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Synthesis of Aluminum-Based Metal Matrix Composites (MMCs) With Lignite Fly Ash As Reinforcement Material

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ABSTRACT

In the present paper, two different lignite fly ashes (FAs) originated from Kardia, Northern Greece (KFA, Class C) and from Megalopolis, Southern Greece (MFA, Class F) were utilized for the fabrication of Al/fly ash Metal Matrix Composites (MMCs). Aluminum-fly ash and aluminum/silicon alloy (Al -12% Si) –fly ash mixtures containing 5%, 10% and 15% w/w fly ash were prepared and compacted. The products were tested for their thermal behavior and then sintered at 600°C for two (2h) and six hours (6h). The density and hardness of the sintered compacts were determined as a function of weight per cent of fly ash particles. Volume changes during sintering of green compacts were also estimated as a function of increasing fly ash weight per cent. Microscopic studies of green and sintered compacts were done to study the effectiveness of sintering. Additionally, the sintered compacts were characterized in terms of their chemical composition and mineralogical structure. Despite the higher porosity of the composites and the development of FA clusters in their metal matrix, there is a significant increase in hardness, especially for the high-calcareous KFA-MMCs. Moreover, the results indicate that the density of the experimental products decreases by the increase of FA participation. The rise of Ca-Si and Si mineral phases is intense, particularly for the composites with the highest percentage presence of KFA (15%) and does not differentiate as a function of the sintering time. However, both the Al and Al-Si MMCs that underwent 2h sintering demonstrate higher hardness than the 6h-sintered.

INTRODUCTION

Fly ash (FA) is the inevitable by-product of Greek lignite burning, due to its high ash content.[1] The annual production of ashes in Greece reaches the amount of 13 million tones. Apparently, more than 70% of this quantity is produced in Northern Greece, while the rest comes from the four units of Megalopolis power plant, which is located in the southern part of the country. In Hellenic ashes, especially in the high calcareous that originate from Ptolemais and Kardia, compounds such as $3CaO{\cdot}Al_2O_3$, $CaO{\cdot}SiO_2$, $4CaO{\cdot}Al_2O_3{\cdot}SiO_2$ or sulfur-calcium-aluminates, are predominant. Hence, they are classified according to ASTM C 618 as Class C.[2-4] No more than 15% of the total Hellenic FA output is systematically utilized and only in cement industry.[5]

Metal Matrix Composites (MMCs) are engineered materials formed by the combination of two or more dissimilar materials (at least one of which is a metal) in order to obtain enhanced properties. Actually, compared to unreinforced materials, they normally demonstrate significantly higher strength, stiffness, hardness and damping capacity.[6] However, the usage of MMCs is limited due to their high production cost. Among the various discontinuous reinforcement used, fly ash is one of the most inexpensive available. Apart from that, its low density renders it substantially interesting for the development of effective and low-cost MMCs.[7, 8]

As concluded from many previous research studies, the strengthening of aluminum alloys with a dispersion of fine ceramic particulates strongly increases their potential in wear resistance and structural applications.[9] In the current work, it is justified that lignite fly ash significantly advances the hardness of the aluminum-based MMCs. Aluminum-fly ash composites have potential applications as covers, pans, casings, pulleys, manifolds, valve covers, brake rotors and engine blocks in automotive, small engine and electromechanical industry sectors.[10] Apart from powder metallurgy, liquid metal stir casting and infiltration techniques are generally applied for the synthesis of FA-reinforced aluminum-based MMCs.[11, 12]

MATERIALS AND METHODS

Fly Ashes

Fly ashes 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 high calcareous, Class C according to ASTM C 618, ash, while Megalopolis fly ash (MFA) is a siliceous, Class F ash. The abovementioned ashes were selected to investigate the effect of their different ingredients on the process of sintering and the development of the mechanical properties of the Al and Al/Si - FA MMCs. The chemical composition of FAs was determined using X-Ray Fluorescence (XRF) spectrometry applying the samples in a pressed powder form and their mineralogical structure by means of X-Ray Diffraction (XRD). The particle size distribution (PSD) of FAs was defined using a particle size analyzer using the wet dispersion method in water.

Synthesis and characterization of MMCs

Aluminum (99.5% metals basis, powder form) and aluminum/silicon 88/12 wt% alloy (99% metals basis, powder form) from Alfa Aesar® Company were selected as the metal matrixes of the composites. Al-fly ash and Al/Si 88/12-fly ash mixtures, containing 5%, 10% and 15% w/w KFA and MFA, were prepared and compacted using Cold Monoaxonic Pressing (CMP). As a matter of fact, two different series of both Al and Al/Si-matrix composites were fabricated. In the first case by incorporating particles of KFA and MFA finer than 56μm, and in the second by incorporating KFA and MFA in an "as received" basis. Six (6) samples for each single combination of type of FA, PSD of FA and percentage participation of FA in Al and Al/Si matrixes were produced; a sum of 144 experimental products was therefore fabricated.

The composites were tested for their thermal behavior by means of Differential Scanning Calorimetry (DSC) in nitrogen atmosphere, at the temperature range of 0-700ºC. The rate of the temperature increase was set at 10ºC /min. Then, the products were sintered (for 2 and 6 hours) at 600ºC in the case of Al-FA compacts and at 520ºC in the case of Al/Si-FA compacts. The calcination took place in an inert atmosphere under constant flow of nitrogen. The sintered compacts were characterized in terms of their chemical and mineralogical composition by means of X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD). The structure of MMCs was also examined by X-ray-coupled Scanning Electron Microscopy (EDAX-SEM). Afterwards, the MMCs underwent analyses for the determination of their hardness according to Vickers method (VHN, corrugation hardness). Actually, those samples produced by the incorporation of FA particles with diameter smaller than 56μm and FA participation of 10% and 15% were picked for that process. The applied weight in the VHN measurement was 6kg. Each tested sample underwent 5 different measurements; their average is given as the final result. Finally, the changes in the density of MMCs before and after sintering were theoretically estimated.

RESULTS AND DISCUSSION

Fly Ashes

Compound	*KFA*	*MFA*
SiO_2	30.16	49.54
Al_2O_3	14.93	19.25
Fe_2O_3	5.10	8.44
CaO	34.49	11.82
Na_2O	1.01	0.53
K_2O	0.40	1.81
MgO	2.69	2.27
P_2O_5	0.34	0.37
TiO_2	0.60	1.35
SO_3	6.28	2.91
MnO	0.07	0.14
LOI	3.95	1.67

Table 1. Chemical composition (%) of Kardia and Megalopolis fly ashes

<u>Chemical and Mineralogical Composition</u>

Table 1 presents the chemical composition of the two FAs used as raw materials. As expected, the significantly different chemical characteristics between the two fly ashes are obvious. In KFA the presence of CaO is predominant as it covers approximately 35% of its chemical composition. On the other hand, MFA is strongly siliceous since almost half of it consists of silicon dioxide. Table 2 includes the main mineral phases presented in the two FAs.

Mineral	*KFA*	*MFA*
Calcite	++	+
Anhydrite	+	-
Quartz	+	++
Feldspar	+	+
Gelenite	+	+
Lime	++	-
Ca Sulphate	-	+

Table 2. Mineralogical composition of Kardia and Megalopolis fly ashes (++: intense presence, +: presence, -: absence)

Particle Size Distribution

Regarding the particle size distribution of fly ashes, it was determined for samples both in an "as received" form and with particles finer than 56μm. For the "as received" MFA, results showed that half of its particles lied under 23.5μm, while 90% of them had a diameter smaller than 100μm. On the other hand, half the particles of grinded MFA lied under 19.8μm and 90% of them had a diameter smaller than 50μm. As far as KFA is concerned, when in "as received" form, 50% of its particles lied below 13.9μm and 90% of them below 110μm. After grinding, 90% of its particles obtained a diameter smaller than 47μm.

Synthesis of MMCs

Fabrication of green and sintered Al-FA and Al/Si-FA products (2h and 6h)

Figures 1 and 2 demonstrate the photos of the produced green products with grinded (left) and "as received" FAs. The external differences between the two composite materials are clear: First of all, the surface of the grinded FA/MMC was much smoother compared with that of "as received"-FA/MMC. Besides, the distribution of FA in the "body" of the material was obviously better in the first case.

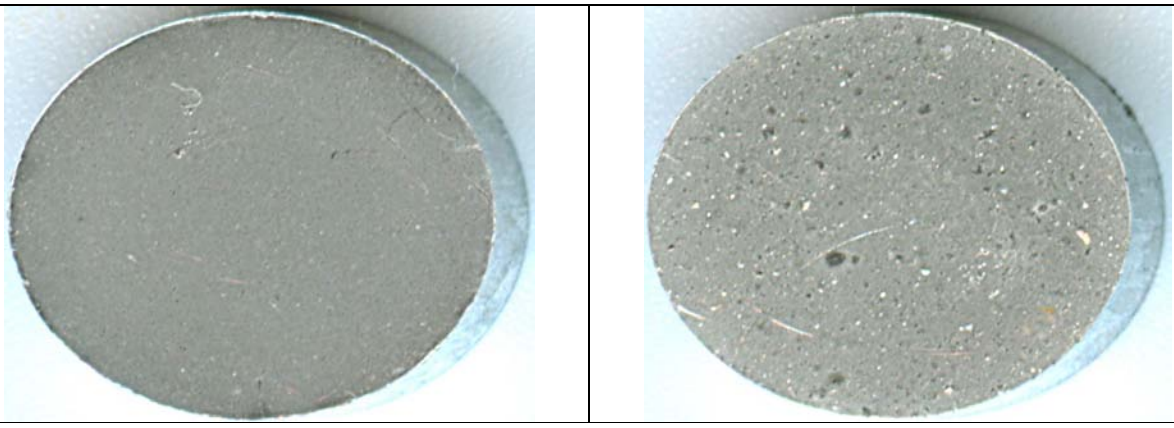


Figure 1. Aluminum-based MMC with grinded MFA.	*Figure 2. Aluminum-based MMC with MFA in an “as received” form.*

After measuring the mass and dimensions of the 2h- and 6h-sintered Al-FA/MMCs insignificant changes in their mass were observed. As a result, it was concluded that oxygen had definitely not been adsorbed upon the surface of the Al-FA/MMCs. However, the height and diameter of the same composites was increased. That increase can be attributed to a possible interchange of oxygen between the aluminum of the matrix and the oxides of the incorporated fly ash, interchange that could led to the formation of alumina (Al_2O_3). As it is known that alumina presents higher volume than the aforementioned materials, it is believed that the above explanation is true.

Regarding the Al/Si-FA composites, after comparing the green to the sintered products, a substantial, post-calcination increase in the mass of those containing fly ash from the region of Megalopolis was observed. In addition, the height and the diameter of Al/Si-FA/MMCs were notably higher than those of Al-FA/MMCs. The type of the material (oil) used to connect the alloy with FA is accountable for that fact. Indeed, during calcination its vapors probably escaped from the “body” of the composite and the porosity of the MMC consequently increased, thus weakening its mechanical properties. Besides, in all the Al/Si-FA MMCs that contained fly ash from the region of Kardia, spherical, superficial and easily-removable clusters were detected (Figures 3 and 4). A possible explanation for the formation of such clusters refers to the high-calcareous nature of KFA that probably makes the melting point of the composites drop.

	
Figure 3. Superficial clusters in Al/Si-5% KFA (<56μm)/MMC	*Figure 4. Superficial clusters in Al/Si-15% KFA(>56μm)/MMC*

Diagrams 1-4 illustrate the percentage mass and volume change of the experimental products as a function of the type of reinforcement material and the hours of sintering. Concerning the MFA-MMCs sintered for 2 and 6 hours, the change in their volume was bigger for the samples with fine-grained fly ash. Regarding the 2h- and 6h-sintered KFA samples, the change did not depend on the particle size distribution of the reinforcement material, but on its percentage participation in the composites. Apart from that, for high FA concentrations, MFA affected both mass and volume changes of the products, stronger than fly ash from the region of Kardia did. It van also be concluded that the changes in the mass of MMCs are more significant when decreasing the mean size of the FA particles. It should be mentioned that the negative mass changes are attributed firstly to the fact that the superficial clusters had been removed before the measurement and secondly to the evaporation of the connection material at the temperatures of sintering.

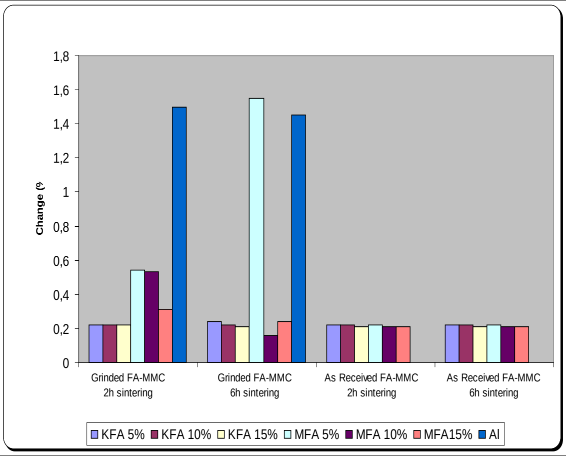


Diagram 1. Volume change (%) of Al-FA/MMCs

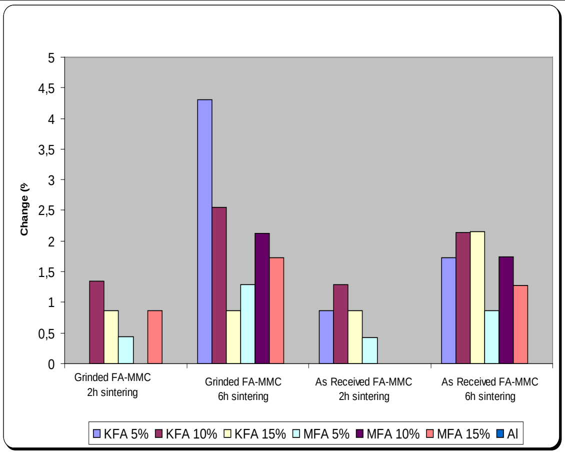


Diagram 2. Mass change (%) of Al-FA/MMCs

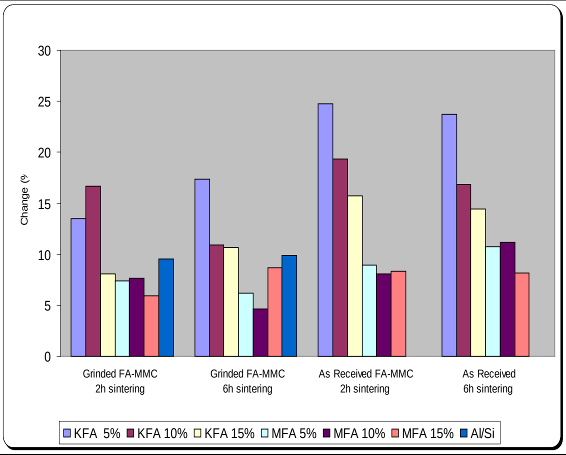


Diagram 3. Volume change (%) of Al/Si-FA/MMCs

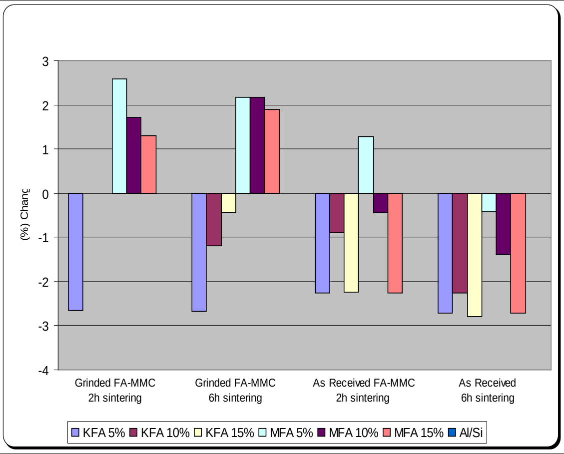


Diagram 4. Mass change (%) of Al/Si-FA/MMCs

Characterization of MMCs

<u>Thermal Behavior of Al-FA/MMCs</u>

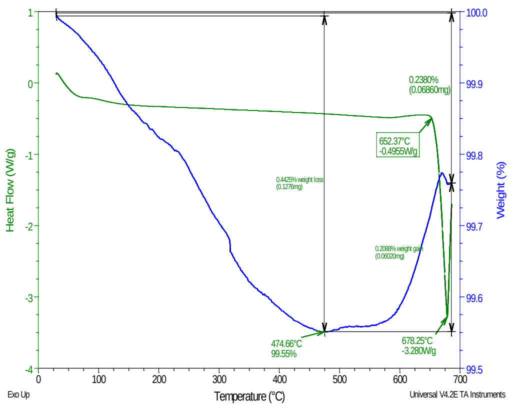


Figure 5. DSC diagram of Al-based MMC with 5% MFA.

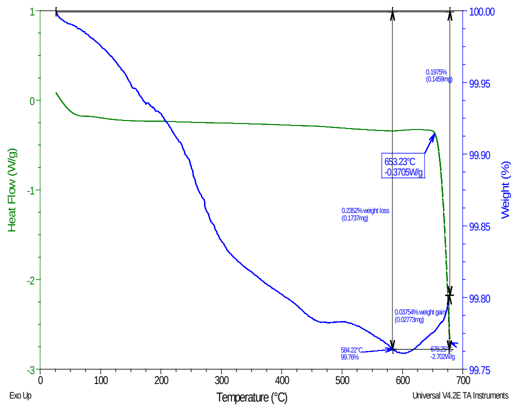


Figure 6. DSC diagram of Al-based MMC with 5% KFA.

Figure 5 illustrates the diagram describing the thermal behavior of the Al/ 5%MFA <56μm- MMC, as determined by the Differential Scanning Calorimetry tests. In this diagram, the green curve describes the flow of the heat into the samples. At the temperature of 652.37ºC a rapid drop of the curve is observed and attributed to the change of form of the sample, which means that the melting point of the composite was by 8ºC lower than that of the pure aluminum. The same curve is minimized at 678.25ºC. The blue curve refers to the change of the mass of the examined sample; a constant slight reduction of its mass up to the temperature of 475ºC can be observed. Actually, at that point, the combustion of the unburned carbon of fly ash took place. Meanwhile, as the temperature increased, the same was happening to the mass change of the sample, on account of extended phase changes.

In Figure 6 the DSC diagram of the Al/ 5%KFA <56μm-MMC is presented. By observing the green curve in this diagram, it is concluded that the melting point of this sample lied at 653ºC, which is 7ºC below the respective point in pure aluminum. Furthermore, that curve is minimized at 678ºC, same as in the case of Al/MFA-MMC. Therefore, it is inferred that the type of lignite FA, when being presented in low concentrations, does not affect the thermal conduction of aluminum-based MMCs. On the other hand, the weight loss in Al-KFA/MMC is significantly smaller than that of the Al-MFA/MMC. At temperature degrees higher than 450ºC the decomposition of the carbonate components of KFA took place. At the areas over 600ºC, an apparent increase in the mass of the sample is observed and attributed to phase changes occurred in KFA.

<u>Crystalline Structure of Al-FA/MMCs</u>

Sintering (h)	*2*	*6*	*2*	*2*
Crystalline Phase	*Al-5% KFA*	*Al-5% KFA*	*Al-10% KFA*	*Al-10% KFA*
Al	++	++	++	++
SiO_2	+	+	+	+
$Si_{64}O_{128}$	-	-	+	-

Table 3. Major crystalline phases identified in Al-MFA/MMCs (2h and 6h sintered) (++: intense presence, +: presence, -: absence)

Tables 3 and 4 present the major crystalline phases of Al-MFA/MMCs and Al-KFA/MMCs respectively. First of all, it is crystal clear that metallic aluminum dominates the mineralogical structure of both Al-MFA/ and Al-KFA/MMCs. Except aluminum, quartz was also identified in MMCs of both FAs. The rest detected minerals vary, mainly depending on the chemical and mineralogical composition of the FAs as well as on the experimental conditions under which they (FAs) reacted with aluminum. Of course, that differentiation is absolutely reasonable because of the significant, chemical and mineralogical, differences between Kardia (calcareous) and Megalopolis (siliceous) lignite fly ashes. Actually, the low concentration of calcareous compounds in MFA obstructed their detection using XRD. Besides, no mixed crystalline phases were identified. Such phases could have developed because of possible reactions between aluminum and FAs. However, the low FA concentrations seem to be prohibitive for those processes. Apart from that, the non-presence of initial mineralogical phases of FAs in the final products, (such as anhydrite, gelenite etc) is also attributed to the small percentage presence of FA in MMCs.

Sintering (h)	*2*	*6*	*2*	*2*
Crystalline Phase	*Al-5% KFA*	*Al-5% KFA*	*Al-5% KFA*	*Al-5% KFA*
Al	++	++	++	++
SiO_2	+	+	+	+
CaO	+	+	+	+
$Ca_{46}(Al_{92}Si_{100}O_{384})$	-	-	+	+
$Ca_{23.20}Mg_{22.4}(Al_{92}Si_{100}O_{384})$	-	-	-	+
$Al_{1.31}$ $(Al_{1.87}Si_{9.61}O_{24})_{0.93}$	-	-	-	+

Table 4. Major crystalline phases identified in Al-KFA/MMCs (2h and 6h sintered) (++: intense presence, +: presence, -: absence)

Microstructure of Al-FA/MMCs

Figure 7 includes selected SEM photos of the Al-KFA/MMCs. First of all, the difference between the even surface of the MMCs reinforced with grinded FA and the uneven of those with “as received” incorporated FA, is obvious. In fact, in the former, FA is better distributed than in the latter, as the same quantity of FA is shared in more of its particles. However, the development of clusters was not avoided even in the case of fine-grained FA/MMCs. On the contrary, they were detected in the microstructure of almost all the Al-KFA/MMCs. In order to solve that problem, the application of ultrasonic radiation before the pressing of the raw materials is considered so that they are better mixed before sintering. Actually, this case is being currently studied in the lab. The distinguished phases observed in both photos of Figure may be some of the crystalline ones identified by the use of XRD. It is consequently supposed that either around an FA particle new phases occur like a thin film, or FA diffuses into aluminum. The aforementioned photos also show the boundaries of the FA grain and were taken to check its adhesion with aluminum. It is worth mentioning that the smoother surfaces of the MFA-reinforced MMCs were ostensibly detected by the microscope. Apart from that, the SEM images showed that the sintering process, in the case of MFA-reinforced MMCs, took place with absolutely no disturbance.

In order concrete conclusions to be drawn, concerning the interactions between the particles of FA and of the metal matrix, EDAX-coupled SEM was implemented. The main goal was to investigate whether diffusion indeed took place or the FA was just incorporated in the matrix due to the thermal softening of the surface of composites. Apart from the classification of the chemical processes took place throughout sintering, EDAX was also applied for the identification of the nature of the superficial clusters presented in Al/Si-KFA/MMCs (Figure 8). The results of those analyses indicate that the clusters consist of a mixture of alloy and fly ash, as the dark areas (Figure 8, Spot A-right photo) present the same composition with the alloy, and the white areas (Figure 9, Spot B-right photo) were characterized by a semi-FA/aluminum nature.

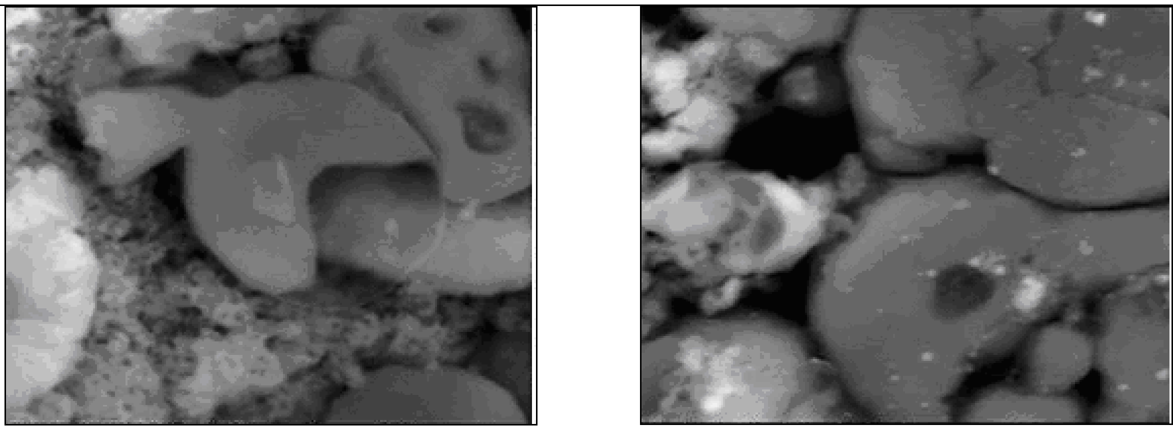
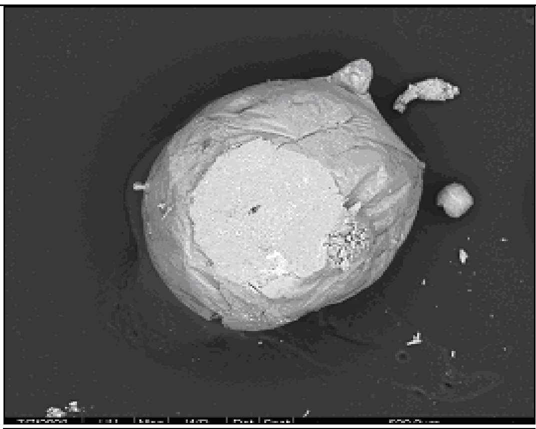
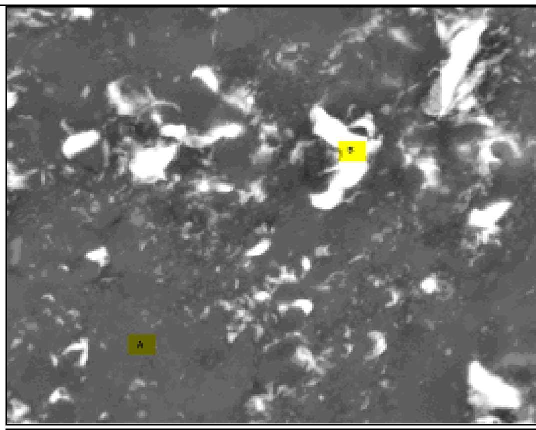
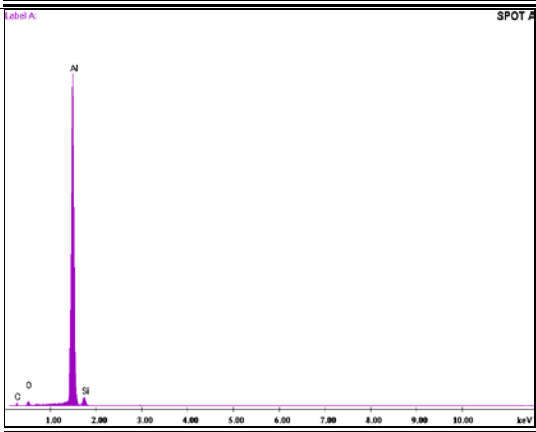


Figure 7. SEM images of Al-KFA/MMCs with grinded (<56μm) KFA (left) and "as received" KFA (right)







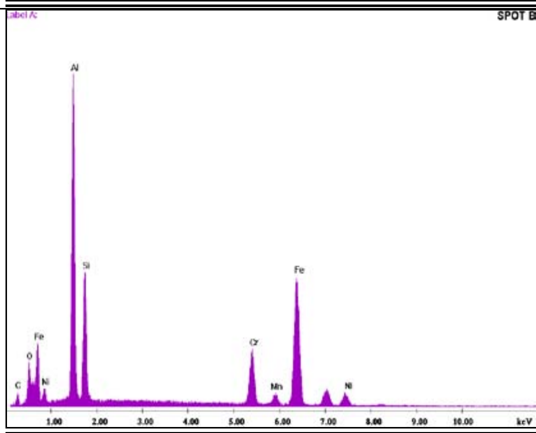


Figure 8. EDAX of the superficial clusters in Al/Si-KFA MMCs (Lower-left: Spot A, lower right: Spot B)

<u>Hardness (Vickers) of MMCs</u>

Diagrams 5 and 6 illustrate the alteration of the superficial hardness of the fabricated MMCs as a function of the type of the incorporated FA and the hours of sintering. First of all, it should be mentioned that all samples presented enhanced hardness comparing to that of pure aluminum. Generally, the KFA-containing samples developed better hardness in comparison with the respective of MFA-reinforced MMCs. We can attribute that fact to the complex Si- and Ca-Si- crystalline phases occurred in KFA-MMCs. These substances, along with the decrease of the melting point of MMCs, had definitely a positive effect on their mechanical properties. Actually, the 2h-sintered MMCs developed better properties than the 6h-sintered samples. It is also observed that the bigger the FA content of MMCs was, the harder their surface became. Indeed, the 2h-Al-15%FA/MMCs demonstrated the higher superficial hardness among all the examined samples. It is therefore believed that no FA presence lower than 15% can satisfactory react with aluminum and subsequently make MMCs develop harder surface than that of pure metals. As far as aluminum/silicon-matrix composites are concerned, both MFA/ and KFA/MMCs obtained better hardness properties after 2 hours of sintering for high FA percentage presence. On the other hand, low FA concentrations seemed to have better influence after 6 hours of sintering.

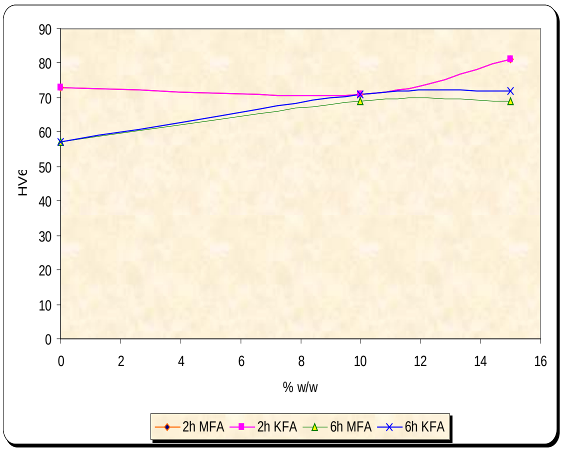


Diagram 9. Hardness (Vickers) of Al-FA/MMCs

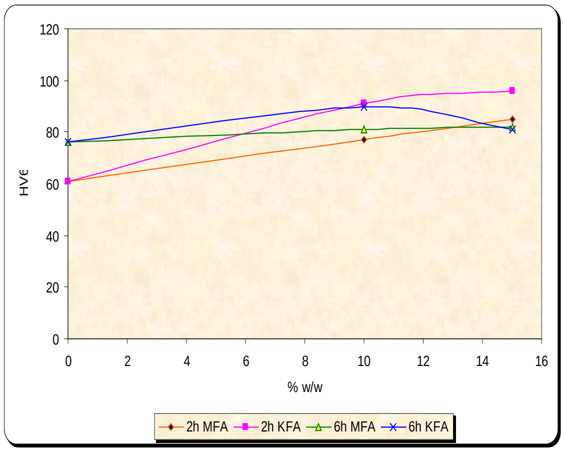


Diagram 10. Hardness (Vickers) of Al/Si-FA/MMCs

CONCLUSIONS

The conclusions drawn from the research study described in this paper can be summarized as follows:

- The samples produced with FA grinded under 56μm presented a better behavior in both the processes of cold pressing and calcination in terms of their final dimensions, volume and porosity

- During the mixing of raw materials it could be useful ultrasonic radiation to be applied in order to break the superficial clusters before pressing and consequently a better distribution of fly ash in the metal matrix to be achieved. In addition, it is necessary a more effective connection material to be found so as the Al/Si-matrix and fly ash to perform a better adhesion

- Regarding the pure Al matrix, the samples containing 15% FA obtained the most attractive chemical, mineralogical and mechanical properties. As for the Al/Si matrix, the incorporation of KFA reduced its melting temperature thus leading to the outflow of mixture through the porous of the sample. This phenomenon was not observed in MFA-containing samples and we therefore conclude that it is the high concentration of calcium that made the melting point of FA drop. Apart from that, the new Si- and Al-Si-phases detected only in Al-KFA/MMCs and not in those reinforced with fly ash from the region of Megalopolis

- 2h-sintered Al/MMCs developed better strength than the 6h-ones. Besides, incorporation of KFA into them leaded to higher strength values in comparison with the siliceous fly ash from the region of Megalopolis. The same behavior was also demonstrated in the case of Al/Si-FA MMCs.

It should be mentioned that this research study is considered the first approach to a project that aims at the advanced reinforcement of aluminum with Greek lignite fly ashes. Apart from optimizing the procedure of powder metallurgy, the elaboration on the stir casting process is planned so as to escalate the participation of FA in MMCs. As a result, their mechanical properties will get enhanced under the simultaneous (and substantial) reducing of their production cost.

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