Pressure-less Ag-Sinter: Necking, Pores Structure and its Properties

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Abstract

Pressure-less Ag-sinter die-attach structure revealed good-networked silver interconnects along with discontinuous shrinkage porosities. A thin sheet test sample is processed to be evaluated with commercially available test equipment. In this study, test samples are stencil printed to a thickness from 70 to 100µm and sintered at 200/250°C for 30/60 minutes (mins). A test sample to a thickness of about 13mm is processed by stacking a few layers of printed Ag-sinter and sintered at 200°C for 1h. Interestingly, good necking is observed in between the silver powder particles, and measured properties for three different porosity levels of pressure-less Ag-sinter are as follows:

- Discontinuous porosities of structure are about 15 to 20%, 20 to 35%, and 45 to 55%, depending on the paste chemistry and formulation (with and without binder)
- Density of these pores structures is from 4.5 to 7.7 g/cc
- Electrical sheet resistivity is from 3.7 to 9.2 µΩ.cm
- Thermal conductivity is from 80 to 190 W/m°K
- Elastic modulus (ultrasonic testing method) is from 7.2 to 38 GPa
    a. Lower the porosity, higher the thermal conductivity and elastic modulus
- Coefficient of thermal expansion (CTE) is about 19.2 to 21.5ppm
- Specific heat capacity (Cp) is about 0.24-0.25 J/g°K
- Both CTE and Cp properties of Ag-sinter are not influenced by porosity in the structure

Key words

Silver sinter, porosity, thermal conductivity, E-modulus, CTE, specific heat capacity, electrical resistivity

I. Introduction

The present silver (Ag) sintered sample (in industry today?) is to a thickness from 30 to 150µm, at low temperatures from 100 to 300ºC for a duration from 30 minutes to 4 hours. Commonly, Ag-sinter possess thermal conductivity between 60 and 200 W/m°K for 200 to 250°C processing temperature and bond line thickness (BLT) greater than 20µm with a variation less than 10µm. Bonded dies reveal greater than 40MPa when well adhered to a gold surface. The sinter profile (temperature and time) depends on the particle size of silver powders (micron to nano) utilized for the synthesis, additives practiced, formulation chemistry, and reactivity of the formulated sinter paste. Information on the characterization of Ag-sinter (scientific tools for measurement, standard test procedures, sample preparation, etc.) is limited to finding thermal, mechanical, and electrical properties [1-5]. Present study enumerates the importance of porosity in the Ag-sinter that impacts its properties. Porosity is measured by cross-section (2-dimensional (2D) area fraction measurement) and density measurement by Archimedes principles [1]. This paper reports a cross-sectional method of measurement. Electrical resistivity of the sintered layer is measured using the 4-probe method. Thermal properties such as specific heat capacity (Cp), coefficient of thermal expansion (CTE), thermal diffusivity, and thermal conductivity of the Ag-sinter are obtained using Differential Scanning Calorimetry (DSC), Thermo-mechanical Analyzer (TMA), and Thermal Interface Material Analyzer (TIMA) [1]. Elastic modulus (E-modulus) is obtained using an ultrasonic method with a sample of thickness of 13mm. The test samples are prepared with a careful formulation of paste vehicle chemistry, avoiding outgassing consequently leading to gas porosities (voids). Presently, the paste is processed with mixed Ag particle sizes (micro to nano).

II. Porosity of Pressure-less Ag-sinter

First, an image is recorded at 2000X magnification using a field-emission Scanning Electron Microscope ((FESEM), Carl Zeiss -Sigma Model), which later converted the image into a binary contrast mode (Ex. pore – black, networked Ag-sinter particles – white). The pore area is measured using Image-Pro 10.0.6 software and % porosities are calculated as a ratio between the pore area and the observed fixed rectangular area [1]. Density of these samples are measured by Archimedes principles and % porosities are calculated as a ratio between the solid rod and the density of measured structure. Denser the sintered structure lower the % porosity (Table 1). A dense Ag-sinter structure is observed for high-metal loading (~90%), 250°C, and a 60 minute sintering profile.

Typical microstructures of ion-milled, pressure-less Ag-sinter with different percent porosities is shown in Fig.1 (revealing porosities for different area fraction of pores). The samples are printed to a thickness from 70 to 100µm and sintered at 200°C to 250°C for 30 minutes to 60 minutes. The microstructure revealed net-worked sintered silver particles by densification on sintering, along with a discontinuous type of shrinkage porosities, leading to an interconnect (this sentence needs to be clarified).

Die shear strength of these six pastes shows a good correlation with the level of porosity and their adhesion to the die and substrate surfaces (Table 1). The paste with a high fraction of porosity of 50% revealed a lower strength of 20MPa, while a low 20% porosity structure showed a higher strength of ~90MPa (Table 2). The high strength is contributed to the high temperature of sintering at 250°C. Necking of the silver particles is clear at a very high magnification of observations from 20kX to 30kX (Figs.1 d & e). Lower porosity and higher shear strength (80 to 94 MPa) of Ag-sinter structure are achieved for a minimum 85% metal loading, mixing sub-micron or nano particles to micro particles, and sintering at a high temperature of 250°C for an hour.

III. Electrical, Mechanical and Thermal Properties of Pressure-less Ag-sinter

Electrical resistivity is measured using a 4-probe tester and calculated using the formulae $\rho = \left(\frac{\pi.V}{ln2.I}\right)t$, where ρ is the sheet electrical resistivity in µΩ.cm, t is the sample thickness in cm, V is the measured voltage, and I is the source current. The Ag-sinter resistivity decreases with a decrease in porosity (Table 1). For about 20% porosity, electrical resistivity is about 2.5 times higher than pure silver at 1.63µΩ.cm. While 50% pores structure revealed 5.5 times higher electrical resistivity than pure silver. Thus, indicating that Ag-sinter particles network is continuous and promotes electron flow effectively possessing as a good interconnect.

Thermal conductivity measurement of pressure-less Ag-sinter by In-plane (lateral) Thermal Interface Materials Analyzer ((LaTIMA), measured as per ASTM D5470 standard, showed interesting results. Thermal conductivity is calculated using the formulae $\lambda = \frac{L.Q}{\omega.t.\Delta T}$ where, ω is the width of the sample, t is the thickness of the sample, L is the length of field measured using an IR camera on a sample, and Q heat flow through the sample. Usually, LaTIMA approach requires ~20mm length x ~10mm width x 100µm thick sample to measure thermal conductivity/diffusivity. It is clear from Table 1 that pressure-less Ag-sinter paste printed and sintered to a thickness of 70 to 100µm with different levels of porosities revealed thermal conductivity from 80 to 190 W/m°K, lower the porosity, higher the shear strength and higher the thermal conductivity.

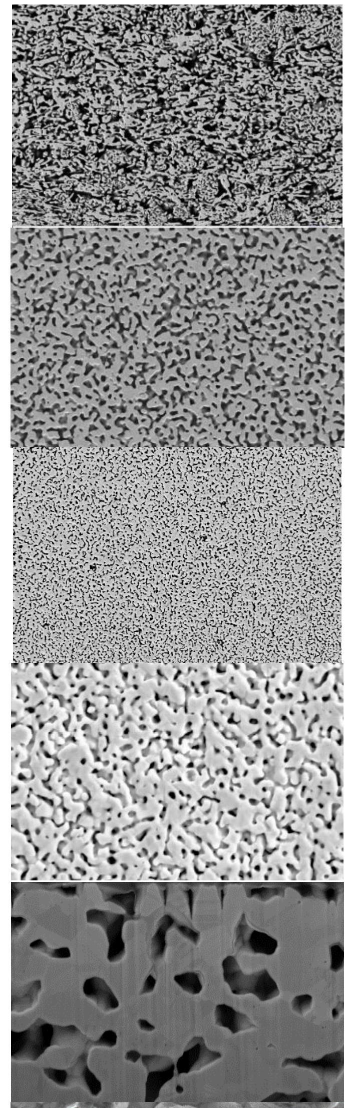

Fig.1 SEM observations of ion-milled pressure-less Ag-sinter for different formulations: (a) about 50% porosity (2kX mag), (b) about 30% porosity (2kX mag), (c) 18% porosity (2kX mag), (d) 18% porosity (6kX mag), (e) 18% porosity (20kX mag), and (f) 30kX magnification of sintered

surface, necking is evident. Sintered at 200ºC to 250°C for 30 to 60 minutes using sinter paste formulated with Ag particles.

Coefficient of thermal expansion (CTE) of pressure-less Ag-sinter with 50% porosities is measured using Thermo-mechanical Analyzer (TMA Q400, TA Instruments model) exhibited 19.2 to 21.5 µm/m°C (ppm). The sample is tested for the temperature range from 25 to 200°C. CTE value is close to reported in the literature [1]. Specific heat capacity measured as per ASTM E1269 standard using differential scanning calorimetry (DSC) revealed about 0.24 J/g°K (Table 1). Pressure-less Ag-sinter Cp and CTE values are close to dense silver sample without porosity, which indicates that the two factors are independent of porosity in the structure.

No.	Material properties Ag - Sinter	Sample Trials					
		With Binder				Without Binder	
		A	B	C	D	E	F
1	Metal loading, %	80-85	87-93	87-93	83-88	89-93	84-86
2	Powder particle size	Micron and sub-micron mixtures					Micro - Nano
3	Sintering Profile	200°C, 60 mins, atm.	200°C, 30 mins, atm.	250°C, 60 mins, N2		200°C, 60 mins, atm.	250°C, 60 mins, N2
4	Porosity, %	45 -55	31-32	22-25	17-21	25 - 35	17 - 19
5	Density, g/cc	4.5-5.0	6.7-7.2	7.3 – 7.7	6.8 - 7.2	6.5 - 7.0	6.9 – 7.2
6	Thermal Conductivity, W/m°K	80	132	145	148	156	190
7	Electrical Resistivity, µΩ.cm	9.18	5.82	4.69	4.45	4.19	3.70
8	E-Modulus, GPa (Sonic Tester)	7.2	22.3	21 - 38			
9	CTE, ppm	19.2 – 21.5					
10	Specific Heat Capacity (Cp), J/g°K	0.24 - 0.25					

Table 1 Measured physical, mechanical, electrical, and thermal properties of pressure-less Ag-sinter (printed and sintered).

The elastic modulus of pressure-less Ag-sinter is measured using 13mm thick Ag-sinter stacked layer sample. As well tested using ultrasonic method [1] through transmission mode as per ASTM C597 standard revealed 22.3 GPa for 30% porosity (Table 1). The sintered silver sample possessed 15 to 55% shrinkage porosity, yet the transfer of sonic wave is not hindered by porosities, conveniently traveled via networked Ag-sinter. The stacked layer is printed a few times one over the other and sintered at 200°C to 250°C for 30 to 60 minutes (length x breadth x thickness: 17.5mm x 16mm x 600µm) with minimal delamination between sintered layers. Thick samples are processed by a similar approach of stacking Ag-sinter layers to a thickness of 17.5mm x 16mm x 13mm. Shrinkage porosities of the sample measured (Table.1) by cross-section revealed 15 to 55% depending on the formulated paste. Other defects such as voids caused by outgassing on sintering or delamination between stacked layers are absent.

No.	Material properties Ag - Sinter	Sample Trials					
		With Binder				Without Binder	
		A	B	C	D	E	F
1	Sintering Profile of the Paste	200°C, 60 mins, atm.	200°C, 30 mins, atm.	250°C, 60 mins, N_2		200°C, 60 mins, atm.	250°C, 60 mins, N_2
2	Die type	Au BSM, 1.4 x 0.8 mm, 150µm	Au BSM, 2 x 2 mm, 290µm	Ni/Ag BSM, 2 x 2 mm, 338µm	Au BSM, 2 x 2 mm, 290µm	Au BSM, 2 x 2 mm, 296µm	Au BSM, 2 x 2 mm, 290µm
3	Lead frame type	Ni/Au QFN		Cu QFN	TO247 Cu, 1.5mm	Ni/Au QFN	TO247 Cu, 1.5mm
4	Die shear strength, MPa	20	62	76	94	73	79

Table 2 Measured die shear strength of pressure-less Ag-sinter with different die back side metallization (BSM) and substrate types.

The present study carefully measured the porosity level of the sintered Ag-structure and reported pressure-less Ag-sinter is about 15 to 50%, its electrical/thermal/mechanical properties strongly depend on the porous structure. Thus, evaluated pressure-less Ag-sinter film/sheet/bar structures meaningfully do represent the die-attach Ag-sinter practiced in the industry of nearly of the same thickness, porosity (15 to 50%) and processed (stencil printing and sintering) with closer steps adopted to test Ag-sinter test samples.

Xu Long et al., reported [2] pressure-less sinter at 200°C for 90 minutes processed with silver nanoparticles. Cross-sectional analysis showed shrinkage porosities from 1 to 17% with a few spots of voids. The thermal conductivity (Laser Flash Method) and Poisson's ratio of pressure-less Ag-sinter is 223.9 W/m°K and 0.363, respectively. The higher thermal conductivity observed for Ag-sinter is due to better densification happened when processed and sintered with nano particles.

Oak-Ridge National Laboratory (ORNL) presented the test measurement of sintered silver under compaction [3]. The reported electrical resistivity of 62% shrinkage porosity Ag-sinter is 8 µΩ.cm (10 MS/m electrical conductivity), measured at room temperature. For the same dense Ag-sinter structure, 75 W/m°K thermal conductivity, 14 GPa E-modulus, 0.2 Poisson's ratio, 20 MPa yield strength, and 20 ppm CTE (measured between 25°C and 250°C) are reported. Samples for testing were prepared [3] by first drying the sinter paste, crushing them into powder. Pellets were processed by pressure-assisted sintering (powder compacted and sintered). It was also concluded that silver grain structure (fine or coarse) processed using micro or nanoparticles does have a significant influence on the electrical/ thermal/ mechanical properties, while the porosity level of the sintered structure has a predominant role in justifying the Ag-sinter properties [3-5]. The present test values are close to the reported one though measured using an entirely different approach (paste formulation) while the level of porosity is the same. Thus, the property of Ag-sinter has a strong correlation with the presence of its level of porosities.

III. Conclusion

Thermal, electrical, and mechanical properties of pressure-less Ag-sinter printed samples with different porosity levels from 15 to 55% are measured using test samples of thickness from 70 to 100µm and sintered at 200 to 250°C for 30 to 60 minutes. For thick samples, a few layers are stacked and sintered to 13mm. These, test samples are evaluated using commercially available equipment and as per standard test procedures. Following are the measured properties of pressure-less Ag-sinter film/sheet/bar:

- Observed porosity is from 15 to 55%, measured by pore area fraction ratio method using 2-dimensional (2D) SEM recorded images. The shrinkage type porosities are discontinuous in type.
- Density is calculated by measuring the mass using Archimedes principles and revealed between 4.5 and 7.7 g/cc.
- Electrical resistivity of the sintered sheet of 70-100 µm thickness, with good Ag-sintered interconnected network structure with 15 to 55% porosity is between 3.7 and 9.2 µΩ.cm.
- Thermal conductivity of 100µm Ag-sinter film with 15 to 55% porosity tested by LaTIMA approach is about 80 to 190 W/m°K.
- Elastic modulus measured by ultrasonic (through transmission mode) of 13mm Ag-sintered rectangular bar with 15 to 55% porosity is between 7.2 and 38 GPa. Lower the porosity, higher the thermal conductivity and elastic modulus.
- Coefficient of thermal expansion (CTE) and specific heat capacity (Cp) of Ag-sinter with 15 to 55% shrinkage porosity is ~19.2 to 21.5ppm and 0.24 to 0.25 J/g°K, respectively. Thus, it indicates that the these 2 factors are independent of porosity.

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