International Journal of GEOMATE, Sept., 2019 Vol.17, Issue 61, pp. 122-128
ISSN: 2186-2982 (P), 2186-2990 (O), Japan, DOI: https://doi.org/10.21660/2019.61.4816
Special Issue on Science, Engineering & Environment

PRODUCTION OF HIGH PURITY Cu MICROPARTICLES AND DEVELOPMENT OF CONDUCTIVE PAINTS USING ELECTROSTATIC COLLOID SOLUTION

Junya Kuroda[1], Risa Uda[1], Honoka Tanabe[1], Kimihiro Yamanaka[1] and *Hirohisa Taguchi[1]

[1]Department of Electrical and Electronic Engineering, School of Engineering, Chukyo University, Japan

*Corresponding Author, 15 Dec. 2018, Revised: 17 Jan. 2019, Accepted: 05 Feb. 2019

ABSTRACT: In recent years, metal microparticles made of Au or Ag have attracted attention as intermetallic bonding materials and low resistance materials of fine interconnects. It is also known that the electron cloud localized on the fine surface of the fine particles has a catalytic effect, and researches on chemical reaction accelerators are being advanced. However, Au and Ag have high material cost, not economical materials. Furthermore, Ag is extremely easily oxidized, and there is a problem in durability of the catalytic effect in the solution. In this research, we considered Cu microparticle formation by Cu three - dimensional tree structure (Cu dendrite). Cu has high electrical conductivity and less oxidizable than Ag. It has an extremely high economic advantage compared with Au. We have succeeded in making high purity Cu dendrites by our previous studies. This Cu dendrite was broken in an aqueous solution using ultrasonic waves. As a result, Cu fine particles having a diameter of about 1 to 10 μm were successfully formed. We also reported that this fine particle was impregnated into a water-soluble paint and succeeded in forming a printer ink with electrical conductivity. Further, by impregnating the methylene blue and Cu dendrite particles are an electrostatic colloidal solution, it was constructed conductive micelles strictures. As a result, we succeeded in strengthening the structure of printed matter using Cu dendrite microparticles.

Keywords: Microparticles, Cu dendrite crystal, Conductive printer ink, Electrical conductivity

1. INTRODUCTION

In recent years, metal microparticles made of Au or Ag have attracted attention as intermetallic bonding materials and low resistance materials of fine interconnects [1]. Metal fine particles typified by Au fine particles are expected to be applied to fields with high added value such as agricultural chemicals in the pharmaceutical field [2]. In addition, in-vehicle exhaust gas treatment and application to fuel cells are under consideration [3]. By atomization, the maximum scientific reaction characteristics can be obtained with minimum precious metal usage [4]. It is also known that the electron cloud localized on the fine surface of the fine particles has a catalytic effect, and researches on chemical reaction accelerators are being advanced [5]. The chemical reaction catalyst forms a reaction intermediate with the reactant. This creates another reaction path with low activation energy required for the reaction [6]. The catalyst itself does not directly participate in the chemical reaction, and itself does not accompany chemical change before and after the reaction. Also, in catalytic effect on metal fine particles, the metal fine particles only supply electrons which are reaction factors from the metal surface in the reaction path, and there is no change in the form of itself. Terminating the reaction pathway in the process of chemical reaction in equilibrium, but only lose catalytic activity as a result[7]. The mainstream of these metal fine particle production methods is a chemical reduction method [8]. A metal salt or a complex is synthesized, and a metal element is precipitated using a reducing action. Finally, it is a technique to obtain nano-sized aggregates by clustering. Using this method, commercial metal nanoparticles are already present. The disadvantage of the chemical reduction method is the precipitation of metallic elements [9]. The precipitated metal element needs to be clustered. The particle diameter formed in this way is the limit of about 1 μm. It fulfills the purpose in utilizing the special surface catalytic effect of metal nanoparticles [9]. However, considering the development of conductive paste and paint, the yield of nanoparticles is important [10]. Chemical reduction forms a reliable metal nanoparticle, but the yield is not high [8]. Another method of forming fine metal particles is a physical generation method from bulk metal. This is called a pulverization method, and it is simply a method of grinding a metal bulk to obtain fine particles. In this method, it is considered difficult to reduce the particle diameter and unify the particle shape [12]. Also, since noble metals such as Au, Ag, Cu have extensibility, physical fracture simultaneously promotes foil formation [13].

In this study, the physical grinding method of high purity Cu dendrite crystal was investigated in order to form Cu fine particles with high industrial utilization

value in high yield and low cost. High purity Cu dendrite crystals were formed by using copper sulfate solution by the application of the plating method. By the method shown in this research, it was possible to form a purity of 99% or more for Cu dendrites, which was a structure containing many impurities so far. Cu dendrite crystals having a tree structure can be obtained. The Cu dendrite crystals can be easily peeled off from the plated substrate. After peeling, Cu dendrite crystals were subjected to ultrasonic vibration in ethanol. As a result, it was physically pulverized to form fine particles with a particle size of 1 to 10 μm. Then we investigated the formation of conductive ink by impregnating the fine particles into the printer ink. Further, by impregnating the methylene blue and Cu dendrite particles are a chargeable colloidal solution, it was constructed conductive micelles strictures. As a result, we succeeded in strengthening the structure of printed matter using Cu dendrite microparticles.

2. EXPERIMENTAL METHOD

2.1 High Purity Cu Dendrite Crystal Formation Method

Figure 1 shows the experimental system schematic used in this study. Basically, the Cu plating method is used. In our previous study, it is known that Cu plating on Zn/Al alloy in concentrated copper sulfate solution forms Cu dendrite structure including Cu/Zn alloy due to poor plating formation [14,15]. In this method, an oxygen-free copper plate placed above the part where Cu dendrite was formed. A gap of 0.4 mm in thickness was formed in order to arrange an oxygen-free copper plate. Since the concentrated copper sulfate solution can penetrate the gap of 0.4 mm, it is possible to form Cu dendrite by the inter-electrode voltage. The copper sulfate solution used was in a supersaturated state. The experimental system was set in the supersaturated copper sulfate solution, and the electroless state was maintained for 5 minutes. In order to provide enough supersaturated copper sulfate solution to the gap 0.4mm oxygen-free copper plate and Zn/Al alloy plates. After that, the power supply was adjusted so as to obtain a current at 40mA for 10 minutes to grow a Cu dendrite structure. The upper electrode plate used in this experiment was an oxygen-free copper plate used for the Hull cell test.

2.2 Cu Fine Particle Formation Method

High purity Cu dendrite crystals formed by the method is a structure entangled two-dimensional growth surface and the three-dimensional growth portion. Figure 2 shows the Schematic diagram of Cu Fine Particle Formation. Dynamically, it has strength enough to pick up a face with tweezers, but this is caused by entanglement of two-dimensional structure

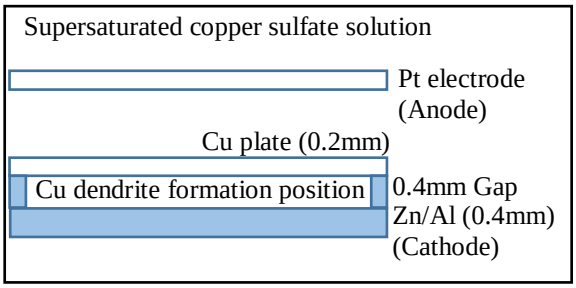


Fig. 1 Schematic diagram of high purity Cu dendrite crystal formation experiment system based on Cu plating method.

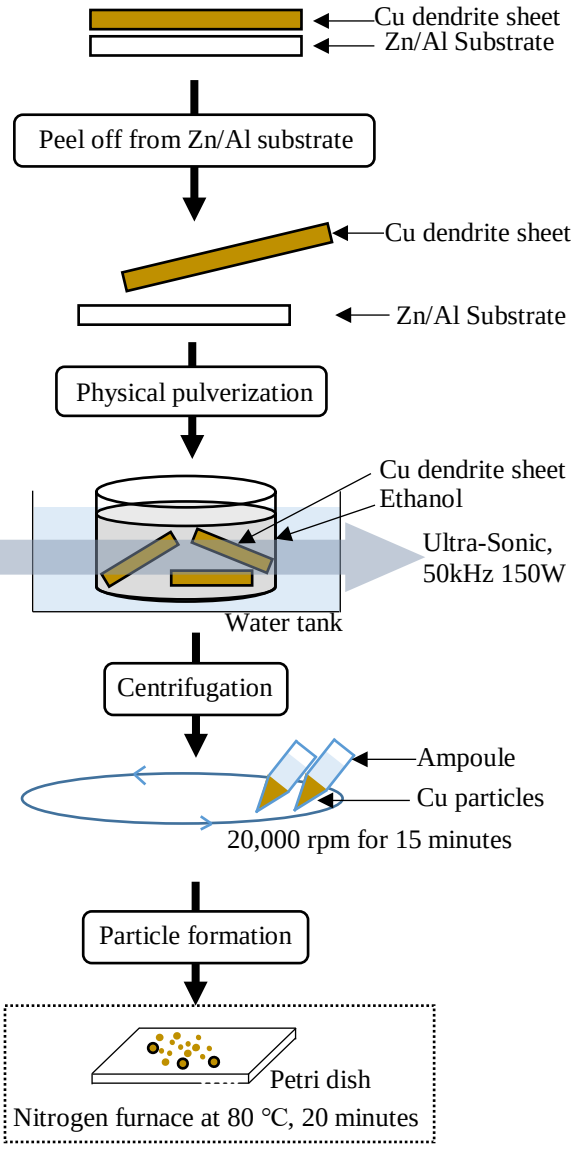


Fig. 2 Schematic diagram of Cu fine particle formation

and three-dimensional structure. Further, since the ZnO crystal is present as a fragile structure on the surface of the growth substrate, it is possible to peel

the Cu dendrite crystal face from the substrate simultaneously and during cleaning in the purified water. The peeled Cu dendrite thin film was held in ethanol, and physical pulverization was carried out using ultrasonic waves of a frequency of 50 kHz and an output of 150 W. After grinding, the water surface of the solution was placed in a dropper, and separation of Cu particles and ethanol was carried out with a centrifuge at 20,000 rpm for 15 minutes. The separated Cu fine particles were transferred to a petri dish, kept in a nitrogen furnace at 80 ° C for 20 minutes to evaporate the ethanol, and particle shape observation was carried out by SEM.

2.3 Conductive Printer Ink Formation

It was investigated to develop a conductive ink as a practical application of Cu particles obtained in this study. Commercially available non-conductive printer ink was impregnated with the Cu fine particles indicated by the above method and dried on the insulating sheet with this ink [16].

As a method of conducting ink, it was also a colloidal solution of copper particles. The methylene blue dye solution, known as the chargeable colloidal solution was mixed copper dendrites particles. Copper particles and methylene blue colloid aggregate to form an electrostatic micelle colloid. The shape of the micelle colloid depends on the original Cu particle diameter. The micelle colloid also becomes huge according to the enlargement of the particle diameter. When planarized under this condition, it becomes a sparse structure. According to the miniaturization of the particle diameter, a dense structure can be constructed by flattening. The Cu fine particle diameter is closely related to the electrical resistance of printed matter. Bonding force at the two-dimensional directions by micellization is enhanced. The expected effect is to have sufficient conductivity at the time of deformation while maintaining conductivity during printing.

Example of two-dimensional branch lobular crystals

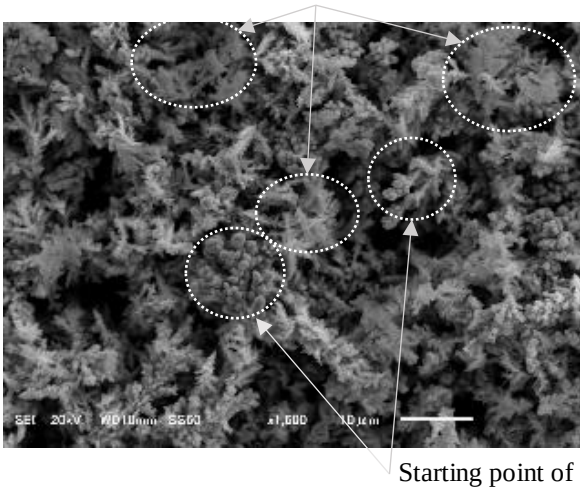


Fig. 3 The SEM image showing simultaneous growth state of two-dimensional crystal and three-dimensional crystal in Cu dendrite.

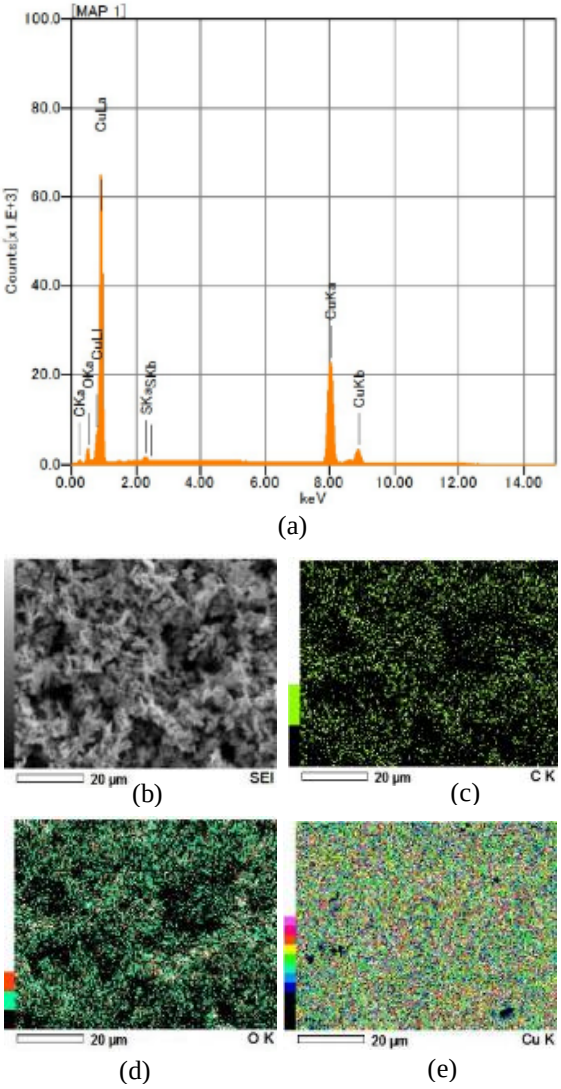


Fig. 4 The surface atomic distribution image and XDS spectrum.

(a) XRS spectrum (b) SEM image
(c) Carbon surface distribution
(d) Oxygen surface distribution

3. RESULTS AND DISCUSSION

3.1 High Purity Cu Dendrite Crystal

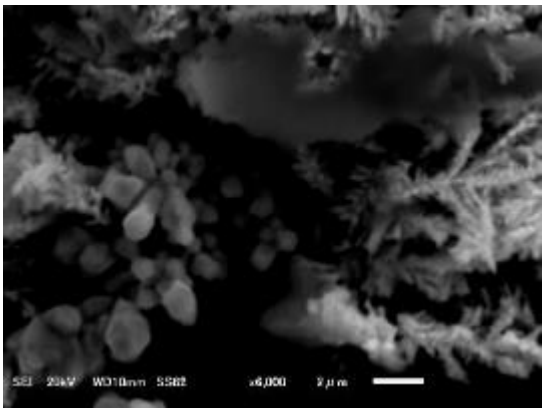
It was placed oxygen-free copper plate directly above the growth surface by Cu dendrite formation process. This effect will be described below. The field effect of the free electron group in the oxygen-

free copper plate inhibited peeling of Zn fragments and upward movement of Zn fragments occurring simultaneously with Cu plating growth. The electric field effect of this oxygen-free copper plate also affected Cu dendrite structure formation. In the previous method, it was three-dimensional growth from the beginning. In the early stage of Cu dendrite crystal growth by this method, two-dimensional planar growth was carried out, and a structure in which branches and leaves extended laterally was formed. However, Cu plating is stably formed at the Al site at the lower part of the plane growth surface, and longitudinal growth is performed. The Cu dendrite structure shown in figure 3 was constructed according to the experimental chart shown in figure 1. The experimental system shown in figure 1 was constructed in the supersaturated copper sulfate solution. In the beginning, it was left for 5 minutes in the electroless state. It is an object of the supersaturated copper sulfate solution be sufficiently impregnated in the gap of 0.4 mm. After that, Cu dendrite was constructed by fixing the inter-electrode current at 40 mA and holding for 10 minutes. After construction, it was washed with ultrapure water to remove sulfate ions. And dried at 80 °C for 20 minutes in a heating furnace in an N_2 atmosphere.

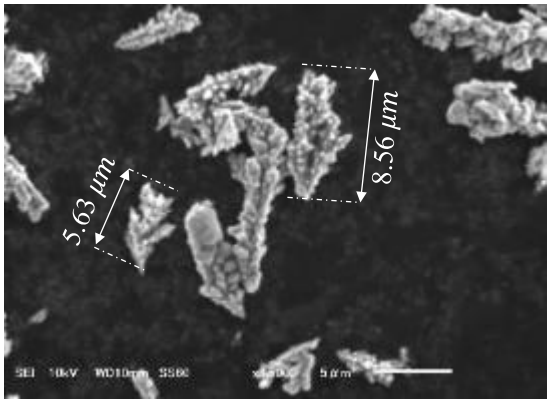
In figure 3, it shows an SEM image in which the two-dimensional growth and the three-dimensional growth surface are simultaneously grown. Although lateral growth of Cu dendrite crystals is confirmed on almost the entire surface, longitudinal growth of granular crystals is confirmed in the part. In the Cu dendrite obtained by the above method, since the longitudinal transport of Zn was inhibited, the Cu concentration reached 99% level. Figure 3 shows the surface atomic distribution image and XDS spectrum. The Cu dendrite surface on which the XDS analysis shown in the figure. 4 was performed is the same as that shown in figure 3. In the surface atomic distribution, Cu or C is mainly observed. Since C and O ware a carbon tape for SEM observation, it means that most of the observed substance was Cu. Both the XRD spectrum and the Cu - kα line lay Cu - lα ray as the main and there were no other atoms other than C observed. As a result, it can be said that the formation of high purity Cu dendrite crystals was successful.

Formation of fine Cu particles

The Cu fine particles obtained by SEM observation are shown in figure 5. The particle shapes are different, and the particle diameter also varies from 1 to 10 μm, but it was found that the particle formation at the μm level was successful. It was found that the shape of the fine particles differs from the granular shape or the plate shape. Basically, because it is a method derived from the pulverization method, it was confirmed that control of both particle size and particle shape is difficult with this method [17]. However, in this method, since all of the obtained Cu dendrite crystals are subjected to a pulverization method, it is possible to atomize all of the Cu dendrite crystals formed.



(a)



(b)

Fig. 5 The Cu fine particles obtained by SEM observation

(a) Granular crystals and branched lobular crystals
(b) SEM image of branch lobe grains

3.2 Conductive Printer Ink Formation

In order to study the industrial application of Cu fine particles prepared in this study, the formation of conductive ink was carried out. Printer ink impregnated with fine Cu particles was measured by a four-terminal method to obtain electric resistivity. Multiple samples were formed to obtain resistivity $4.22*10^{-5}\Omega$-m. However, it was confirmed that the resistivity is about 10 times in some samples. This indicates that there is a dispersion in Cu fine particles that realizes conductivity. It is necessary to study in the future to have good dispersion.

Overview photograph of mixing the methylene blue and copper dendrite particles shown in figure 6. The blue color of methylene blue and the color of copper particles were mixed, and it became a brown print. Figure 7 shows SEM observation of the sample after printing. It could be confirmed as methylene blue colloid was coated with Cu. In the EDS analysis

Fig. 6 Overview photograph of mixing the methylene blue and copper dendrite particles

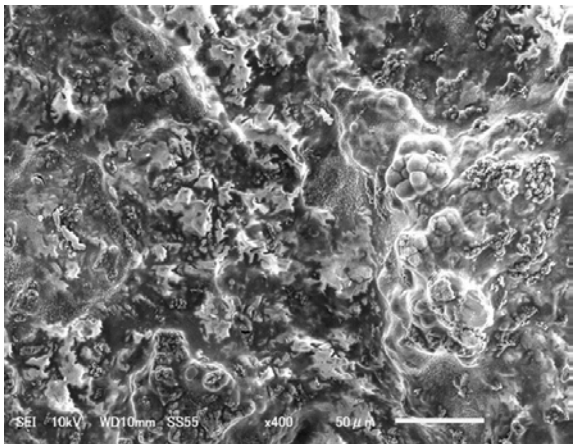


Fig. 7 The SEM image showing mixing the methylene blue and copper dendrite particles

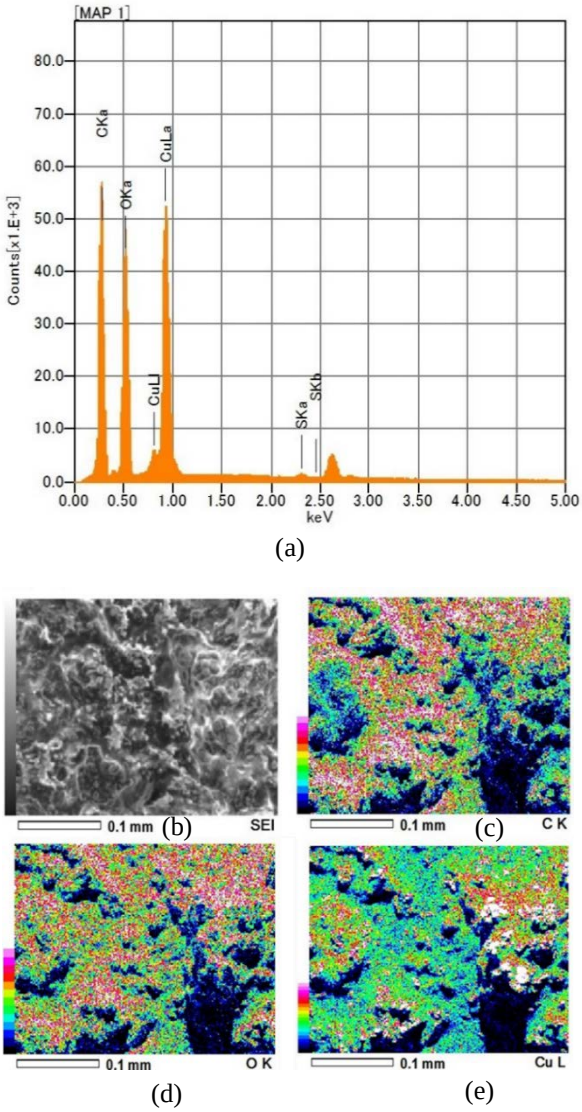


Fig. 8 The surface atomic distribution of mixing the methylene blue and copper dendrite particles and XDS spectrum

of Figure 8, carbon is overlapped and detected in the area where Cu is distributed. As shown in the EDS spectrum of figure 8 (a), sharp peaks of carbon and oxygen are confirmed. It is a clear organic matter spectrum [18]. Thus, the observation object is mixed Cu and organics. In mass%, carbon was 45.5%, oxygen was 30%, and Cu was 24%. We succeeded in micelle formation and structure strengthening of expected methylene blue and Cu particles. However, the resistivity of this sample was about $10^{-1}\Omega$-m by the four-terminal method. Methylene blue is a positively charged stain. Therefore, it repelled with the copper particle Cu^{2+} in the solution, and it does not contribute to decrease in resistivity.

4. CONCLUSIONS

In this research, we got the following conclusion. When placing an oxygen-free copper plate above the

(a) XRS spectrum (b) SEM image
(c) Carbon surface distribution
(d) Oxygen surface distribution
(e) Cupper surface distribution

Cu dendritic growth portion, upward movement of Zn fragments derived from the Zn/Al substrate was inhibited, and as a result, it was found that high purity Cu dendrite crystals could be formed. Next, by executing ultrasonic pulverization of this Cu dendrite crystal in ethanol, it is possible to convert all of the produced high purity Cu dendrite crystal into fine particles having a particle size of about 1 to 10 μm. Finally, by imprinting fine particles formed by this method into printer ink and executing printing, succeeded in forming printed matter with conductivity although there was a deviation between samples. Further, by impregnating the methylene blue

and Cu dendrite particles are an electrostatic colloidal solution, it was constructed conductive micelles strictures. As a result, we succeeded in strengthening the structure of printed matter using Cu dendrite microparticles.

5. ACKNOWLEDGMENTS

The authors are grateful to the Chukyo University Research Found for financial assistance with this research. This work was supported by JSPS KAKENHI Grant Number 18K040272.

6. REFERENCES

[1] Garci C. C., Murtazin A., Groh S., Horvatica V., and Niemaxa K., Characterization of single Au and SiO2 nano- and microparticles by ICP-OES using monodisperse droplets of standard solutions for calibration, Journal of Analytical Atomic Spectrometry, No. 25, 2010, pp.645-653.

[2] Adschiri T., Hakuta Y., and Arai K., Hydrothermal Synthesis of Metal Oxide Fine Particles at Supercritical Conditions, Industrial & Engineering Chemistry Research, Vol. 39, No. 12, 2000, pp. 4901-4907.

[3] Morawsk L., Ristovski Z., Jayaratne E. R., Keogh D. U., Ling X., Ambient nano and ultrafine particles from motor vehicle emissions: Characteristics, ambient processing and implications on human exposure, Atmospheric Environment, Vol. 42, No. 35, 2008, pp. 8133-8138.

[4] Zhang J. F., Zhou Y., Yoon J. and Kim J. S., Recent progress in fluorescent and colorimetric chemosensors for detection of precious metal ions (silver, gold and platinum ions), Chemical Society Reviews, Vol.9, 2013, pp.4738-4761.

[5] Kikuta T., Uchino T., Akao N., Akahoshi Y., Koura T., Development of Micro-Particles Accelerator with Pulse Formation, Procedia Engineering, Vol. 103, 2015, pp. 279-286.

[6] Daszkowski T., Eigenberger G., A reevaluation of fluid flow, heat transfer and chemical reaction in catalyst filled tubes, Chemical Engineering Science, Vol 47. No. 9, 1992, pp. 2245-2250.

[7] Zhang J., Vukmirovic M. B., Xu.Y., Mavrikakis M., Adzic R. R., Controlling the Catalytic Activity of Platinum-Monolayer Electrocatalysts for Oxygen Reduction with Different Substrates, Angewandte Chemie, Vol. 117, 2005, pp. 2170-2173.

[8] Giro-Paloma J., Martínez M., Cabeza L. F., Fernández A. I., Types, methods, techniques, and applications for microencapsulated phase change materials (MPCM), Renewable and Sustainable Energy Reviews, Volume 53, 2016, pp.1059-1075.

[9] Muhaimin M., and Bodmeierb R., Effect of solvent type on the preparation of ethylcellulose microparticles by solvent evaporation method with double emulsion system using focused beam reflectance measurement, Polymer International, Vol. 66, Iss. 11, 2017, pp.1448–1455.

[10] Inoue M., Itabashi Y., Tada Y., Development of bimodal electrically conductive pastes with Ag micro- and nano-fillers for printing stretchable E-textile systems, Proc. of European Micro-electronics Packaging Conference, 2015.

[11] Dichiara A. B., Yuan J., Yao S., Sylvestre A., Zimmer L., and Bai J., Effective synergistic effect of Al_2O_3 and SiC microparticles on the growth of carbon nanotubes and their application in high dielectric permittivity polymer composites, Journal of Materials Chemistry A, No. 2, 2014, pp.7980-7987.

[12] Lee J. G., Kim D. Y., Kim T. G., Lee J. H., Deyab A., Lee H. W., Kim J. S., Yang D. H., Yarin A. L., Yoon S. S., Supersonically Sprayed Copper−Nickel Microparticles as Flexible and Printable Thin‐Film High‐Temperature Heaters, Advance Materials Interfaces, No. 4, 2017, pp.1700075(1-8).

[13] Torresdey J. L. G., Parsons J. G., Gomez E., Peralta J., Troiani H. E., Santiago P., and Yacaman M. J., Formation and Growth of Au Nanoparticles inside Live Alfalfa Plants, Nano Letters, 2002, Vol.2, No. 4, pp 397–401.

[14] Xiao Y., Li M., Wang L., Huang S., Du X., Liu Z., Interfacial reaction behavior and mechanical properties of ultrasonically brazed Cu/Zn–Al/Cu joints, Materials and Design, NO. 74, 2015, pp. 42-49.

[15] Wu Z. G, Sandlöbes S., Wu L., Hu W., Gottstein G., Kerzel S. K., Mechanical behavior of Zn–Al–Cu–Mg alloys: Deformation mechanisms of as-cast microstructures, Materials Science and Engineering A, Volume 651, No,10, 2016, pp. 675-687

[16] Natori A.Y., Canestraro C.D., Roman L.S., and Ceschin A.M., Modification of the sheet resistance of ink jet printed polymer conducting films by changing the plastic substrate, Materials Science and Engineering: B Vol. 122, Issue 3, 2004, pp 231-235.

[17] Richard S., Rajadurai J. S., Manikandan V., Influence of particle size and particle loading on mechanical and dielectric properties of biochar particulate-reinforced polymer nanocomposites,

International Journal of Polymer Analysis and Characterization, Vol. 21, No. 6, 2016, pp.462–477.

[18] Wang X., Zhou W., Liang G., Song D., Zhang X., Characteristics of maize biochar with different pyrolysis temperatures and its effects on organic carbon, nitrogen and enzymatic activities after addition to flavor-aquic soil, Science of The Total Environment, Vol. 538, No.15 2015, pp.137-144.