Proceedings of the EUROCOALASH 2012 Conference,
Thessaloniki Greece, September 25-27 2012
http:// www.evipar.org/

Pressure infiltration technique for the synthesis of A356 Al/high-Ca fly ash composites

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Keywords: Metal Matrix Composites (MMCs), lignite fly ash, liquid metal infiltration, wear, compression strength

Abstract

In the present paper eight types of A356 Al-fly ash composites were synthesized using pressure infiltration technique, by utilizing Class C fly ash (FA). Actually, such a strongly calcareous FA was for the first time used in MMCs-manufacturing by liquid metal infiltration techniques. After testing their mineralogy and chemistry, certain FA size-fractions were used for the fabrication of the composites and their particular properties were linked to the level of the successful synthesis of the materials, the development of their microstructure and their wear strengths. The effect of using ground FA particles on the structure of composites and their tribological performance was also investigated through this study. It was concluded that using fine FA particles can strongly advantage the properties of composites and that grinding of fly ash facilitates MMCs-manufacturing by pressure infiltration and it also advantages their wear properties.

1. Introduction

Metal Matrix Composites (MMCs) find a wide range of applications, including aerospace and automobile, thanks to their excellent combination of physical, mechanical and tribological properties [1, 2]. However advanced those composites may be, their usage remains limited on account of their high production cost. Coal/lignite fly ash is one of the most abundant and inexpensive materials that can be used to reinforce aluminium alloy composites. Techniques such as powder metallurgy, liquid metal stir casting and pressure infiltration have been applied in the past for the synthesis of FA-reinforced aluminum-based MMCs [3-8]. FA-reinforced aluminum matrix composites are also termed as “ashalloys” [9].

Pressure infiltration technique can be used for synthesizing MMCs with high volume fraction and uniform distribution of particles in the matrix. It has been applied in the past for fabrication of MMCs containing fibrous and particulate reinforcements [10-13]. In fact, previous research works have studied pressure infiltration technique for different composite systems, such as Al-Ni, Al-SiC particles, Al-SiC foam, Al-glass fiber, Al-Al_2O_3 etc [14]. Studies on the tribological characteristics of Al-MMCs containing various reinforcements are available in the literature [15-17]. However reports on the wear characteristics of "ashalloy" composites are still limited [18].

In the current study A356 Al-fly ash composites were fabricated by the use of pressure infiltration. Actually, very fine, fine and middle-sized particles of highly calcareous and siliceous FA were used to produce FA-60% vol.-containing composites. Indeed, such highly calcareous fly ash was for the first time used for "ashalloy" composites-fabrication by infiltration techniques. Free CaO of fly ash did not result in substantial drawbacks concerning the synthesis of composites. Chemical, mineralogical and shape properties of certain FA particle fractions were examined and correlated to the development of microstructure and tribological properties of the manufactured composites.

2. Materials and Methods

2.1 Fly ash

FAs were collected from the electrostatic precipitators of the lignite-fired power stations of Kardia, Northern Greece and Megalopolis, Southern Greece. Kardia fly ash (KFA) is a highly calcareous, Class C according to ASTM C 618, ash, while Megalopolis fly ash (MFA) is a siliceous, barely Class C ash. The abovementioned ashes were selected to investigate the effect of their different ingredients on the development of the microstructure and properties of A356 Al-FA MMCs. The FAs were separated into their different size fractions by manual screening, by using the respective sieves. XRF analysis of KFA showed that CaO ranges from 49.59% in the very fine particles to 39.89% in the coarse particles, SiO_2 from 22.89% to 34.12%, SO_3 from 4.15% to 0.24% and F_2O_3 from 5.22% to 6.94%. In MFA, SiO_2 ranges from 45.55% in the fine particles to 54.90% in the coarse ones, CaO from 16.31% to 10.04%, Fe_2O_3 from 10.60 to 13.52, with a minimum of ~11.70% in the middle-sized MFA particles and SO_3 from 2.5%, in the very fine particles, to practically zero in the coarse particles.

2.2 Synthesis of composites

In this study, composite materials were fabricated by pressure infiltration of both ground and non-ground fly ash particles with A356 alloy melt. Infiltration was performed in a custom furnace consisting of a water cooled stainless steel chamber with resistive heating elements inside. Approximately 70 g fly ash was packed into the bottom half of alumina crucibles with a graphite spacer disc placed on top of the fly ash preform. A 65 g-charge of A356 was added on top of the spacer and the crucible inserted into a custom machined graphite tube holder inside the furnace. The furnace was sealed and evacuated and then heated to 800 °C and held for ~30 min to ensure melting of the alloy. The pressure was then increased to 2.1 MPa using Ar gas forcing the melt into the spaces in the packed fly ash bed. The furnace was cooled under pressure and the samples removed after solidification was complete and pressure removed. 8 types of composites were fabricated using a combination of type and treatment of fly ash.

2.3 Characterization of composites

Microstructure of composites was examined by means of Energy-Dispersive X-ray Spectrometry (EDS-SEM, JSM-6300 JEOL). Dry sliding wear tests were conducted in air at ambient atmosphere using a Pin-on-Disc machine (CSEM High Temperature Tribometer, operated by the authorized personnel of CERECO S.A.) according to ASTM G 99-90. Pins of specimens were tested against spheres of alumina (Al_2O_3, diameter: 6mm). Prior to actual wear tests, sliding surfaces of test specimens were rubbed on 400/600 grid SiC emery paper. The surface of disc was polished to a surface roughness of 0.1 ± 0.02 R_a, using a series of abrasive papers. Experiments were conducted under dry conditions, at room temperature (25ºC, relative humidity: 65 ± 5%). The linear speed and sliding distance were 0.05 m/s and 94.20 m respectively. The load was 2 N. The rotational frequency of tested samples was set at 95 rpm; a total of 3,000 rounds were made by each sample. The wear rate was derived by the ratio WV / (FN x SD) (where WV the worn volume, FN the normal applied load and SD the total sliding distance). The coefficient of friction was evaluated by measuring the track cross sectional area and height, at ten different points on the wear track, using CSEM REVETEST Scratch-Tester. The worn volume was calculated by multiplying the average track area with the circumference of the slide circle. Worn surfaces and wear debris of the tested composites were also examined by EDS-SEM.

3. Results and Discussion

3.1 A356 Al-fly ash composites

Synthesis and microstructure of composites

Table 1 shows the synthesized “ashalloy” composites along with their encoding used within this study.

Table 1. Composites synthesized by pressure infiltration technique

Encoding	Metal	Ceramic (foam)	FA particles (μm)
C01	A356 Al	60% vol. KFA	(0-25)
C02	A356 Al	60% vol. KFA	(25-40)
C03	A356 Al	60% vol. KFA	(40-90)
C04	A356 Al	60% vol. KFA	(25-40) ground
C05	A356 Al	60% vol. MFA	(0-25)
C06	A356 Al	60% vol. MFA	(25-40)
C07	A356 Al	60% vol. MFA	(40-90)
C08	A356 Al	60% vol. MFA	(25-40) ground

Focus was put upon fine and ground fly ash particles in order for the mechanical properties of the materials to be advanced by the addition of low-diameter fly ash particles. Apart from that, there was no previous literature-report on synthesis of aluminum-based composites with such highly calcareous and simultaneously very fine fly ash particles. Moreover, ground Class C and Class F fly ash particles were for the first time comparatively tested for their efficiency to be used in composites-manufacturing by means of pressure infiltration technique. Previous reports[8] of “ashalloys”-manufacturing with other techniques (powder metallurgy) indicate that the incorporation of ground FA particles into aluminum has a positive effect on the properties of composites. FA particle fraction of (25-40)μm was particularly selected to be ground as it is rich in the -mechanically desirable- siliceous components and, simultaneously, its particles-diameters lay within a mechanically-acceptable range of microns. The goal of grinding this certain fraction was the glass phase to be broken and to subsequently make the active siliceous ingredients of FA particles release.

Figure 1 shows SEM pictures of the manufactured composites. Table 2 shows the chemical analyses of selected spots within the micrographs of composites. Actually, chemical analyses facilitated the process of identification of specific procedures that took place while molten alloy was being infiltrated into fly ash. Indeed, in spots where Ca and Fe were detected, it was obvious that a kind of metal/fly ash mixture was predominant. FA particles were identified in the mixture either as separate particles or as clusters. In fact, FA-clusters were extensively formed on account of the electrostatic forces that made separate particles coalescence and, to some extent, may harm the mechanical properties of composites[19]. Figures 1.a and b show panoramic micrographs of the homogenous surfaces of C02 and C04 respectively, indicating the successful infiltration of molten alloy into highly calcareous fly ash. Microstructure of all composites showed good contact between the alloy matrix and the surface of the fly ash particles. However, in regions near the contact surfaces of two touching particles, lack of proper infiltration (porosity) occurred. In addition, it was clear that infiltration of alloy into ground FA particles resulted in a better homogeneity of the final product. Indeed, grinding of FA seems to advantage the composites, not only chemically, but also in terms of their more likely successful manufacturing.

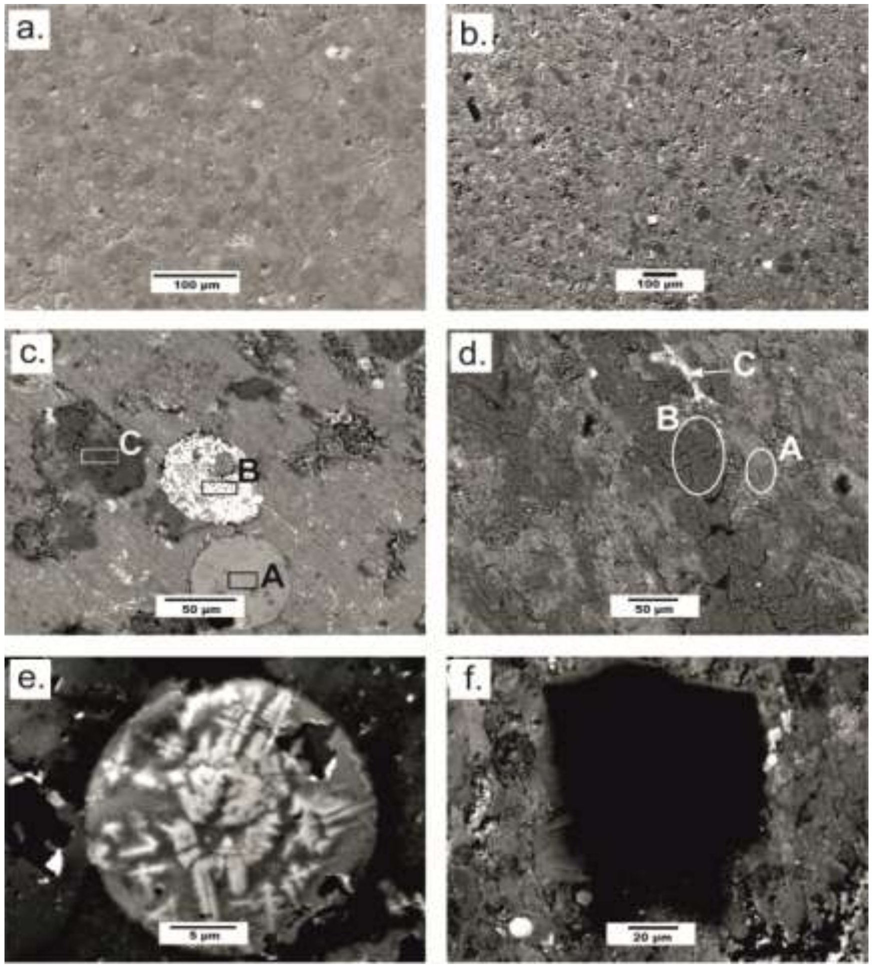


Fig. 1 (a) SEM micrograph of C02 at the scale of 100 μm. (**b)** SEM micrograph of C04 at the scale of 100 μm. (**c)** SEM micrograph of C04 at the scale of 50 μm. A: High-Ca area; B: High-Fe area; C: High-Al area. (**d)** SEM micrograph of C08 at the scale of 50 μm. A and B: High-Al areas; C: High-Fe area. (**e)** Highly ferrous spherical structure on the surface of C08. **(f)** Void observed in a fly ash-interparticle region of C06.

Figure 1.c shows the surface of C04 in a higher analysis. The spherical and elliptic structures identified on the surface of the composite (marked spots: A, B & C) were formed after the infiltration of alloy into ground FA. The chemical analyses of those spots (Table 2: A1, B1 & C1) indicated that alloy/fly ash mixtures were dispersed throughout the main mass of the material. On the other hand, there were specific places where only particular compounds were intensely concentrated, thus indicating the presence of FA clusters within the composite. Good homogeneity was also achieved in composites containing highly siliceous, ground FA particles, as it can be seen in Figure 1.d, which shows an SEM picture of C08. Table 2 also shows the chemical analyses of the marked spots A, B and C of this certain picture (A2, B2 &C2). Regarding the distribution of elements within the main mass of the products, as well as the dispersion of FA particles into them, the tendency presented by MFA-containing composites was same as for the KFA-containing materials. However, less spherical structures were identified in the second case, a possible sign of less porosity being present in raw fly ash. Figure 1.e shows a typical

spherical structure of those mainly identified on the surface of MFA-containing composites. This particular sphere (diameter: ~20μm) was highly ferrous, a result of the predominance of MFA in this certain spot. Part of Fe_2O_3, SiO_2 and CaO of both KFA and MFA can react with aluminum and silicon of matrix, up to 850°C, according to the chemical equations 3-5 [6, 14, 20, 21].

$$2Al_{(l)} + 3/2SiO_2 \rightarrow 3/2Si_{(s)} + Al_2O_{3(s)} \quad (3)$$
$$2Al_{(l)} + Fe_2O_{3(s)} \rightarrow 2Fe_{(s)} + Al_2O_{3(s)} \quad (4)$$
$$CaNa_2(CO_3)_2 + 2SiO_2 \rightarrow CaSiO_3 + Na_2Si + 2CO_2 \quad (5)$$

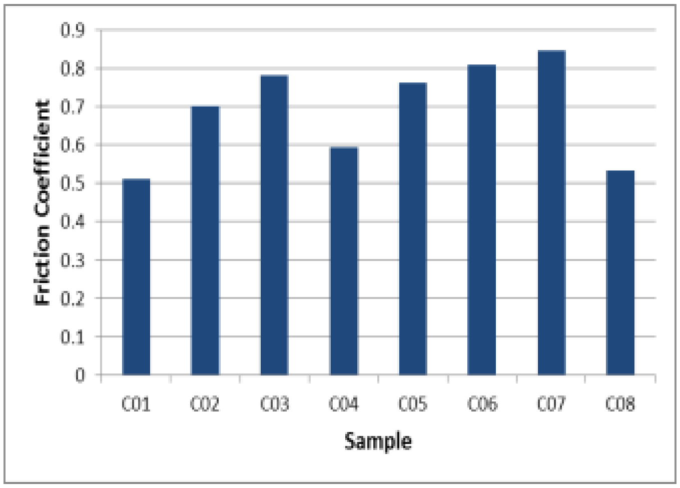
In some cases voids were observed within the composites. Such holes had a diameter range of 5-30μm and were not deliberately introduced and hence a priori undesirable. They had actually formed because of the incomplete infiltration that happened on some occasions, which was mainly attributed to the low applied pressures. In the SEM pictures of Fig. 2 it could also be seen that pores were generally presented at interparticle contact regions, where a high applied pressure is required for the melt to infiltrate. Such pores have also been observed in many different MMC-systems [22, 23]. Figure 1.f shows the biggest void observed in the composites through this study. Another form of porosity may be also present in both KFA and MFA composites as fly ash contains solid along with hollow particles (cenosheres). This form of porosity is desirable since it reduces the weight of the final products.

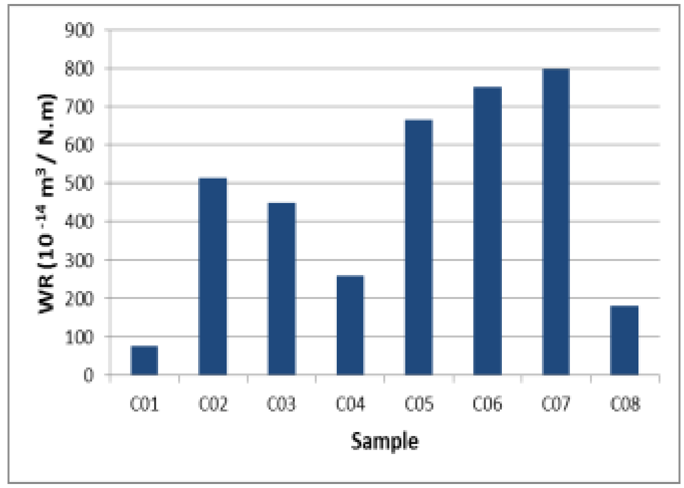
Table 2. Spot chemical analysis of pictures included in Figure 2. (A1, B1, C1: A, B and C spots of middle-left picture / A2, B2, C2: A, B and C spots of middle-right picture

Compound	A1 (%)	B1 (%)	C1 (%)	A2 (%)	B2 (%)	C2(%)
Al_2O_3	21.47	3.51	72.87	98.20	69.30	66.69
SiO_2	38.50	3.55	16.00	1.43	20.51	16.49
Fe_2O_3	8.93	92.09	6.45	0.13	2.49	16.36
CaO	28.70	0.64	3.53	0.04	6.27	0.05
SO_3	0.34	0.25	0.86	0.06	1.50	0.08
Na_2O	0.99	0.60	0.10	0.02	0.02	0.36
TiO_2	0.99	0.12	0.16	0.01	0.01	0.02

Tribological performance of composites

Figure 2 comprehensively shows the main results (friction co-efficient and wear rate) of the wear performance-tests that the synthesized composites underwent in order to study the effect of type of FA, FA-particle size distribution and grinding on the development of their wear properties.





In general, the KFA-containing composites presented better tribological properties than those produced with MFA. Indeed, calcium of KFA extensively reacts with Si of the alloy, thus resulting in the formation of complex Si- and Ca-Si-phases[8] that appear to advantage wear-strength of composites. This particular tendency was later confirmed by EDS-analysis. It was also found that: the finer the FA-particle, the lower the friction coefficient, an outcome that can be attributed to: a) the general advancement of the mechanical properties of materials caused by the usage of fine reinforcement-particles b) the more calcareous nature of fine FA particles that helps the formation of hard Ca-Si phases[8] and c) the particular minerals that were more intensely presented in fine FA particles (such as lime in KFA and quartz in MFA). In fact, it seems that a combination of those factors plays the most important role in the development of the tribological properties of "ashalloy" composites as those with ground FA particles showed the best results among all manufactured composites. Actually, grinding of FA, on the one hand reduces the particle-diameter of reinforcements and on the other makes the glass phase be broken and the active siliceous ingredients release, thus resulting in better mechanical properties of composites. It is noted that the worn surfaces of composites showed considerable curling-up along the specimen edges, as well as craters and ploughing. Both smooth and rough crater regions could be seen on the worn surfaces of the composites and it runs parallel to the sliding direction, indicating that mechanism of wear is probably adhesive [18]. Plastic ploughing and cutting were clearly less in KFA-containing composites than those in MFA-composites, mainly because of the calcareous compounds presented in the former.

4. Conclusions

Below, the main conclusions of this research study are summarized:

- It was proved that highly calcareous nature of fly ash does not obstruct the synthesis of A356-fly ash composites by pressure infiltration technique. Rather, the subsequent development of Ca-Si phases appears to advantage the tribological performance of those composites.
- Grinding of fly ash facilitates manufacturing of composites and it also advantages their wear properties. Indeed, ground FA particles have no glass phase (they therefore contain more active

ingredients) and they simultaneously lay within an acceptable range of particle-diameter without "carrying" the chemical drawbacks (i.e. high free CaO) of the very fine FA particles.

- Occasional presence of voids was observed in regions where FA particles were very close to each other and attributed to the low applied pressure.
- For both highly calcareous and highly siliceous fly ashes, the optimum -in terms of tribology- particle fraction to be used in A356 composites manufacturing by pressure infiltration is (25-40) μm, after grinding.
- Using fine FA particles can strongly advantage the properties of composites. However, due to electrostatic forces, fine FA particles intensely tend to form clusters, thus restraining the good dispersion of fly ash within the alloy-matrix. The next big challenge in "ashalloy" composites-manufacturing is to achieve the maximum level of de-agglomeration of fly ash particles in order composites with high strength to be manufactured.

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