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Development of pitch-based carbon–copper composites

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Abstract Carbon–copper composites with varying copper to carbon ratio of 0.66–1.5 (by weight) were developed from coal-tar-pitch-derived green coke (as such or modified with natural graphite) as carbon source and electrolytic grade copper powder at different heat treatment temperatures (HTTs) of 1000–1400 °C. The physical, mechanical, and electrical properties differ depending upon the HTT and also on copper to carbon ratio (Cu/C). The composites prepared at HTT of 1100 °C having Cu/C ratio of 0.66 and 0.9 exhibited a high bending strength of 150 and 140 MPa, bulk density of 2.63 and 2.81 gm/cm^3, electrical resistivity of 1.6 and 0.96 m Ω cm and shore hardness of 88 and 84, respectively, in spite of well-known inadequate wettability between copper and carbon. Increasing the temperature from 1100 °C for processing of the composites deteriorated the properties mainly due to the loss of copper through melting above 1100 °C as revealed by X-ray, scanning electron microscopy, thermal analysis and EDAX studies.

Introduction

Carbon (graphite)–copper composites are versatile materials useful as brushes for engines and generators in electrical applications and as shaft materials, bearings etc. for tribological or mechanical engineering applications [1–3]. These composites exhibit the unique characteristics of both the components, i.e., thermal and electrical conductivities of the copper and low thermal expansion coefficient, lubricating and corrosion-resistance properties of the graphite [3, 4]. Carbon–copper composites also find use in microwave travelling wave tubes as multistage depressed collector in place of copper because carbon has a relatively low secondary electron emission coefficient when compared to copper [5, 6]. These composites are generally prepared by powder techniques as these techniques offer the possibilities of producing uniform quality composites with relatively low machining costs [3, 4, 7, 8]. The carbon–copper composites have also been reported to be prepared by other methods using expensive equipments, viz, by impregnating a carbon substrate with a molten copper or its alloy [9], by hot isostatic pressing technique [10] or by high frequency induction heating at high pressures [11]. It may be however important to mention here that there are limitations to the use of above-said methods mainly due to the poor affinity/wettability between copper and graphite, which leads to weak interfaces with negative effects on the structural, mechanical and electrical properties [7, 12, 13]. The lack of wetting between copper and graphite (carbon) during the composite processing has been reported to be improved by coating the graphite particles or carbon fibres with copper using electroless coating techniques before consolidation [13–15]. This has resulted in the improvement of copper–graphite (or carbon fibre) interface thereby leading to enhancement in the properties of the composites.

Queipo et al. [16] reported the use of binder coal tar pitch (CTP) due to their low cost, easy availability and good wetting behaviour during the processing of carbon–

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copper composites. This coating of graphite with pitch was done to study the influence of thermal treatment of CTP with graphite (synthetic and natural) at a temperature of 420 °C for 1 h in nitrogen atmosphere on the interface formed when mixed with copper with a purpose of getting improved properties of carbon–copper composites. It was observed by Queipo et al. [16] that the bulk density, flexural strength and electrical properties of carbon–copper composite (using treated natural graphite) were improved to 2.0–2.58 gm/cm^3, 39–46 MPa and 0.2–0.7 m Ω cm, respectively, when compared to values of 1.66 gm/cm^3, 29–36 MPa and 0.93 m Ω cm for carbon composites but without the inherent ductile properties of the copper in the resulting composites.

The present authors through this communication have attempted to develop carbon–copper composites (C–Cu composites) by incorporating copper into the self-sintering green coke (GC) powder derived by the heat treatment of a commercially available CTP. The authors have already reported that the CTP-based self-sintering carbon (GC) powder has unique properties and it is used to produce carbon monolith and carbon–ceramic composites [17–22]. It is expected that when GC is mixed with copper powder, it is likely to result in dense C–Cu composites with good mechanical and electrical properties. A search of literature reveals that study on the development of C–Cu composites using a mixture of self-sintering GC powder (as such or modified with graphite) and copper is not so far reported. The present article gives an account of this attempt and the results obtained therefrom.

Experimental procedure

Development of GC powder and carbon monolith (batch A)

A special commercially available QI-free CTP procured from Konark Tar Products Ltd, India, was characterized and subjected to heat treatment temperature (HTT) of 500 °C to obtain the so called GC (also called raw coke). The GC thus prepared was then ground into a fine powder using planetary ball mill at 250 rpm for 5 h. The powder was characterized and moulded into rectangular plates of the size 40 × 15 × 5 mm^3 using a conventional hydraulic press at a pressure of 200 MPa. These green plates were carbonized at 1000 °C in nitrogen (purity 99.9%) atmosphere by employing a heating rate of 20 °C/h up to 250 °C and 10 °C/h from 250 to 1000 °C to obtain carbon monolith. The plates were characterized and further heat treated up to 1400 °C by employing heating rate of 100 °C/h up to 1000 °C and 15 °C/h up to 1400 °C in nitrogen atmosphere to obtain final plates of batch A.

Development C–Cu Composites (batches B–H)

Six batches (B–G) of C–Cu composites were developed from the mixtures of the GC powder and electrolytic grade copper powder (Acros Organics, 99% pure) keeping the Cu/C weight ratio of 0.66, 0.9, 1.0, 1.1, 1.3, and 1.5. The various GC–Cu mixtures were ball milled in a planetary ball mill for about 5 h at 250 rpm which were oven dried for 1 h, moulded into rectangular plates of 40 × 15 × 5 mm^3 using hydraulic press at the pressure of 200 MPa. The moulded plates were heat treated at different temperatures (1000 °C or higher up to 1400 °C) in nitrogen atmosphere as mentioned above to get C–Cu composite batches B–G. In addition, the GC used in batch A was mixed with 25% natural graphite to get modified GC, ball milled for 5 h with copper powder to get Cu/C ratio of 0.72 in the C–Cu composites, moulded into rectangular plates and heat treated at different temperatures (1000 °C or higher) as mentioned above to obtain C–Cu composites batch H.

Characterization

The precursor CTP and GC powder were characterized with respect to various parameters such as quinoline insoluble (QI), toluene insoluble (TI), softening point, specific gravity, coking value (CV) and volatile matter. The carbon (C) and hydrogen (H) contents were determined using Euro Vector Elemental Analyzer and C/H atomic ratios were calculated from C and H contents so obtained. Weighed quantity of CTP, GC and powdered mixtures of C–Cu composites (batches B, C and D) were heat treated in nitrogen from 300 to 1000 °C in steps at the rate 200 °C/h to determine residual mass upon heat treatment (Thermogravimetric analysis, TGA). Carbon monolith batch A derived from the moulded GC powder and C–Cu composites (batches B–H) were characterized with respect to bulk density, weight loss and volume shrinkage after the heat treatment at 1000 °C and higher up to 1400 °C. The bending strength and electrical resistivity of the carbon monolith after heat treatment to 1400 °C were also measured by three point bending test using Instron Universal Testing Machine (model 4411) and using a laboratory developed four-probe apparatus, respectively [22]. The bending strength, electrical resistivity and shore hardness of the C–Cu composites were determined after they were heat treated at 1000 and 1100 °C. The bending strength of few batches was also determined after heat treatment to temperatures of 1300 and 1400 °C, respectively. The C–Cu composites (batch B) heat treated to 1000, 1100, 1200 and 1400 °C was also characterized by X-ray diffraction analysis by employing D-8 Advanced Bruker Powder X-ray diffractometer using CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å) and scanning electron microscopy (LEO-440 and ZEISS-EVO MA10).

Results and discussion

Characteristics of raw materials

The characteristics of the precursor CTP and the GC powder are given in Table 1. The CTP was observed to have low softening point of 86.6 °C and specific gravity of 1.27. It can be seen from the values that precursor CTP possessed a QI content of 0.2%, TI content of 22.6% and CV of 43.8% which are lower as compared to those of GC powder which showed QI of 97%, TI of 99% and CV of 91%. This increase in QI, TI and CV of GC powder is attributed to the removal of volatile matter on pyrolysis of precursor CTP at the temperature up to 500 °C during GC preparation and also to the dehydrogenative condensation and polymerization reactions between various molecular species of the CTP. This observation is also supported by the weight change observed in thermal analysis study given in Fig. 1 which showed sharp decrease in weight of residue of CTP up to 500 °C beyond which the weight loss decreases very slowly up to 1000 °C. In comparison it is seen that GC powder shows a gradual and low weight loss from a value of nearly 100% at 300 °C to 92% at 1000 °C. This is further confirmed by the decreasing hydrogen content from a value of 4.77% for CTP to 2.68% for GC powder (Table 1) and increasing C/H atomic ratio value from 1.61 to 2.86 for CTP and GC powder derived therefrom, respectively.

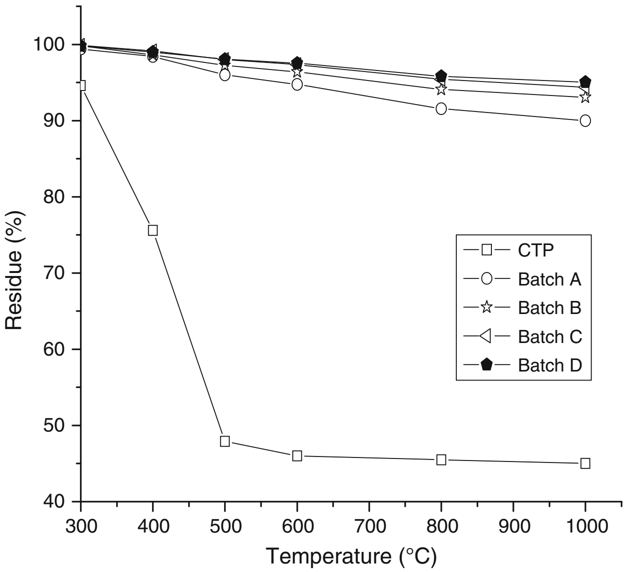


Fig. 1 Thermal analysis graph for coal tar pitch and C–Cu composites batches A–D

Table 2 Characteristics of coal-tar-pitch-based carbon monolith batch A

S. No.	Characteristics	HTT (°C)	Batch A
1.	Bulk density (gm/cm^3)	RT	1.30
		1000	1.65
		1400	1.81
2.	Weight loss (%)	1000	8.6
		1400	11
3.	Volume shrinkage (%)	1000	27.5
		1400	35.0
4.	Electrical resistivity (m Ω cm)	1000	4.8
		1400	2.9
5.	Bending strength (MPa)	1400	79
6.	Shore hardness	1400	103

Characteristics of CTP-based carbon monolith (batch A)

The characteristics of the carbon monolith batch A developed using GC powder are given in Table 2. It is observed that the green carbon monolith (without sintering) possessed a bulk density of 1.30 gm/cm^3 at room temperature which increases up to 1.65 gm/cm^3 and finally to 1.81 gm/cm^3 after the HTT at 1000 and 1400 °C, respectively. This increase in

Table 1 Characteristics of precursor coal tar pitch and green coke powder

S. No.	Characteristics	Precursor coal tar pitch	Green coke
1.	Softening point (°C)	86.6	–
2.	Specific gravity	1.27	–
3.	Quinoline insoluble content (%)	0.2	97
4.	Toluene insoluble content (%)	22.6	99
5.	Coking yield (%)	43.8	91
6.	Volatile matter (%)	56.2	8.2
7.	β-Resin (%)	22	2
8.	Carbon (%)	92.39	91.35
	Hydrogen (%)	4.77	2.68
	Atomic C/H ratio	1.61	2.86

bulk density is a consequence of significant volume shrinkage (27.5%) observed during carbonization of GC plates (i.e. from room temperature up to 1000 °C) which is attributed to the increase in skeletal density of the carbon phase during this conversion of GC to carbon. The weight loss due to removal of volatile takes place gradually during this solid transformation from GC to carbon. It is further observed that the weight loss and volume shrinkage from 1000 to 1400 °C is relatively less and this is attributed to the removal of most of the volatile matter from GC on carbonization to 1000 °C. The electrical resistivity of the carbon monolith plates decreases from 4.8 to 2.9 m Ω cm as the HTT is increased from 1000 to 1400 °C. This is attributed to the increasing proximity between the carbon particles resulting from increasing volume shrinkage as well as bulk density of the carbon monolith and also to the marginal enhancement of the pregraphitic order of the material (GC) upon heat treatment from 1000 to 1400 °C which would favour better electrical conductivity. The characteristic values for the bending strength and shore hardness of the monolithic carbon plates after the heat treatment of 1400 °C were observed to be having reasonably high values of 79 MPa and 103 respectively.

Characteristics of C–Cu composites (batches B–H)

The characteristics of the C–Cu composites batches developed with GC (batches B–G) and of composites developed using GC modified with natural graphite (batch H) are given in Table 3. It is seen from the values that the bulk density of GC-based plates (without sintering) is 1.30 gm/cm^3 (Table 2) and the green density values (before sintering) for C–Cu composites are higher and found to be in the range of 1.93–2.95 gm/cm^3 for batches B–G having Cu/C weight ratio varying between 0.66 and 1.5 (Table 3). This increase in green bulk density is due to

Table 3 Characteristics of C–Cu composite batches

Characteristics	HTT (°C)	Composition of C-Cu composite batches (weight percentage) along with Cu/C ratio						
		B Cu/C 40:60 (0.66)	C Cu/C 47.4:52.6 (0.9)	D Cu/C 50:50 (1.0)	E Cu/C 52.4:47.6 (1.1)	F Cu/C 56.5:43.5 (1.3)	G Cu/C 60:40 (1.5)	H Cu/C 41:58 (0.72)
Bulk density (gm/cm^3)	RT	1.93	2.10	2.25	2.41	2.48	2.95	2.19
	1000	2.51	2.75	2.86	3.10	3.19	3.32	2.66
	1100	2.63	2.81	2.92	3.17	3.25	3.37	2.73
	1300	2.64	2.80	–	–	–	–	–
	1400	2.62	2.76	–	2.98	3.04	3.03	–
Weight loss (%)	1000	6.20	5.0	4.68	4.08	3.18	3.65	4.58
	1100	6.90	5.3	4.90	4.25	3.94	3.80	4.80
	1300	8.10	8.9	–	–	–	–	–
	1400	10.1	13.5	–	13.0	12.8	14.9	–
Volume shrinkage (%)	1000	28.66	28.2	25.5	23.0	23.5	22.5	21.6
	1100	31.35	31.0	26.6	27.0	25.8	24.4	23.7
	1300	32.00	32.0	–	–	–	–	–
	1400	34.70	35.0	–	–	–	–	–
Electrical resistivity (m Ω cm)	1000	2.30	1.53	1.40	1.20	0.82	0.66	1.16
	1100	1.60	0.96	0.85	0.80	0.68	0.58	0.80
	1300	1.07	0.60	–	–	–	–	–
	1400	1.20	0.70	–	0.42	0.23	0.21	–
Bending strength (MPa)	1000	135	125	100	94	92	75	94
	1100	150	140	105	83	80	70	87
	1300	120	90	–	–	–	–	–
	1400	70	60	–	60	–	60	–
Shore hardness	1000	90	86	84	82	81	79	84
	1100	88	84	79	78	79	75	83
	1300	87	83	–	–	–	–	–
	1400	85	80	–	73	74	75	–

Note: The figures in the parenthesis refer to Cu/C ratio (by weight) the higher density of metallic copper present in these composites and further the density is expected to increase as the copper content is increased in these composites. The green (bulk) density of the composite (batch H) developed with modified GC (i.e. with addition of natural graphite) with Cu/C ratio of 0.72 is 2.19 g/cm^3 (Table 3) which is higher than that of batch C (2.10 gm/cm^3) developed with GC as such with Cu/C ratio of 0.9. This is attributed to the better compression resulting from lubricating effect of natural graphite besides it possesses a higher density of 2.26 gm/cm^3 as compared to the GC whose density is around 1.3 gm/cm^3. The same trend of increasing bulk density is noticed for various batches of C–Cu composites (having different Cu/C weight ratios) heat treated to 1000 °C which is attributed to the self sintering property of the GC resulting in high volume shrinkage with a relatively low weight loss at 1000 °C as seen in TGA graph in Fig. 1 for few C–Cu composite batches (B–D), since the Cu powder present in the composite does not undergo any weight loss or volume shrinkage. The increase in the bulk density for batch H developed with modified GC as carbon source (Cu/C weight ratio = 0.72) from room temperature to 1000 or 1100 °C is found to be less than the values observed for batches B (Cu/C weight ratio = 0.66) and C (Cu/C weight ratio = 0.9) which may be due to the reduced quantity of GC in the composite (batch H) because both natural graphite and copper do not undergo any weight loss or volume shrinkage on heat treatment. It is important to mention here that the bulk density of all the composites decreases on further heat treatment at 1300 and 1400 °C and this is attributed to the loss of copper from the composite plates resulting from the melting and removal of Cu which starts at temperatures above the melting point of copper, i.e. 1080 °C.

It may be noted that the bulk density of pitch-based carbon–copper composites developed by Queipo et al. [16] using pitch graphite mixture and copper powder possessed densities of 2.36 and 2.58 gm/cm^3 for Cu/C ratio of 0.71 and 1.06, respectively. In the comparison, carbon–copper composites developed in the present investigation with GC mixed with natural graphite and copper (batch H) with Cu/C ratio of 0.72 and with GC and Cu mixtures (batches D and E with Cu/C ratios of 1.0 and 1.1, respectively) possessed bulk densities of 2.66, 2.86 and 3.10 gm/cm^3, respectively at a HTT of 1000 °C, thereby showing that the present process gives more compact and dense C–Cu composites.

The values for the volume shrinkage of the composites given in Table 3 show that the volume shrinkage increases as HTT is increased to 1100 °C or higher which is due to self-sintering property of GC. The volume shrinkage, however, decreases as the Cu content is increased (batches B–G) which is expected since it is the GC component of the composites which shows volume shrinkage and copper does not undergo any volume shrinkage or weight loss on heat treatment. It is also seen that the increase in the weight loss of the composites from 1100 to 1400 °C is higher in the composites with increasing copper content as compared to the increase in weight loss from 1000 to 1100 °C and this is attributed to the loss of Cu from the C–Cu composite as mentioned earlier.

The electric resistivity of these composites given in Table 3 for batches B–G shows that the electric resistivity is decreased from a value of 2.30–0.66 m Ω cm at 1000 °C and from 1.60 to 0.58 m Ω cm at 1100 °C as copper to carbon ratio (weight ratio) in the composites is increased from 0.66 to 1.5, respectively. This is attributed to the self-sintering property of GC which increase the proximity among the carbon particles due to increasing volume shrinkage or bulk density and also to the high conductivity of the copper present in C–Cu composites. The batch H (Cu/C ratio of 0.72) exhibits a value of 1.16 m Ω cm at 1000 °C and 0.8 m Ω cm at 1100 °C which is lesser than the values observed for batches B (2.3 and 1.6 m Ω cm) and C (1.53 and 0.96 m Ω cm) at 1000 and 1100 °C, respectively, whose Cu/C ratios are 0.68 and 0.9, respectively. This may be attributed to the lubricating effect of natural graphite which when added to the GC (i.e. batch H) results in better compaction (as observed by bulk density values at room temperature) and consequent better electrical conductivity values at 1000 and 1100 °C, respectively. Further, it is also known that natural graphite

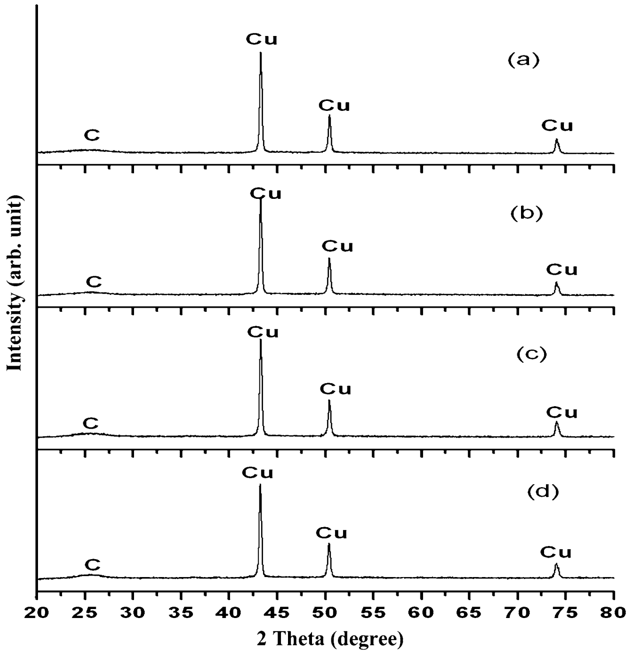


Fig. 2 X-ray diffraction patterns of C–Cu composite batch B (Cu/C weight ratio = 0.66) heat treated to (*a*) 1000 °C, (*b*) 1100 °C, (*c*) 1200 °C, (*d*) 1400 °C

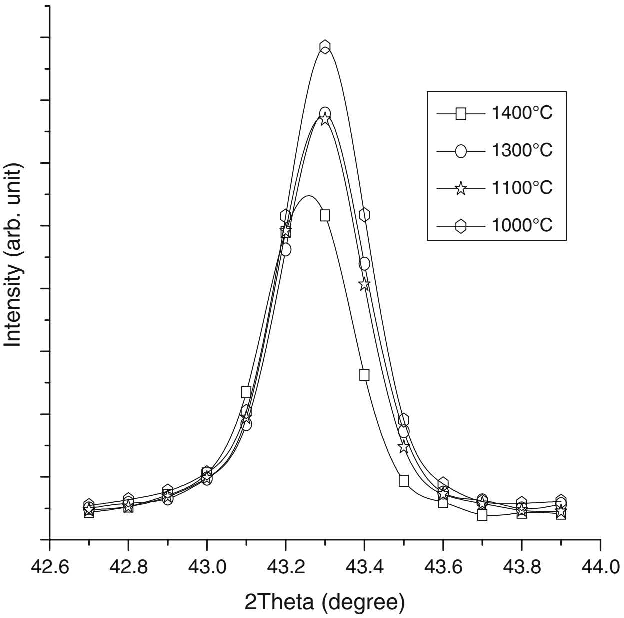


Fig. 3 X-ray diffraction patterns of C–Cu composite batch B, Cu/C weight ratio = 0.66 (after scale expansion from $2\theta = 42.6°$ to 44°)

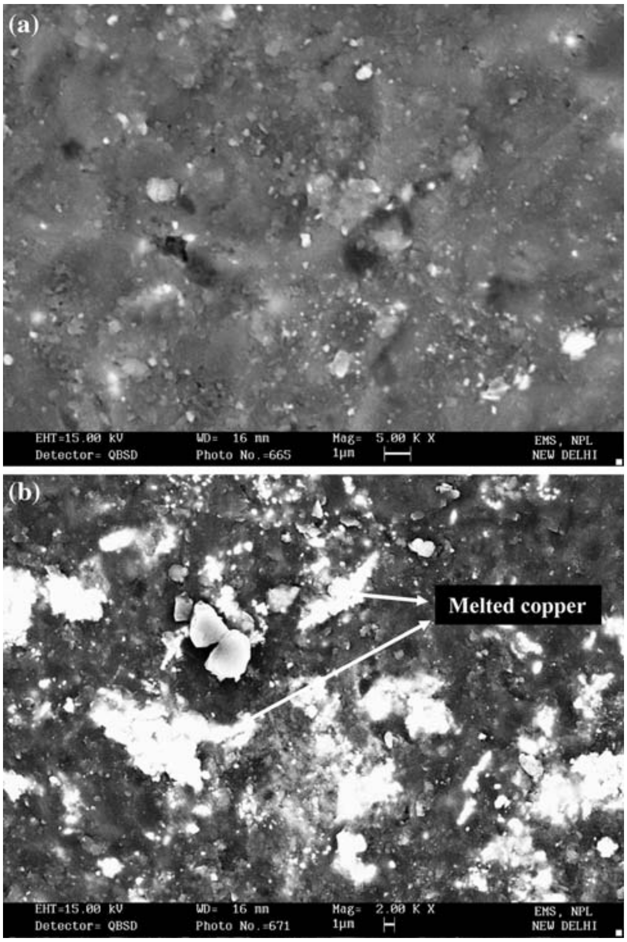


Fig. 4 Scanning electron micrographs of C–Cu composite batch C (Cu/C weight ratio = 0.9) heat treated to **a** 1100 °C and **b** 1400 °C

possess higher electrical conductivity as compared to the monolithic carbon from GC.

It is also seen that bending strength is maximum in composites (batch B) having a higher quantity of GC which helps in making a dense composites due to the self sinterability of the GC powder. The bending strength of the

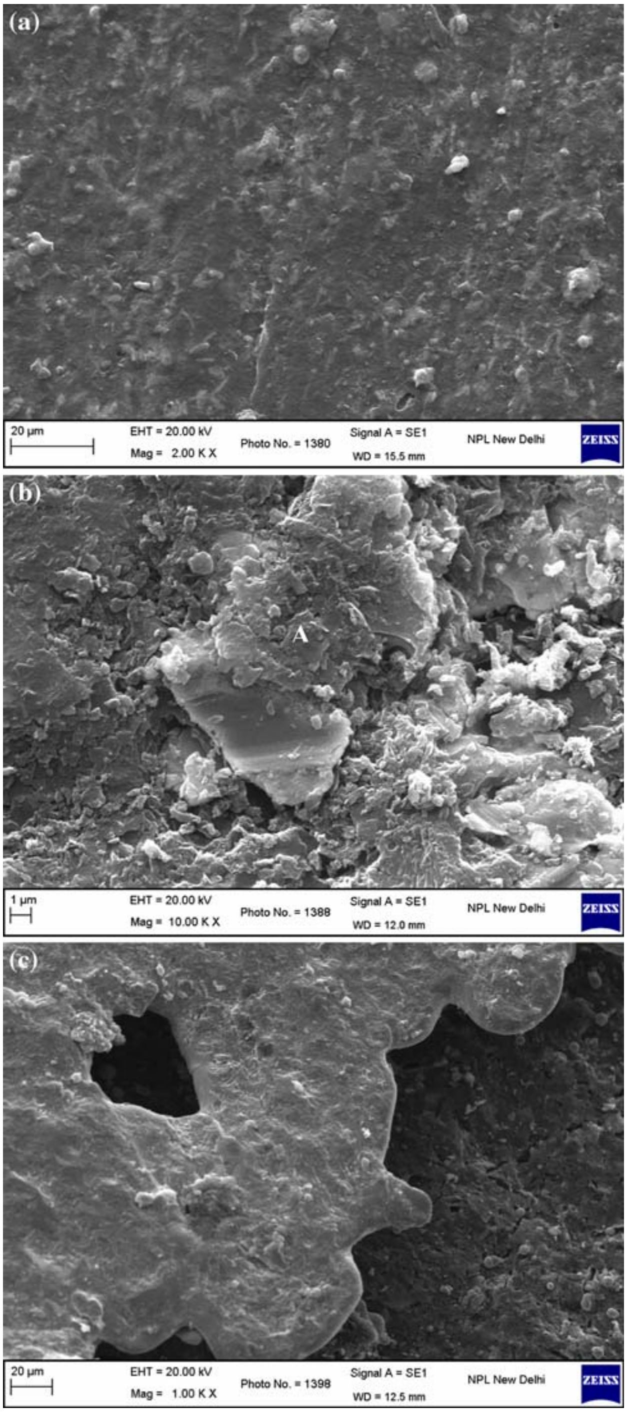


Fig. 5 Scanning electron micrographs of C–Cu composite batch G (Cu/C weight ratio = 1.5) heat treated to different temperatures **a** 1100 °C, **b** 1400 °C and **c** fractured surface (HTT 1400 °C)

composites at 1000 °C is decreased gradually from a value of 135 MPa for batch B to 75 MPa for batch G and this is due to the decreased quantity of GC or increased quantity of copper in the composites (batches B–G) and also to the lack of wettability between copper and carbon [9, 16].

It is further observed that the bending strength values of 94 MPa for batch H which contains natural graphite in addition to GC derived carbon is lesser than the values of 135 and 125 MPa observed for batches B and C, respectively, which may be attributed to the presence of natural graphite in batch H as it is known to decrease bending strength significantly. It is also noticed from the values that the bending strength increases for batches B and D as the HTT increases from 1000 to 1100 °C while it decreases from batch E to G. This observation probably indicates that the limiting Cu/C weight ratio and limiting HTT in these composites is around 0.9 and 1100 °C for obtaining better bending strength. The bending strength was further found to decrease as the HTT is increased from 1100 to 1400 °C which may be attributed to the slight improvement of pregraphitic order in the C–Cu composites and also to the melting and subsequent removal of copper from the composites at these temperature as seen from higher weight loss resulting in voids that was also observed from SEM studies which are explained under the subheading SEM analysis. The shore hardness values of the composites decrease gradually from 90 to 79 as the copper content is increased which is also in agreement with the results reported earlier [16].

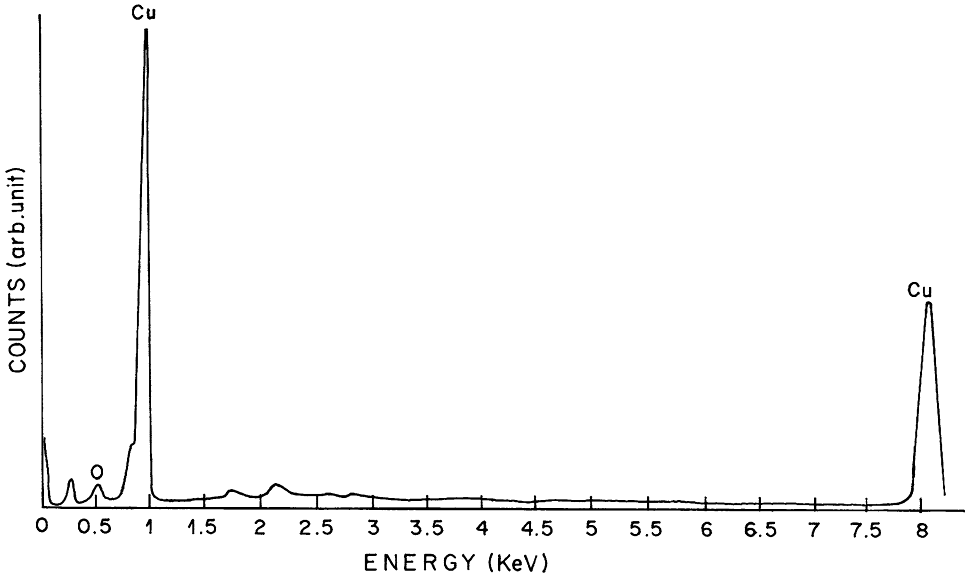
X-ray analysis

The X-ray diffraction pattern of C–Cu composites (batch B with Cu/C weight ratio 0.66) heat treated to different temperatures from 1000 to 1400 °C is given in Fig. 2. The X-ray diffraction pattern shows characteristics peaks of copper at $2\theta = 43.29°$, 50.43° and 74.13°. The peak due to carbon is not very prominent since the GC-derived carbon at 1000–1400 °C is generally turbostatic. X-ray powder pattern of composites (batch B) heat treated to 1000 and 1400 °C were plotted after expanding the 2θ scale from 42.6° to 44° and the same is given in Fig. 3. It is seen from this figure the intensity of the copper peak at $2\theta = 43.29°$ is found to decrease as the HTT is increased from 1000 to 1400 °C. This observation also supports the melting of the copper which starts above 1080 °C resulting in the loss of copper which in turn leads to reduced values of bulk density, bending strength and increased values of electrical resistivity and weight loss at temperatures above 1100 °C.

SEM analysis

The scanning electron micrographs of the C–Cu composites batch C (Cu/C ratio of 0.9) and batch G (Cu/C ratio of 1.5) heat treated to 1100 and 1400 °C are given in Fig. 4a–b in back scattered mode and Fig. 5a–c in secondary emission mode, respectively. The micrographs (Figs. 4a, 5a) show that the copper is distributed into the carbon matrix of the composites (heat treated to 1100 °C) and no clear interface between copper and carbon is visible in these composites. It is also seen from micrograph (Figs. 4b, 5b) that copper has melted on heat treatment of composites above 1100 °C leading to the formation of agglomerates (marked 'A' in Fig. 5b) of copper formed through flowing of copper on melting. This observation was confirmed by the EDAX analysis of the copper agglomerate shown in Fig. 5b and the EDAX pattern is given in Fig. 6 which shows mainly characteristic peaks of copper at 0.9 and

Fig. 6 EDAX analysis of C–Cu composite batch G (Cu/C weight ratio = 1.5) HTT to 1400 °C



8.1 keV. The voids seen in Fig. 5c in SEM studies supports our observation mentioned earlier under the subheadings characteristics of C–Cu composites and X-ray analysis that copper is lost through melting at temperatures above 1080 °C resulting in the deterioration of physical, mechanical and electrical properties.

Conclusion

Carbon–copper composites could be developed using CTP-based GC and commercial copper powder. The composites showed improved bulk density, bending strength and enhanced electrical properties up to the HTTs of 1100 °C in spite of lack of wettability between carbon and copper. The bending strength and bulk density decreases as HTT is increased above 1100 °C which is attributed to the melting and subsequent removal of copper in these composites.

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