

Effect of the Surface State of Particle and the Polyol Decomposition on the Copper Nanoparticle Sintering Process

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ABSTRACT

It is well known that the metal nanoparticle features a melting point depression as opposed to the bulk metal material because of the size effect. It is possible for the metal nanoparticle to sinter at a relatively low temperature and we are interested in the metal nanoparticle as a conductive material for the printed electronics applications. This study investigated the effect of the surface state of the copper nanoparticles and the polyol decomposition on the copper nanoparticle sintering process using the copper particle because of its advantageous cost and the polyol as the typical solvent. When the oxidation degree of the copper nanoparticle was low, the ketones were detected as the decomposition material, and since the ketones have a weak reduction capability, the effect of the nanoparticle on the sintering of the copper nanoparticles was low. However, in the case of the higher oxidized copper nanoparticles, the carboxylic acids were detected as the decomposition material, which had a leaching effect and the copper oxide was reduced in association with the decomposition process, the effect on the sintering of the copper nanoparticle was high. The optimization of the oxidation degree of the copper nanoparticle and the interaction between the oxidized copper nanoparticle and the polyol accelerated the grain growth of the sintered particles and the electric resistivity decreased. The crack in the obtained sintered film decreases. The oxidation degree is one of the most important factors for the development of the copper nanoparticles in the future.

1. INTRODUCTION

It is known that the metal nanoparticle shows many different characteristics from the bulk materials. One of the characteristics is to increase the influence of the surface energy on the stability of the condition. The ratio of metal atom existing on the surface increases with the decrease of the particle radius, and the stability of the condition is not determined by the volume free energy but the surface energy. It displays some characteristics, such as the drastic depression of the apparent melting point, the improvement of the activity of the catalyst, etc. On the other hand, the increment of the surface area with the size miniaturization favors an easy aggregation of particles, an easy oxidation, and an easy sedimentation of particles. The size and the stability of each particle are needed for the utilization of the metal nanoparticle.

The synthesis of metal nanoparticles and the optimization of the size have progressed recently and the conductive materials to be utilized in the printing electronics are being developed. The gold, the silver and the copper are investigated as the conductive material¹⁾⁻³⁾. We are interested in the copper, because it is cheap in cost and has a high resistance to the ion migration⁴⁾. It is well known that

the sintering behavior of the copper nano particles is affected not only by size but by the surface state or by the oxidation degree. The copper nanoparticles are required to sinter and to prevent them from oxidation at the same time in the case of using as the electric conductive material during the heating process. The sintering between particles decreases the electric resistivity because of the forming the conductive path, but the oxidation of the particles increases the resistivity. A lot of researchers pursued capping the copper surface with the organic protecting materials to prevent it from the oxidation. The process needed to sinter the particles in a reducing atmosphere such as the hydrogen or the formic acid atmosphere^{5), 6)}, following to remove the organic protector on the surface by oxidation sintering efficiently. However it is shown that there are some problems to use the hydrogen or the formic acid in the practical use or the safety perspective, and the cost is high to build a specific sintering furnace and the exhaust apparatus.

Among its characteristics, in Furukawa Electric the development of a copper nanoparticles is being advanced to adopt to reducing atmosphere less sintering by reduction of the surface protecting agent on particles. Our developed copper nanoparticles are expected to provide the high electric conductivity by utilizing the copper nanoparticles paste combined with the solvent having the

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reduction capability.

This paper reported the analysis of the sintered process on the copper nanoparticles, which had the different surface state and the degree of oxidation, and the polyol was used as the solvent because of its reduction capability. In the previous study, it was effective to use the copper nanoparticle paste composed of the copper nanoparticle and the polyol system for sintering the copper nanoparticles, because the polyol was decomposed at low temperature with the catalysis effect of the copper⁷⁾. However the mechanism of the above reaction is still unknown, the effect of the reaction between the copper nanoparticles and the polyol on the sintering of the particle was investigated.

2. EXPERIMENT

2.1 Material

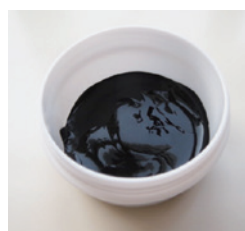
The copper nanoparticles used for the experiment were synthesized at the different conditions and the average radius, the degree of oxidation and the surface modification amount (the content of carbon) on the particles were shown in Table 1. The average radius of the particles was measured with the scanning electron micrograph (SEM), the diffraction strength ratio of Cu₂O (111) and Cu (111) measured with the X-ray diffraction (XRD)⁹⁾ was evaluated as the degree of oxidation, and the surface modification on the particles was analyzed with the Infrared carbon-sulfur absorption spectrometer.

Table 1 Copper nanoparticles in detail.

No.	Particle	Average particle diameter (nm)	Oxidation degree (ICu ₂ O/ICu)	Carbon content (mass %)
1	Nanoparticle A	23	0.15	0.66
2	Nanoparticle B	30	0.05	0.19
3	Nanoparticle C	20	0.51	1.45
4	Nanoparticle D	25	0.5	0.49

2.2 The Analysis of the Decomposition Process of the Solvent

The copper nano paste was prepared by the dispersion of the copper nanoparticles in the polyol solvent. The appearance of the paste was shown in Fig.1. The glycerin was used as the typical polyol in the experiment. The copper nanoparticles paste was picked in the pyro foil for heating and baked at several heating conditions, and the generating components were analyzed. The measurement condition in detail was shown in Table 2.1 and 2.2.



Paste	Copper nanoparticle paste
Solvent	Glycerin
Solid component	50 mass %
Atmosphere	Nitrogen
Sintering time	10 min.
Sintering temperature	250°C

Figure 1 Furukawa Electric copper nanoparticles.

Table 2.1 Condition of the pyrolysis (Py) measurement.

Apparatus	Japan Analytical Industry Co. Curie Point Pyrolyzer JCI-22
Heating method	High frequency induction heating
Sample weight	2 mg
Pyrolysis condition	160°C × 15 sec 220°C × 15 sec 280°C × 15 sec
Carrier gas	Helium
Preheating	150°C

Table 2.2 Condition of Gas chromatography mass spectrometer (GC/MS) measurement.

Apparatus	Thermo Electron Co. TRACE GC ULTRA / TRACE DSQ
Column	Thermo Electron Co. TR WAX 30 m, 0.25 ml D=0.25 μm
GC program	40°C (4 min) → 10°C / min → 250°C (10 min)
Ionization method	Electron Ionization (EI) method
Ion source temperature	250°C
MS transfer line temperature	300°C
Detecting method	Full Scan (m/z=33 ~ 500)

The copper nano paste was coated on the glass substrate to investigate the effect of the reaction between the copper particles and the polyol on the sintering of the particles. The coated paste was heated in the nitrogen atmosphere and the sintered film was obtained. We investigated the relationship between the electric resistivity of the sintered film and the sintered state measured with the SEM.

3. RESULT

3.1 The Analysis of the Thermal Decomposition of the Copper Nanoparticles With the Pyrolysis-gas Chromatography-Mass Spectrometry (Py-GC/MC)

The thermal decomposition components for the paste of the copper nanoparticles B detected with the Py-GC-MS at 160, 220 and 280°C were shown in Fig.2. The ketones,

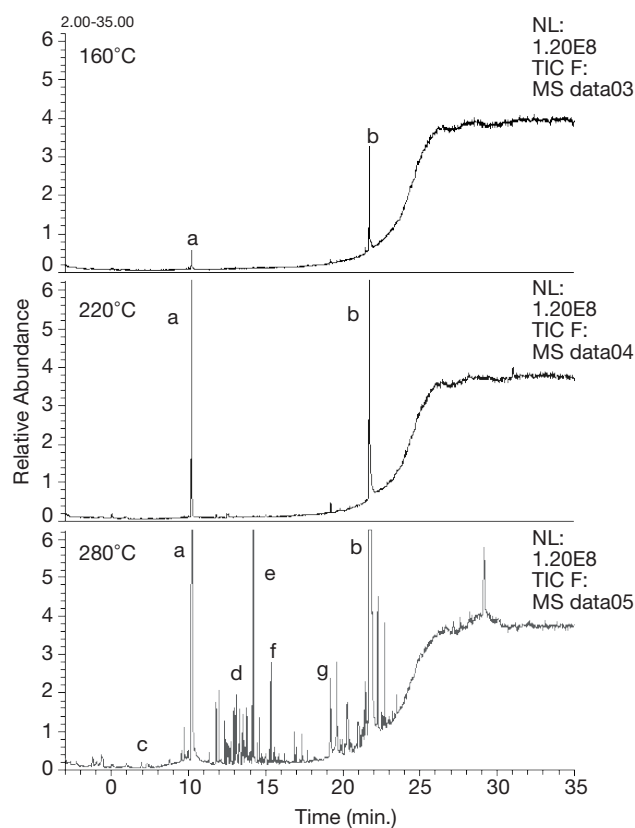
the diol compounds and some kinds of carboxylic acids, other than the glycerin of the solvent, were detected in response to the heating temperature, and more types of the decomposition were detected with the elevation of the heating temperature. It was assumed that the glycerin was thermally decomposed in the presence of the copper catalyst and the organic materials were detected as the decomposition components because the activation of the copper nanoparticles increased with the elevation of the temperature. The relationship between the decomposition behavior of polyol and the state of the copper nanoparticle was investigated including the previous study regarding the decomposition of the glycerin. According to the Hung's report⁵⁾, the polyol, such as the glycerin, tends to decompose to the ketones and the diols under the copper catalyst. On the other hand, the carboxylic acid was generated when the polyol was decomposed under the copper oxide catalyst, according to the B. Mane's report⁹⁾. The lactam compounds detected at high temperature of 280°C in the measurement was assumed to be the decomposition of the surface modification on the particles. The paste using the other copper particles was thermally decomposed at the same condition of the experiment and the decomposition compound was investigated. The results in each particle condition, investigated at 280°C because a lot of amount and types of the decomposition compound at its temperature were detected, are shown in Fig.3.

When the lower oxidized copper nanoparticle A and B were used, the main decomposition compound of the glycerin was the acetol. The copper nanoparticle B has the highest activity, according to the detected amount of the acetol and the types and the amount of the other decomposition. Since the copper nanoparticle B had less amount of the surface modification than the copper nanoparticle A, we assumed that the surface modification influenced on the activity of the decomposition of the glycerin.

On the other hand, it featured to detect the acetic acid and the formic acid in the case of using the high oxidized copper nanoparticle C and D. The detected peak of the acetol was very small for the copper nanoparticle C which had high oxidation and a large amount of the surface modification. However not only the acetol but the acetic acid and the formic acid were detected for using the particle D which had high oxidation but less amount of the surface modification.

The activity of the copper nanoparticles was influenced from not only the oxidation degree but the modifier on the particles. A number of small peaks which we were not able to identify were detected in the analysis. Some material detected relatively large amount of peaks was found to be the intermediate on decomposition of the glycerin or the reacted material between the intermediates. Moreover we assumed that the small detected materials were generated from the impurities in the solvent or the impurities in the particles.

The organic products generated from the decomposition of the glycerin were influenced by the catalyst effect of the copper oxide and the surface modification state on the surface of the particles. The decomposition rate has to be considered on the basis of the above two factors.



a	Acetol	d	Acetic acid	g	2-Pyrrolidone
b	Glycerin	e	Propylene glycol		
c	Ally alcohol	f	Dioxane-5-ol		

Figure 2 The Py-GC/MS result of the copper (Cu) nanoparticle B sample.

3.2 The Kinetic Analysis for the Decomposition of the Polyol Solvent

The decomposition of the solvent was analyzed using the result of the Py-GC/MS. Since the result of the Py-GC/MS is influenced by the change of the measuring environment, the absolute value is difficult to evaluate. We carried out the semi quantitative evaluation using the amount of the acetol and the acetic acid for the Py-GC/MS results at the high temperature as the standard, which were common products to the copper nanoparticles paste. The temperature dependency of the absolute value of the detected amount was analyzed.

The temperature dependency of the generation rate of the acetol and the acetic acid for each copper nanoparticle was shown in Fig. 4 and Fig. 5, as the Arrhenius plot. The generation rate of the acetol was shown in Fig.4. In the case of lower oxidation of the copper nanoparticle (A, B), the generation rate of the acetol was higher at each

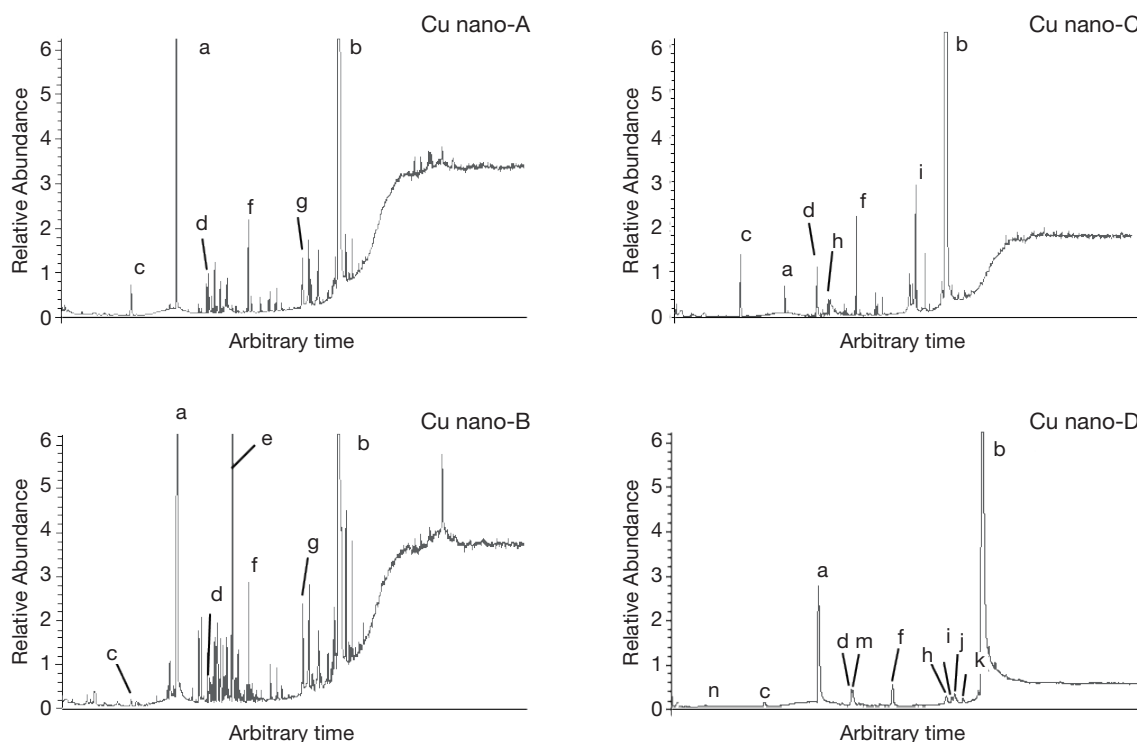


Figure 3 Py-GC/MS results at 280°C for various Cu nanoparticle samples. (a: Acetol, b:Glycerin, c:Ally alcohol, d:Acetic acid, e:Propylene glycol, f:Dioxane-5-ol, g:2-pyrrolidone, h: Formic acid, i, j, k:Unknown m:Acetol acetate n:Vinyl acetate)

temperature, and the rate for the particle B was the highest among them. As for the temperature dependency, the generation rate was higher with the increment of the temperature, but since the gradients of each plot in the decomposition reaction of the glycerin to the acetol were not different in various temperature, the mechanism of the decomposition reaction of glycerin was the same. In the case of the particles with high oxidation degree, the generation of the acetol decreased, especially the generation rate for the particle C with a lot of surface modification decreased drastically at the lower temperature. This meant that the surface oxidation degree and the surface modification would influence on the decomposition reaction.

Fig. 5 shows the generation rate of the acetic acid. The gradient on the plots was mild and we assumed that the activation energy of the acetic acid generation would be lower than in the acetol case and the generation rate of the acetic acid would be low. The generation rate using the high oxidized copper nanoparticle C was high at the high temperature and low at the low temperature. However in the case of the copper nanoparticle D with the high oxidation degree and a lot of surface modification, the reactivity and generation rate tended to be low. According to the result of Fig. 4 and Fig.5, the gradient of the generation rate is the same for particles which had the different oxidation degree or surface modification amount. It was assumed that the generation mechanism of the acetic acid would be the same for each copper nanoparticle. However, the ability to generate of the ace-

tol or the acetic acid was different from the oxidation state or the surface modification amount.

In order to exclude the effect of the surface modification amount, without the data for the large different surface modification state, the reaction rate ratio between the generation of the acetol and the acetic acid at 280°C, where the reaction rate was relatively high, were plotted against the oxidation degree of the copper nanoparticles and the result was shown in Fig. 6. The ratio of the reaction rate of the acetic acid / the acetol was increased with the increment of the oxidation degree. If the copper nanoparticle acted as the catalyst on the decomposition of the glycerin solvent, in the case of the low oxidation degree of the copper nanoparticle, the glycerin decomposed with the generation of the acetol, but in the case of the high oxidized copper particle, very close to the copper oxide state, the glycerin inclined to decompose with the generation of the acetic acid, the acetol was prevented from generating. Even when the reaction started from the same material, it proceeded in the different direction under the catalyst of the copper nanoparticles. The oxidation degree of the copper nanoparticle was one of the important factors to control the decomposition reaction of the glycerin.

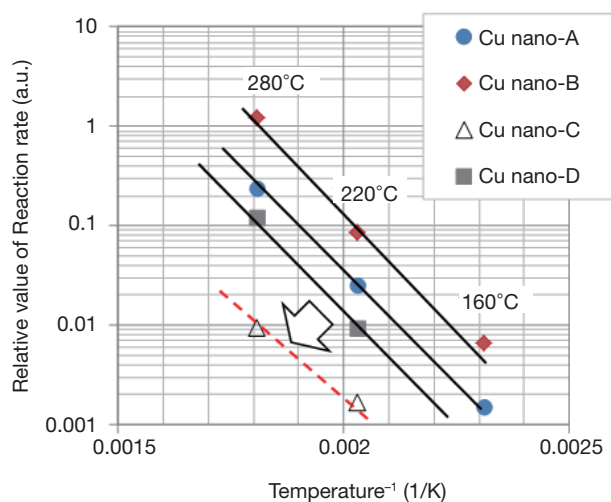


Figure 4 Temperature dependency on the acetol formation.

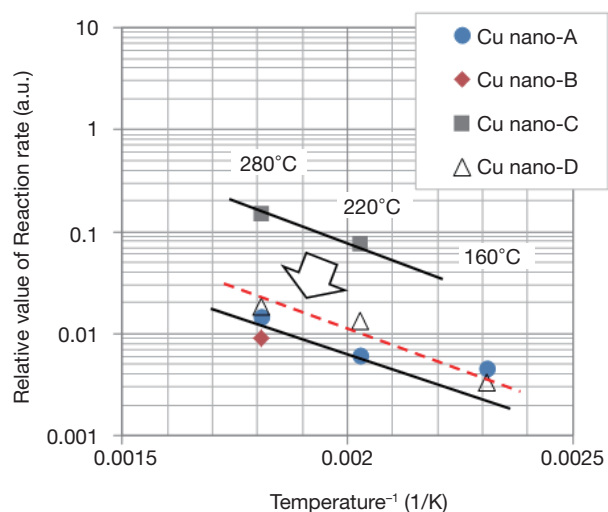


Figure 5 Temperature dependency on the acetic acid formation.

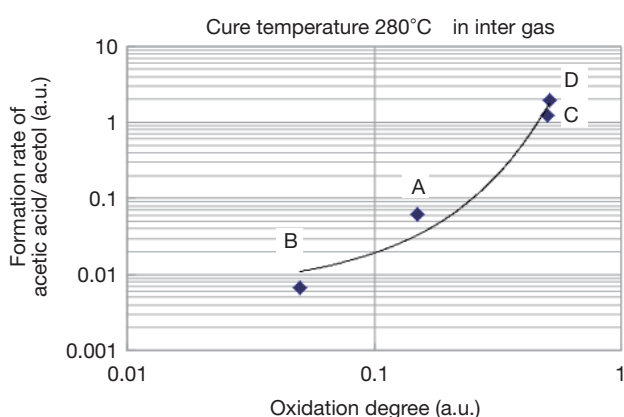


Figure 6 Effect of the oxidation degree on the formation rate of the acetic acid / acetol at 280°C.

4. DISCUSSION

4.1 The Mechanism of the Glycerin Decomposition on the Oxidation Degree

The decomposition reaction process of the glycerin was

different from under the copper catalyst or under the copper oxide catalyst. In the case of the copper catalyst, the main decomposed product was the ketones, such as the acetol, and the ketones had the less reduction capability. It presumed that the reduction of the copper was occurring with the hydrogen molecular or the hydrogen radical from the hydroxyl group of the glycerin. It was difficult to reduce the copper nanoparticles completely because the main generated products had the less reduction capability.

In the case of the reaction under the copper oxide catalysts, the decomposition product of the glycerin was the carboxylic acids, which had the leaching effect of the copper oxidation through the formation of the complex and the copper oxide was reduced by the further proceeding of the decomposition reaction, according to the Carvalho's report¹⁰. The oxidation and reduction of the copper repeated until the acetic acid was consumed completely in the thermal reaction system and the sintering seemed to be accelerated. The chemical equation was shown below.



The reaction scheme between the decomposition of the glycerin and the different oxidation degree of the copper nanoparticles is shown in Fig.7, according to the analysis result and the previous study research. When the glycerin used in the experiment reacted under the copper nanoparticle catalyst, the dehydration occurred and the acetol was generated. The hydrogen radical generated from the dehydrogenation coordinated on the surface of the copper nanoparticle, the radical increased the activity of the copper nanoparticle surface and accelerated the sintering between particles. By contrast, the decomposition of the glycerin under the copper oxide catalyst, which is different from the copper catalyst, the aldehyde or the acetic acid was formed because the C-C bond cleavage occurred, and it presumed that the sintering of the particles accelerated more.

4.2 The Effect of the Decomposition Component of the Glycerin on the Sintering of the Copper Nanoparticles

The relationship between the variation of the decomposition reaction of the glycerin and the oxidation state of the copper nanoparticles, the reduction of the copper and the sintering state of the copper nanoparticles were investigated. The copper nanoparticle paste was prepared using the copper nanoparticles with two different degree of oxidation and the solvent being the glycerin. The paste containing 50 weight % of copper of the total paste weight was printed on the glass substrate with the squeegee method. The paste was spread uniformly at the thickness of 100 μm and was sintered for 10 min. at 250°C in the nitrogen atmosphere. After sintering, the sintered film was cooled down to the room temperature in the nitrogen atmosphere. The sintered film was observed with the SEM and the result was shown in Fig.8

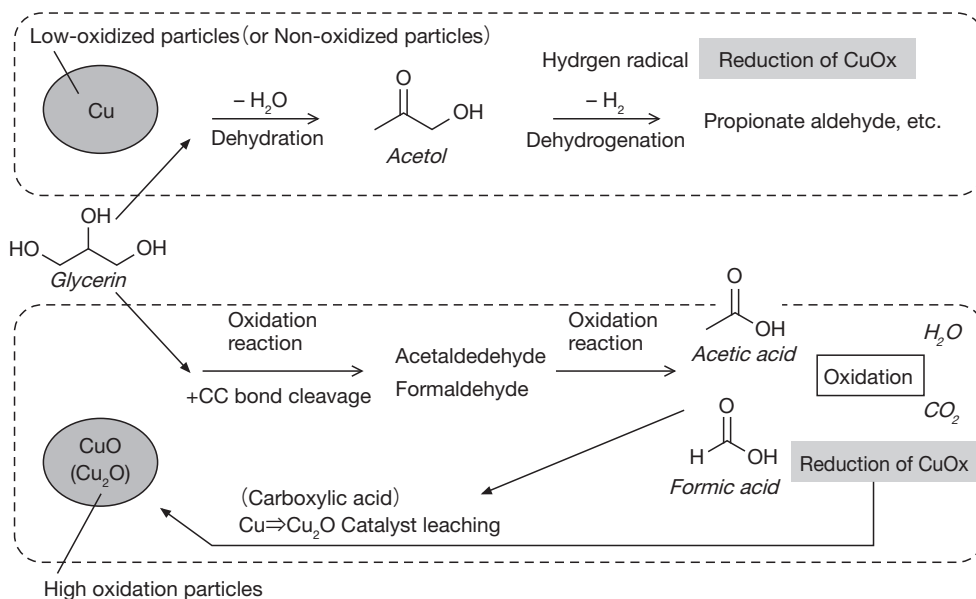


Figure 7 Schematic pathway of the glycerin decomposition reaction on Cu/ Cu₂O catalyst.

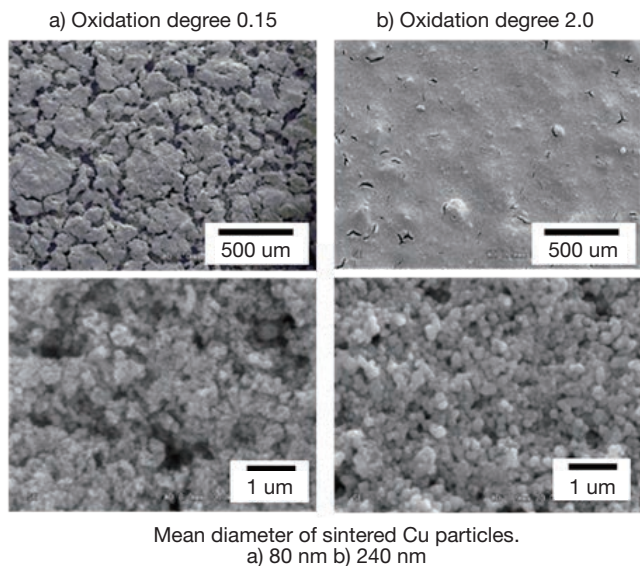


Figure 8 SEM images of the sintered Cu paste.

The sintering performance of the high oxidized particle was compared with the low oxidized one. It was observed more grain growth of the sintered particle size on using the high oxidized particle comparing with the use of the low oxidized copper nanoparticle. The average diameter grew around 10 times after the sintering from the primary diameter of 20 to 40 nm before the sintering for the high oxidized copper nanoparticle. In the case of using the low oxidized copper nanoparticle, the sintered particle size grew around 4 times from the primary diameter.

The crack of the sintered film was occurring with the shrinking of the film during the drying or the decomposition of the solvent by heating. It prevented the film from cracking in the case of using the high oxidized particle. Since the oxidation and the reduction were repeated with

the leaching effect and the sintered particle size grew, the growth of the particle size made less crack. The degree of oxidation of the particle influenced the sintered state of particles and the forming of the sintered film.

The effect of the oxidation degree of the particle on the electric resistivity was investigated. The sintered films were made using the copper nano paste with the different degree of oxidation and measured the electric resistivity. The result was shown in Fig.9. The resistivity decreased with the increment of the oxidation degree and we succeeded to decrease to $3 \times 10^{-4} \Omega \cdot \text{cm}$ in the experiment. The purpose of the experiment was to compare with the particles with the different degree of oxidation and we plan to get the sintered film with further lower resistivity with the suitable solvent formula or the particle size.

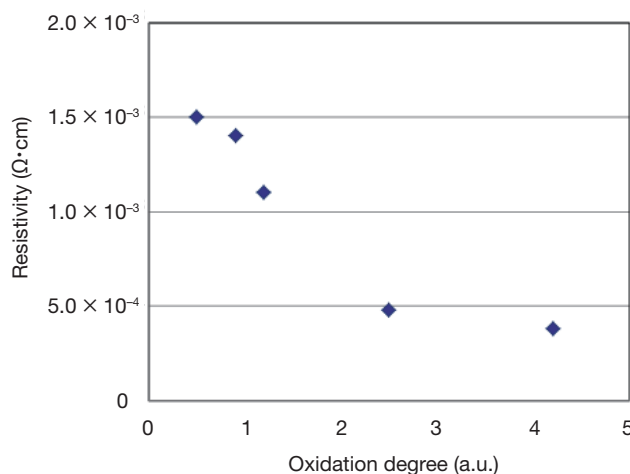


Figure 9 Electric resistivity of the sintered Cu paste.

5. CONCLUSION

The copper nanoparticle paste consisting of the copper nanoparticle and the glycerin was investigated. The glycerin was decomposed with the copper catalyst effect and the decomposition improved the sintering ability of the paste.

The mechanism of the decomposition reaction in the copper paste during sintering was clarified on the basis of the review of the previous study related to the decomposition of the glycerin and the analysis of the decomposition component for the heated copper paste containing the copper nanoparticle and the glycerin with the Py-GC/MS.

The degree of oxidation of the copper nanoparticle influenced the decomposition process of the polyol used as the solvent and the generated products were different depending on the decomposition reaction path

The different amount of the surface modification, influenced the reaction rate of the decomposition of the polyol.

According to the analysis result of the copper nanoparticles with the Py-GC/MS, the oxidation of the copper nanoparticle dependence on the sintering of copper was investigated. In the case of the low oxidized copper nanoparticle, since the ketones of the main decomposition product of the glycerin and the solvent had the weak reduction capability, the sinter ability did not accelerate. As for the high oxidized copper nanoparticle paste, since the glycerin was decomposed to the carboxylic acids which had the leaching effect of the oxidation of copper through the complex formation and the reduction of the copper oxide in the further decomposition process, the sintering of the copper nanoparticle was accelerated.

The interaction between the high oxidized copper nanoparticle and the polyol improved the growth of the sintered particle and the formation of the sintered film, the oxidation degree is the important factor for developing the copper nanoparticle.

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