JOURNAL OF MATERIALS SCIENCE 17 (1982) 1041–1048

Metal-shell char particulate composites using copper-coated particles

K. GOPAKUMAR, T. P. MURALI, P. K. ROHATGI
Regional Research Laboratory (CSIR), Trivandrum 695019, India

Optimum conditions to obtain uniform and continuous coatings of copper on 125 μm size coconut shell char particles (by using Fehling formaldehyde solution, activating char surfaces by copper tartarate complex followed by copper coating) are reported. 30 wt % of copper, in the form of coatings with almost theoretical density, could be depostied on shell char particles in the present investigation. Copper-coated shell char particles were dispersed in Al–11.8 wt % Si alloy melts using the vortex method and the melts were poured into moulds to produce cast Al–alloy shell char particulate composites, with higher recoveries than those obtained with uncoated shell char particles. Copper shell char composites using coated char particles were also successfully made by powder metallurgy techniques. As a result of 4 wt % dispersions of coconut shell char in the as-sintered copper shell char composites (a) hardness decreases from 45 BHN to 35.7 BHN (b) density decreases from 7.9 g cm^{-3} to 7.06 g cm^{-3}, (c) electrical resistivity increases from 5 μ ohm cm to 10.05 μ ohm cm in close agreement with calculated value, and (d) wear rate and friction coefficient under dry conditions decrease from 6.635×10^{-11} cm^2 and 0.250, to 3.89×10^{-11} cm^2 and 0.129, respectively, suggesting that these composites can be used in antifriction applications. Repressing and annealing increases the density and hardness, and decreases the electrical resistivity values of the as-sintered pieces.

1. Introduction

Coconut shell char particles can be attractive dispersoids in Cu and Al matrices because of their good thermal properties, wear resistance, reasonably good solid lubricating properties [1], and low density. In addition, shell char is a renewable resource available in large quantities at costs much lower than graphite [2].

The problem encountered in dispersing untreated coconut shell char particles in Al-alloy melts is their poor wettability with the melts. To overcome a similar problem with graphite, the wettability of graphite with the matrix was improved by pretreating the particles [3], the addition of surface active agents to the melt together with the particles [4] and by coating the surface of particles by copper or nickel [5]. Copper-coated graphite [5] and copper coated mica [6] have been successfully dispersed in Al–Al alloy melts by liquid metallurgy techniques. Further use of Cu-coated graphite particles to produce Cu graphite composites by powder metallurgy (PM) methods is likely to result in better distribution and improved bonding between particles and the matrix [7–10].

In this paper, we report a relatively inexpensive process of coating copper on coconut shell char particles which does not use costly salts, such as $PdCl_2$ or $AgNO_3$, to activate particles before electrolytic coating of copper. In addition, the process has an additional advantage since the sodium potassium tartarate used in the coatings can be recovered and reused [11]. Mechanical and electrical properties of Al alloy shell char and Cu-shell char composites produced (using Cu-coated shell char particles) by both liquid and powder metallurgy techniques are reported.

2. Materials

2.1. Coconut shell char particles

Coconut shell char particles, (average size 125 μm) obtained by charring coconut shell powder in the

0022–2461/82/041041–08$03.46/0

temperature range 900 to 950° C in a mild steel container (coated with refractory clay) without access to air, was used in the coating experiments. The chemical composition of the shell char used is: C, 84.85 wt%; volatiles, 10 to 12 wt%; moisture, 4.2 wt%; ash, 1.1 wt%; P, 0.03 wt%; S, 0.02 wt%. Shell char particles have a true density of 0.8 g cm^{-3} with a porosity of 31%. Copper tartrate solution and Fehling–formaldehyde solution were prepared as reported in a previous communication [12].

3. Experimental procedure

3.1. Adsorption

50 g of coconut shell char particles (of average size 125 μm) were heated to 400° C for 2 h in the absence of air and were cooled in a dessicator. They were tranferred to 0.01 mol% CuT solution (pH 7 to 8) at room temperature (30° C), and stirred at 10 to 15 rpm with a glass stirrer. Copper adsorbed on to the surface of char particles was monitored by:

(a) measuring the decrease in copper concentration of the bulk of CuT solution by periodically taking out 2 ml of solution and analysing for copper using a spectrophotometric method; and

(b) taking out adsorbed char particles and analysing them for copper.

3.2. Activation

This step is for reducing the adsorbed CuT to elemental copper which acts as an activation site to initiate subsequent copper coating. The solution containing char particles with adsorbed Cu–T complex was filtered, washed free of CuT with double distilled water, and the residue was transferred to 37% V/W formaldehyde solution at a pH of 8.5 to 9.5 at room temperature and was stirred at 10 to 15 rpm for 1 h.

3.3. Copper coating

Activated particles were tranferred to a 10 lit beaker containing an electroless Fehling formaldehyde solution of concentration: $CuSO_4 \cdot 5H_2O$ 100 g; sodium potassium tartrate (Rochelle salt), 250 g; 37% V/W formaldehyde solution, 60 ml. The solution was stirred at 30 to 40 rpm periodically, checking the pH and maintaining a constant pH of 8.5 to 9.5 by the addition of NaOH (50 g). Copper on the coated powder was evaluated (a) by the decrease in Cu-concentration of the coating solution and (b) by analysing for copper by periodically taking out the coated powder sample by a volumetric method. A 30% copper coating was achieved in about 2.5 h.

3.4. Preparation of composites

3.4.1. Cast composites

3 to 5 kg of LM6 alloy was melted, de-gassed using purified N_2 for 5 min, and stirred at about 400 rpm using a mechanical stirrer. Copper-coated shell char particles were then added into the vortex. After the addition of the powder the melt containing suspensions was stirred for 2 to 3 min and poured into suitable permanent moulds.

3.4.2. Powder metallurgy produced composites

Samples of the copper-coated powder were blended for 2 h with pure copper powder (100 μm size) to get mixtures containing 2, 4, 6, 8 and 10 wt% of shell char using a double-cone blender. The blended powder mixtures were compacted to cylindrical samples of dimensions 12.5 mm x 16 mm in a die at pressure of 180 MN m^{-2}. The green compacts were sintered at 1000° C in a hydrogen atmosphere for 1.5 h. One set of sintered composites were repressed at 200 MN m^{-2} and annealed at 400° C in hydrogen for 30 min.

The electrical resistivity values were measured by the four-probe method; the compressive strengths were measured by an Instron machine; and the wear resistance were measured using a pin on disc machine.

4. Results and discussions

4.1. Adsorption of CuT complex on coconut shell char particles

Fig. 1 shows that weight per cent of copper deposited reaches a maximum of 2.3 wt% after 15 min of treatment and thereafter it remains constant; the amount of copper deposited is independent of the concentration of CuT solution [13]. The rate of CuT adsorption and the amount of CuT adsorbed on shell char particles (2.3 wt% Cu in 15 min) is high compared to the rate of adsorption on TiO_2 particels [12] (0.91 wt% Cu in 30 min).

4.2. Activation

It was found necessary to maintain the pH of the formaldehyde solution between 8.5 and 9.5 to obtain the maximum reduction of adsorbed complex in the minimum time. At low pH values

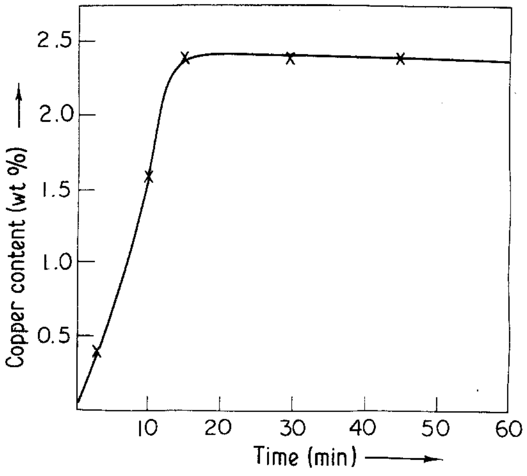

Figure 1 Variation of Cu–T complex absorbed on shell char with time.

reaction rates are low; at higher pH values free copper will be present in the solution.

4.3. Copper coating from Fehling–formaldehyde solution

The electroless technique of coating copper from a Fehling–formaldehyde bath involves the reduction of copper tartrate to metallic copper by alkaline formaldehyde [14].

It was possible, under the conditions of the present investiagation to coat up to 30 wt% of copper on the shell char particles (see Fig. 2). Deposition of copper in the pH range 8.5 to 9.5 increases linearly with concentration of copper ions up to a certain limit, and then decreases with time as a result of drop in pH of the coating solution. The pH level has to be maintained at 8.5 to 9.5 by subsequent addition of NaOH solution for the coating to continue at the initial rate. A temperature above 50° C leads to deposition of Cu_2O, and therefore, the present coating experiments were conducted at 30° C.

The possible reactions involved in the process may be represented as follows:

(a) decomposition of formaldehyde in presence of alkali

$$HCHO + OH^- \rightarrow H^- + HCOO^- ; \qquad (1)$$

(b) the absorbed CuT becomes reduced to Cu as

$$Cu^{2+} + 2H^- \rightarrow Cu^0 + H_2 ; \qquad (2)$$

(c) The Cu acts as a catalyst for a further Fehling–formaldehyde reaction

$$Cu^{2+} + 2HCHOO + 2OH^- \rightarrow Cu^0 + 2\,HCHOO^- + H_2 . \qquad (3)$$

4.4. Density

The measured densities of copper-coated shell char particles compare well with the theoretically calculated ones (Fig. 3) indicating that the coatings are reasonably dense.

4.5. Optical microscope studies

Optical micrographs of shell char particles show that the particles are porous and measured macropore size ranges from 20 nm to 100 nm. Fig. 4a, b and c shows the progress with time of copper coating on shell char particles. In the initial stages the copper coating is discontinuous; with increasing time separate islands of the copper coating form bridges and become continuous. Fig. 4c

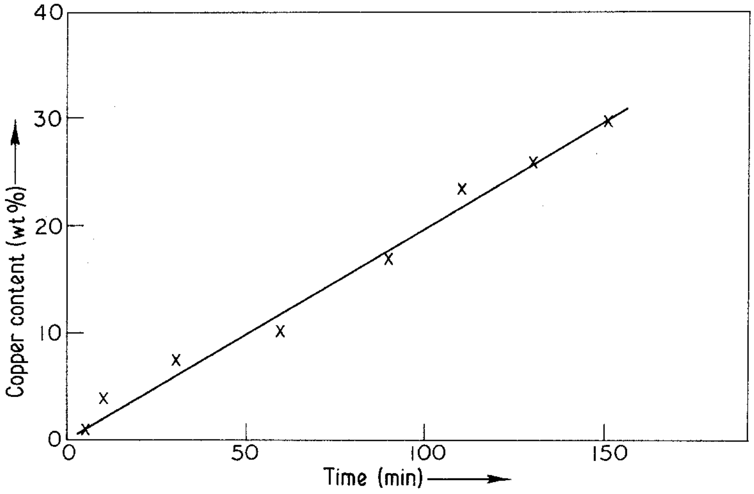

Figure 2 Progess of Cu-coating on shell char particles with time.

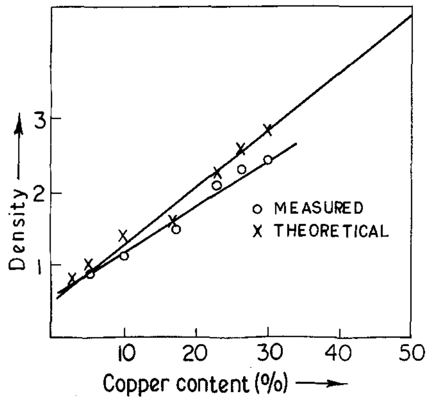

Figure 3 Comparison of measured densities of Cu-coated shell char particles containing different weight per cents of Cu with theoretically calculated densities.

shows a shell char particle after treatment for 150 min and a continuous thick coating of copper can be seen. This is in accordance with Schlesinger [15] who has shown that initial deposition of copper occurs discontinuously at selective sites during the early stages of growth. Only during the later stages of deposition, neighbouring islands of copper begin to touch each other and form a truely continuous coating [16].

4.6. Cast composites

Fig. 5a and b shows macro and micro photographs of Al–11.8 wt% Si–3 wt% shell char (made using copper coated shell char) cylindrical castings (50 mm x 150 mm) whose surfaces are machined to 1 mm depth, showing uniform dispersion of char particles. The density of char particles is 0.8 g cm^{-3} and the measured density of coated char particles (30%) is 2.0 g cm^{-3} which is close to the density of Al–11.8 wt% Si alloy. Hence, the flotation and segregation of char particles is minimal in the liquid metal bath and in the casting; a reasonably uniform dispersion of char particles was observed even at the bottom portion of the casting. Copper-coated shell char particles have been dispersed in molten Al–11.8 wt% Si alloy with recoveries higher than those of the uncoated char particles. Typical mechanical properties of Al–11.8 wt% Si alloy containing 3 wt% char particles are: UTS, 12 to 13 kg mm^{-2}; hardness, 75 to 80 BHN; elongation, 2%; and UCS, 43 kg mm^{-2}.

4.7. Powder metallurgy produced composites

Fig. 6a shows the macrophotograph of the copper shell char bushes and copper shell char contract materials fabricated by the powder metallurgy technique. Fig. 6b shows that there is a uniform dispersion of shell char particles in the matrix of copper.

4.8. Mechanical properties of composites

The density and hardness values of as-sintered and as-repressed composites decrease with increasing

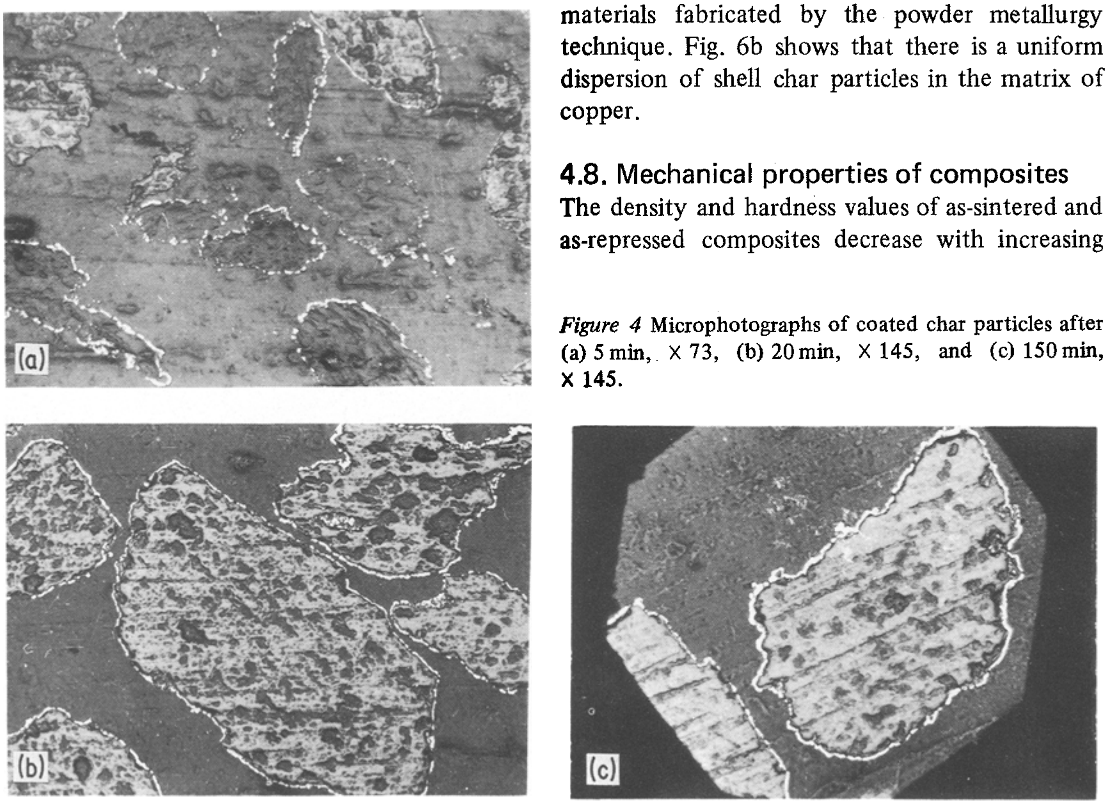

Figure 4 Microphotographs of coated char particles after (a) 5 min, X 73, (b) 20 min, X 145, and (c) 150 min, X 145.

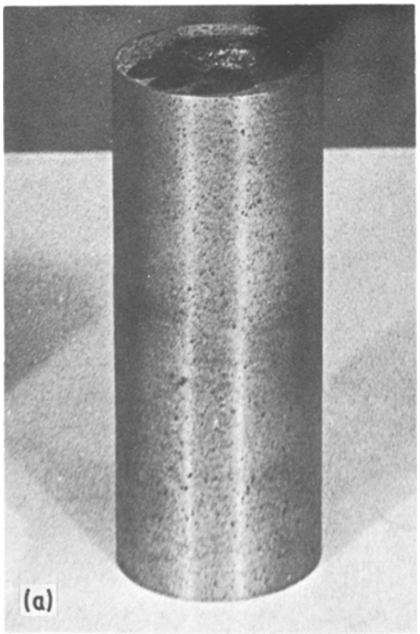

Figure 5 (a) Macrophotograph of Al–11.8 wt% Si–3 wt% char cylindrical casting (50 mm × 150 mm). (b) Microstructure of Al–11.8 wt% Si–3 wt% char (using copper-coated char), × 60.

volume-fraction of char particles (see Table I). Since coconut shell char comprises light porous particles (density, $d = 0.86\,\text{g cm}^{-3}$) compared to the matrix copper ($d = 0.97\,\text{g cm}^{-3}$) decrease in density values are expected. The decrease in density values are more when compared to theoretical densities calculated according to rule of mixtures, probably due to the porosity in the as-sintered composites; however, further repressing at $200\,\text{MN m}^{-2}$ and annealing at 400° C increases the density values (Table I). The decrease in hardness values may be due to the lower hardness of char particles [17] (40 to 45 BHN) compared to the hardness value of 70 BHN for the matrix. Further repressing and annealing of the as-sintered composites reduced the porosity content of the composites, and improved the hardness values by about 50%, as can be seen from Table I.

The density values of as-sintered Cu–10 wt% char composites ($5.8\,\text{g cm}^{-3}$) are lower as compared to densities of Cu-graphite composites [9] produced using Cu-coated graphite particles. However, Cu–10 wt% char composites have higher hardness values (40 BHN) compared to Cu-graphite composites (25 BHN).

Wear rates and friction coefficient, μ, values decrease due to the dispersion of coconut shell char particles in copper matrix. Typical wear

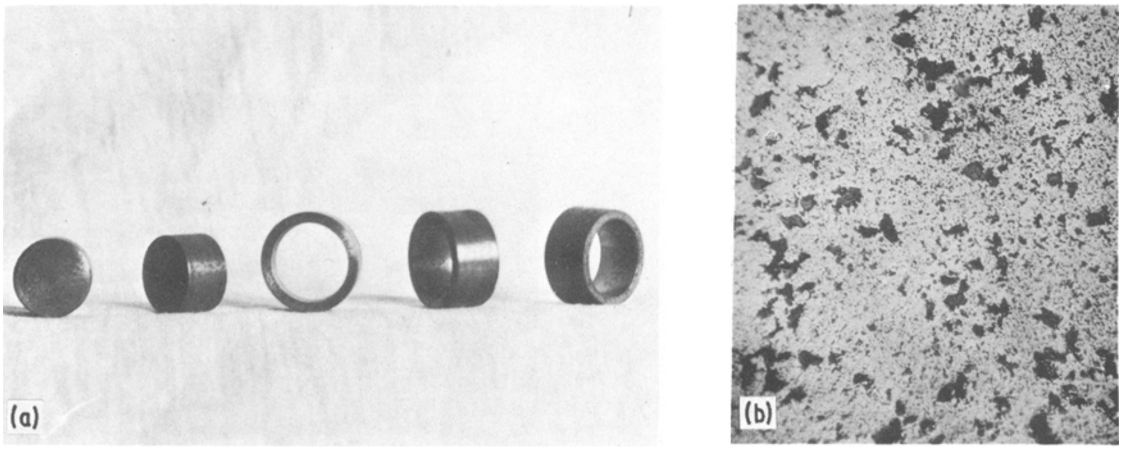

Figure 6 (a) Macrophotograph of Cu–4 wt% char bushes and contact brush material. (b) Microstructure of Cu–4 wt% char composite, × 66.

TABLE I Mechanical properties of Cu–shell char composites

Char content	Density (g cm^{-3})		Hardness (BHN)	
	As-sintered	Repressed	As-sintered	Repressed
0			45	70
2	7.48	8.20	40	68
4	7.06	7.80	35.7	65
6	6.60	7.45	32.5	60.5
8	6.22	7.10	29.6	55.5
10	5.80	6.80	22.3	40.0

rate and μ-value for copper–4 wt% char composite are 3.89×10^{-11} cm^2 and 0.129 compared to the matrix wear rate and μ-value of 6.635×10^{-11} cm^2 and 0.250, respectively, at a sliding speed of 0.56 m sec^{-1} and at a load of 80 N.

Typical stress–strain curve under compression of Cu–4 wt% shell char composite is shown in Fig. 7. Compression strength of the composite is 23 kg mm^{-2}. The presence of 4 wt% shell char particle decreases the compressive strength of copper by 30 wt%. However, Cu–4 wt% shell char composite, under compressive stress can undergo large strains (0.3 to 0.4) before fracture, which suggests that these composites can be further worked into different shapes by mechanical working operations. A further SEM picture of the top surface of a compressed specimen (see Fig. 8) shows deformation including necking and bridging of char particles. The average l/d ratio of the particle is about 10 compared to the average l/d ratio of 1.5 to 2.2 for the original 125 μm char particles in the as-sintered composites.

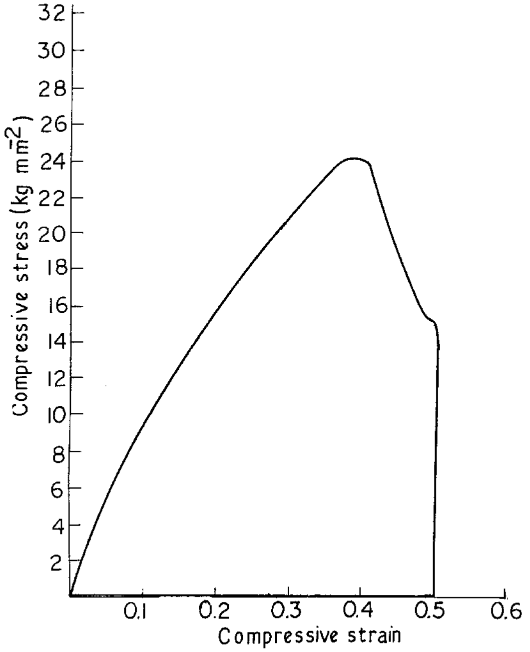

Figure 7 Compressive stress–strain diagram for sintered Cu–4 wt% shell char composites.

5. Electrical resistivity of Cu–char composites

Measured values of electrical resistivity of as-sintered Cu–2 to 10 wt% char composites, and repressed and annealed composites are shown in Table II. Since the resistivity of char particles is of the order of 2.1×10^4 ohm cm compared to the resistivity value of 5 μohms cm for Cu blank made in the present investigation, increases in the resistivity values due to additions of char are expected. Measured values are compared with theoretically calculated values using the following three formulae:

$$\rho = \frac{2\rho_d + \rho_m + V_d(\rho_d - \rho_m)}{2\rho_d + \rho_m - 2V_d(\rho_d - \rho_m}, \qquad (1)$$

where ρ is the electrical resistivity of the composite (in μohm cm), ρ_m is the electrical resistivity of the matrix (in μohm cm), ρ_d is the electrical resistivity of the dispersed particles (in μohm cm) and V_d is the volume-fraction of dispersed particles, given by Maxwell [18] for the specific resistance

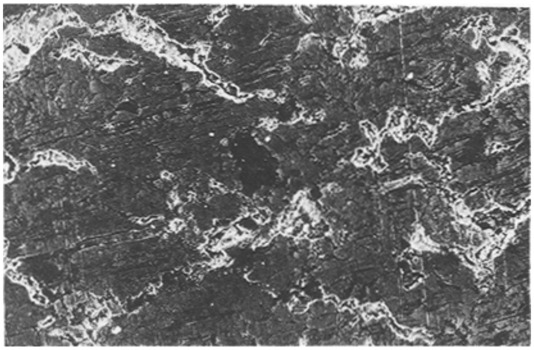

Figure 8 SEM photograph of top surface of a compressed Cu–4 wt% char composte, × 210.

TABLE II Electrical resistivity values

Volume-fraction of matrix	Volume-fraction of dispersed coconut shell char	Measured value of resistivity (μohm cm)		Theoretically calculated value of resistivity (μohm cm)		
		As-sintered	Repressed	Equation 1	Equation 3	Equation 2
0.82	0.18	8.754	8.25	6.645	6.0968	6.8493
0.69	0.31	10.05	9.564	8.6395	7.2456	9.3457
0.59	0.41	17.52	12.754	10.2118	8.4729	12.987
0.505	0.495	28.5	19.324	12.3510	9.898	19.4174
0.445	0.555	47.5	41.5	14.194	11.232	29.8590

of a system where one phase is dispersed within another,

$$\rho = \frac{\rho_m}{(1 - 1.5V_d)} \tag{2}$$

for the electrical resistivity of a system containing spherical inclusions of an insulating material in a highly conducting medium [19], and

$$\rho = \frac{\rho_m \rho_d}{V_m \rho_d + V_d \rho_m}, \tag{3}$$

where V_m is the volume-fraction of the matrix, for the resistance of two phases in parallel [20].

Closest agreement with the measured values (Table II) is obtained from the Equation 2 derived by Van Beak [19]. Electrical resistivity values for as-sintered composites are high, while for repressed samples, the resistivity is lowered and is in close agreement with the values predicted by Equation 2. Apparently, on pressing the as-sintered samples the inhomogenities and porosity are decreased. Cu–shell char composites made by the powder metallurgy techniques in the present study have a lower density and greater hardness compared to Cu–graphite composites [8] made under similar conditions. Further, Cu–shell char composites wear less, and have lower values of coefficient of friction compared to matrix Cu, made in the present study under dry conditions of sliding. This suggests that these composites have the potential for use as electric contact material.

6. Conclusions

(a) It is possible to deposit continuous coatings of copper (between 10 and 30 wt% on the the surface of pretreated coconut shell char particles, first by activating the surface of the particles by Cu–T complex followed by copper coating using Fehling–formaldehyde solution.

(b) Maximum adsorption of copper tartrate complex occurs within 15 min (2.3 wt% Cu) and thereafter the rate of adsorption remains constant with time.

(c) It is possible to disperse copper-coated shell char particles in cast Al-alloys by the vortex method and cast the composite melts in suitable permanent moulds to get cast Al–shell char particulate composite.

(d) It is possible to prepare copper-shell char composites by pressing and sintering copper-shell char powders and 100 μm-size copper powder.

(e) As a result of 4% dispersions of coconut shell char in as-sintered Cu-shell char composites (1) density decreases from 7.9 g cm^{-3} (of matrix) to 7.06 g cm^{-3}, (2) hardness decreases from 45 BHN to 35.7 BHN, (3) electrical resistivity increases from 5 μohm cm to 10.05 μohm cm, which agreed well with theoretically calculated value according to Van Beak, and (4) wear rate and friction coefficient under dry conditions decreases from 6.635 x 10^{-11} cm^2 and 0.250 to 3.89 x 10^{-11} cm^2 and 0.129, respectively, indicating that these composites will be good for antifriction applications. Repressing the as-sintered composites at 200 MN m^{-2} and annealing them at 400° C for 1 h increases the density and hardness values and decreases the electrical resistivity values.

Acknowledgement

The authors are grateful to Shri S. G. K. Pillai (RRL), Shri A. Natarajan and Shri Y. K. Rao (VSSC) for optical microscopic studies. Thanks are also due to Shri Peter Koshy and Shri Vijaya Kumar (RRL) for SEM photographs. They are also thankful to Shri N. T. George, Defence Metallurgical Research Laboratory, Hyderabad, for useful discussions.

References

1. P. K. THAMPAN, "The Coconut Palm" (Green Villa Publishing House, Cochin, India 1975).

2. US Patent Number 3853635, 10 December, 1974.
3. M. K. SURAPPA, PhD Thesis, Indian Institute of Science, Bangalore, India, 1979.
4. P. K. TOHATGI, B. C. PAI and P. C. PANDA, *J. Mater. Sci.* 14 (1979) 2277.
5. F. A. BADIA and P. K. ROHATGI, *AFS Trans.* 77 (1969) 402.
6. DEONATH, PhD Thesis, Indian Institute of Science, Bangalore, India, 1977.
7. M. N. MURTHY, Proceedings of the 14th Seminar on Electrochemistry, November 1973 (Electrochemical Society of India, Karai Kudy) pp. 44–50.
8. G. S. BHATTACHARJEE, S. L. N. ACHARYULU, N. T. GEORGE and R. V. THAMHANKAR, *Trans. PMAI* 2 (1975) 54.
9. L. V. CHOZNOGUZ, A. N. LESHCHENKO, V. P. POPOV, D. S. YAS' and A. K. KARAULOV, *Soviet Powder Metall. Metal Ceram.* 18 (1979) 688.
10. D. S. YAS', V. I. PAVLENKO and V. B. PODMOKOV, *Poroshk. Metall.* 1 (1976) 31.
11. K. GOPA KUMAR, C. PAVITHRAN and P. K ROHATGI, *J. Plating Surace Finishing,* July (1981) 61.
12. K. GOPA KUMAR, C. PAVITHRAN and P. K. ROHATGI, *J. Mater. Sci.* 15 (1980) 1588.
13. *Idem,* unpublished work (1980).
14. W. GOLDIE, "Metallic Coating on Plastics" (Electrochemical Publications Ltd, England, 1974).
15. M. SCHLESINGER, "The Basic Principles of Electroless Deposition, Science and Technology of Surface Coatings" edited by Brian and Chapman and J. C. Anderson (Academic Press, London and New York, 1974) p. 176.
16. J. P. MARTON and M. SCLHLESINGER, *J. Electrochem. Soc.* 115 (1968) 16.
17. C. L. MARTELL, "Industrial Carbon" (Van Nostrand Publishing Ltd, USA, 1947).
18. J. C. MAXWELL, "A treatise on Electricity and Magnetism" Vol 1, 3rd Edn, (Clarendon Press, Oxford, 1982) p. 440.
19. L. K. VAN BEAK, "Progress in Dielectrics" Vol. 7 (Heywood Publishers, London, 1967) p. 69.
20. L. H. VAN VLACK, "Materials Science for Engineers" (Addison-Wesley Publishing Co, London, 1973) p. 407.

Received 11 May
and accepted 9 September 1981