Effect of Sintering Temperature on Stress Relaxation Behavior of Sintered Nano-sized Ag Particles

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A tensile test and a stress relaxation test were carried out using nano-sized Ag particles pressureless sintered at two levels of temperature to investigate the effects of sintering temperatures on the creep mechanism of sintered nano-sized particles. Inverse analysis using micro scale FEM model revealed that the creep stress exponent of the compact portion in the sintered nano-sized Ag particles was close to the value of dislocation creep. However, the sintered nano-sized Ag particles have a different type of creep mechanism from that of bulk Ag, regardless of sintering temperature levels. This creep is considered to be resulted from the low quality grain boundary structure. And the grain boundary quality does not improve with an increase in sintering temperature. Since the deformation in the low quality grain boundary is considered to be dominant on microscopic behavior of sintered body, sintered nano-sized Ag particles exhibit extremely brittle behavior compared to pure metals.

Key Words: Ambient Temperature Creep, Sintering Temperature, Sintering Ag Nano-particles, Grain Boundary, FEM, EBSD

1. Introduction

The operating temperature of next-generation power devices is estimated to be higher than 473 K1). In this context, the material of nano-sized Ag particles having both high thermal-stability and the capability to allow low temperature bonding is receiving a great deal of attention as a die attach material2). However, investigations of the mechanical properties necessary for reliability design have not been moved forward adequately because of experimental difficulties. The author, et al. have demonstrated in their past experiment that pressureless sintered nano-sized Ag particles show extremely low elastic modulus and exhibit stress relaxation at a high rate at ambient temperature 3). According to the creep deformation mechanism map for bulk Ag, delineated by Ashby, et al., creep strain rate at ambient temperature is $10^{-9}$/s and so it is predicted that high rate stress relaxation will not occur4)-9). This indicates that the creep deformation mechanism for sintered nano-sized Ag particles is different from that for bulk Ag, suggesting that another new creep deformation mechanism exists – its specifics remain unknown though. Although creep deformation is a critical factor in considering joint reliability, a thorough investigation is desired. So, in this study, a tensile test and a stress relaxation test were carried out using nano-sized Ag particles sintered at two levels of temperature to investigate the effects of sintering temperatures on the creep mechanism of sintered nano-sized particles.

2. Experimental Method

2.1 Specimen

Paste of nano-sized Ag particles with an average diameter of 100 nm was used in this study. The temperature of the paste was raised at a 60-minute ramp rate from ambient temperature to the sintering temperatures which were then held for 30 minutes to make pressureless sintered plates for fabricating specimens. The sintering temperatures were 423 K and 573 K. The plates obtained from sintering at each temperature were shaped into the geometry shown in Fig.1 for mechanical testing. Fig.2 shows the microstructures of sintered nano-sized Ag particles. Sintered nano-sized Ag particles have the porous structure with numerous pores. With increasing sintering temperature, an average grain size increased to about two times the original size, resulting in compacted structure having decreased porosity; the porosity was 29.6 % at 423 K and 12.4 % at 573 K.

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2.2 Mechanical Testing

Tensile testing was performed to obtain stress-strain curves. The initial strain rate was $10^{-3}$/s with the inclusion of reliability analysis in thermal fatigue deformation. The test temperatures were three levels of 298 K, 373 K, and 423 K.

Stress relaxation behaviors were obtained by giving tensile strain to the specimens at the initial strain rate of $10^{-3}$/s which was held for 1500 seconds. The test temperatures were 298 K, 358 K, and 423 K. In order to investigate deformation mechanisms, creep properties were obtained analytically, by the method described below, from the load-time curves that can be obtained from the stress relaxation test.

In all of the tests, a micro mechanical testing machine complete with a piezo actuator (Saginomiya: LMH207-20) was used. Displacements were measured with the capacitive sensor installed near the specimen fixing jig. For heating the specimen, the ceramic heater installed inside the specimen fixing jig was used and the test temperatures were controlled to maintain ±2 K. The appearance of the test machine used is shown in Fig. 3.

2.3 Creep Analysis

Creep properties of the compact portion were analyzed in this study to investigate creep deformation mechanisms of sintered nano-sized Ag particles. The properties were found by the finite element method (FEM) through inversely analyzing micro scale FEM models developed by reproducing the internal structures. Creep deformation was assumed to obey the steady-state creep law shown in the equation (1).

$$\dot{\varepsilon}_{ss} = A \sigma^n$$

Where, $\dot{\varepsilon}_{ss}$ is the steady-state strain rate, $\sigma$ is the stress, $n$ is the stress exponent, and $A$ is the material constant. Fig. 4 shows the 3D micro scale FEM models with the reproduction of the internal structures of sintered nano-sized Ag particles. These models were constructed by giving element divisions to 3D-CAD models generated by way of combining cross-sectional images of specimens observed at intervals of 40 nm. For cross-sectional...
surface observations, FIB-SEM (Focused Ion Beam-Scanning Electron Microscope) was used. The element type of tetrahedron 10-node was employed; the numbers of nodes for the models were about 180000 for 423 K and about 210000 for 573 K. A solver of ANSYS ver. 16.0 was used.

2.4 Microstructural Observation

Sintered Ag particles were sputtered by Ar ions to observe microstructures. A field emission-type scanning electron microscope (JEOL: JSM-7001F) was used for the observation. The quality of sintered interfaces (grain boundary) was examined through performing orientation analysis by Electron Backscatter Diffraction (EBSD).

3. Results

3.1 Stress-Strain behaviors

Results of the tensile testing at each test temperature are shown in Fig.5. The stress-strain curves in Fig.6 show microscopic results that include pores in the sintered nano-sized Ag particles.

In regard to the 423 K data, the testing was not continued to the fracture because of the actuator’s limitation on strokes. At 298 K, the Ag particles sintered at any sintering temperatures exhibited strain hardening after yielding and fractured at the strain of about 3%, exhibiting brittle properties unlike pure metals. With an increase in sintering temperature, yield strength became high and fracture ductility was lowered. At 373 K, yield stress was reduced to 1/3-1/4 of that at ambient temperature. Furthermore, recovery type stress-strain curves were exhibited after yielding with no exhibition of strain hardening. And there was no difference in strength depending on sintering temperature levels that was observed at 298 K. At 423 K, the yielding stress was further lowered and the ductility improved compared to 298 K. As in the case of 373 K, differences in strength by sintering temperature were not observed. The stress-strain curves transferring to recovery type indicates that creep deformations were taking place. These results represent that creep of sintered nano-sized Ag particles starts at a relatively low temperature, suggesting that creep deformation do not suspend by increasing sintering temperature.

3.2 Stress Relaxation behaviors

Results of the stress relaxation testing are shown in Fig.6. Regardless of sintering temperature levels, sintered nano-sized Ag particles exhibited a stress-relaxation phenomenon in which stress started to decrease over time from the ambient temperature of 0.24 \( T_m \). The results combined with the aforementioned tensile testing results indicate that sintered nano-sized Ag particles start to creep from the ambient temperature (0.24 \( T_m \)). And these results show that the microstructure become compacted by an increase in sintering temperature, which means that creep does not cease although the microscopic strength increases.

Fig.7 shows the relationship between the steady-state strain rate and stress of the compact portion obtained by inverse analysis using micro scale FEM models on the assumption that stress relaxation is dominated by power law creep. The stress exponent or the gradient of a straight line was, at any sintering temperature level, about 5-8, close to the value of dislocation creep mechanism. And the effects of sintering temperatures on creep strength and stress exponent are insignificant. Especially at 423 K, there were practically no variations in creep strength caused by...
and according to sintering temperature levels and it was predicted that increasing sintering temperature should promote sintering and improve creep strength. However, the effects of sintering temperatures on creep properties were not of particular note. In other words, the number of pores decreased with an increase in sintering temperature, so the creep strength increased apparently but it can be thought that the properties of the compact portion did not improve with increasing sintering temperature. The values of the elastic moduli for compact portion were 23-45 GPa for the nano-sized Ag particles sintered at 423 K and 45-60 GPa for those sintered at 573 K, slight increases with an increase in sintering temperature. These values are still low compared to the elastic modulus of bulk Ag and an increase in sintering temperature does not improve mechanical properties of the compact portion.

4. Discussion

As shown in Table 1 and Table 2, the elastic modulus of the compact portion tends to increase with increasing sintering temperature. It is, however, still low compared to bulk Ag, which leads to the prediction that there should be some structure in the sintered Ag particles to lower the elastic modulus. As sintered materials of nano-sized metal particles commonly have many grain boundaries formed by sintering (sintering interfaces), such a low elastic modulus may possibly be resulted from the low strength of the grain boundaries. Thus, following investigations were made with a focus on the grain boundaries formed by sintering.

### Table 1

| Temperature [K] | 298 | 358 | 423 |
|-----------------|-----|-----|-----|
| Sintered at 423 K | 45  | 40  | 23  |
| Sintered at 573 K | 60  | 53  | 45  |
| Bulk Ag         | 78  |     |     |

### Table 2

| Diffusion path | $n$ | $Q$ [kJ/mol] | $\sigma = 10$ [MPa] | $\sigma = 50$ [MPa] |
|----------------|-----|--------------|---------------------|---------------------|
| Sintered at 423 K | 5-8 | 128          | 90                  |
| Sintered at 573 K |      | 115          | 72                  |
| Bulk Ag         | 5   | 190          | Lattice             |

First, the elastic modulus will be explored. Fig.8 shows crystallographic orientation mapping images of the grain boundary neighborhood for sintered nano-sized Ag particles and bulk Ag. Black dotted portions show the regions where the CI (Confidence index) is lower than 0.1. A CI value is a reliability index in determining orientation; it is known that if defects such as dislocations and voids exist, the CI value is lowered. With a look at Fig.8, the CI values of grain boundaries were low either in sintered nano-sized Ag particles or bulk Ag. In this regard, it should be noted that the low CI region (which shows the presence of grain boundaries) was narrow in bulk Ag, whereas it was wide in the sintered Ag particles. It seems that the width of the low CI value regions of the grain boundaries became narrow.
with increasing sintering temperature - indicating that vacancies and other defects are included in the neighborhood of the grain boundaries formed by sintering, which means that the quality of the grain boundaries is low compared to bulk Ag. A similar case of broad low CI value regions in copper plating films has also been reported\(^\text{10}\). The strength (bonding strength) of the low quality grain boundaries was low and, for this reason, the elastic modulus of the sintered Ag particles is thought to be low compared to bulk Ag. As shown in Fig.8, the quality of grain boundaries tends to improve, indicating that the elastic modulus increases with an increase in sintering temperature.

Next, creep will be investigated. As shown in Table 2, the creep stress exponent of the compact portion of sintered nano-sized Ag particles shows the value close to the dislocation creep mechanism of metals. And the activation energy is about half of that in bulk Ag for lattice diffusion at any sintering temperature levels. In bulk metal materials, these data show the creep caused by dislocation pipe diffusion. However, if the creep deformation mechanism of sintered nano-sized Ag particles in this study is same as that of bulk Ag, the strain rate becomes \(10^{-10}/s\), making it difficult to observe creep. And it is suggested that creep at high rates in sintered nano-sized Ag particles has the mechanism different from that of bulk metals.

In a recent study, two types of low temperature creep have been discovered; one occurring by cross-slip in FCC metals\(^\text{11-12}\) and the other occurring by grain boundary sliding, as shown in Table 3. In HCP metals, low temperature creep has also been discovered: it occurs by grain boundary sliding of dislocations pushed out to the boundaries by the internal stress in the metal\(^\text{13}\). These low temperature creeps, however, have a feature that the activation energy is extremely low and are not consistent with the creep in this study for which the activation energy is half of the lattice diffusion. Given that the quality of the grain boundaries is low and the grain size is submicron in the sintered nano-sized Ag particles used in the study, creep is presumably occurring in the low quality grain boundaries. In other words, a phenomenon similar to grain boundary diffusion must be occurring because of numerous defects included in the grain boundary neighborhood. Fig.9 shows the results of microstructural observations before and after the tensile tests with a focus on the grain boundaries formed by sintering. The observations were made at test temperature of 413 K when the nominal strain was 4 %. A comparison between microstructures of pre- and pro- tensile tests confirms that grain boundaries deform like ice pillars and the width widens in the circled places. It can be thought that the neighborhood of sintered nano-sized Ag particles has the structure that includes many defects like vacancies, leading to diffusion in the grain boundary even in the low temperature region, causing such deformations.

| Material          | Creep start | \(n\) | \(Q\) [kJ/mol] | Creep mechanism       |
|-------------------|-------------|-------|---------------|-----------------------|
| Sintering Ag      | 0.24 \(T_m\) | 5-8   | 70-130 (Ag 190) | Unknown               |
| (This study)      |             |       |               |                       |
| Al                | 0.3 \(T_m\) | 5     | 30 (Al 142)   | Cross-slip            |
| Cu                | 0.3 \(T_m\) | 2.2   | 15 (Cu 211)   | Cross-slip            |
| Mg Alloy (AZ31)   | 0.41 \(T_m\) | 4 or more | 80 bellow (Mg 134) | Slip-induced GBs     |

It is generally known that in metals of polycrystalline with an average of less than one micron size, the grain boundaries exhibit the structural characteristics that the grain boundaries act as an obstacle to dislocations and plastic deformation transit to intergranular from grain interior. Especially in nano-order crystals, dislocation is difficult to move. And the volume ratio of the grain boundaries increases significantly, so the properties themselves of the grain boundaries are known to have effects on the properties of micro-sized materials\(^\text{14-16}\).

Hence, on the assumption that creep dominates deformation in the grain boundary, the stress relaxation test was reproduced by FEM analysis using 2-dimensional scale models as shown in Fig.10. The internal structure of sintered nano-sized Ag particles was reproduced for the models on the assumption that the grain boundary had a certain volume and it was the only area of creep occurrence. The portions in black color were the structure of the grain boundary and the portions in gray color were crystal grains in Fig.10. The grain boundary nature was determined as an elasto-creep body and the steady state creep law in the equation (1) was used. The grain was determined as an elasto-plastic body, assuming the occurrence of partial yield. The equation (2) shows the yield condition and equation (3) shows the strain hardening law. The elastic modulus of the grain was 78 GPa for bulk Ag. The creep and elasto-plastic material constants were determined
by inverse analysis so that FEM analysis results coincide with experimental results. The creep constant of the sintered interface was determined by referring to the creep properties of the compact portion.

\[ f(\sigma, \varepsilon_p) = \sigma - C_i = 0 \]  
\[ \dot{\chi}_i = \frac{2}{3} \sum C_i \dot{\varepsilon}_p - C_i \dot{\chi}_i \dot{p} \]  

Where \( \dot{\chi} \) is the back stress rate, \( n \) is the number of elements, \( \dot{\varepsilon}_p \) is the plastic strain rate, \( \chi \) is the back stress, \( \dot{p} \) is the accumulated plastic strain rate, \( C_1, C_2 \) and \( C_3 \) are the material constants. The reproduction results of the stress relaxation test are shown in Fig.11. Analysis values agree well with experiment values in solid lines and the plastic deformation and stress relaxation of sintered nano-sized Ag particles were reproduced by the FEM model. That is, it is considered that the grain boundary formed by sintering dominates creep. Table 4 shows material properties obtained. The stress exponents of creep were close to those obtained from the stress relaxation experiment, which physical implications are not known at the present moment. The elasticity of the grain boundary improved with an increase in sintering temperature, whereas the creep constant stayed pretty much the same. The results suggest that in nano-sized Ag particles pressureless sintered, the grain boundary includes many defects without improving the quality. Furthermore, since the deformation of the grain boundary governs the microscopic behavior of the grain boundary, the ability of sintered nano-sized Ag particles to absorb the strain energy generated during deformation is extremely low. This seems to be the cause of the extremely brittle behavior compared to pure metals as shown in Fig.6. The deformation mechanism needs to be further explored.

### Table 4 Material constants for 2D micro scale FEM models.

|                        | Sintered at 423 K | Sintered at 573 K |
|------------------------|-------------------|-------------------|
| Sintered interface     | \( E \) [GPa]     | \( n \)           | \( A_i \)          |
|                        | 4                 | 5.7               | \( 7.0 \times 10^{14} \) |
|                        | 15                | 5.7               | \( 8.0 \times 10^{14} \) |
| Ag grain               | \( E \) [GPa]     | \( C_1 \)         | \( C_2 \)         | \( C_3 \)         |
|                        | 78                | 15                | 15               | 15               |
|                        |                   | 30000             | 40000             |
|                        |                   | 280               | 280               |

![Fig.10](image1.png)

2D micro scale FEM models involving low quality grain boundary.

![Fig.11](image2.png)

Stress relaxation curves obtained by experiment and FEA using 2D micro scale model.
as the analysis of the mechanism using the models in this study was simplified.

5. Conclusion

1) In the range of the study, pressureless sintered nano-sized Ag particles exhibit a different type of creep from that of bulk Ag, regardless of sintering temperature levels.

2) The creep stress exponent of the compact portion in the sintered nano-sized Ag particles was about 5-8 and the activation energy was about 70-130 kJ/mol.

3) This creep is considered to be resulted from the low quality grain boundary structure that includes many defects. And the grain boundary quality does not improve with an increase in sintering temperature.

4) Since the deformation in the grain boundary of low quality is considered to be dominant on microscopic behavior of sintered body, sintered nano-sized Ag particles exhibit extremely brittle behavior compared to pure metals.

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