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Evaluation of Cu-coated graphite compacts prepared by pulsed current activated sintering process

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Cu-coated graphite powder for weight reduction and a high thermal conductivity was fabricated using a chemical reaction process. First, 4 g of graphite powders, which was treated using an activation and wetting process, was added to an aqueous solution of copper (Cu) sulfate; also, zinc (Zn) powders (such as 35, 40, 45, and 50 wt.%) was added as a transposition solvent to the aqueous solution and stirred for 1 hr for a transposition reaction. After the addition of the fabricated powders mixture to a 75 wt.% DI water: 10 wt.% H₃PO₄: 10 wt.% H₂SO₄: 5 wt.% mixture, tartaric acid was added to the aqueous solution to produce a passivating oxide film, followed by a drying for 24 hrs. The particle size of the fabricated powder, which is coarser than the initial graphite powder, is approximately 3 μ m to 4 μ m, and the low-intensity oxide peak of the XRD pattern of the fabricated powders is due to the low Zn powder content. With the use of the Cu-coated graphite powder, Cu-coated graphite sintered bodies were fabricated using a pulse current activated sintering (PCAS) process. The Cu-graphite sintered bodies were evaluated using FE-SEM, EDS, XRD, a particle analysis, and the Archimedes method.

Key words: Chemical reaction process, Cu-coated graphite, Microstructures, Electric conductivity, Thermal conductivity.

Introduction

The information processing abilities for bulk storage and highly integrated electronics are greatly needed in industrial applications in terms of optical communications, photoelectrons, LEDs, and RF packages; however, the application components generate a large extent of heat compared to other applications. It is very important to effectively transmit and control heat for application performances. Components such as electric and electronic equipment accompany the electron movements; therefore, the more that the integration and high output are progressed, the more the amount of heat that is generated from the electric and electronic equipment. When the generated heat cannot be released rapidly, the heat-based deterioration of the outside of the electric and electronic equipment becomes severe, and the performance and lifetime of the corresponding product are drastically degraded, thereby reducing the reliability of the product [1-8]. To solve this problem, the heat is emitted conventionally using a heat-sink material made of copper (Cu), whereby an excellent thermal conductance is provided, and a metal material like aluminum (Al) is applied to the outside of the electric and electronic equipment. But, when a metal is used as the heat-sink

material, the material easily drops out due to the cracking that is caused by the difference of the thermalexpansion coefficient between the heat-sink material and the junction-base metal; consequently, the heat-sink material is welded to the part where the phenomenon is occurring, or the problem regarding the remarkable degradation of the product is excessively generated by the large mass, which is the metal-characteristic property that is due to the high thermal-expansion coefficient.

A non-metal-group inorganic material like silicon carbide (SiC) or aluminum nitride (AlN) is lightweight in comparison with aluminum (Al) or Cu, and the suitability regarding its use as a substrate material is confirmed by a low thermal-expansion coefficient. A disadvantage, however, is the thermal conductivity of such materials that is less than 200 W/mk; therefore, carbon (C)-base composite materials (e.g., C fibers, C nanotubes, graphite, etc.) are proposed to improve this problem.

In this paper, Cu-coated graphite powders was fabricated according to a chemical-reaction process, and Cu-coated sintered bodies were fabricated using a pulse current-activated sintering method to achieve a low thermal expansion coefficient and a high thermal conductivity. The Cu-coated graphite powder and compacts were evaluated using field-emission scanning electron microscopy (FE-SEM), energy dispersive Xray spectroscopy (EDS), X-ray diffraction (XRD), a particle analysis, and the Archimedes method.

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Experimental Procedure

In the chemical reaction process for which graphite powder (Qingdao Kropfmuehl, > 99.5%, d(0.5) 7.2 μ m) is used, the Cu is displaced from the Cu-sulfate solutions by zinc (Zn); regarding the involved mechanisms, a description is provided in [reference]. Briefly, the displacement of the Cu from the Cu-sulphate solution with the use of Zn-reducing agents can be achieved as follows:

$$CuSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Cu(s)$$
(1)

For the graphite powder coatings, the Cu-sulfate solution and glacial acetic acid (AcOH) are used. Upon the completion of the chemical reaction, the displaced metal ion (Cu²⁺) becomes neutralized; however, for a brief initial period, the charge of the Cu²⁺ is positive. After a reaction with acid, graphite powder typically comprises polar surface groups. In the present case, the graphite powder after the reaction with the AcOH comprises a carboxyl group (R-COOH), leaving the powder with a negative charge and coating the Cu²⁺ with the positive charge on the powder. The AcOH also maintains the activated state of the powder surface so that the coating is uniform [9].

Fig. 1 shows the FE-SEM image and XRD patterns of graphite powder, wherein the graphite powder is flake-shaped and only graphite phase peaks are evident. First, the 4 g of graphite powder was subject to an activation treatment in an electric furnace at 400 °C for 1 hr; this treatment barely affected the mechanical properties of the graphite powders within an experimental accuracy. The 4 g of graphite powder was then dipped in 2 ml of the AcOH to further improve the wettability of the graphite surface in relation to the metal that is to be coated. Subsequently, 600 ml of a 1 M Cu-sulfate solution was added to the activator bath, and a displacing agent (zinc powder) was added to displace the metal from the solution. The bath was stirred well to uniformly disperse the powders in the solution for 1 hr. The completion of the chemical-reaction process was indicated by the color changes of the solution and the powders. The Cu-coated graphite powder was then treated in an acid-stabilizer bath (75% D.I water + 10% $H_2SO_4 + H_3PO_4 + 5\%$ tartaric acid) for 20 min, thereby



Fig. 1. FE-SEM image and XRD pattern of graphite powder.

reducing the tarnishing of the coated Cu. The coated powders were washed thoroughly with water prior to an 80 °C drying. The uniformity of the coating was studied according to the microstructure, and the thickness of the coating layer was studied using a particle analysis. The compositions of the graphite and Cu were studied using EDS, and this was followed by the study of the phase of the Cu-coated graphite powder using XRD.

After the Cu was coated on the graphite powder by the chemical reaction process, the graphite powder was sintered by a pulse current activated sintering (PCAS) method. Fig. 2 shows a schematic diagram of the apparatus that was used for the PCAS process, which



Fig. 2. Schematic diagram of apparatus for PCAS process.



Fig. 3. Schematic representation of temperature, pressure and shrinkage displacement profile during PCAS process.

includes a 25 V, 1000 A dc-power supply (provided a pulsed current for 12 ms with an off time of 2 ms through the sample and the die) and a 10 ton uniaxial press. First, the system was evacuated, followed by the application of a standard uniaxial pressure. A DC pulse current was then activated and maintained until a negligible densification rate was obtained, as indicated by the observed shrinkage of the sample. The sample shrinkage was measured in real time using a linear gauge for the vertical displacement. The temperature was measured using a K-type thermocouple. Depending on the heating rate, the electrical and thermal conductivities of the compact, the relative density of the compact, and the temperatures on the surface and in the center of the sample could differ. The sintering-treatment heating rates are 60 °C, 100 °C, and 150 °C. After the temperature reached 600 °C, a uniaxial pressure of 60 MPa was applied. After the completion of the sintering treatment at 800 °C, the current was turned off, and the sample was allowed to cool to room temperature. The entire densification process for which the PCAS technique was used consists of the following four major control stages: chamber evacuation, pressure application, power application, and cool-down. The four major sintering stages are schematically shown in Fig. 3. The relative densities of the sintered samples were measured using the Archimedes method. The compositional and microstructural analyses of the compacts were studied by XRD and FE-SEM. The electronic conductivity was studied using a non-destructive tester, and the thermal conductivity was studied using the laser flash analysis (LFA) and differential scanning calorimetry (DSC).

Results and Discussion

For the particle analysis, 35 wt.%, 40 wt.%, 45 wt.%, and 50 wt.% reducing agents were used. The results of the particle analysis with the lowest reducing agent wt.%, 35 wt.%, shows an increase of the particle size of the Cu-coated graphite powder from the initial graphite particle size of d(0.5) 7.2 µm to d(0.5)12.6 µm; similarly, for the 40 wt.%, 45 wt.%, and 50 wt.% reducing agents, the size values of 13.4 µm, 12.9 µm, and 13.1 µm, respectively, are shown. The amount of the displacement in the aqueous solution according to the reducing-agent saturation is calculated as follows:

$$G_A = 100/(1 + (X_B M_B / X_A M_A)),$$
 (2)

where G_A is the weight percent of A, X_A is the atomic percent of A, X_B is the atomic percent of B, M_A is the atomic weight of A, and M_B is the atomic weight of B. Through the use of Eq. (2) here, a 35.7 wt.% reducing agent is supersaturated to the Cu, and this is the reason for the inconsistent progression of the displacement process.

2Theta Fig. 5. XRD patterns of Cu-coated graphite powders at different Zn contents; a) 35 wt.%Zn, b) 40 wt.% Zn, c) 45 wt.% Zn and d)

50 wt.% Zn.

Fig. 4 shows the microstructure images of the Cucoated graphite powder at different Zn contents wherein the Cu-coated particles are almost irregularly shaped. In the microstructure images, the bright area is the Cu and the dark area is the graphite; since the heavy elements (high atomic number) backscatter the electrons more strongly than the light elements (low atomic number), they appear brighter in microstructure images. The BSEs (backscattered electrons) are used to detect the contrast between the areas with different chemical compositions. Fig. 4 shows the uniform coating, but the Zn composition and a large quantity of oxygen were detected for the 40 wt.%, 45 wt.%, and 50 wt.% reducing agents, while the Cu contents are lower than that of the 35 wt.% reducing agent; this means that the reducing agents are supersaturated above 40 wt.%. The results of the microstructure and EDS analyses show that the Cu-coated graphite powder does not differ according to the quantity of the reducing agent, and the oxides increase the occurrence frequency, thereby increasing the impurity amounts.



Fig. 4. FE-SEM images of Cu-coated graphite powders at different Zn contents; a) 35 wt.%Zn, b) 40 wt.% Zn, c) 45 wt.% Zn and d) 50 wt.% Zn.



Fig. 5 shows the XRD patterns of the Cu-coated graphite powder for the different reducing agent quantities. As shown in Fig. 5, only the graphite (006) and Cu (111), (200), and (220) peaks were observed for the 35 wt.% reducing agent, indicating that no impurities were added during the chemical-reaction process. The case of the 40 wt.% reducing agent is similar to the 35 wt.% case, but also, the CuO (111) phase was detected since the reducing agents are slightly supersaturated. In the cases of the 45 wt.% and 50 wt.% reducing agents, the CuO (111), CuO (200), CuO (220), graphite (110), and Cu₂O (110) phases were detected. Also, the peak intensities of the Cu (111), Cu (200), graphite (006), and Cu (220) phases decreased quietly compared with those of the 35 wt.% and 40 wt.% reducing agents.

The XRD patterns show that beyond saturation reducing agents were added and the Cu oxides were fabricated, which decrease the powder properties. The grain size and the internal strain were calculated using the Stokes and Wilson's formula [10], as follows:

$$b = b_d + b_e = k\lambda /(d\cos\theta) + 4\varepsilon \tan\theta, \qquad (3)$$

where *b* is the full width at half-maximum (FWHM) of the diffraction peak after the instrumental correction; b_d and b_e are the FWHM for a small grain size and a low internal strain, respectively; *k* is a constant (with a value of 0.9); λ is the wavelength of the X-ray radiation; *d* and ε are the grain size and the internal strain, respectively; and θ is the Bragg angle. The parameters *b* and *bs* follow Cauchy's form according to the following relationship: $B_0 = b + b_s$; here, B_0 and b_s are the FWHM of the broadened Bragg peaks and a standard sample's Bragg peaks, respectively. The approximate average grain sizes of the Cu-coated graphite powder for the different reducing agents increased gradually, as follows: 3.27 µm, 3.48 µm, 3.06 µm, and 3.02 µm.

The variations of the shrinkage displacement and the temperature with the change of the heating rate during the sintering of the Cu-coated graphite powder for which the PCAS process was used are shown in Fig. 6. When an electric current was applied, the shrinkage displacement increased by up to 550 °C, and then abruptly, the shrinkage displacement was nearly constant at above that temperature. When the temperature reached approximately 800 °C, the densification rate became nearly negligible, and the samples densified to the almost-theoretical density of approximately 1,080 sec, as will be further discussed below. The sintered relative densities of the 60 °C/min, 100 °C/min, and 150 °C/min heating rates are 6.722 g/cm³, 6.673 g/cm³, and 6.348 g/ cm³, respectively. These results are attributed to two causes. First, because a high Joule heating occurs at the point of contact between the particles due to an induced current, the spread of the atoms is accelerated; in addition, the performance of the sintering at a low temperature is



Fig. 6. Variation of shrinkage displacement of Cu-coated graphite compacts with sintering temperature and sintering time during PCAS process under 60 MPa at 800 °C.

considered as easier because the spread of the atoms is accelerated in an electric field. Second, when pressure is applied during the sintering, the driving force of the sintering is increased; Eq. (2) shows the increased driving force, F, as follows:

$$F_{\rm D} = \gamma + (P_{\rm a}r/\pi), \tag{4}$$

where γ is the interfacial energy, and Pa and r are the applied pressure and the particle radius, respectively. Consequently, these results suggest that, compared with the conventional sintering processes, the most obvious advantages of the PCAS process are faster heating rates, shorter processing times, and relatively lower temperatures during the sintering, all of which allow for the limitation of the grain growth and clean grain boundaries [11, 12].

Fig. 7 shows the FE-SEM images of the polished surfaces for the sample that was heated to 800 °C at a pressure of 60 MPa. As shown in Fig. 7, for each of the heating rates, the microstructure in the FE-SEM images consists of the nanophases of the graphite and the copper grain. The abrupt increase of the shrinkage displacement at the ignition temperature is due to the density increase that is the result of the change of the molar volume that is associated with the formation of the consolidated Cu-coated graphite sintered bodies.

Fig. 8 shows the XRD patterns of the Cu-coated graphite sintered bodies after the PCAS process. All of the peaks are those of Cu and graphite and impurities are nonexistent. The average grain sizes of the Cu-coated-graphite sintered bodies at the different heating rates are approximately $4.74 \,\mu\text{m}$, $4.83 \,\mu\text{m}$, $4.59 \,\mu\text{m}$, and



Fig. 7. FE-SEM images of Cu-coated graphite compacts sintered at different heating rate during PCAS process; a) 60 °C/min, b) 100 °C/min, and c) 150 °C/min.



Fig. 8. XRD patterns of Cu-coated graphite compacts sintered at different heating rate during PCAS process; a) 60 °C/min, b) 100 °C/min and c) 150 °C/min.



Fig. 9. Electronic conductivity of cu-coated graphite compacts sintered at different heating rate during PCAS process; a) 60 °C/ min, b) 100 °C/min, and c) 150 °C/min.

4.65 mµ. The grain of the Cu-coated graphite powder, however, shows a fine structure that was obtained without any grain growth during the PCAS process.

The electrical conductivity of the Cu-coated graphite

 Table 1. Thermal conductivity Cu-coated graphite compacts sintered at different measuring temperature.

Measuring temperature (°C)	Diffusivity (mm ² /s)	Specific heat (J/gK)	Thermal condzuctivity (W/mK)
Room temperature	38.02	0.46	110.17
50°C	36.49	0.46	108.18
100°C	34.64	0.48	107.13

sintered bodies at different heating rates is shown in Fig. 9, wherein the conductivity, with a minimum of approximately 38, increases slightly to a maximum of approximately 43 with the decreasing of the heating rate. The reason for this behavior is the nearly linear increase of the relative density of the Cu-coated graphite from 6.348 g/cm^3 to 6.722 g/cm^3 , whereby the electron path was closely made for a fast motion.

The thermal conductivity of the Cu-coated graphite sintered bodies at the 60 °C/min heating rate for different measuring temperatures is shown in Table 1. The thermal conductivity equation is as follows:

$$\mathbf{K} = \mathbf{a}^* \mathbf{C}_{\mathbf{p}}^* \boldsymbol{\rho},\tag{5}$$

where a is diffusivity (mm²/s), C_p is specific heat, and ρ is density [13]. The highest density of the Cu-coated graphite sintered bodies for the 60 °C/min heating rate was measured according to the thermal conductivity. While the highest thermal conductivity was achieved at room temperature, the thermal conductivity of another sintered body is almost similar; therefore, regarding the Cu-coated graphite sintered bodies, a uniform thermal conductivity can be achieved at any temperature.

Conclusions

The results of the particle size analysis show that the particle size of the Cu-coated graphite powder for the 35 wt.% reducing agent, the lowest wt.% reducing agent, is d(0.5) 12.6 µm; however, the sizes for the 40 wt.%, 45 wt.%, and 50 wt.% reducing agents are similar to that of the 35 wt.% at 13.4 µm, 12.9 µm, and 13.1 µm, respectively. The XRD patterns show that only the graphite (006) and Cu (111), (200), and (220) peaks were observed for the 35 wt.% reducing agent, since 35 wt.% is the most favorable reducing agent condition. The sintered densities of the 60 °C/min, 100 °C/min, and 150 °C/min heating rates are 6.722 g/ cm³, 6.673 g/cm³, and 6.348 g/cm³, respectively. The electronic-conductivity results, for which the sintered bodies of the 60 °C/min, 100 °C/min, and 150 °C/min heating rates were used, show that the lowering of the heating rate resulted in a gradual increase of the electronic conductivity. The thermal-conductivity results of the sintered body that was fabricated at the 60 °C/ min heating rate show an increase from 107 w/mK (measuring temperature of approximately 100 °C) to 110 w/mK (measuring temperature of approximately room temperature).

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