted particles	2024Al	8
Squeeze casting	70-65	90-150 µm	Commercial purity	9
Stir casting	6, 12	Narrow size range (53-106 µm) and wide size range (0.5-400 µm)	A356	10
Stir casting	6, 12	Narrow size range (53-106 µm) and wide size range (0.5-400 µm)	A356	11
Stir casting (Vortex)	6-50 vol %	Ni-coated fly ash	Novel ZnAl22	12
Powder Metallurgy	0-16 wt %	Cu-20%Zn		13
Pressureless infiltration	20 vol %	36-50 µm	Al-3Si-15Mg	1,2

Table 4 Various fly ash/alloy systems studied by different processing routes.

One of the main issues to consider when dealing with composites processed with fly ash is the tendency for the development of new or secondary phases. This of course is closely related to aluminum alloy composition. The presence of new phases may have an impact on both, the corrosion and mechanical behavior of the composites. As for the former, two other possibilities can be considered at the same time; chemical and galvanic corrosion. Chemical corrosion is more common when one of the phases can be easily dissolved when exposed to given atmosphere, as in the case of aluminum carbide (Al_4C_3) – formed by the dissolution of SiC in liquid aluminum – which reacts with water. The second possibility is easier to associate to the formation of galvanic couples between the matrix and a given phase or between two phases. And the damage can go from mild to severe. To illustrate the implication of such condition, in Fig. 4, a photomicrograph of an Al/SiC/$MgAl_2O_4$ composite undergoing severe corrosion is shown.

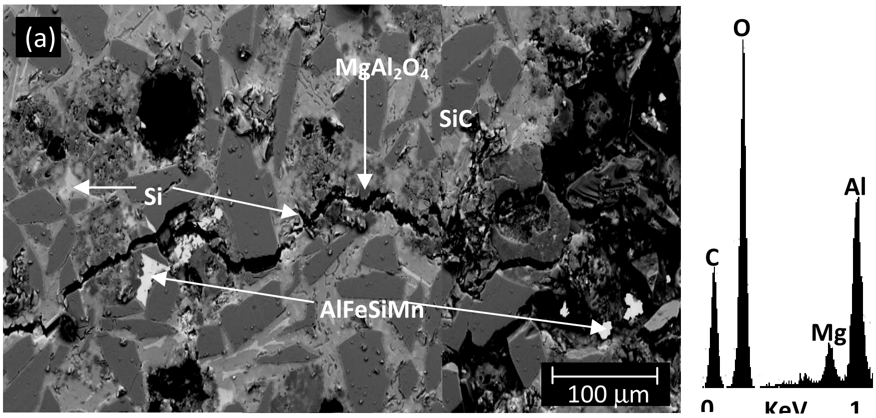

Fig. 4 Photomicrograph of an Al/SiC/$MgAl_2O_4$ composite prepared with fly ash via pressureless infiltration [2].

Interestingly, corrosion can be prevented by adequate optimization of the processing parameters, i.e., processing time and temperature, atmosphere and alloy composition, amongst others. Perhaps the latter influences decisively the formation secondary phases. The photomicrograph in figure 5 illustrates the sound microstructure of an Al/SiC/$MgAl_2O_4$ composite processed under optimized conditions with fly ash, eleven months after fabrication.

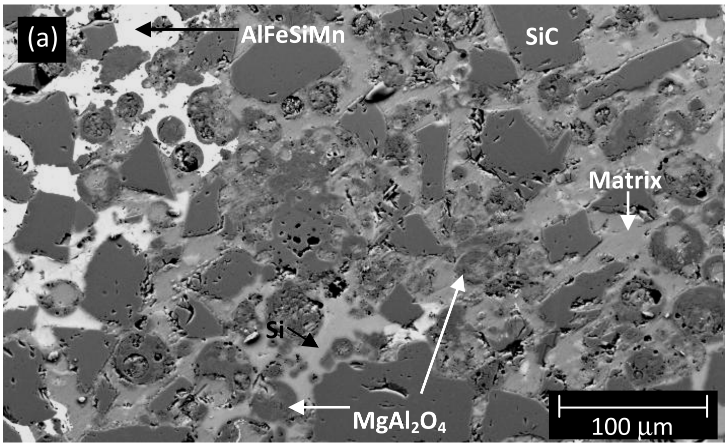

Fig. 5 Micrograph of an Al/SiC/$MgAl_2O_4$ (fly ash) composite processed under optimal conditions. Condition observed 11 months after processing[2].

2.3 Resulting properties of Al/fly-ash composites

A number of mechanical properties have been reported for fly ash composites. These include: hardness, compressive strength, damping capacity, adhesive and sliding dry behavior, and even some magnetic characteristics[2, 3, 5, 7-11]. G. H. Wu et.al., [7] measured the damping properties of fly ash 6061 Al composites with various reinforcement diameters and with about 40 vol % porosity (enclosed within the hollow sphere fly ash particle) using the forced vibration mode and the bending-vibration mode on the multifunctional internal friction apparatus. The damping capacity is a measure of a material's ability to dissipate elastic strain energy during mechanical vibration or wave propagation. The composites were prepared using the squeeze casting technique, applying a vertical pressure to force molten aluminum to infiltrate into the fly ash preform completely, maintaining the pressure for about 5 min until the solidification is completed. The results indicated that the damping capacity of the fly ash 6061 Al composite with smaller reinforcement diameter is higher than that with larger reinforcement diameter in both vibration modes. In the bending-vibration mode, there is a more significant increase in the damping capacity of the as-received commercial 6061 Al due to the addition of fly ash particles and the damping capacities of the fly ash/6061 Al composites can reach (2-3) x 10^{-2}, which is more than two times of the maximum values measured in the force vibration mode. In a different investigation [9], the authors developed a new method to predict the compressive strength of cenosphere-aluminum syntactic foams, showing the relation between the relative wall thickness of the cenosphere and the compressive strength of such foams.

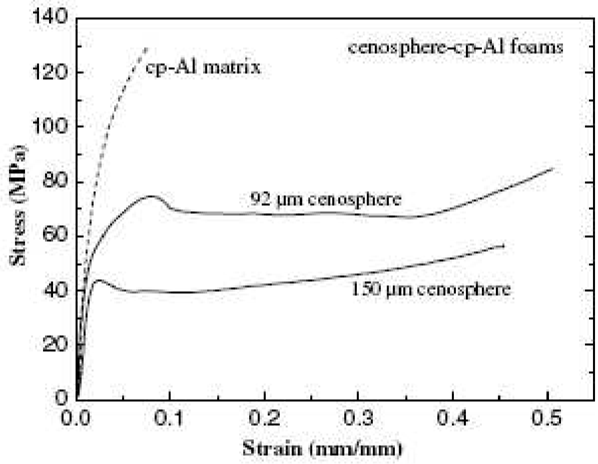

Fig. 6 Compressive response of the cenosphere-cp-Al syntactic foams[9].

Quasi-static compression tests indicated that the annealed cenosphere-aluminum syntactic foams can deform plastically at relatively higher stress (~45-75 MPa) and their energy absorbing capacity can reach ~20-35 MJm^{-3}.

Using an alloy of Al-7Si-0.35 Mg, T. P. D. Rajan and co-workers [14] studied the effect of three different stir casting routes on the microstructure and properties of fly ash (13μm average particle size) composites. Among liquid metal stir casting, compocasting (semi solid processing), modified compocasting followed by squeeze casting routes evaluated, the latter resulted in a well-dispersed and relatively agglomerate and porosity free fly ash particle dispersed composites. Interfacial reactions between the fly ash particle and the matrix leading to the formation of $MgAl_2O_4$ spinel and iron intermetallics are more in liquid metal stir cast composites than in compocast composites.

Sudarshan and Surappa [10] found that composites reinforced with narrow size range of fly ash particles exhibit superior mechanical properties compared to composites with wide size range particles. These findings were obtained after the evaluation of various mechanical properties of fly ash composites fabricated by the stir-casting technique and hot extrusion, using A356 Al alloy and fly ash particles with narrow (53-106 μm) and wide (0.5-400 μm) size range. Hardness, tensile strength, compressive strength and damping characteristics of the unreinforced alloy and composites were measured. Bulk hardness, matrix microhardness, 0.2% proof stress of A356 Al-fly ash composites are higher compared to that of the unreinforced alloy. Additions of fly ash lead to increase in hardness, elastic modulus and 0.2% proof stress. It should be recognized that many investigations have been performed on the evaluation of compressive strength, involving various testing parameters. For instance, D. P. Mondal et al., [15] studied the effect of strain rate and relative density on compressive deformation of closed cell aluminum-fly ash composite foam and correlated plateau stress and densification strain with strain rate and relative density. The authors developed an empirical relation, following the power relation of plateau stress with strain rate and relative density. K. V. Mahendra et. al., [16] prepared composites with Al-4.5 wt. % Cu varying fly ash contents in 5, 10, and 15 wt. %, using stir casting. They studied the effect of fly ash on the fluidity of the composites. Density, hardness, impact strength, dry sliding wear, slurry erosive wear and corrosion performance were evaluated.

In another investigation Surdahan et. al., [11] studied the dry sliding behavior of Al-fly ash composites (A356 alloy) and compared with that of the Al alloy, Al_2O_3 and SiC composites, finding that the wear resistance of Al-fly ash composites is almost similar to that of Al_2O_3 and SiC reinforced Al-alloy. The load effect on wear rate of A356 alloy and the corresponding composites is shown in Fig. 7. In Fig. 7 C6S stands for composites with 6 v% fly ash particles (sieved), C12S for composites with 12 v% fly ash particles (sieved) and C12AR for composites with 12 v% fly ash particles (as received).

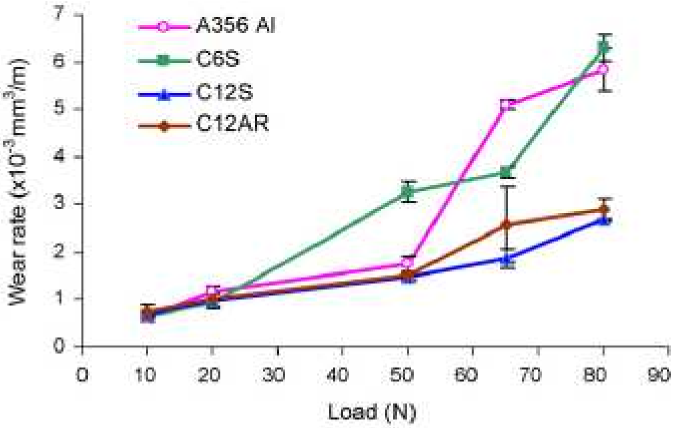

Fig. 7 Effect of load on wear rate of A356 alloy and its composites by weight loss method [11].

At high loads (>50 N), where fly ash particles act as load bearing constituents, the wear resistance of A356 Al alloy reinforced with narrow size range (53-106 μm) fly ash particles were superior to that of the composites having the same volume fraction of the particles in the wide size range (0.5-400 μm). Adhesive wear is dominant in unreinforced alloy, whereas abrasive wear is predominant in composite. At higher load, subsurface delamination is the main mechanism in both the alloy as well in the composites. A more elaborate discussion was made after examining the worn surfaces, subsurfaces and debris in the microscope.

In the work by Z. Dou and co-workers [8], the cenosphere and precipitator fly ash particulates were used to produce two kinds of aluminum matrix composites with the density of 1.4-1.6 g cm^{-3} and 2.2-2.4 g cm^{-3} separately. The electromagnetic shielding effectiveness (EMSE) properties of the composites were measured in the frequency range 30.0 kHz-1.5 GHz. The results indicated that the EMSE properties of the two types of composites were nearly the same. The tensile strength of the matrix aluminum decreased by addition of fly ahs particulate and the tensile strength of the composites were 110.2 MPa and 180.6 MPa separately. The fractographic analysis showed that one composite fractured in a brittle manner and the other in a micro-ductile manner.

3. SUMMARY

This review shows that there are some central issues necessary to address before fly ash composites reach their full potential on a commercial scale.

1. Due to these differences in chemical composition, it is difficult to compare the properties of composites obtained so far. And this isn’t just matter of adjusting chemical composition as is the case for the aluminum alloys.
2. In order to obtain the highest properties, it is better to use a narrow size range of fly ash particles. This implies preconditioning operations with associated cost.
3. Fly ash particles may also change in shape during processing, for instance, when they are compacted at high pressures. In this respect, the use of processing routes not involving considerable levels of pressure or mechanical manipulation, like the pressureless infiltration route, are more attractive.
4. Associated to the processing route is the type of aluminum alloys used. For pressureless infiltration it is essential that the alloy wets the solid fly ash. A prior study on the wetting aspects is recommended.
5. The current literature also shows that although most of the composites proposed have been evaluated in mechanical testing, there is no document supporting an extensive corrosion evaluation, not only by electrochemical testing but also in humidity tests at room and above ambient temperature.
6. Damping, capacity, tensile strength, and compressive strength are some of the properties mostly evaluated. However more work needs to be done, because, as some authors affirm, the influence of strain rate on the compressive deformation behavior of aluminum metal foams is yet to be understood.
7. An important conclusion that can be drawn is that fly ash may not be useful without previous preparation; its use in the as-received condition would rather be uncommon.

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