JMEPEG (1997) 6:785-791

Effects of Porous Carbon on Sintered Al-Si-Mg Matrix Composites

J.U. Ejiofor and R.G. Reddy

The influence of microporous particulate carbon char on the mechanical, thermal, and tribological properties of wear-resistant Al-13.5Si-2.5Mg alloy composites was studied. Large increases in surface area due to the formation of micropores in coconut shell chars were achieved by high-temperature activation under CO_2 gas flow. Activated char particles at 0.02 V_f were used to reinforce the alloy. The composites were fabricated via a double-compaction reaction sintering technique under vacuum at a compaction pressure of 250 MPa and sintering temperature of 600 °C. At more than 35% burn-off of the carbon chars at the temperature of activation, 915 °C, the total surface area remained virtually unaffected. The ultimate tensile strength and hardness decreased by 23% and 6%, respectively; with increasing surface area of the reinforcement from 123 to 821 m^2g^{-1}. The yield strength and the percentage of elongation decreased by a factor of 2 and 5, respectively. No significant change in sliding wear rate was observed but the coefficient of friction increased by 13% (0.61 to 0.69). The coefficient of linear thermal expansion was reduced by 16% (11.7×10^{-6} to 9.8×10^{-6} °C^{-1}), and remained unaffected at more than 35% burn-off. Energy-dispersive spectrometry of the particles of the activated chars showed that oxides of potassium and copper coated the open surfaces. Failure at the matrix-char interface was observed, and this was attributed to localized presence of oxides at the interfaces as identified by electron probe microanalysis. Poor wetting of the oxides by magnesium at the sintering conditions resulted in formation of weak matrix-char interface bonds.

Keywords metal-matrix composites, sintering, wear

1. Introduction

Aluminum-silicon alloy composites are known for their good wear-resistant properties and have been fabricated for a great number of tribological applications (Ref 1, 2). One of the fabrication techniques, reaction sintering, produces parts with up to 30% porosity, and subsequent secondary processing practices such as extrusion and rolling are common in achieving further densification. Reaction sintering is usually applied to parts that have a low coefficient of friction and require light loading, less than 45 lb, as well as to those with inherent lubricating properties (Ref 3). The theory of sintering has been well documented (Ref 4, 5) and the process is fairly well understood.

For every synthetic composite in service, excellent bonding between the matrix and the reinforcement phase (which guarantees high interfacial strength as well as effective performance in a reasonable period of time) is an important requirement. Current practices aimed at achieving this requirement include: (a) proper selection of wettable material mates; (b) mechanical, chemical, and thermal treatments of the reinforcing phase; (c) alloying of the matrix with surface active elements; and (d) spontaneous growth of reinforcement phases, the in-situ method. Previous studies (Ref 6) on Al-11.8Si alloy (with additions of 3 to 6% Mg) reinforced with coconut shell char and prepared by the vortex method have reported good bonding and excellent tribological properties. Up to 40 vol% coconut shell char as a reinforcement was possible. Preferential segregation of magnesium near the inner surface of the pores of the char particle was reported. In addition, the tensile properties and hardness of the alloy were found to decrease with additions of char particles. Ejiofor and Reddy (Ref 7) recently studied the reaction sintering of Al-13.5Si-2.5Mg alloy (magnesium added as a surface active element) reinforced with primary-carbonized coconut shells, a form of carbon char. They achieved adequate alloy-char interfacial bonds at 0.02 V_f char with significant reduction in dry sliding wear and coefficients of friction and thermal expansion. Progressive reductions in sintered density followed additions of char particles. Some of the results, however, fell within the range for electromechanical antifriction applications.

In related work, Satyanarayana et al. (Ref 18) reinforced Al-11.8Si alloy melt with preheated coconut shell char via the mechanical stirring technique. They reported increases in the densities and mechanical properties of the composites, and this disagrees with the findings by Murali et al. (Ref 6) and those of later investigators (Ref 9, 19, 20). Satyanarayana et al. also observed a superior adhesive wear resistance and decreasing coefficient of friction.

It is well known, however, that large surface area provides the excess surface energy that drives sintering in powdered materials. Excess energy is readily obtained in fine, irregularly shaped powder particles with interconnected pores. Chars are a group of non-graphitizable carbon made from organic materials that do not become fluid during the carbonization process. They have very high surface area (relative to the graphitizable carbon), which is further increased on activation. The use of steam and carbon dioxide in the production of activated carbon by partial gasification has been reported for a number of precursors, including brown coal, olive stones, and coconut shells (Ref 10-12). Depending on the medium used, a significant in-

---

J.U. Ejiofor, Shelco Foundries, Inc., Jacksonville, AL 36265, USA (formerly of the Department of Metallurgical and Materials Engineering, The University of Alabama); **R.G. Reddy,** Department of Metallurgical and Materials Engineering, The University of Alabama, P.O. Box 870202, Tuscaloosa, AL 35487-0202, USA.

crease in surface area was observed. In general, steam appears to produce a larger mesopore volume (width 2 to 50 nm) than carbon dioxide, the latter favoring micropore development. The ability of fine particulate carbonaceous matter to form interconnected micropores after both chemically enhanced activation and high temperature "physical" activation has been exploited by different process industries. However, the influence of the increased surface area of the particles of the activated carbon on the synthesis of structural or tribological materials has not been systematically studied. Instead, most studies have focused on adsorption of gases, decolorization of sugar, refining of oils, purification of water, and so on (Ref 13-15). Common precursors used for activated carbon are bones, coconut shells, natural carbons, and petroleum residues.

We have undertaken a study of the influence of micropores in activated carbon char on the sintering of a hypereutectic Al-13.5Si-2.5Mg alloy. The objective was to evaluate the macroscopic properties of the resulting composites. The effects of char additions on the densities of the composites are also discussed.

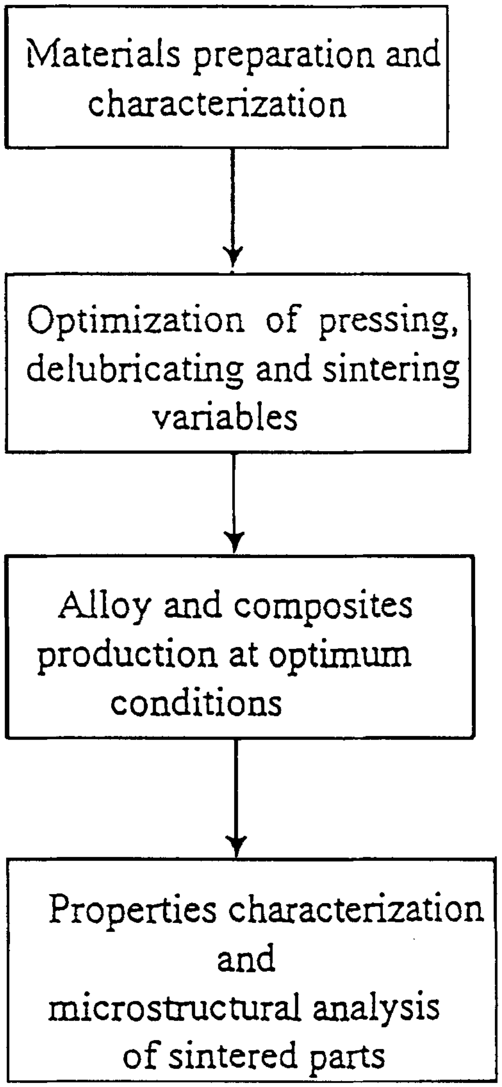


Fig. 1 Composites processing flowsheet

2. Experimental Procedure

A conventional, double-compaction powder processing technique was used in fabricating the composites. A flowsheet is given in Fig.1. The details of the technique are given elsewhere (Ref 9, 19, 20), so only the preparation of the reinforcements is described in this paper. The composition of the reinforcement precursor, coconut shell, is shown in Table 1. The shells were fragmented and carbonized in a closed thick mild steel pot. The maximum temperature of the primary carbonization was 655 °C. The process was considered complete when the escape of gases was no longer visible. The air-cooled chars were ground to less than 300 μm. They were annealed under dry liquid nitrogen at 300 °C for 1 h. The composition of treated samples is given in Table 2. In order to detect formation of graphite crystals on the char, x-ray diffraction analysis (XRD) was carried out. Energy-dispersive spectrometry (EDS) was used to reveal the extent of oxidation of the chars. These analyses are shown in Fig. 2(a) and (b).

Secondary carbonization and subsequent physical activation of the samples was carried out under high-purity dry nitrogen with very low dewpoint (and flow rate, 4.0 L/min). The chars were heated to 850 °Cand held for 5 to 10 s. The heating rate was 15 °C/min and the pressure was 1 bar. The samples were cooled in the furnace. Carbon dioxide was used as the activation medium with a flow rate of 4.0 L/min while the sample was heated to 915 °C. Samples were activated to various burnoff percentages in order to vary the amounts of porosities. Formation of micropores was measured by total particle surface area. At the end of the activation process, the samples were furnace-cooled. Both the secondary carbonization and the activation were preformed in a gravimetric tube furnace assembled from a Donaldson vertical split tube furnace and a Cahn RH Electrobalance (Cerritos, CA; Ref 16). The powdered carbon char sample was contained in a suspended silica glass cylindrical crucible. The dimensions of the cylinder were 11 mm internal diameter, 2 mm thickness, and 44 mm internal depth. Silica

Table 1 Composition of coconut shell powder

Constituent	Value, wt%
Moisture	12.00
Ash	0.62
Lignin	29.35
Solvent extracts	2.71
Pentosan	28.11
Cellulose	26.20
Anhydride	0.92
Others	0.09

Table 2 Composition of coconut shell char before activation

Element	Value, wt%
C	77.15
H	2.88
N	0.24
S	<0.1
P	0.018
Others	19.71

shots were placed at the bottom of the crucible to create channels for the upward-moving gases. The elemental compositions of the activated samples were analyzed using the Carlo Erba 1106 Elemental Analyzer. The time of activation, percentage burn-off, and elemental composition are given in Table 3. The Brunauer-Emmett-Teller technique was applied in measuring the surface area of the reinforcements using the Carlo Erba Sorpty model 1750 (Cerritos, CA). Typical scanning electron micrographs of the activated carbon char are shown in Fig. 3. The white deposits observed in the micrographs are the ash compounds.

Composites of Al-13.5Si-2.5Mg containing 0.02 V_f activated carbon chars were fabricated according to the optimal conditions determined in our previous studies (Ref 7, 9), such

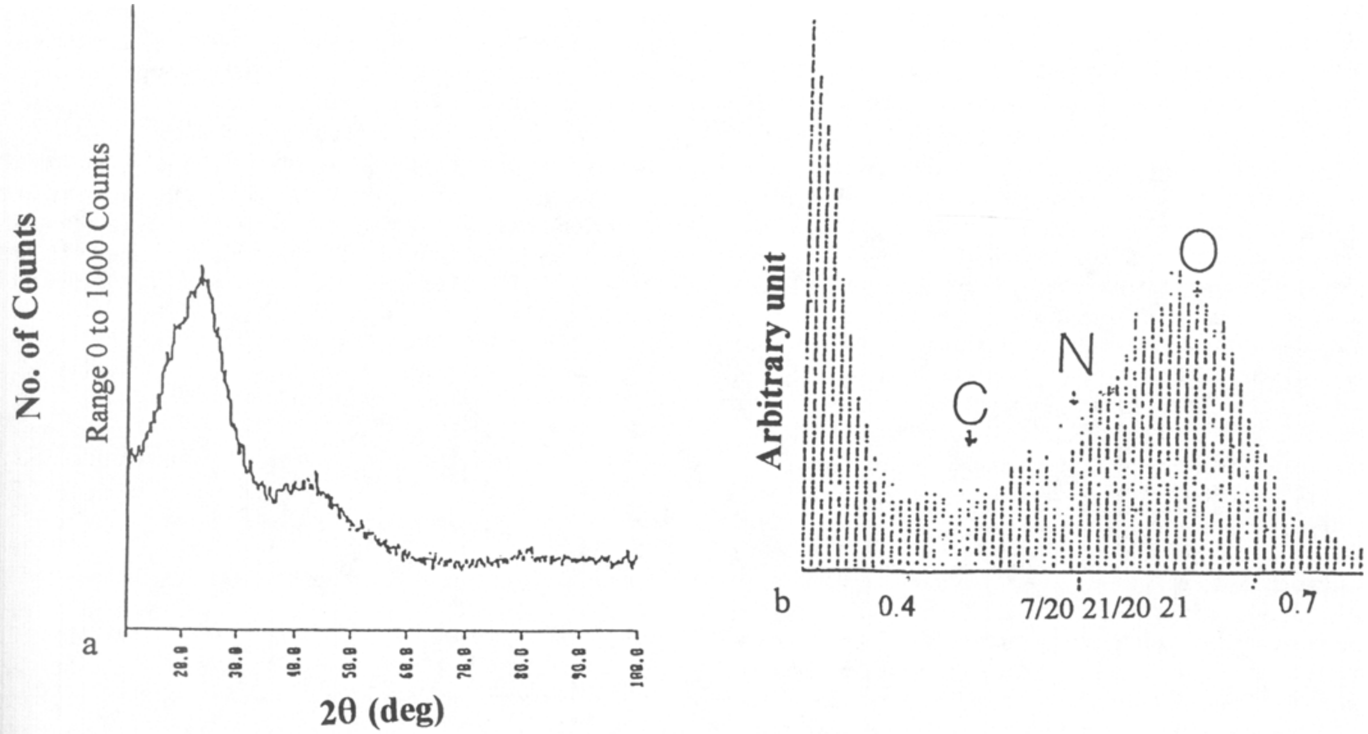
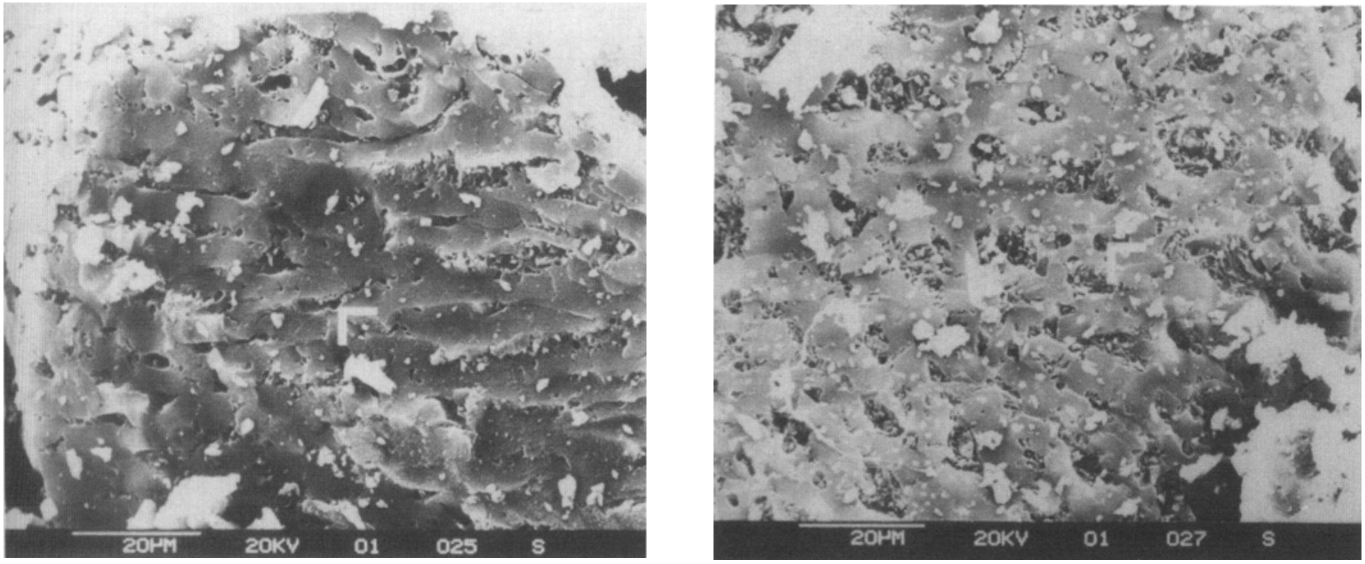


Fig. 2 Primary carbonized coconut shell char. (a) X-ray pattern revealing absence of peaks. (b) EDS showing presence of oxygen



(a) **(b)**

Fig. 3 Typical scanning electron micrographs of activated coconut shell char. (a) 21.7% burn-off. (b) 48.5% burn-off. White deposits represent ash products as: 1% particulate stearic acid and 0.5% aluminum stearate were used as lubricants; a compaction pressure of 250 MPa was used to produce a flat tensile test specimen; delubrication was performed at 300 °C for 1 h under nitrogen gas; vacuum sintering was done at 600 °C using a diffusion pump with a tube pressure between 1.7×10^{-1} and 4.42×10^{-1} Pa; and a backing pressure of 0.08 MPa was applied to consolidate the green samples. Thermal, tribological, and mechanical properties of the fabricated composites were subsequently determined.

3. Results and Discussion

As shown in Fig. 2(a), graphitization of the char particles did not occur during the primary carbonization process. The high amounts of cellulose and lignin given in Table 1 indicate that coconut shells contain some amounts of organic fibers. Table 2 and Fig. 2(b) show the low yield of elemental carbon in the char. This may have resulted from hydrogenation as well as from air oxidation of carbon during primary carbonization. This thermal decomposition process removes the noncarbon elements (hydrogen, oxygen, traces of sulfur and nitrogen) in a gaseous form. The resultant disorganized carbon particles are then deposited in some interstices, leaving a small amount of unfilled interstices. Secondary carbonization removes the disorganized carbon, exposing the surface of the elementary crystallites to the action of the activation agent, which is carbon dioxide in this case. According to Wigmans (Ref 17), the activation process does result in carbon removal via active sites and in some other reactions, all of which lead to the development of porosity with increasing burn-off. These mechanisms explain the increase in surface area, the changes in pH, and the carbon yields at burn-offs during the physical activation (Table 3). The surface area increased from 123 (unactivated char) to 821 m^2g^{-1} (activated char, at 48.5% burn-off). Laine et al. (Ref 12) have reported an increase in surface area (measured by a nitrogen adsorption technique) of chemically activated coconut shell from about 420 to 1250 m^2g^{-1} for temperatures ranging from 300 to 600 °C. Table 3 also shows that there was significant loss of material in the initial 1 to 1.5 h of the high-temperature activation. Virtually no weight loss was observed and carbon content remained unchanged at higher percentage of burn-offs. This suggests that activation beyond this time period did not affect selective combustion (removal) of carbon from active sites by the diffusing carbon dioxide, thus allowing creation of pores. Other reactions (Ref 12) and dilation of the micropores may be responsible for the observed small increase in surface area.

As was the case with use of unactivated char, reinforcing the matrix alloy with progressively more porous char led to declines in the ultimate tensile strength, yield strength, and percent elongation of the composites. This behavior is presented in Fig. 4. The ultimate tensile strength and the hardness decreased by 23 and 6%, respectively. A marginal decrease in the

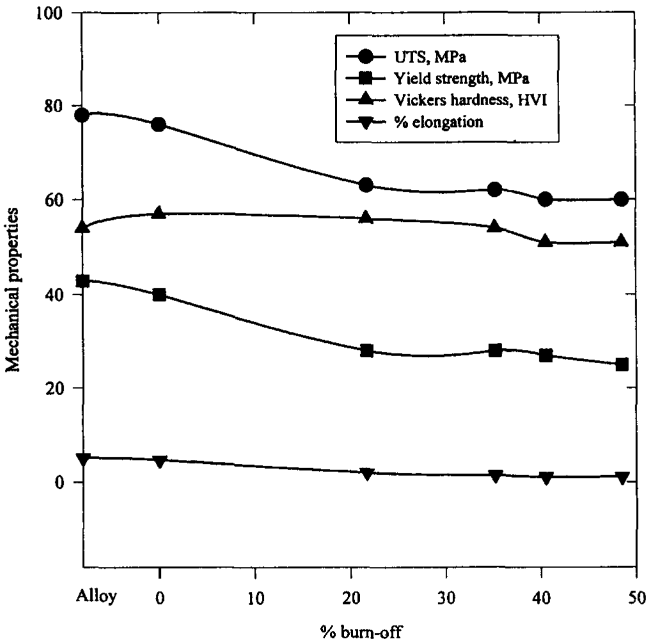


Fig. 4 Effects of percent burn-off of chars on the mechanical properties of the composites

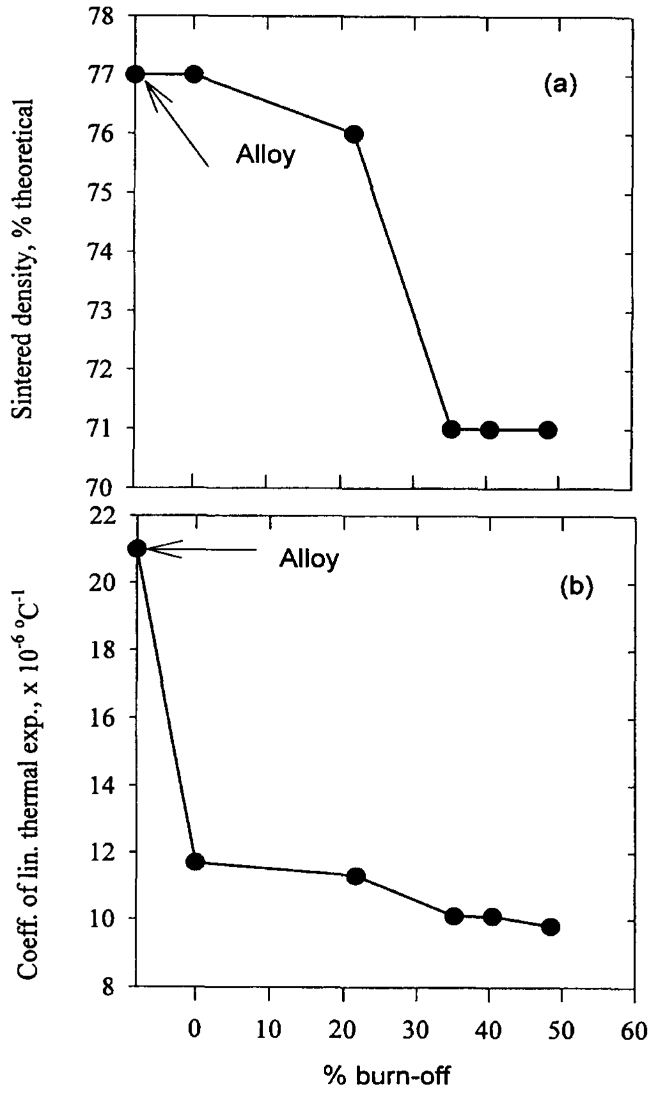


Fig. 5 Effects of percent burn-off of chars on (a) sintered density and (b) coefficient of linear thermal expansion of the Al-13.5Si-2.5Mg composites

sintered density of the composites (77 to 71 MPa) also occurred, as shown in Fig. 5(a). This reduction in strength does not necessarily imply a poor service performance of the composites, because their specific densities are not adversely affected. The yield strength decreased by almost a factor of 2, while the percent elongation reduced by a factor of 5.

Examination of the fractured surfaces revealed a potential cause for the decline in mechanical properties. Potassium and copper oxides were detected on the char particles by x-ray analysis, with more concentrations of copper at higher burn-off (Fig. 6). These are combustion products, such as ash, which are alkaline in nature and are likely to be responsible for the rise in pH of the chars with activation time. Typical ash constituents include alkali oxides, alkaline earth oxides, and silica. Thermodynamic considerations suggest that magnesium in the matrix alloy is expected to reduce oxides of copper and potassium, thus aiding in formation of chemical bonds. However, the deposits of these oxides are capable of affecting the wetting action of magnesium as well as the amount necessary to cause the required interfacial bonds. Significant reactions and bonding at the interface due to diffusion may not have occurred, probably because of a limited proportion of molten magnesium (melting point, 650 °C) at the sintering temperature. This is because it is necessary to have an adequate thin film of liquid-phase magnesium on the oxide substrates and subsequent bonding due to atomic diffusion in order for strong bonds to form between the char and the matrix particles. As activation time is increased, and thus the burn-off percentage, the amount of these oxides are expected to rise. This rise will progressively hinder sintering, leading to decreases in the mechanical properties of the composites as shown in the results (Ref 20).

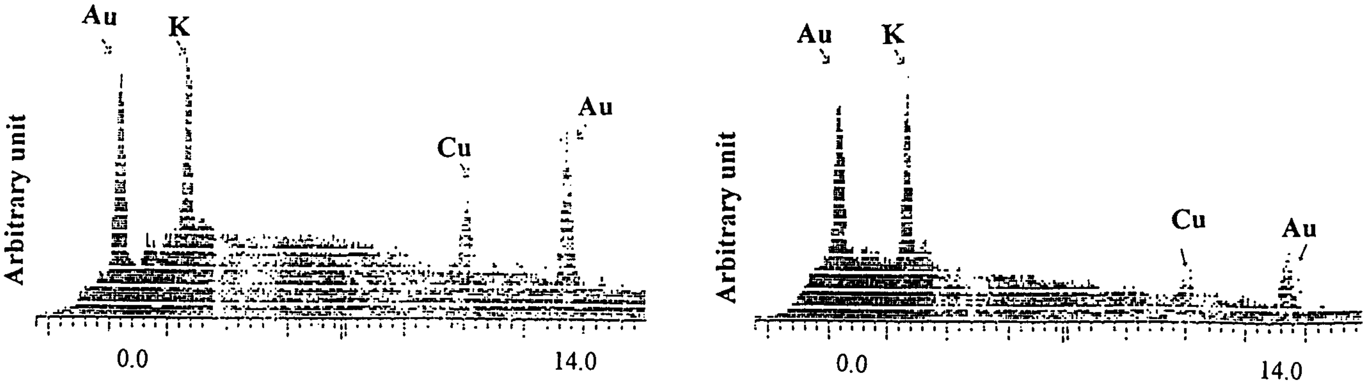
This critical effect of the oxides was revealed by electron probe microanalysis (EPMA) of the fracture surface of a tension-failed composite containing 0.02 V_f of the 48.5% burn-off char. An interfacial failure suggestive of poor bonding was observed. As shown in Fig. 7, the fracture path traversed at the char-matrix interfaces with potassium, silicon, and a very low concentration of magnesium on the surfaces. But earlier (Ref 6) and recent investigators (Ref 7) have reported excellent bonds between Al-Si-Mg alloy and particulate carbon char containing no oxide products at the open surfaces. The presence of the oxides is therefore attributable to the reductions in the mechanical properties of the composites. It can also be deduced that excellent bonding would be achieved if sintering temperature were high, but not so much as to lead to formation of the intermetallic carbide phase.

Further, carbothermic reduction of copper oxide is thermodynamically possible at the sintering conditions, especially with supply of oxygen by the carbon dioxide flow. This is not, however, the case with potassium oxide, which is more stable relative to carbon monoxide gas. These phenomena are expressed in Fig. 7, which shows only the presence of potassium peak at the fracture surface of the interface-failed composite, indicating a possible migration of copper into the matrix.

Figure 5(b) shows that a 16% reduction in the linear thermal expansion of the reference alloy was achieved when 48.5% burn-off char was the reinforcement. This is attributed to the increased volume of pores in the activated char, as can be seen in the figure where the respective values decrease with increasing total surface area of the chars. Figure 8 shows that the sliding wear rate of the composite filled with unactivated char decreased by a negligible amount when the chars were acti-

Table 3 Percentage burn-off, surface area, weight loss, pH, and composition of the activated char particles

Activation time, min	Burn-off, %	Surface area, m^2g^{-1}	Weight loss, %	pH	Composition, wt% C	H	N	P	S
0	0.0	123	0.00	4.9	77.15	2.88	0.24	0.02	<0.1
105	21.7	624	26.31	6.9	88.59	0.44	0.22	...	<0.1
110	35.2	800	28.99	7.3	90.33	0.24	0.13	0.05	<0.1
160	40.5	815	29.01	7.3	90.33	0.20	0.07	0.02	<0.1
200	48.5	821	29.02	7.8	90.36	0.21	0.17	0.04	<0.1



(a)

(b)

Fig. 6 X-ray spectra of the activated chars at (a) 21.7% burn-off and (b) 48.5% burn-off, revealing oxides of potassium and copper

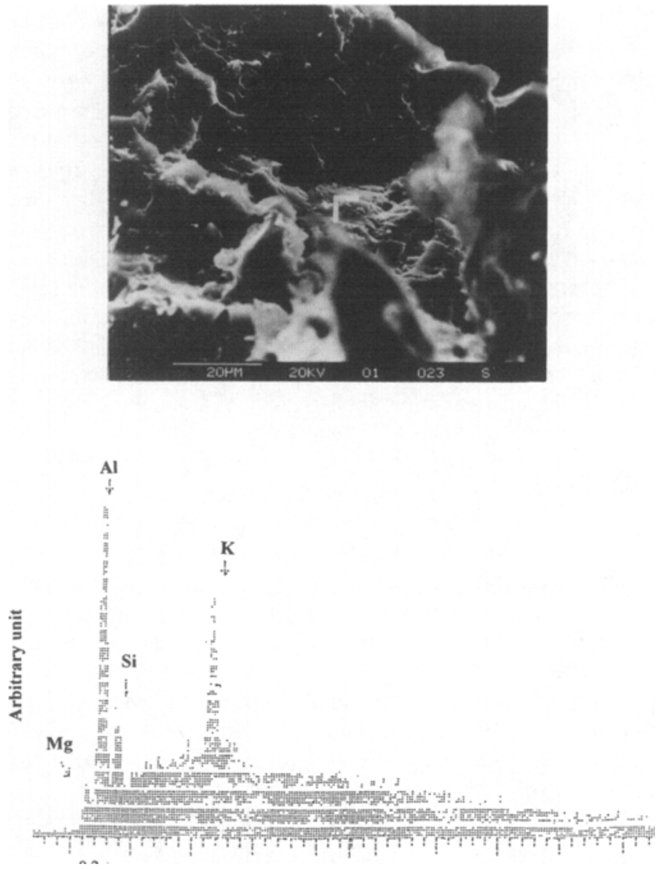


Fig. 7 Scanning electron fractograph and EPMA of fracture surface of Al-13.5Si-2.5Mg alloy containing 0.02 V_f char activated at 48.5% burn-off

vated, while the coefficient of friction remained virtually unaffected (increasing from 0.61 to 0.69, at 48.5% burn-off). The wear rate decreased from 1.7×10^{-7} to 1.66×10^{-7} g/cm^{-1}. Although the optimum amount of coconut shell char in the matrix alloy is 2 vol% for sliding wear under a loading of 10 lb (Ref 7), the wear reduction observed appears to be an anomaly. Composite materials with weak bonds are expected to be vulnerable to wear and mechanical failures because of poor and disproportionate load distributions. The anomaly is explained by the redox reactions of the thermal process. Oxides of sulfur could form by the reactions between oxygen in the activation chamber and the sulfide in the particle. The Gibbs energy is high for a chemical reaction to take place between magnesium and sulfur at the sintering temperature, forming magnesium sulfide (Ref 21). This final compound is known to increase the coefficient of friction between two bodies (Ref 18). The coefficient of friction increased by only 13% in the present study, but friction contributed by surface asperities (made of a self-lubricating material such as carbon) often lead to seizures that do result in errors in measurement of wear rate.

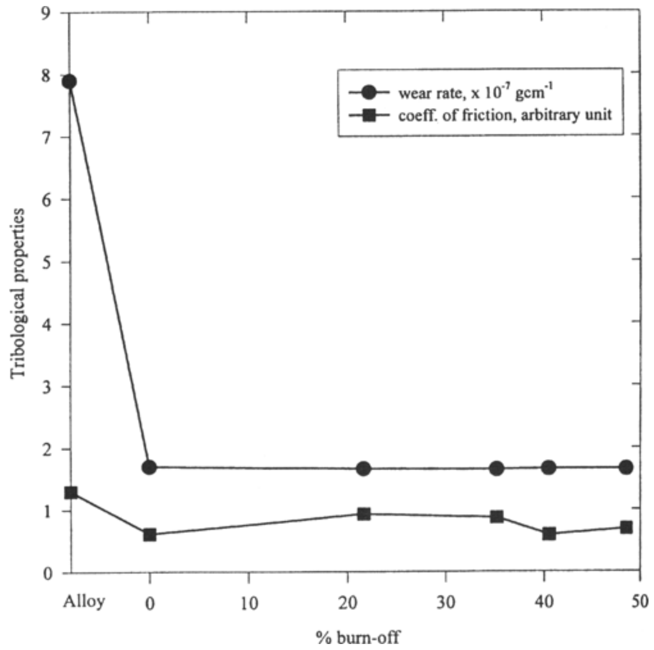


Fig. 8 Effects of percent burn-off of chars on sliding wear rate and coefficient of friction of the Al-13.5Si-2.5Mg composites

4. Conclusions

This study has provided a basis for the potential use of porous reinforcements, such as carbon, in Al-Si-Mg alloys in producing lightweight composites with high specific strength via the powder metallurgy technique. Further specific findings include:

- Activation of coconut shell char at high temperature (≥915 °C) does not increase pore formations at burn-offs beyond 35%.
- The ultimate tensile strength and the hardness values of the Al-13.5Si-2.5Mg alloy decreased by 23 and 6%, respectively, when the alloy was reinforced with 0.02 V_f activated char of surface area 821 m^{2}g^{-1}. Yield strength and the percent elongation of the composites decreased by factors of 2 and 5, respectively. With less porous carbon (unactivated char), the mechanical properties remained virtually unaffected, except the Vickers hardness, which increased from 54 to 57. This increase has been attributed to good interfacial bonding and the high hardness value of carbon.
- The EDS analysis showed that oxides of potassium and copper were formed around the particles of the activated char. Failure at the matrix-char interfaces was observed. Silicon, a low concentration of magnesium, and localized potassium oxide were identified at the fractured surfaces by EPMA. The interface failure was attributed to poor wetting and bonding (caused by the oxides) between the surfactant, magnesium, and the char particles at the sintering temperature, 600 °C.
- The sliding wear rate of the Al-13.5Si-2.5Mg alloy reinforced with 0.02 V_f activated char (48.5% burn-off) is not different from that of the alloy containing unactivated carbon char. On the other hand, the coefficient of friction of the former is, on average, 11% higher than that of the latter composite. The coefficient of linear thermal expansion decreased by only 16% (11.7 to 9.8) when activated char was used as the filler phase, and it remained constant at burn-offs greater than 35%.

Acknowledgments

We are pleased to acknowledge the financial support of this research provided by the National Science Foundation. We also thank Dr. J.J. Freeman of the Dept. of Chemistry, Brunel University, London, for assistance in the activation work and technical discussions. We are also grateful to the staff of the Materials Technology Dept., Brunel University, London, for the use of some bench facilities.

References

1. B.M. Cox, P. Enright, D. Doutre, and R. Provencher, Advances in Commercialization of Shape Casting of Aluminum Composites, *Proc. Int. Conf. on Cast MMCs,* D.M. Stefanescu and S. Sen, Ed., American Foundryman Society, 1993, p 180
2. A.M. Banerji, M.K. Surappa, and P.K. Rohatgi, Cast Aluminum Alloys Containing Dispersion of Zircon Particles, *Metall. Trans.,* Vol 14B, 1983, p 273-293
3. A.D. Roosato, T.D. Vreeland, and F.B. Prinz, Manufacture of Powder Compacts, *Int. Mater. Rev.,* Vol 36 (No. 2), 1991, p 45-61
4. R.L. Sands and C.R. Shakespeare, *Powder Metallurgy: Practice and Applications,* George Newmans Ltd., London, 1986, p 79-107
5. B.H. Alexander and R.W. Baluffi, *Acta Metall.,* Vol 5 (No. 11), 1957, p 666
6. T.P. Murali, M.K. Surappa, and P.K. Rohatgi, Preparation and Properties of Al-Alloy Coconut Shell Char Particulate Composites, *Metall. Trans.,* Vol 13B, 1982, p 485-494
7. J.U. Ejiofor and R.G. Reddy, Microstructural and Tribological Properties Evaluation of Char-Reinforced Al-Si Alloy Composites, *Proc. TMS Conf. on Automotive Alloys,* S.K. Das, Ed., TMS, 1997, p 95-112
8. K.G. Satyanarayana, B.C. Pai, M.R. Krishnader, and C.G. Nair, Aluminum Alloy Metal Matrix Composites for Engineering Applications, *Proc. Int. SAMPE Symp.,* SAMPE, 1987, p 880-889
9. J.U. Ejiofor, B.A. Okorie, and R.G. Reddy, "Synthesis and Property Analysis of Char-Reinforced Al-Si Alloy Composites," J. Matls. Sci., Chapman & Hall Publ., Nov 1997 (in press)
10. J.J. Freeman, F.G.R. Gimblett, R.A. Hayes, Z. Mohd. Amin, and K.S.W. Sing, Preprints, *IUPAC Symposium on Characterization of Porous Solids (COPS II),* IUPAC/Univ. Alicante, 1990, p 366-368
11. K. Tashiro, M. Kobayashi, and H. Tadokoro, *Macromolecules,* Vol 10, 1977, p 413
12. J. Laine, A. Calafat, and M. Labady, Preparation and Characterization of Activated Carbons from Coconut Shell Impregnated with Phosphoric Acid, *Carbon,* Vol 27, 1989, p 191-195
13. J. van Driel, *Activated Carbon: A Fascinating Material,* A. Capelle and F. de Vooys, Ed., Norit N.V., The Netherlands, 1983, p 40
14. J.T. Cookson, *Carbon Adsorption Handbook,* P.N. Cheremisinoff and F. Ellerbusch, Ed., Ann Arbor Science, Ann Arbor, MI, 1980, p 241
15. W.M. Priest, Jr. and R.A. Mosher, *ACS Symposium Series,* Vol 200, 1982, p 225
16. J.J. Freeman and F.G.R. Gimblett, Studies of Activated Charcoal Cloth, Part II: Influence of Boron-Containing Impregnants on the Rate of Activation in Carbondioxide Gas, *Carbon,* Vol 25, 1987, p 565
17. T. Wigmans, Industrial Aspects of Production and Use of Activated Carbons, *Carbon,* Vol 27, 1989, p 13-22
18. T.S. Eyre, Wear Mechanisms, *Proc. Conf. of Institution of Metallurgists on Materials Selection for Wear Resistance,* Brunel University, London, 1979, p 1-19
19. J.U. Ejiofor, B.A. Okorie, and R.G. Reddy, Powder Processing and Properties of Zircon-Reinforced Al-13.5 Si-2.5Mg Alloy Composites, *J. Mater. Eng. Perform.,* Vol 6 (No. 3), 1997, p 326-334
20. J.U. Ejiofor and R.G. Reddy, Developments in the Processing and Properties of Particulate Al-Si Composites, *JOM,* Oct 1997 (in press)
21. N.A. Gokcen and R.G. Reddy, *Thermodynamics,* Plenum Publishing, New York, NY, 1996