Spark plasma sintering of graphite–aluminum powder reinforced with SiC/Si particles

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A B S T R A C T

The growing demand for lightweight materials for a variety of engineering applications has led to increased researches on graphite and graphite aluminum composites. An attempt is made in this work to investigate the electrical conductivity of unreinforced graphite aluminum (Gr–Al) powder and graphite aluminum (Gr–Al) powder reinforced with 10 wt.% SiC and 10 wt.% Si using the spark plasma sintering techniques. In addition, a study of the microstructure and hardness of the resulting composite was done after full sintering at a pressure of 50 MPa and temperature of 550 °C. It was observed that the addition of 10 wt.% SiC and 10 wt.% Si improved the electrical conductivity of Gr–Al powder between 18.9 °C and 287 °C. The results of the composites showed that a relative density of 97.1% was achieved for Gr–Al sample sintered at 550 °C while 96.1 and 95.4% were obtained for Gr–Al 10 wt.% Si and Gr–Al 10 wt.% SiC respectively. The micro-hardness values are 26 ± 5, 26 ± 4 and 20 ± 3 HV1.0 for Gr–Al (550 °C), Gr–Al 10 wt.% Si and Gr–Al 10 wt.% SiC respectively. The peak ratio values are very much improved in the hybrid composites produced. The study has shown that hybrid Gr–Al composite is a promising material for improved peak ratio and electrical conductivity.

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1. Introduction

The high demand for lighter materials to replace aluminum and its alloys, particularly in the automobile and aerospace industries [1,2], has led to various researches and each of these efforts has produced one product or the other with various advantages and shortcomings [3]. Graphite (Gr) is known to be a material with high thermal conductivity, low coefficient of thermal expansion, low density and having a self-lubricating ability [4,5]. This has made it find applications in electronics as heat sinks [6,7], as die materials in sintering furnaces and recently, in the production of carbon pistons and engine block cylinder liners [8,9]. Despite all the interesting properties of graphite which make it useful in a wide range of engineering applications, it is however very difficult to consolidate [5]. Thus there has been a proposal for a graphite–particle dispersed composite produced by compacting graphite particles coated with a high thermal conductivity metal such as copper, silver or aluminum [3,10–15]. However, due to the problem of having good wettability between graphite and metal in the production of dense, high thermal conductivity composites, different efforts have been adopted to improve wettability and adhesion of graphite with the metal [16–18].

Studies have been reported on coating carbon fibers with silicon dioxide layers as well as using low melting point metals (Te, Bi, Pb, Sn, etc.) to improve wettability of graphite [3,16]. Zoltan et al. [16] observed that better performance of hybrid composites can be obtained if porosity is eliminated by improving the wettability of the reinforcing particles. Landry et al. [18] found that for graphite at temperatures less than 1273 K, aluminum and aluminum alloys do not wet graphite whatever the microstructure and texture of graphite materials.

A number of studies have been reported on varying fabrication techniques to improve the tribological properties [19–21], thermal properties [22,23], seizure resistance [24], and machinability [25] of graphite–aluminum composite. Most of these studies are however observed to be focused on casting, vacuum hot pressing, and pressure infiltration methods which have been reported to be hindered by three well known facts: (i) gasification of graphite, which initiates below the melting point of aluminum; (ii) reaction between aluminum and graphite to form aluminum carbide, an unstable compound with very poor mechanical and thermal properties and (iii) poor wettability of the Al/Gr interface [4]. Little or nothing has been reported on the use of spark plasma sintering (SPS) techniques, which has recently been found to be an effective technique for fabrication of metallic and ceramic-based composites.

The advantages of SPS over other production methods include fast sintering, lower sintering temperatures, avoidance of grain coarsening, prevention of unwanted reactions among the different phases, effective consolidation and production of near net shape materials [26–29]. As there were limited reports in the literature on the spark plasma sintering of graphite–aluminum powder [3] as well as on the electrical resistivity during spark plasma sintering [30], it was decided in this

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study, to investigate the spark plasma sintering behavior of graphite–aluminum powders and their electrical resistivity during sintering. It is conceptualized that the additions of SiC and Si particles as reinforcements are expected to improve the wettability and the infiltration of the metal into the graphite matrix, while information on densification behavior of the powders during sintering will be useful in understanding the electrical conductivity (inverse of electrical resistivity) and will also serve as data base for the use of graphite–aluminum in sintering furnaces and in electronics. Attention was focused on investigating the effect of the sintering temperature on densification process, porosity, microhardness, sintering, resulting microstructures and peak intensity ratio.

2. Experimental procedure

The starting powders used in this experiment are graphite–aluminum (Element Six Production, PTY Ltd. Company) Si (Alfa Aesar) and SiC (Carborundum Co. Ltd., Trafford Park, Manchester) powders with particle size of 80 μm, 45 μm, and 50 μm, respectively. The mixing of the powders in the pre-determined compositions (Table 1) was done using a T2F tubular mixer using a plastic bottle containing tungsten carbide balls, at a ball to powder ratio of 5:2 for 1 h at a speed of 101 rpm. The blended powders were sintered to discs of 30 mm in diameter using spark plasma sintering system model HHPD 25 manufactured by FCT Germany. The pressure in the chamber of the furnace was maintained at 1 mbar during consolidation while uni-axial compression was done throughout the sintering process with 50 MPa. Sintering was performed at a dwell time of 10 min at temperatures of 500, 550 and 580 °C using.

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>77.98</td>
<td>12.86</td>
<td>6.95</td>
<td>1.47</td>
<td>0.60</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Fig. 1. SEM micrographs of initial powders (a) Gr–Al, (b) SiC and (c) Si.

Fig. 2. XRD patterns of initial powders (a) Gr–Al, (b) Gr–Al 10 wt.% SiC and (c) Gr–Al 10 wt.% Si.

Table 1
Elemental composition of the as-received Gr–Al powder.
52 °C/min heating rate. The temperature was continuously measured by a pyrometer inserted at the upper punch at 5 mm from the surface of the sample which records temperatures close to that of the inside of the sample. The linear shrinkage of the powder compact was monitored by measuring the relative displacement of the graphite punch.

Electrical resistivity of the powder during sintering was measured with a non-conducting die made of Si₃N₄, special punches made of molybdenum with a copper base. A force of 10 kN was applied to create contact with the powder and power of 8 kW was used with an increment of 2 kW every 2 min after the temperature was stabilized. When the displacement rate starts increasing, showing the occurrence of sintering, the process was stopped. To understand the effect of densification of the powder on resistivity, the instantaneous relative densities of the powders were obtained using the equation \( D_l = D_f(h_f/h_i) \) [31] where \( D_f \) is the final relative density of the sample measured by Archimedes’ method, \( h_f \) and \( h_i \) are the final and instantaneous heights of the samples, respectively.

The measured density was reported as the arithmetic mean of three different measurements taken from the same sample. The microhardness was measured using a Vickers indentation method at a load of 100 gf with a dwell time of 15 s and the test result for each sample was the arithmetic mean of ten successive indentations with standard deviations. Qualitative phase and morphological analysis were done on the starting powders and the sintered samples using a High Resolution Field Emission Scanning Electron Microscope (JEOL JSM-7600F) incorporated with an EDX detector (Oxford X-Max) with INCA X-Stream2 pulse analyzer software, and Back Scattered Electron detectors. Imaging was done using an electron beam accelerating voltage of 15 kV, a probe current of \( 0.5 \times 10^{-9} \) A, a working distance of 8 mm between the sample surface and the electron beam pupils, and a high chamber vacuum gauge of \( 8.7 \times 10^{-4} \) Pa which are all suitable operating parameters towards obtaining high quality and statistically reliable results, both for imaging and for EDX elemental compositional analysis. The INCA analyzer software was set to 70 second acquisition time and at a process time of 2 s. Phase analysis of powders and sintered discs was also

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**Fig. 3.** Displacement and displacement rate against temperature for the sintered samples (a) Gr–Al at 500 °C, (b) Gr–Al at 550 °C, (c) Gr–Al at 580 °C, (d) Gr–Al 10 wt.% Si at 550 °C and (e) Gr–Al 10 wt.% SiC at 550 °C.
performed using EMPYREA diffractometer with Cu Kα radiation, and analyzed using Highscore plus software.

3. Results and discussions

3.1. Morphology and SEM analysis

The SEM micrographs in Fig. 1 show the morphology and the distribution of the particles present in Gr–Al, SiC, Si powders while the elemental composition of the as-received powder is presented in Table 1. The graphite particles have a flake-like morphology and the aluminum particles are uniformly distributed with both irregular and round shapes.

The X-ray diffractographs of the starting powders presented in Fig. 2 revealed the presence of SiO₂. The observed SiO₂ could result from the oxidation of Si, which may in turn serve as a wetting agent at the graphite/graphite and graphite/metal interfaces. The high amount of SiO₂ in Fig. 2c can be attributed to the increase of Si from the reinforcement. This is also expected to bring about good wettability and strong bonding between the particles [11].

3.2. Displacement and displacement rate

Fig. 3 shows the displacement and displacement rate against temperature curves of the Gr–Al and reinforced Gr–Al sintered samples. Generally, three peaks can be easily identified from the displacement rate curve. A fourth peak was noticed in Fig. 3c which might be as a result of the melting of the binder and the oxide layer. Also, in Fig. 3d, a deviation from the general shape of the displacement rate against temperature curve can be observed. This could be attributed to the addition of silicon which has been said to cause a substantial drop in the fabrication temperature, thus reducing the gasification of graphite and strongly limits the reaction between aluminum and graphite [4].
According to the work of Diouf and Molinari [32], the phenomena during heating which are responsible for densification and presented as four peaks are: rearrangement of powder particles due to the initial pressure, localized deformation, bulk deformation and extensive sintering by mass transport phenomenon but in the present work, the particle rearrangement and the localized deformation merged together as a peak, followed by the bulk deformation and then extensive sintering.

### 3.3. Electrical conductivity

The variation of electrical conductivity of Gr–Al, Gr–Al 10 wt.% Si and Gr–Al 10 wt.% SiC powders with temperature and instantaneous relative density are shown in Fig. 4. It can be observed that electrical conductivity of Gr–Al increases with temperature and instantaneous relative density, but further improvement was achieved with the addition of Si and SiC. This observation may be as a result of the fact that addition of impurities decreases the resistivity and hence increases electrical conductivity [33,34]. At temperatures between 18.9 °C and 287 °C (Fig. 4a), the electrical conductivity of Gr–Al 10 wt.% Si is slightly higher than that of Gr–Al 10 wt.% SiC which may be attributed to the fact that silicon lowers the melting point of aluminum and improves its infiltration into the matrix. It is interesting to note that between 289.35 and 298.1 °C the response of the three powders to electrical current was the same. This suggests the availability of equal amount of free charge carrying electron necessary for electrical conductivity. Beyond this point, a drop in electrical conductivity of Gr–Al 10 wt.% Si was noticed which could be attributed to the decrease in the densification above 300 °C. This observation has been noted by earlier researchers who observed that as the percentage of silicon increases in aluminum alloys, densification decreases [35,36]. The slightly higher electrical conductivities of the Gr–Al and Gr–Al–SiC would permit heat flow through the powders with corresponding increased densification as observed in Fig. 4b. The good thermal properties of Gr and SiC would lead to local heat generation caused by the Joule heating occurring at the particle–particle contact [31]. Despite the fact that graphite is a semi-metal, it has been identified to be a good electrical conductor, particularly at the basal plane [3]. The slight improvement in electrical conductivity can be attributed to the arrangement of the graphite particles and the local heat generated between graphite/graphite and graphite/metal particles. SiC being a ceramic seems to promote localized heat increase which leads to thermal diffusion. This can translate to electrical conductivity increase, because more electrical charge carrying electrons will be available. However, SiC can be observed to have lowered the instantaneous relative density thereby accounting for the comparatively lower electrical conductivity of the Gr–Al 10 wt.% SiC compared to the Gr–Al composite.

The low temperature gasification of graphite observed by Rodriguez-Guerrero et al. [4] may suggest the presence of gaseous phases occurring during resistivity measurement. However, the addition of Si and SiC as observed in Fig. 5 may have reduced this gaseous phases [4] thereby resulting in the improvement in electrical conductivity.

### 3.4. The relative density of the sintered samples

After the resistivity measurement, which was stopped before full sintering began, the powders were fully sintered at higher temperatures and pressure. Gr–Al powder without Si and SiC addition was preliminarily sintered at different temperatures (namely: 500 °C, 550 °C, and 580 °C) so that the proper sintering temperature for full densification can be selected. At a sintering temperature of 580 °C, melting and spraying of molten metal on the graphite die were noticed. This observation was also reported by Zheng et al. [37]. The graph of relative density against temperature for Gr–Al samples presented in Fig. 6 shows that the best densification was obtained at temperature of 550 °C (Table 2). This led to the choice of 550 °C as the sintering temperature for Gr–Al 10 wt.% SiC and Gr–Al 10 wt.% Si hybrid composites which resulted in relative densities of 95.4 and 96.4%, respectively (Fig. 7).

The value of the relative density of Gr–Al 10 wt.% SiC compared to that of Gr–Al 10 wt.% Si is in agreement with the findings of Shehata et al. [38]. They observed that by increasing the proportion of ceramic particles the porosity is also increased due to difficulty of compressing

### Table 2

<table>
<thead>
<tr>
<th>S/N</th>
<th>Sintering temp. (°C)</th>
<th>Samples name</th>
<th>Sample thickness (cm)</th>
<th>Sample diameter (cm)</th>
<th>Measured density (g/cm³)</th>
<th>Theoretical density (g/cm³)</th>
<th>Relative density (%)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>Gr–Al</td>
<td>0.39</td>
<td>3</td>
<td>2.258</td>
<td>2.375</td>
<td>95.1</td>
<td>4.9</td>
</tr>
<tr>
<td>2</td>
<td>580</td>
<td>Gr–Al</td>
<td>0.24</td>
<td>3</td>
<td>2.125</td>
<td>2.375</td>
<td>89.5</td>
<td>10.5</td>
</tr>
<tr>
<td>3</td>
<td>550</td>
<td>Gr–Al</td>
<td>0.39</td>
<td>3</td>
<td>2.307</td>
<td>2.375</td>
<td>97.4</td>
<td>2.9</td>
</tr>
<tr>
<td>4</td>
<td>550</td>
<td>Gr–Al–10 wt.% SiC</td>
<td>0.41</td>
<td>3</td>
<td>2.227</td>
<td>2.438</td>
<td>95.4</td>
<td>4.6</td>
</tr>
<tr>
<td>5</td>
<td>550</td>
<td>Gr–Al–10 wt.% Si</td>
<td>0.45</td>
<td>3</td>
<td>2.277</td>
<td>2.370</td>
<td>96.4</td>
<td>3.9</td>
</tr>
</tbody>
</table>
the hard ceramic particles in a ductile matrix, similar to the current work. The addition of Si particles on the other hand has been observed by Rodríguez-Guerrero et al. [4] to improve wettability and the fast infiltration of aluminum into the graphite matrix. However, it has been observed that as the percentage of Si increases in aluminum alloys the density reduces [38]. This could be the reason for the comparatively lower relative density of Gr–Al 10 wt.% Si compared to that of Gr–Al sintered at 550 °C (Table 2).

It can be observed from Fig. 6 that at full sintering with a sintering temperature of 550 °C, the relative density of Gr–Al was comparatively the highest as compared with the maximum instantaneous relative density attained during resistivity measurement. It should be understood that during electrical resistivity measurement, only the minimum pressure required for electrical contact was applied, while a non-conducting die was used to allow the total current to pass through the powders to enable full assessment of the thermal sensitivities of the powders under study. However, during consolidation at the actual sintering temperatures, the maximum pressing force for full densification was applied. The least density observed for the fully sintered Gr–Al–SiC as compared with Gr–Al could therefore be attributed to the possible ceramic nature of SiC. Graphite and aluminum both have metallic properties, though to different degrees, but adequate to allow passage of electric current and improve the densification of the composite.

3.5. Microstructural and phase analysis

The microstructure of the samples sintered at 500, 550 and 580 °C is presented in Fig. 7 and that of samples reinforced with SiC and Si is presented in Fig. 8. At the sintering temperature of 500 °C, pores are observed which are as a result of poor densification in the sample. Some large, well rounded and un-deformed particles can also be observed showing that they are not sintered. Few deformed particles can be observed which give the extent of the densification achieved in the sample. Well sintered particles resulting in strong bonds and fewer pores are observed at an increased sintering temperature of 550 °C.
(Fig. 7b). Pores are also noticed at the sintering temperature of 580 °C due to melting of the binder and the oxide layer. Already sintered particles, with no visible initial particle shapes, are also noticed. These must have occurred before the melting, of the binder and oxide layer.

Good bonding resulting from well sintered particles can also be observed in the sample reinforced with 10 wt.% Si. These are all pointers to improved mechanical properties. Not well sintered sample with undeformed particles was obtained after reinforcing with 10 wt.% SiC. Pores can also be seen in the micrograph which shows the reason for the lower relative density obtained for this sample.

The XRD results in Fig. 9 show the distribution of the phases observed as the temperature increases from 500 °C to 580 °C. For samples sintered at 500 and 550 °C (Fig. 9b and 9c), there are no significant changes in the phases present in the initial powder and the sintered samples. This implies that there are no interfacial reactions between the particles. Only graphite and stilinite (AlSiO) are observed at the sintering temperature of 580 °C (Fig. 9d) which may be as a result of the melting noticed during the sintering process. The XRD of the sintered samples reinforced with Si and SiC are presented in Fig. 10 and 11 with phases similar to those in the initial powders except for the non-existence of some Si and SiC phases identified in the initial powders. For Si, it might have resulted into the formation of SiO2 due to Si picking up available oxygen by oxidation. In the literature the presence of Al4C3 phase which has detrimental effects on the bonding and therefore the mechanical properties is often reported when other conventional methods are used [2]. The absence of this phase in the present work confirms the possibility of avoiding its formation when spark plasma sintering is used. The SiC particles can only be seen in one phase, which might be attributed to the undeformed SiC particles observed in the SEM micrograph. The peak ratio which signifies how the binder or coating metal is able to provide the composite with high thermal conductivity [3] is given in Table 3. It is defined as the ratio of the second peak value (intensity of the second highest peak) to the first peak value (intensity of the first highest peak) obtained from the X-ray diffraction of a metal portion in the composite.

From Table 3, a significant improvement in the peak intensity ratio can be observed in the hybrid composites with Gr–Al 10 wt.% SiC having a value of 53.07% despite its relative density of 95.4% compared to Gr–Al sintered at 550 °C with a value of 32.30% and relative density of 97.1%. The improvement is thought to be as a result of the melting temperature of SiC (2730 °C) creating localized heating that effected the infiltration of aluminum into the graphite matrix.

3.6. Microhardness

Fig. 12a shows the graph of micro-hardness against sintering temperature for Gr–Al sintered at 500 °C, 550 °C, and 580 °C. The hardness values obtained are a reflection of the densification after sintering and the homogeneity of the reinforcing materials. Gr–Al sintered at 550 °C had the highest hardness value while that sintered at 580 °C had the lowest value. Again, this is due to the poor densification and melting obtained at 580 °C. The addition of SiC and Si particles reduced the hardness values (Fig. 12b) which may be due to the higher level of porosities obtained as a result of the densification after the sintering process.
3.7. Fracture surface analysis

The SEM micrographs of the fractured surfaces of graphite–aluminum samples sintered at 500 °C, 550 °C, and 580 °C are shown in Fig. 13. Large undeformed particles with cleavages can be observed at 500 °C as well as intergranular fracture and necking which indicated that full sintering was not achieved at this temperature. However, at 550 °C, dimples could be observed along with well deformed and few undeformed particles. The appearance of dimples on the fracture surface signified the occurrence of necking. The differences in features observed in Fig. 13a and b are most probably as a result of the pressure applied and the differences in the sintering temperatures which affected the level of densification of the particles. In Fig. 13c, all the particles are well deformed and the occurrence melting of the binder which led to the formation of AlSiO as earlier stated resulted in transgranular fracture and voids observed.

Fig. 14 shows the SEM micrograph of the fractured surfaces of graphite aluminum composite reinforced with 10 wt.% SiC and 10 wt.% Si. The Gr–Al 10 wt.% Si composite shows well deformed material with only very few observable particles (Fig. 16a). Strong bonding with fewer pores can also be observed which may probably be as a result of the well distributed binder and oxide layers (AlSiO). Addition of SiC (Fig. 14b) can be observed to have resulted in weak bond between the SiC particles and the matrix which could be attributed to the difficulty in deforming SiC particles as reported by earlier researches [33].

4. Conclusions

Spark plasma sintering was used to study the electrical conductivity of unreinforced Gr–Al and Gr–Al reinforced with 10 wt.% Si and 10 wt.% SiC particles. Under the SPS conditions used the following conclusions can be derived:

The addition of 10 wt.% Si and 10 wt.% SiC improved the electrical conductivity between 18.9 °C and 287 °C.

The instantaneous relative density showed that SiC lowers the densification of Gr–Al powder while the addition Silicon had little improvement on it as the temperature increases.

The study showed that Gr–Al sintered at 550 °C without any reinforcement had the best performance in terms of the relative density, micro hardness and the resulting microstructure.

It was also observed that the sintering temperature can still be increased in order to obtain full densification.

For the hybrid composite, it was clear that addition of 10 wt.% Si and 10 wt.% SiC as reinforcement increased the peak ratio of Gr–Al composite.
References


