

Characterization and Reliability of Ag Nanoparticle Sintered Joint for Power Electronics Modules

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Abstract

Nowadays, numerous power electronics application requires operation at high temperatures. In order to address increasing change of reliability problems in power die attachments for high temperature and high reliability applications, sintering Ag nanoparticles has been used as bonding material for this work.

Firstly, quantitative microstructure characterization of as-sintered Ag joints has been carried out. The resulting normalized thickness, pore size and porosity decreased, and grain size increased with increasing the sintering time. A time dependence of the form $t^{1/n}$ with n close to 2 or 3 can be further derived for the kinetics of the thinning, densification and grain growth within the sintered Ag joints. From the results can be seen, sintering kinetics is still in the intermediate stage, the densification had not been completed, and Ag grain would continue growing afterwards, which could further explain degradation behaviours of sintered joints during isothermal ageing tests and thermal cycling tests.

Secondly, sintered Ag joints with four kinds of substrate metallization have been subjected to isothermal ageing tests at temperatures of 150 °C, 200 °C and 250 °C for up to 32 days. The different microstructure patterns of sintered joints with four substrate finishes during isothermal ageing tests have been presented and compared, which could use the results to explain part of the degradation behaviours of the sintered Ag joints during thermal cycling tests and guide selection of suitable substrate finish for the die attachments in high temperature power electronic system.

Furthermore, thermal cycling tests have been carried out to investigate the reliability of two sizes of sintered Ag joints and solder joints during temperature cycling between -55 °C to 125 °C and -55 °C to 150 °C. Microstructure evolution of sintered Ag joints was investigated by non-destructive and destructive characterization methods, which revealed the factors which could effect on the degradation during thermal cycling tests. With microstructure features of sintered joints observed from X-ray tomography and SAM, because a specific specimen can be evaluated over its lifetime, a true image of microstructure evolution of damage during operation can be obtained, and crack and degradation can be observed three-dimensionally.

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LIST OF SYMBOLS FOR THE MATH LISTS

h_0 : the mean of the total thickness series of the as-dried paste of Ag nanopartcles

h : the mean of the total thickness series of the sintered Ag joint

$\bar{r}$: the the mean of the total pore size data series

P : the mean of the porosity data series

$\bar{d}$: the average Ag grain size

ΔK : the integral breadth

θ : the diffraction angle

λ : the wavelength of X-ray

d : an apparent Ag grain size

c : the average dislocation contrast factor

β : the dimensionless shape factor

$\Delta\theta$: the line widening at half the maximum intensity

r : the radius of a pore measured from the black and white image

S : the area of a pore measured from the black and white image

P_{tr} : the percentage of thickness reduction

t : the sintering time

$\bar{d}_0$: the value of $\bar{d}$ for the as-dried paste of Ag nanoparticles.

x_0 : the epitaxial layer thickness for as-sintered joint

D : the diffusion coefficient at temperature of T

E : the activation energy

R : the energy constant which is 8.3145 J/mol*K;

T : the Kelvin temperature

A : the collision frequency factor

CHAPTER 1 Introduction

1.1 Challenges in joint technology for power electronics reliability

Power electronics is an equipment which could control and convert electrical power by means of power semiconductor device. Nowadays, power electronics is widely used throughout the energy supply chain [1][2]. The typical packaging of a power electronic is illustrated schematically in Figure 1- 1. The module consists of several layers of materials such as Direct Bonded Copper (DBC) substrates, conductor, semiconductor chip, wire bonds, encapsulation, metal bars and protective casing [3][4].

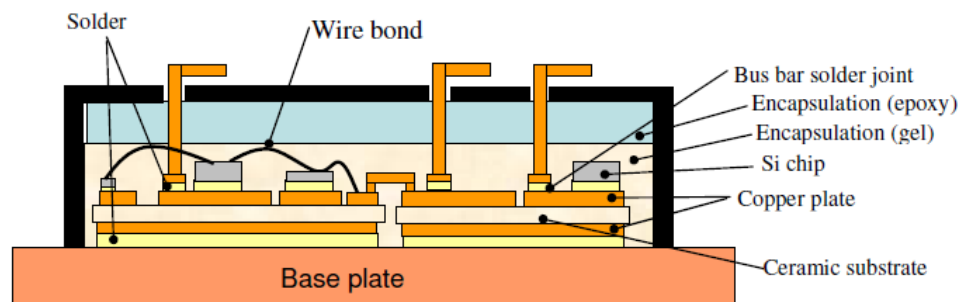


Figure 1- 1: Schematic diagram of a power electronics module structure

The conventional technology for power electronics interconnection normally involves die-attaching one terminal of the semiconductor device to a substrate with solder joints, and wire-bonding gold or aluminium wires to the other terminal. However, because of the interconnect technology limitations, the junction temperature cannot get exceed 150 °C, it is cannot meet the requirement of the wide band gap devices applied in high temperature environments, which theoretically allow junction temperature up to a limit of 600 °C. Therefore, the limitation of interconnect technology of power

electronics limits the further development of high temperature power electronics [5][6].

The traditional solution for power die attachment operating at high temperature is the use of high lead materials, such as $\text{Pb}_2\text{SnAg}_{2.5}$ [7][8]. However, Pb-containing solders will be removed from even high temperature electronics sooner or later because of the toxicity of lead. In 2006, the WEEE (European Union Waste Electrical and Electronic Equipment) Directive and RoHS (Restriction of Hazardous Substances) Directive came into effect prohibiting the inclusion of significant quantities of lead in most consumer electronics produced in the EU [9][10][11]. Besides environmental pressure, other motivations of eliminating lead from electronic solder materials include hazardous waste disposal concerns, workplace safety considerations, etc.

To address the increasing challenge of reliability problems in power die attachments for high temperature applications, a few die attach materials as Pb-containing solder alternative have been reported.

Transient liquid phase (TLP) soldering is a relatively new soldering process that joins materials using an interlayer. The interlayer melts and the interlayer element diffuses into the substrate materials during heating process, causing isothermal solidification [17][18]. Such bonds can be as strong as the bulk substrate material [19]. However, TLP bonding is specialized bonding technique that can be time-consuming and expensive compared to other joining methods [20][21], as Figure 1-2 shows.

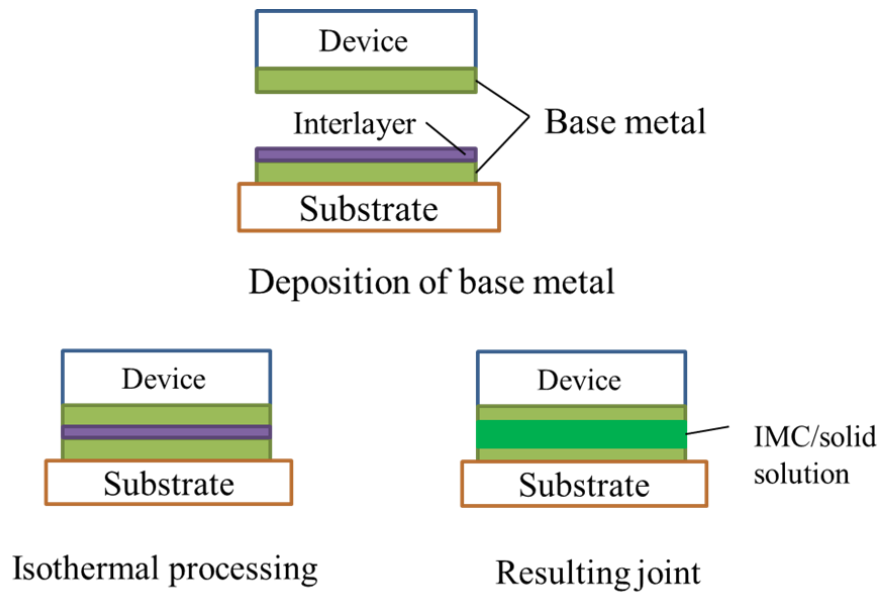


Figure 1- 2: Schematic plated TLP soldering process

The technique of locally brazing the metallic elements without necessitating raising the semiconductor chip and substrate to a high temperature has been investigated by several groups at Johns Hopkins University and Louisiana State University in USA, and Technische Universität Berlin in Germany [22][23], because temperature sensitive devices may be damaged or destroyed by the global heating during the bonding process. However, as Figure 1-3 shows, local brazing using reactive Al/Ni foil, which can localize the reaction-induced high temperature within around the joints, were nanostructured and prepared using sputtering process, and hence are extremely expensive. Besides the materials cost, failure mechanism of die cracks during thermal cycling test have been revealed and has not been fully understood [24].

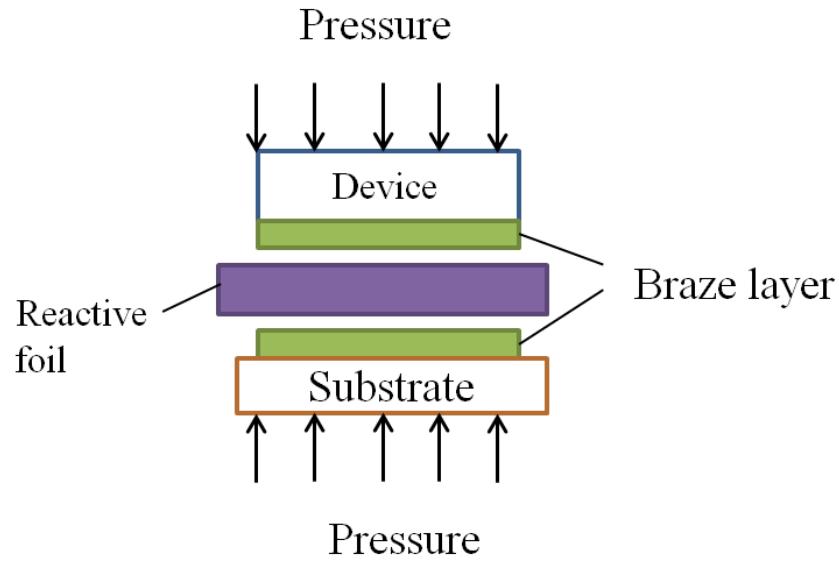


Figure 1- 3: Schematic of locally brazed joining process

Liquid solder is considered to be another potential method for improving reliability of solder joints, which can be used at temperatures below 125 °C [7][25][26]. Low melting point (MP) solder, e.g. the eutectic In-Sn (MP~119 °) or Sn-Bi (MP~139 °) solder were applied and melted, so the stresses on the joints were released [25]. The component is mechanically attached to the substrate by an underfill or glob-top. Surface tension will ensure that the liquid solder interconnect remains in contact with the terminations on the component and the substrate, and that electrical contact between them is maintained, as Figure 1-4 shows. In such high-temperature liquid-phase solder interconnects, the role of the barrier metal is crucial. The barrier layer's function is to slow down IMC formation between the solder and the substrate. In order for mechanical adhesion to develop between the solder and the contact metallization, there must be growth of an IMC at the interface, but excessive IMC formation may cause brittle failure [25][26].

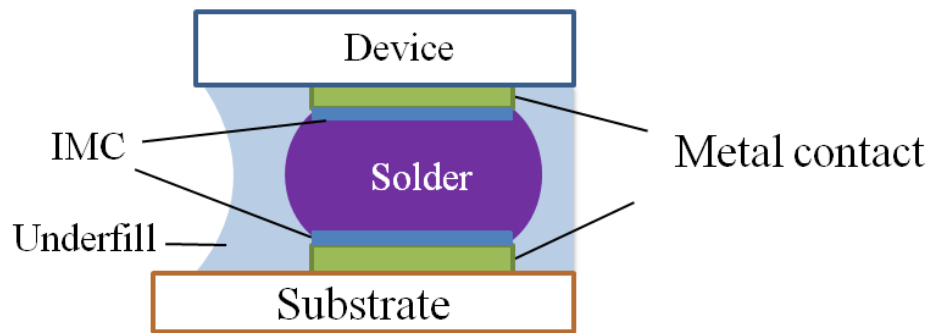


Figure 1- 4: Schematic of utilizing liquid solder connection to the substrate

Metallic or ceramic nanoparticles may be added into the lead-free solders to refine the microstructure, slow down the growth of interface IMCs and improve the mechanical properties at elevated temperatures. Co, Ni and Pt nanoparticles added into Sn-Ag based solders were found to be effective to reduce the growths of IMCs and to improve the drop test performance and increase reliability [27][28]. As we can see from the literature [27][29], some metallic and IMC nanoparticles react with solder materials during reflow to establish good bonding between the reinforcement particles and the solder matrices. However, the compatibility between the inert reinforcement materials and most of the solder alloys matrices remains a problem. At least, inert reinforcement particles should be chosen to be wetted well by solder materials. It is difficult to distribute nanoscale reinforcement particles in solder matrices homogeneously to prepare composite solders. Furthermore, all these are just basic research, and no data are reported about the results of using these reinforced solders in real electronic assemblies.

Besides, some other emerging solder alloys have been reported for improving the reliability of the solder joints operating in high temperature environments. Zinc is known to be another choice as a high-temperature die attachment material. Zinc has a melting temperature of 419.5 °C. With alloying materials such as aluminium and tin, the melting temperature of Zinc can be at range of 300 °C to 400 °C [30]. Zn-Al solder with a melting point of 380 °C has been investigated for die attachment [31]. Experimental results indicated that the

Zn-Al solder joints are stable when subjected to thermal cycling of -40 °C to 200 °C and -40 °C to 250 °C, with neither serious damages, nor delamination after 4000 cycles. However, care must be taken when using this solder for die attachment because the reflow has to be carried out at temperatures above 400 °C to achieve effective solder joint. In reality, this condition is difficult to satisfy without detrimental effect on other components of the package.

1.2 Motivation and objectives of the present thesis

In order to improve the reliability of the solder joints operating in high temperature environments, another alternative is use of high melting point metals, such as silver, platinum or copper. Silver has the second best thermal conductivity and the best electrical conductivity. Gold and platinum are also too expensive and have worse electrical and thermal properties, which cannot be candidate either. Copper is cheaper than silver, however, it oxides quickly at high temperature in the air. Silver has a melting point of 961 °C and good mechanical properties. Also, silver is an environmental friendly material.

Used as a die attachment and/or joining material, silver is generally processed with sintering technology. Sintering of silver is a heating process that makes silver particles be bonded together, which can result in significant strengthening and improved thermal, electrical and mechanical properties when compared with even high temperature solder alloys. Because the sintered joints can be formed by atomic diffusion and particle consolidation, the processing temperature can be much lower than the melting temperature. For example, the sintered Ag joints can be formed at significant low temperature and work at relative high temperature.

To address the increasing challenge of reliability problems for solder alloys and conductive adhesives commonly used for semiconductor die attachments in high-temperature and high reliability applications, several alternatives have been discussed. Of the above-mentioned alternative joining materials and technologies, sintering Ag nanoparticles has been used as bonding material for this work.

Unlike solder reflowing where solder joints are formed through liquid wetting, solid-liquid interfacial reaction and solidification, there are re-arrangement of Ag nanoparticles, densification and reduction in porosity and grain growth

occurring during the sintering process. These microstructural features in the sintered Ag joints depend on both the formulation of the paste and the sintering parameters such as heating rate, sintering temperature, pressure and time, and have effects on the thermal and electrical performance and thermomechanical reliability of the sintered Ag joints in service.

In the existing literature [20][21], the values of thicknesses and porosity of the sintered Ag joints are reported. However, there is no work which has been carried out to explore the variation in those reported values and their quantitative dependence on the sintering parameters. Such a quantitative characterization in Chapter 3 would provide a better description to further optimize the process and predict the performance and reliability of the sintered joints used in power electronic systems.

Furthermore, numerous power electronics application requires operation at high temperatures. Currently, the oil and gas industry is one of the largest users of high-temperature power electronics. Most systems are expected to operate continuously at high temperature for 5 years or more but without much thermal cycling [32]. Another application for power electronics is aircraft, which uses power electronics at high temperature. The driving force for developments in this industry comes from a better fuel efficiency aiming to increase the performance and reliability of the aircrafts. Obviously very high reliability is expected, despite long operating life (10 - 30 years) and frequent deep thermal cycling (several take-offs and landings per day) [32]. Therefore, reliability of sintered Ag joints has been investigated under conditions of isothermal ageing and thermal cycling to reveal the application of sintered joints and microstructure evolution of sintered joints in high temperature environments.

In Chapter 4, in order to guide the selection of suitable substrate finish for the die attachments in high temperature power electronic systems, sintered Ag joints with four kinds of substrates finish have been investigated during isothermal ageing. The results show microstructure evolution of sintered joints with different substrates finish in high temperature ageing. Through analysis and comparison of the obtained microstructure features with those observed, they also can provide insight into the relevant degradation/failure mechanisms of the sintered Ag joints occurring in the thermal/power cycling tests.

Under passive thermal cycling tests, the reliability of sintered joints has been reported in literature. However, most results were evaluated by bonding strength from shear tests and characterized by cross-sectional SEM images. In Chapter 5, in order to investigate microstructure evolution and degradation of sintered joints during thermal cycling, nondestructive methods including X-ray tomography and SAM have been applied to reveal the effects on the crack initiation and propagation in the same sintered joints over time.

1.3 Structure of the thesis

Chapter 1, this chapter introduces challenge of reliability problems in power die attachments for high temperature and high reliability applications, and several technologies and materials under research and development may be as potential alternatives to address this reliability problem. It also outlines the objectives and structure of this thesis.

Chapter 2 presents a literature review to gain a better understanding of this research work. Firstly, development of sintering Ag technology have been reviewed; secondly, effects of sintering parameters including nanoparticle size, sintering pressure, sintering temperature profile and substrate on the quality of sintered joint are reviewed; thirdly, sintered joint reliability is reviewed, which includes the high temperature storage reliability, effect of sintering parameters on reliability, and comparison with solder joints in terms of reliability and microstructure characterization during reliability tests.

In Chapter 3, microstructural features of sintered attachments are quantitatively characterized with scanning electronic microscopy, transmission electron microscopy, X-ray diffraction and image analysis method.

In Chapter 4, sintered joints with four kinds of substrate metallization have been subjected to isothermal ageing tests at temperatures of 150 °C, 200 °C and 250 °C for up to 32 days. Microstructure evolution of sintered joints with those different metallization substrates during isothermal ageing has been presented and compared.

In Chapter 5, thermal cycling tests have been carried out to investigate the reliability of two sizes of sintered Ag joints and solder joints during temperature cycling between -55 °C to 125 °C and -55 °C to 150 °C. During thermal cycling, non-destructive and destructive characterization methods have been used as

characterization methods for revealing microstructure evolution of sintered Ag joints during thermal cycling.

Chapter 6 summarizes the experimental work covered in this thesis and suggests future work.

1.4 Research contribution

The main contribution of this work is investigation and identification of microstructure evolution of sintered Ag joints during isothermal ageing and thermal cycling tests, which provide insight into the relevant degradation/failure mechanisms of the sintered Ag joints occurring in tests. The specific contributions include the following:

(1) With quantitative microstructure characterization of as-sintered joints, the resulting normalized thickness, pore size and porosity decreased, and grain size increased with increasing the sintering time. A time dependence of the form $t^{1/n}$ with n close to 2 or 3 can be further derived for the kinetics of the thinning, densification and grain growth within the sintered Ag joints. It can be known that sintering kinetics is still in the intermediate stage, the densification had not been completed;

(2) Microstructure evolution of sintered Ag joint with four kinds of substrate finishes have been investigated during isothermal ageing. For bare copper substrates and substrates with Ag finish, because of oxide layer effects, sintered layer degraded along the substrate interface and ultimately separated from substrate surface, and it presented much denser microstructure. For sintered joints with Ag/NiP metallization and Au/NiP metallization substrates, the degradation of cracks initiated and propagated randomly and separately in sintered joints.

(3) Surface roughness of substrate has shown significant influence on the densification of sintered joint, and can result in different degradation microstructure of sintered joint during thermal cycling. Therefore, surface roughness should be considered carefully during the substrate selection;

(4) Three dimensional X-ray computed tomography has been used as non-destructive observation tool for characterization to reveal microstructure evolution of sintered joints during thermal cycling, which shows the progressive accumulation of damage with the same sintered joints during thermal cycling.

CHAPTER 2 Literature review

2.1 Introduction

In this chapter, development of silver sintering technology has been first reviewed. Sintering is a heating process which makes particles bond together, leading to strengthening and improving electrical, thermal and mechanical properties [60][61], however, high-temperature sintering has the risk of damaging device. In order to achieve low-temperature sintering technology, reducing particle size and pressure-assisted sintering have been considered as two effective ways [57][60][61].

Microstructure characterization of sintered joints has also been reviewed in this chapter to gain knowledge of the effects of materials and sintering parameters including nanoparticle size, pressure, temperature profile, substrate, etc. on the quality of the sintered joints. These can provide further insights into understanding reliability behaviour of sintered joints.

Reliability tests have been normally conducted to evaluate the bonding quality and application performance of sintered joints. In this chapter, reliability concerns for sintered joints application have been reviewed, which include high temperature storage reliability, and comparison of reliability between sintered joint and soldered joints.

2.2 Development of sintering Ag technology

As early as 1989, Schwarzbauer invented the sintering of microscale Ag particles used for mounting electronic devices [33]. However, this required high sintering temperature. In order to obtain highly dense microstructure of sintered joint, above 750 °C of high sintering temperature had to be applied for sintering microscale Ag paste, which might probably damage devices, substrates and other interconnection materials.

In order to lower the sintering temperature below 300 °C, Schwarzbauer et al. applied external pressure of 30-50 MPa on the chip/substrate assembly to speed up the sintering kinetics [33]. Zhang et al. investigated the sintering mechanism of Ag pastes, which revealed that applying external pressure would help the densification process by eliminating some fraction of pores through compression, increasing the contact area between the Ag particles [34]. With a pressure of about 40MPa, the Ag die attach layer underwent significant densification and presented good thermal and electrical conductivity. The sintered silver joints were also reported to be highly reliable. However, the requirement for such high pressure still bears risk of cracking or surface damage of the joining components, and it would significantly have the limitation of production throughput, manufacturing process, and it also places critical demands on substrate flatness, thickness of the chips, etc.

Zhang et al. [35] improved sintering technology significantly by replacing the Ag microscale particles with Ag nanoscale particles. To make it suitable for screen stencil-printing dispensing like solder paste or microscale Ag paste, some organic components such as dispersants, binders and thinners were mixed into the nanoscale Ag particles [36][37]. Wang et al. [38] found nanoscale Ag paste provides good mechanical support and exhibits densified microstructures after sintering as an alternative interconnection material for high-power semiconductor devices. Lu et al. and Bai et al. [39][40] showed results that electrical and thermal conductivities of sintered Ag joints were found to be 3–5 times higher than those of solder, and 10 times higher than those of conductive epoxy.

Therefore, reducing particle size and pressure-assisted sintering have been considered as two effective ways to achieve low-temperature sintering technology.

2.3 Microstructure characterization of sintered Ag joints

2.3.1 Effect of original nanoparticle size

The effect of grain size of Ag nanoparticle has been investigated and measured during the sample preparation process, and considered as one of the factors for

effective sintering [38][41][42]. The effect of two different grain sizes of Ag paste on the joint strength has been compared by Ide et al.[43]. Grain sizes of Ag nanoparticle (11 nm) paste and Ag fine particle (100 nm) paste have been measured by transmission electron microscopy (TEM) and further applied as die attachment. Joint strengths of as-sintered samples sintered with both grain sizes of paste were obtained through shearing tests. The shear strength of the joints sintered with 11 nm nanoparticle paste was 25-40 MPa, which was significantly higher than those sintered with 100 nm fine particle paste of 0.5-10 MPa, as Figure 2- 1 shows.

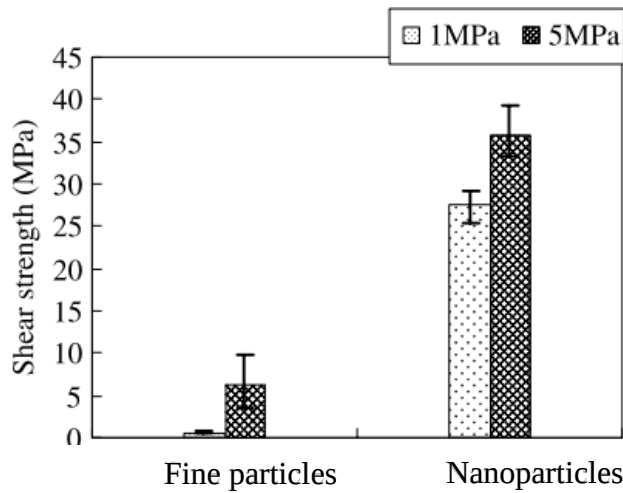


Figure 2- 1: The shear strength of sintered Ag joins with fine particles and nanoparticles (the error bar shows the maximum and minimum values) [43]

Besides, microstructure of sintered nanoparticle Ag joint and sintered fine particle joint have been characterized by scanning electron microscope (SEM) [43][44]. With the same sintering parameters, the sintered Ag nanoparticle (11 nm) joint had denser interfacial microstructure than that using Ag fine particle of 100 nm in size [43]. Moreover, Bai et al. [44] also revealed that the densification rate of 30 nm Ag nanoparticles was much higher than those of 100 nm Ag nanoparticles, as Figure 2- 2 shows.

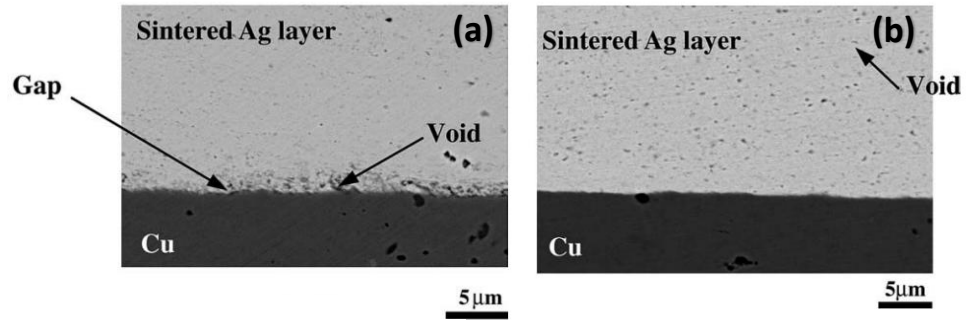


Figure 2- 2: Microstructure images of sintered Ag joints with (a) fine particle and (b) nanoparticle [43]

Furthermore, the fracture morphology of the sintered joint has been examined through SEM after shear test [43]. The fracture position of the joint sintered with nanoparticles (11 nm) Ag paste was predominantly in the sintered joint, while the fracture position of the joint sintered with fine particle (100 nm) Ag paste was mainly around the interface between sintered joint and substrate.

In literature [43], Ide et al. inferred that the difference of interfacial microstructure caused the shear strength variation. Because the nanoscale Ag particle might increase contact area between Ag particle and substrate surface, which can further improve bonding quality and increase interfacial bonding strength. Therefore, sintered joint using nanoscale grain size of Ag particle paste shows better bonding quality.

2.3.2 Effect of sintering pressure

As an alternative to solder die attach, pressure-assisted sintering technology was demonstrated by Zhang et al. in 2002 [34]. SEM micrographs of Ag pastes under various sintering conditions have shown microstructure characterization of as-sintered Ag pastes. It can be seen that the application of sintering pressure significantly increased the densification of the sintered layer. With higher the sintering pressure, it was showed the decrease of porosity and increase of shear strength. This improvement due to following main reasons:

(1) External pressure forces the Ag particles close together, which could increase contact area between the Ag particles and enhance their contact at the interfaces with the chip and substrate, these would further increase bonding strength [62].

(2) External pressure helps the densification process by eliminating some fraction of pores through compression, so the rearrangement of the nanoparticles can increase density [46][60].

As Figure 2- 3 shows, the sintering pressure has shown effect on the density (ρ) and shear strength (τ) [56]. The densities of sintered joints are 58% and 90% with sintering pressure of 0 MPa and 30 MPa. The shear strengths are 7 MPa and 47 MPa with sintering pressure of 0.3 MPa and 30 MPa. With higher sintering pressure, the density and shear strength are increasing at the same time. However, the too large external pressure makes the automation and application difficulty and also is a potential to damage the device or substrate.

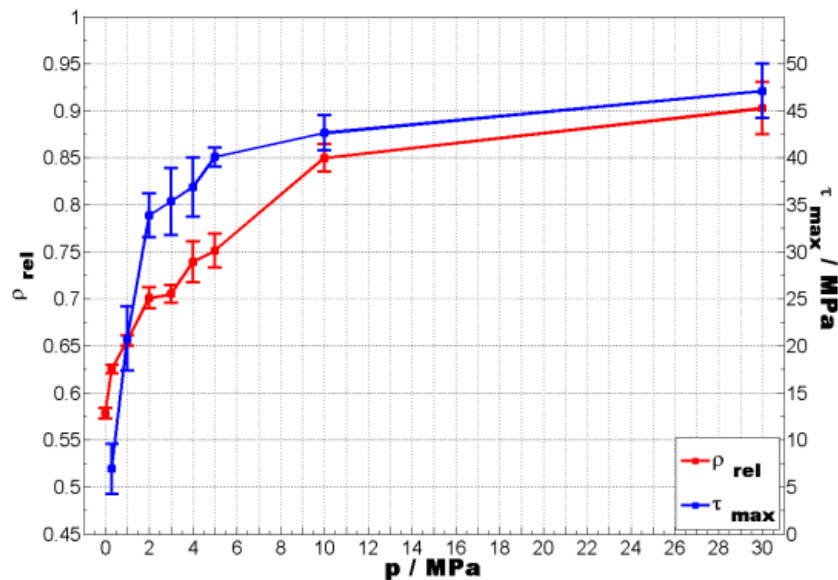


Figure 2- 3: Relative density (ρ) and maximum shear strength (τ) of sintered Ag joints sintering for 60s at 275 °C versus sintering pressure [45]

2.3.3 Effect of sintering temperature profile

In literature [44][46], with microstructure characterization and shearing tests of as-sintered Ag joints, relationship between sintering parameters and shear strength has been discussed.

Yan et al. [47] revealed the shear strength as a function of sintering temperatures with sintering pressure of 5 MPa for sintering 5 minutes and 30 minutes. As

Figure 2- 4 shows, when sintering temperature increased from 160 °C to 250 °C, the shear strength increased sharply from 9 MPa to 50 MPa. However, after sintering temperature exceeding 250 °C, the value of shear strength fluctuated around 50 MPa.

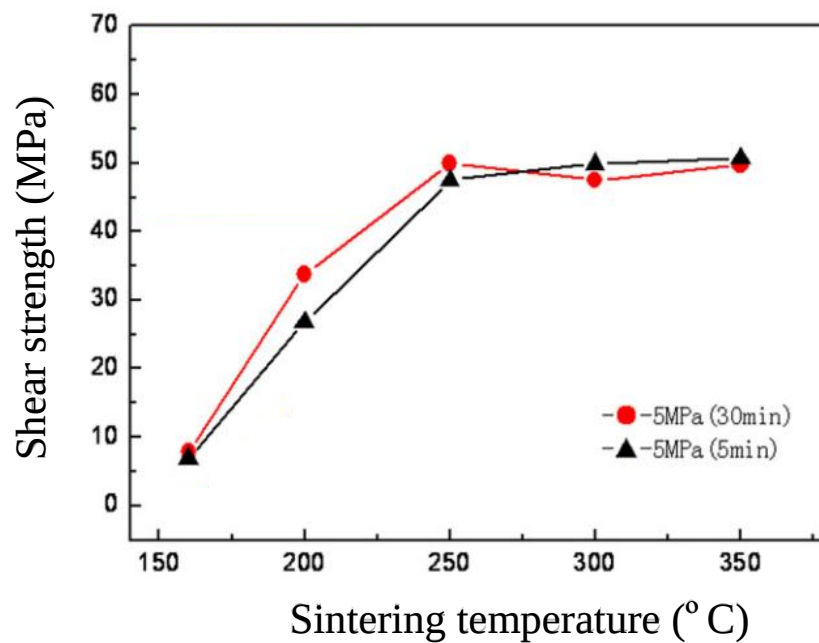


Figure 2- 4: Results of shear tests for sintered joints with sintering pressure of 5MPa and sintering time of 30 min and 5 min [47]

Kim et al. [42] investigated the microstructure evolution of Ag paste screen-printed on a silicon substrate as a function of sintering temperature as Figure 2-5 shows. When sintered at 150 °C for 30 minutes, the surface of the Ag nanoparticle paste showed the similar particle sharp and size as as-dried paste. While sintered at 200 °C for 30 minutes, the clusters were built through connections. As sintering temperature increased to 250 °C, the surface of sintered Ag nanoparticle paste drastically changed from discrete Ag nanoparticles to continuous and consolidated ones. After sintering at 300 °C, because of the solvent evaporation, the volume of the screen-printed sintered joint showed more significantly shrinkage. At the same time, more pores showed up in the sintered joint.

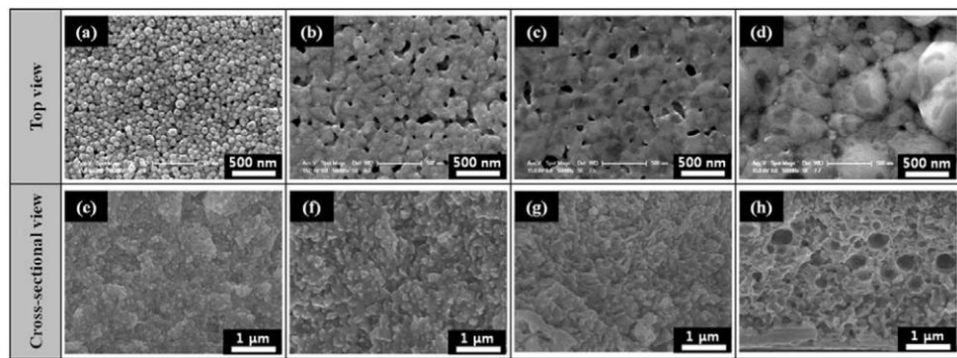


Figure 2- 5: Images of nanoparticle Ag paste sintered at various temperatures: (a) and (e) at 150 °C; (b) and (f) at 200 °C; (c) and (g) at 250 °C; (d) and (h) at 300 °C [61]

Wang et al. [48] revealed the SEM images of the fracture surfaces of sintered joints with different sintering temperature. While the sintering temperature went up to above 300 °C, from the SEM images, the densification could not be improved.

Therefore, good bonding quality is related to nanoparticle size, applied pressure, dispersant, etc., Above a certain sintering temperature may not

improve or even slightly degrade the bonding quality of the sintered joint [48][49][50].

Alarifi et al. [51] investigated the relationship between neck size of the Ag nanoparticle and sintering holding time of 1 minute, 3 minutes, 5 minutes, 10 minutes and 30 minutes at sintering temperature of 200 °C. The microstructure SEM results showed that neck growth was observed after 1 minute holding time, it continued growing till 5 minutes. Then the neck size became almost constant.

Wang et al. [48] also revealed that the effect of holding time and temperature rate on the densification mechanism by microstructure characterization of SEM images. For the nanoparticle paste used in the literature [48], the holding time of 60 min and heating rate of 10 °C/min are most effective and optimal for the sintering process. The result showed the prolonging the holding time cannot benefit the evolution of microstructure. Similarly, if the heating rate is higher than 10 °C/min, unstable volatilization of the organic solvent is more likely to cause partial sintering.

As mentioned previously, in order to achieve a well sintered joint and good bonding quality, nanoparticle size, sintering pressure, sintering temperature, holding time as well as heating rate have interactional effects on the final sintering results. Imposing low pressure can be compensated by higher temperature and long holding time to make sure dispersant evaporation and interface adhesion. Similarly, with limited sintering temperature, higher sintering pressure and longer holding time should be applied.

Above all, exceeding high enough sintering parameters, which could not have further positive effect on quality of sintered Ag joints, however, it might damage device and degrade the sintered joint at the same time.

2.3.4 Effect of substrate

In literature [47][48][50][52][53], Ag nanoparticles have been successfully used as bonding materials on different surface metallization substrates. In order to prevent oxidation during sintering process, nickel was deposited on the surfaces of the substrates, which can be served as a barrier layer [52].

Henaff et al. [54] investigated that effect of substrate metallization on the thermal and mechanical performance of sintered Ag joins. DBC substrate with Au/Ni metallization was applied as the bonding substrate. Thermal cycling test has been conducted to evaluate the reliability of sintered joints. After 2400 cycles between -40 °C to 150 °C, no crack or fracture can be observed by SEM cross-sectional microstructure characterization.

Bai et al. [52] conducted thermal cycling test from 50 °C to 250 °C for sintered Ag joints with Ag/Ni, Au/Ni DBC substrates and Ag metallized copper substrate. The failure criterial was based on 50 % decrease in shear strength of sintered joint. The sintered joints with Ag/Ni and Au/Ni DBC substrates withstood 4000 and 6000 cycles, as Figure 2- 7 shows, while the sintered joint with copper substrate only failed at 500 cycles, as Figure 2- 6 shows. Bai et al. concluded the sintered Ag joints with copper substrate was exposed to higher thermally-induced stresses than sintered Ag joints with Ag/Ni and Au/Ni metallized DBC substrates, because the combination of Cu substrate and SiC device has a substantially larger CTE mismatch than those of DBC substrates/SiC [52].

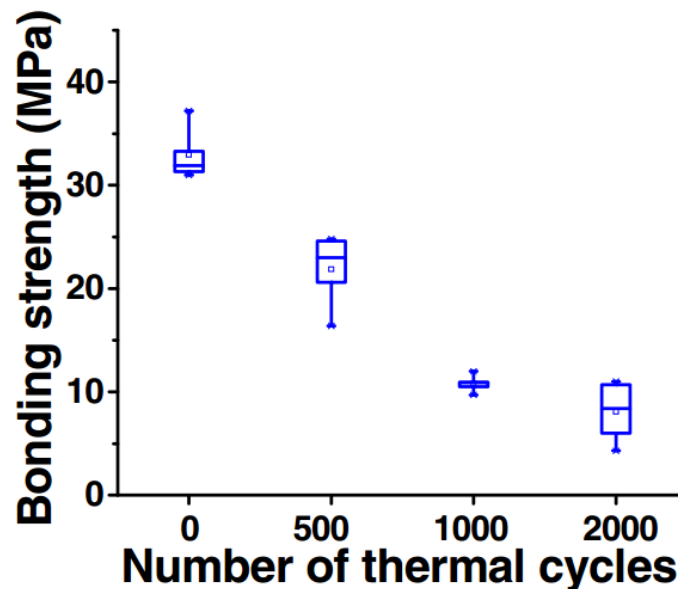


Figure 2- 6: Shear tests results of sintered joints with copper substrate during thermal cycling between 50 °C to 250 °C [52]

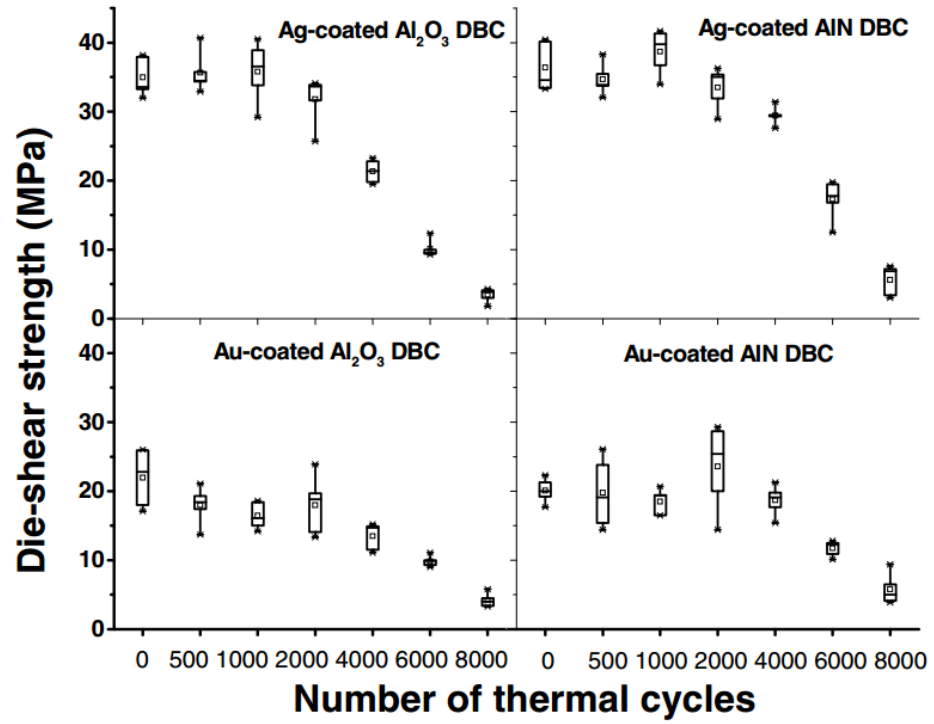


Figure 2- 7: Shear tests results of sintered joints with different DBC substrates during thermal cycling between 50 °C to 250 °C [52]

In literature[55][56][57], the formation of epitaxial layer in sintered joints has also been observed and discussed. Akada et al. [55] showed TEM images and diffraction patterns of the Ag/Au interface sintering at 300 °C, as Figure 2- 8 shows. The diffraction pattern of Ag near interface corresponded to that of Au. As lattice image observation of the interface shows, the crystal orientation of Ag corresponded to that of gold. It is considered that the epitaxial layer of Ag was formed and it is oriented in the direction of the Au crystal.

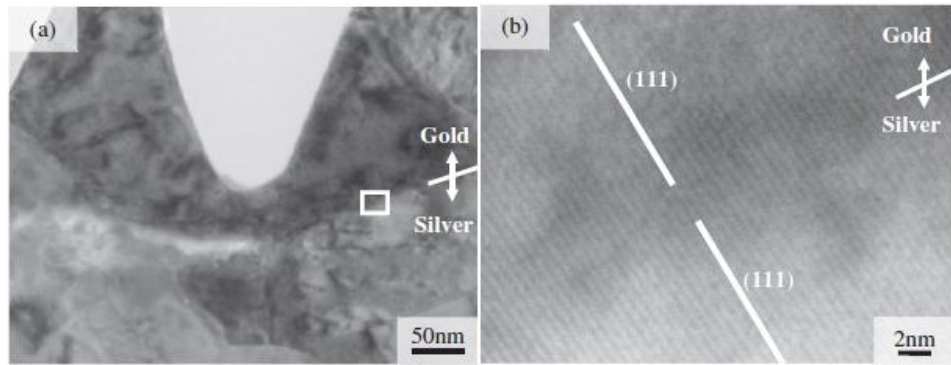


Figure 2- 8: TEM and lattice images of the Ag/Au interface sintering at 300 °C
(a) Bright-field image. (b) Lattice image [55]

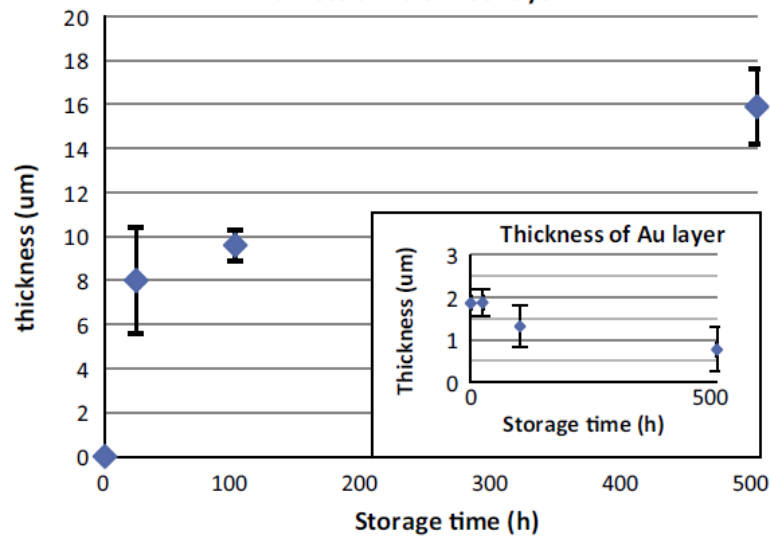


Figure 2- 9: Thickness of epitaxial layer as function of isothermal ageing time.
Insert shows thickness of the residual Au plating [57]

Paknejad et al. [57] also showed the grain structure of the plated Au led to diffusion of Au into the sintered Ag joint by atomic diffusion. It concluded that voids migrated away from the Ag/Au interface and into sintered Ag joint leading to formation of the epitaxial layer and high porosity region, which probably weaken the bonding strength of the sintered joint. As Figure 2- 10 shows, the region above epitaxial layer showed high porosity and nearly

delaminated. The thickness of epitaxial layer increased with more storage time, while thickness of Au layer decreased, as Figure 2- 8 shows.

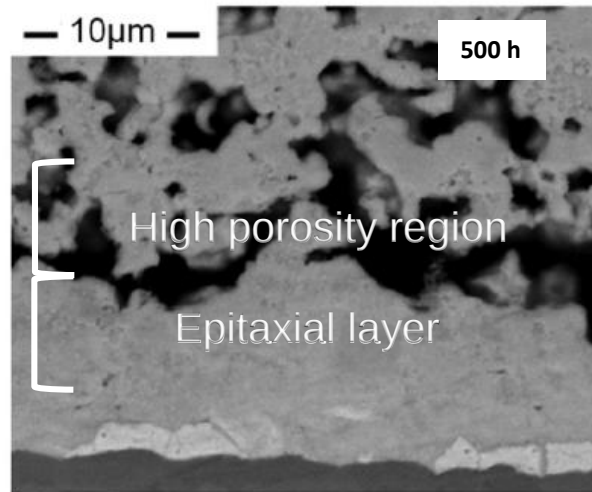


Figure 2- 10: SEM images of sintered joint ageing for 500 hours at 300 °C
[57]

From the literature [58][59], roughness of substrates surface is another factor which has influence on the bonding quality of sintered joints. Navarro et al. [58] evaluated the influence of different surface roughness on the shear strength of sintered joint. It has been shown that when roughness of substrates surface increased, the die shear strength decreased, as Figure 2- 11 shows. Buttay et al. [59] showed the cross-sectional SEM images of sintered joint with raw DBC and polished DBC. As Figure 2- 12 shows, the sintered joint with polished DBC with lower roughness value had better bonding quality.

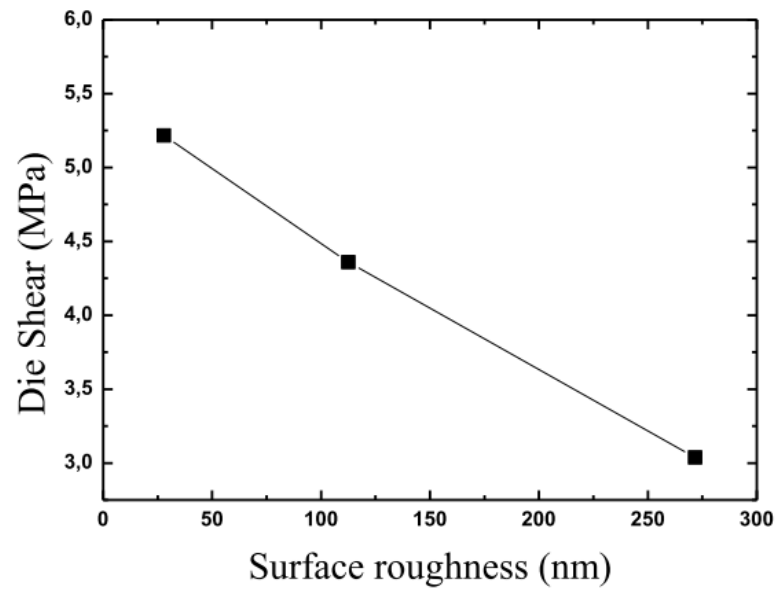
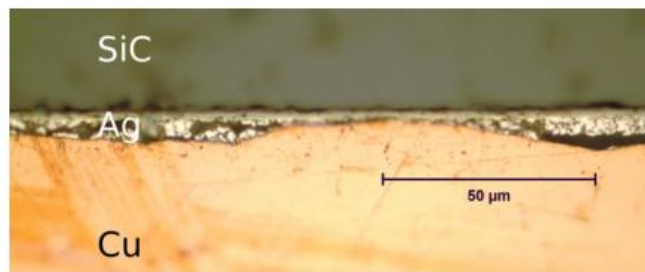
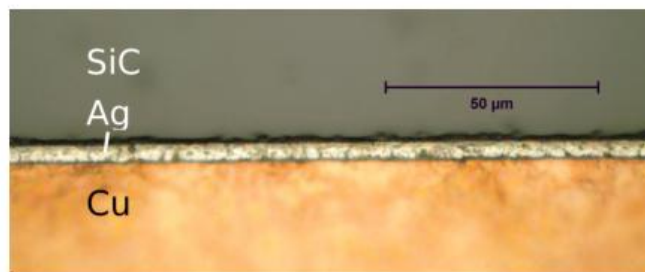


Figure 2- 11: Results of shear tests of sintered joints with different roughness substrates [58]



(a)



(b)

Figure 2- 12: Cross-sectional images of sintered joints with raw DBC (a) and polished DBC substrate (b) [59]

2.4 Reliability of sintered Ag joints

2.4.1 High temperature isothermal ageing tests

Li et al. [60] conducted shear tests on sintered Ag joint (1mm×1mm) with Ag/Ni electroless plated substrate during thermal ageing test. At ageing temperature of 85 °C, isothermal ageing time showed effect on shear strength of die attach. According to results, the shear strength declined to 99.65%, 91.99%, 78.40% and 79.09% at 24 hours, 168 hours, 720 hours and 1000 hours, respectively. After 1000 hours, the shear strength of sintered joint was about 22 MPa. As Figure 2- 13 shows, during isothermal ageing, the degradation of sintered joints has occurred.

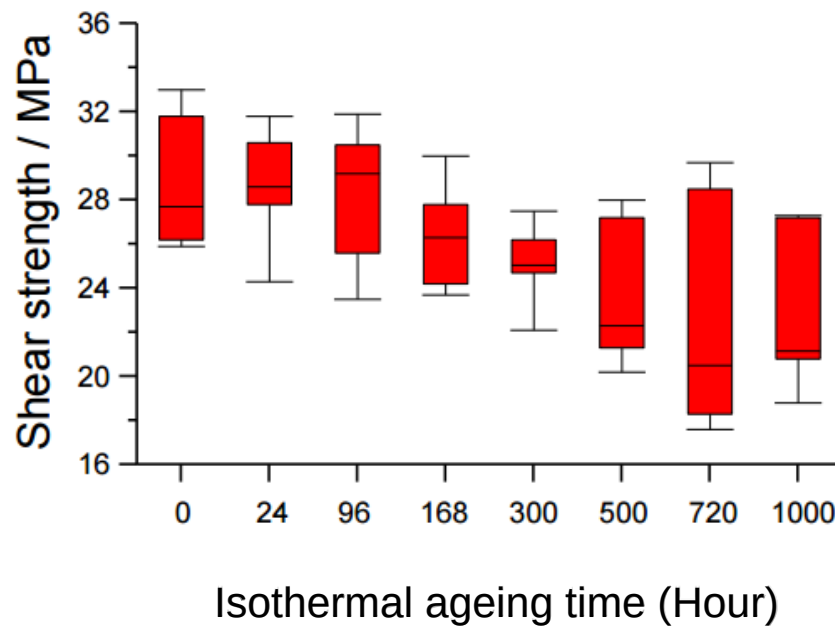


Figure 2- 13: Results of shear tests of sintered joints during isothermal ageing at 85 °C [60]

Paknejad et al. [57] has reported that degradation of sintered joints with Au/Ni metallization substrates during isothermal ageing at 300 °C. For the sintered

joints with Au/Ni metallization substrates, samples were pressure-free sintered on substrate with 2 μm Au/Ni metallization layer. As SEM images of cross-section samples show, there were void-free layer on substrate surface and the layer thickness grew with isothermal ageing time.

As discussed in the literature [57], it was observed that the shear strengths of sintered Ag joints with Au/Ni substrate were decreasing during isothermal ageing at 300 $^{\circ}\text{C}$, as Figure 2- 14 shows.

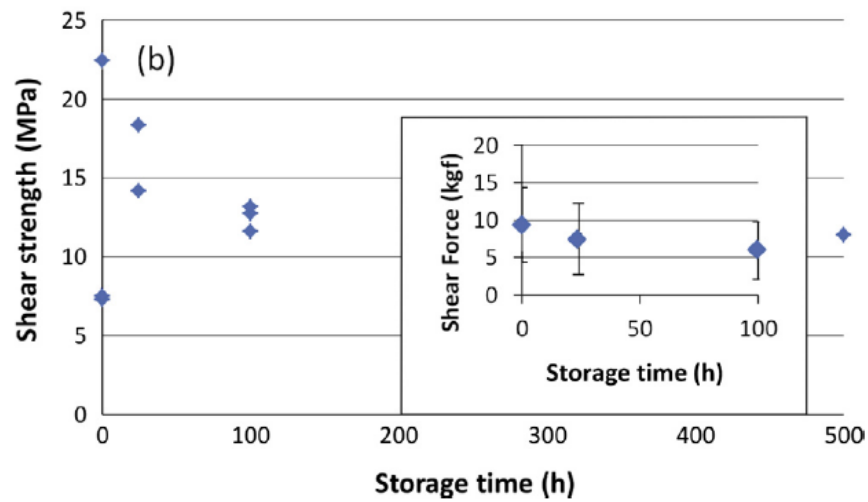


Figure 2- 14: Shear strength on Au substrates (main body shows individual shear test results and insets show shear strength of all samples including those which fractured during the test) [57]

There is limited literature for the high temperature storage reliability of sintered joint. In literature, shear strength was normally used for evaluating the reliability of sintered joint during isothermal ageing. However, in order to get knowledge of relevant degradation mechanisms of the sintered Ag joints during isothermal ageing, it is very important to understand the microstructure evolution during isothermal ageing, thus the reliability of sintered joint can be predictable and evaluable.

2.4.2 Comparison of reliability between sintered joints and solder joints

In literature [16][50][61], thermomechanical reliability of sintered Ag joints has been compared with solder joint during passive temperature cycling test. It has been revealed that the sintered Ag joints performed better thermomechanical reliability than that of typical solder joints.

In literature [61], for the thermal cycling test between -5 °C to 175 °C, it has been demonstrated that sintered Ag joints in good condition can survive about 1000 cycles, while in the same condition, $\text{Sn}_{96.5}\text{Ag}_3\text{Cu}_5$ and $\text{Pb}_{95}\text{Sn}_5$ have only passed 70 and 150 cycles, respectively. For power cycling test with the same samples, the sintered devices showed results of 208000 cycles to failure, while the soldered ones failed with a characteristic lifetime of 11970 cycles. In literature [50], for -45 °C to 250 °C thermal cycling test, die shear strength of sintered Ag joints varies from 25 MPa to 15 MPa while $\text{Au}_{88}\text{Ge}_{12}$ solder showed a decrease of the shear strength from 50 MPa to 15 MPa.

2.4.3 M

2.4.3 Characterization and evaluation of samples during reliability test

In previous literature, microstructure characterization of sintered joints were normally conducted and observed by destructive methods, such as SEM, TEM, etc. However, as one of an infinite number of potential planes is examined, such results might be at risk of misinterpretation. Furthermore, this approach cannot have the same specimen monitored and evaluated over an entire period of its lifetime [62].

Non-destructive test utilizes various non-invasive measurement techniques, such as ultrasonic and radiography to determine the integrity of the samples without destroying the usefulness of them. Scanning acoustic microscopy (SAM) and X-ray computed tomography are very powerful non-destructive tools for characterization and evaluation of microstructure evolution.

As Figure 2- 15 shows, Boettage et al. [63] also showed voids in sintered joints have been detected by SAM and presented comparison of SAM results between good bonding interface and delaminated interface. Boettage et al.

presumed the substrate metallization quality was the root cause for the delamination.

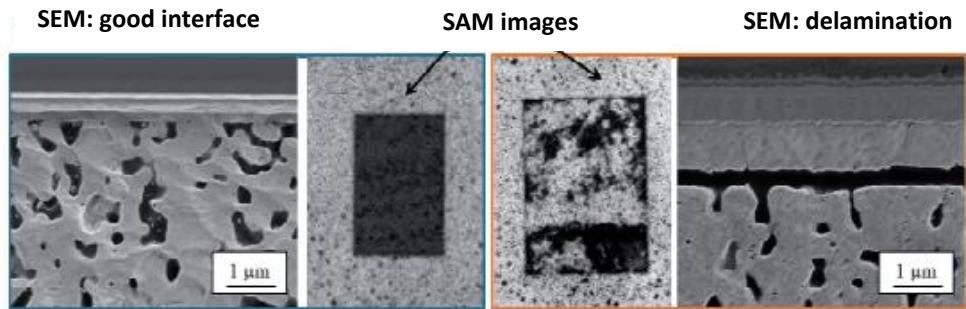


Figure 2- 15: Differences in bonding quality of silver-sintered interfaces in dependence of the backside metallization. Centre: SAM images. Left/Right: SEM images of the cross sections after defect target preparation [63]

X-ray computed tomography has been proved to be a reliable technique to obtain the 3D microstructure of materials to a satisfactory resolution. Because a specific specimen can be evaluated over its lifetime, a true image of microstructure evolution of damage during operation can be obtained, and crack and degradation can be observed three-dimensionally [62]. Furthermore, multiple virtual cross-sectional images can be presented.

Chen et al. [64] compared the X-ray tomography image of as-sintered joint with those of as-soldered joint. The results of X-ray tomography images showed that there were more voids in the soldered joint, and the porosities of sintered joint and solder joint are 0.52% and 2.41%, respectively, as Figure 2-16 shows. However, the X-ray tomograph was not further conducted to investigate the degradation of sintered joint and soldered joint.

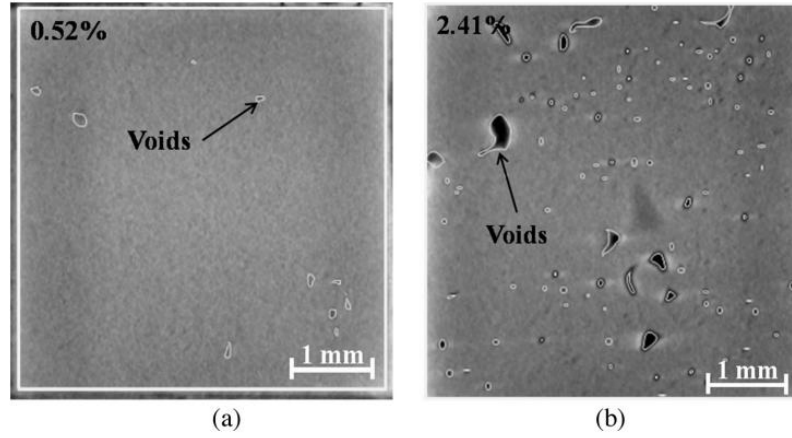


Figure 2- 16: X-ray tomography images of (a) as-sintered Ag joint and (b) as-soldered SAC305 joint [64]

Agyakwa et al. [62] demonstrated the potentials to observe the progressive accumulation of same wires during passive thermal cycling between $-55\text{ }^{\circ}\text{C}$ and $190\text{ }^{\circ}\text{C}$. From X-ray tomography images, cracks can be seen emerging from the extreme ends of the bonds after 517 cycles, as Figure 2- 17 shows.

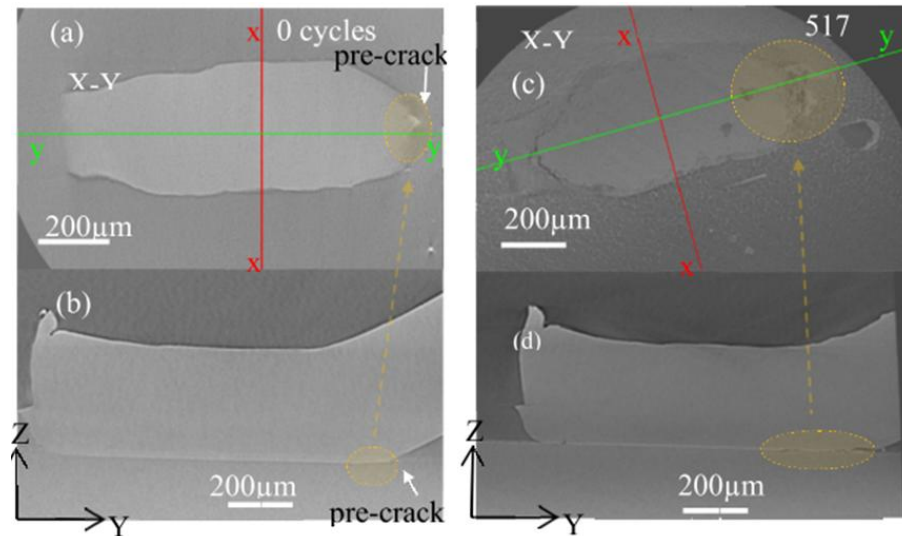


Figure 2- 17: Virtual cross-sectional images of wire bond by X-ray tomography [62]

Li et al. [16] presents a comparative investigation of thermomechanical reliability of four kinds of bonding materials under passive thermal cycling between -60 °C and 190 °C, -55 °C and 190 °C, which included $Pb_{5}Sn$, $Au_{12}Ge$, $Zn_{5}Al_{0.1}Ge$ solder alloys and sintered Ag joints. Microstructure of samples has been characterized by X-ray tomography during thermal cycling. From the virtual cross-section images it could be seen that there is no appreciable effect observed in sintered joint and solder joints after 640 cycles, as Figure 2- 18 shows.

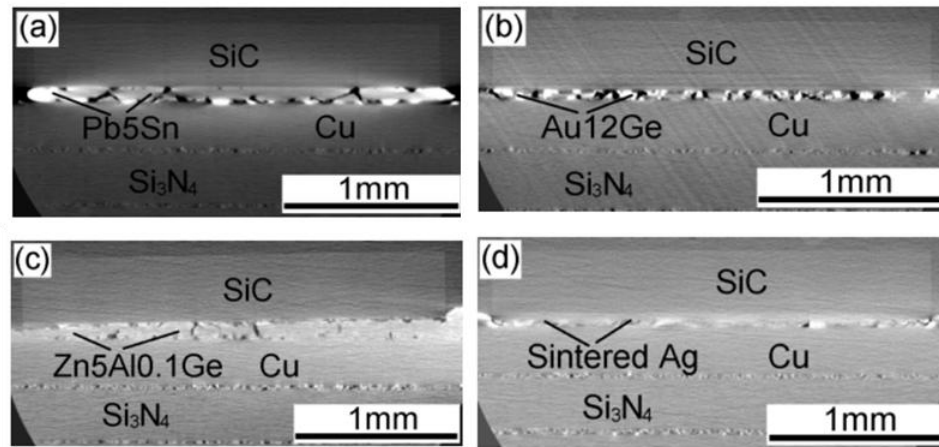


Figure 2- 18: X-ray images obtained from samples after 640 cycles: (a) $Pb_{5}Sn$, (b) $Au_{12}Ge$, (c) $Zn_{5}Al_{0.1}Ge$ solder alloys and (d) sintered Ag joints [16]

For sintered Ag joints, there is very limited literature for non-destructive reliability evaluation by X-ray tomography technology. However, in recent years, most researches on reliability of sintered Ag joints were focused on the shear strength test to evaluate the bonding quality or cross-sectional SEM images to reveal the degradation of sintered Ag joints. In this respect, additional insight attainable from X-ray computed tomography is both unique and invaluable, particularly in relation to observation of degradation development in three-dimensional space for the same sintered Ag joint.

2.5 Summary

This chapter includes three main parts: development of sintered Ag joints technology, microstructure characterization and reliability of sintered Ag joints. Pressure-assisted sintering and nanoscale Ag particles use are two effective ways to lower the sintering temperature.

In order to achieve good bonding quality, nanoparticle size, sintering pressure, sintering temperature, holding time and temperature rate have interactional effects on the final sintering results. In literature, the reliability of solder joints has been compared with that of sintered Ag joint at the same condition. It can be seen that the sintered Ag joints have got better reliability than solder joints during isothermal ageing and thermal cycling. Non-destructive methods for microstructure characterization have been reviewed, which can provide more information of degradation microstructure.

CHAPTER 3 Microstructure

characterizations of as-sintered Ag joints

3.1 Introduction

Microstructural features of sintered Ag joints are different from those of the reflowed solder joints, and there is rearrangement of Ag nanoparticles, densification and reduction in porosity and grain growth occurring during the sintering process. In this chapter, the microstructural features of sintered Ag joints (13mm ×13 mm) for power die attachments which were prepared at 240 °C and 5 MPa for 3 to 17 minutes were quantitatively characterized with SEM (scanning electronic microscopy), TEM (transmission electron microscopy), XRD (X-ray diffraction) and binary image analysis method. The microstructural features characterized in this chapter include the thickness, pore size, porosity and grain size. SEM is used to observe the bonding quality at the interfaces, micro-scale voids and the defects around the interfaces and within the joints, as well as the thickness uniformity of the joints across the entire bonding area. TEM and XRD are used to measure grain size and dislocation density of sintered joints. Binary image analysis can be used for measuring the thickness, pore size and porosity values from the images obtained by SEM.

From literature review, it can be seen that there is a wealth of studies on the formulation of the Ag nanoparticle pastes, manner and pattern of printing paste, sintering process, mechanical and thermo-mechanical properties, as well as thermal cycling and power cycling reliability. However, there is no work which has been carried out to explore the variation in those values of microstructural features and their quantitative dependence on the sintering parameters. In this chapter, characterization of sintered Ag joint microstructures with SEM, TEM and XRD is necessary to obtain the information about the densification, uniformity, grain size and voids/defects, which are necessary for investigating the effects of the sintered parameters on the quality of the sintered joint. Such a

quantitative characterization would provide a better description to further optimize the process and predict the performance and reliability of the sintered joints used in power electronic systems.

3.2 Experiment procedure

3.2.1 Materials

The paste of Ag nanoparticles used was obtained from Cookson Electronics (South Plainfield, NJ 07080, USA), and has been formulated for pressure-assisted die attachment on Ag or Au finish. The average size of the Ag nanoparticles was about 20 nm. This Ag nanoparticle paste was mixed the Ag nanoparticle powder with some organic vehicle, such as binder, surfactant, as well as thinner. The binder usually holds the dispersed Ag nanoparticles together in order to avoid cracking of sintering joints during drying and sintering stages. The surfactant can keep Ag nanoparticles from agglomeration. The thinner is used to adjust viscosity for ease of dispensing or printing.

The substrates used to attach Si devices for measuring thickness, pore size and porosity of the sintered Ag joints were Si₃N₄-based substrates. They were cut into 22 mm × 17 mm coupons from received 44 mm × 34 mm substrates which consist of 0.32 mm thick Si₃N₄ ceramic tiles sandwiched by 0.3 mm thick Cu actively brazed on both sides. The surface finish on the as-received substrates was 5 μm thick NiP. An additional Ag layer of about 2 μm in thickness was further deposited with brush plating on the NiP finish. The Si devices attached on the Si₃N₄-based substrates were 13 mm × 13 mm × 0.35 mm Si insulated gate bipolar transistors (IGBTs) with around 1/1 μm thick Ni/Ag metallization on their back sides.

The substrates used to prepare the samples for measuring the grain size of the sintered Ag layers were 25 mm × 15 mm × 0.1 mm Ag foil substrates. After printing and drying the paste of Ag nanoparticles on the Ag foil substrates, a piece of 20 mm × 10 mm × 0.1 mm Fe foil was placed on the top of each of the samples for applying the pressure during the final sintering stage.

3.2.2 Sintering process

The sintered Ag samples were prepared using a home-made press. The paste of Ag nanoparticles was first printed on all the substrates with 100 μm thick

stainless steel stencils. In the case of the Si_3N_4 -based substrates, the size of the printed paste was $16 \text{ mm} \times 16 \text{ mm}$ on each of the substrates. In the case of the Ag foil substrates, the size of the printed paste was $20 \text{ mm} \times 10 \text{ mm}$ on each of the substrates. Then all the substrates printed with the wet paste were moved into an oven to dry at 130°C for 30 minutes.

The thicknesses of the dried paste on the Si_3N_4 -based substrates were first measured using a Zeta-20 optical profiler (Zeta Instruments, San Jose, CA 95131). During the measurement, both the horizontal and vertical resolutions were less than $1 \mu\text{m}$. Then one Si IGBT was placed on the central area of the dried paste on each of the Si_3N_4 -based substrates, and fixed with Kapton tape. The sample was turned upside down and put on 1 mm thick silicone rubber situated on the cold plate of the press. The final sintering was performed at temperature of 240°C and pressure of 5 MPa for 3, 5, 9 or 17 minutes before releasing the pressure and cooling the sample down to room temperature within 3 minutes. Figure 3- 1 shows the schematic sample geometry and temperature / pressure profile used to prepare these samples.

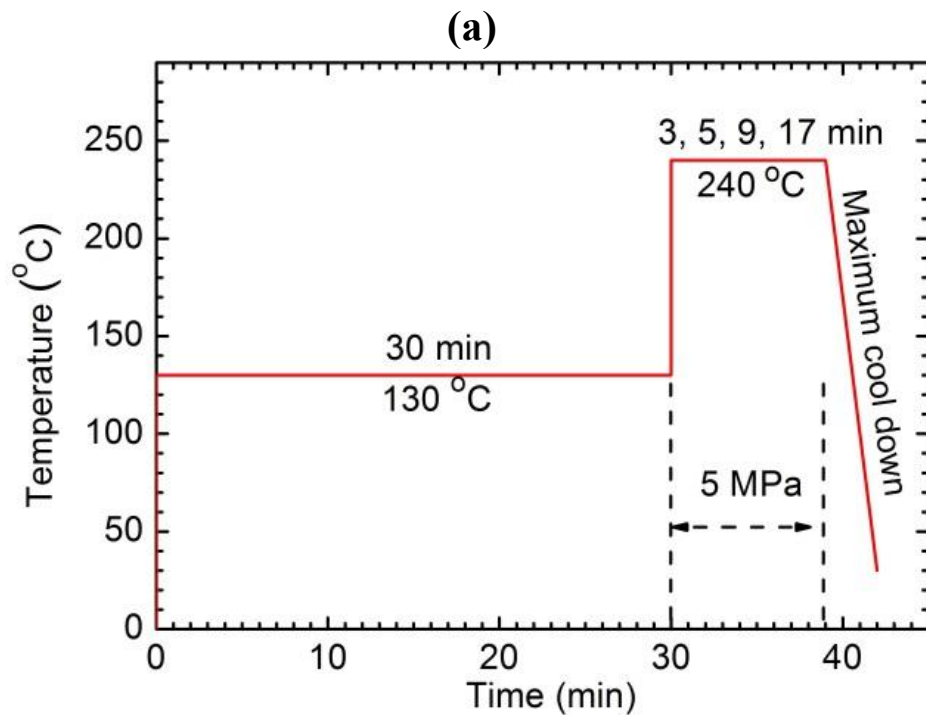
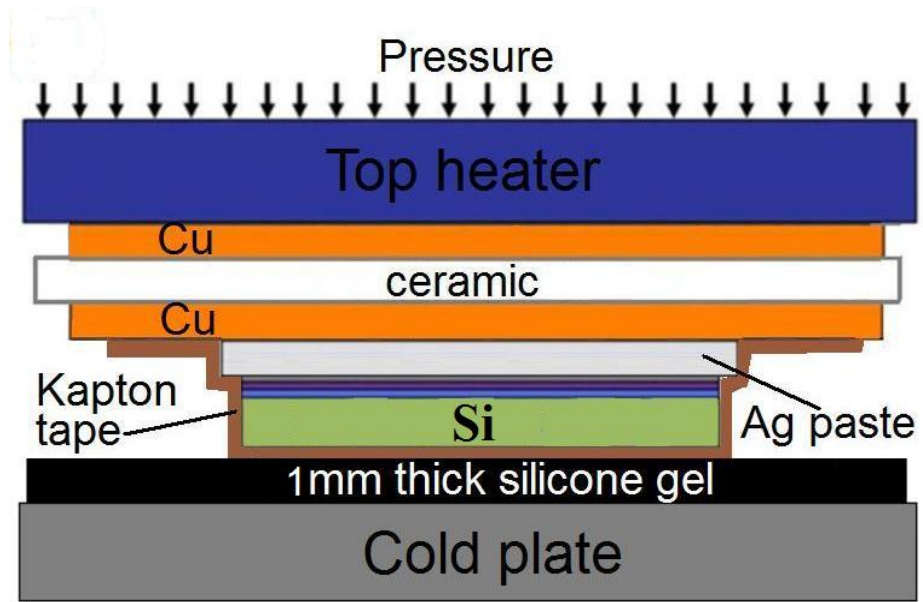


Figure 3- 1: Schematic diagrams of sample geometry (a) and temperature and pressure profile (b) used during the sintering process. Note that the dimensions of sample geometry are not to scale.

Each of the four Ag foil substrates with printed and dried Ag paste was covered by one piece of Fe foil, and then moved onto the cold plate of the press directly.

The final sintering was also carried out at temperature of 240 °C and pressure of 5 MPa for 3, 5, 9 or 17 minutes before releasing the pressure and cooling the sample down to room temperature within 3 minutes.

3.2.3 Microstructure characterization

3.2.3.1 Cross sectional process

The process of specimen preparation for SEM is as Figure 3- 2 shows:

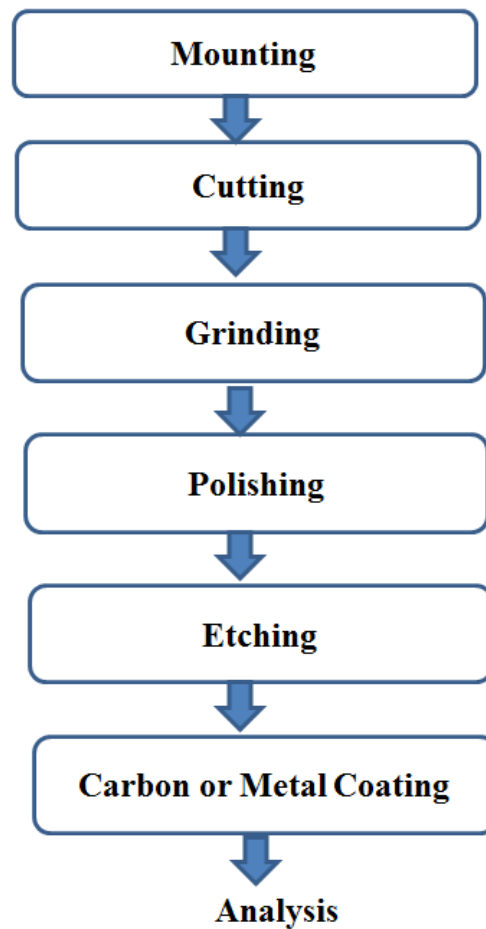


Figure 3- 2:Cross section process of sample preparation

First, the sample was placed upright within the mould, which was then filled with an edge retaining resin and hardener mix and allowed to cure for 24 hours. A BUEHLER ISoMet 1000 fitted with a diamond-impregnated blade was then used to cut the samples close to the plane of interest.

The mounted samples were ground with 600, 800, 1000 and 1200 grit SiC papers each for 50 seconds. A BUERHLER AutoMet 250 Grinder-Polisher was used for grinding. The samples were further polished using diamond slurries of 3 and 1 μm , both for 10 min, ensuring that the deformation introduced during the previous steps were removed. A final polish was then done using an Al_2O_3 suspension with a grit size of 0.1 μm .

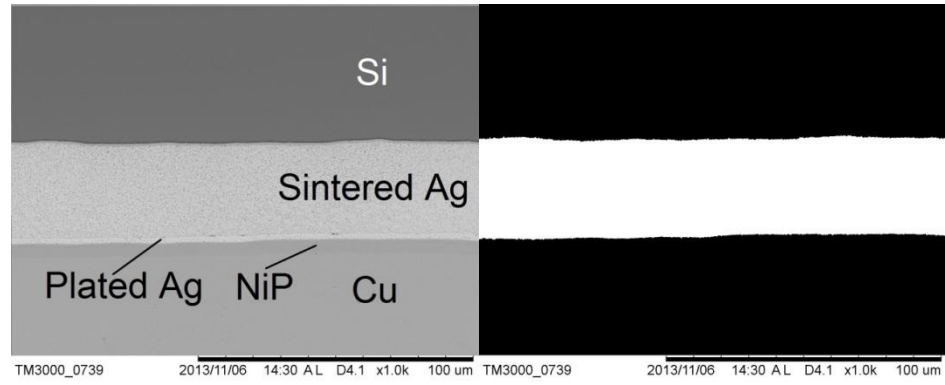
A UNITRONICS PE-200 industrial bench top plasma processing system was employed for plasma etching in this work. Each polished sample was placed in the chamber for a plasma time of 15 min. The setting for purge vent was 59s and the gas was set to stabilize for 30s after etching.

Prior to SEM analysis, the samples were coated with a thin conducting film (platinum).

3.2.3.1 Thickness and pore

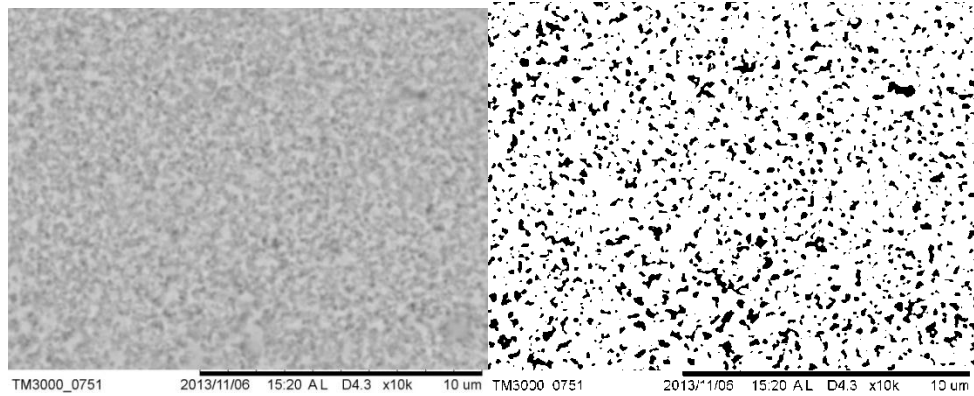
A Hitachi TM300 desktop SEM was employed to observe the microstructure features and take images from the etched samples for measuring thickness, pore size and porosity of the sintered Ag joints. For each sample, ten SEM images 1280×960 pixels in resolution and $170 \times 127 \mu\text{m}$ in size were taken for measuring the thickness, and another ten SEM images 1280×960 pixels in resolution and $17 \times 12.7 \mu\text{m}$ in size were taken for measuring the pore size and porosity. All the SEM images were evenly taken along the entire 13 mm length of the Si IGBT on the etched sample, and the SEM images used to measure the pore size and porosity were taken in the middle areas of the sintered Ag layer in the through-thickness direction.

All the thickness, pore size and porosity values were measured using the binary image analysis which was accomplished using the Image Analysis Toolbox Version 5.0.2 of MATLAB R14SP2 (Mathworks Inc.). The key steps were to enhance the as-taken grey level SEM images and then produce the corresponding binary images to extract the specific Ag layers or the pore features within the Ag layers, as detailed in the previous work [65]. Figure 3- 3 presents representative SEM images and binary images used to measure the thickness, pore size and porosity values.



(a)

(b)



(c)

(d)

Figure 3- 3: (a) One representative SEM image and (b) the corresponding black and white binary used to measure the thickness values; (c) one representative SEM images and (d) the corresponding black and white binary used to measure the pore size and porosity values for the sample of attaching one Si IGBT on the Si_3N_4 -based substrate at 240 °C and 5 MPa for 5 minutes.

A data series for the thickness was obtained from the intercepted lengths of the extracted Ag layer in the through-thickness direction, which were subtracted by 2 μm to account for the brush-plated Ag layer on the NiP finish, on each of the black and white binary images similar to Figure 3- 3(b). The average value of the thickness series obtained from each binary image was calculated and used to represent the thickness at the middle point of the cross section where the SEM image was taken. The 10 thickness series obtained from the 10 SEM images were further merged as a total thickness series for the corresponding sample. The results of statistical analysis in terms of mean, standard deviation, coefficient of variation, minimum and maximum values of the total thickness

series were calculated to compare the thickness and its variation among the 4 samples prepared with sintering times of 3, 5, 9 and 17 minutes.

The pore size was expressed as “apparent” radius and we calculated as:

$$r = \sqrt{S/\pi} \quad 3-1$$

Where r is the “apparent” radius, S is area of a pore measured from the black and white image similar to Figure 3- 3(b). A data series for the pore size were obtained from each of the SEM images used to measure the pore size and porosity. Similar to thickness, the average value of the pore size series was calculated and used to represent the pore size at the middle point of the cross section where the SEM image was taken. The 10 pore size series obtained from the 10 SEM images were further merged as a total pore size series. The mean, standard deviation, coefficient of variation, minimum and maximum values of the total pore size series were calculated to compare the pore size and its variation among the 4 samples prepared with sintering times of 3, 5, 9 and 17 minutes.

The measurement of porosity is relatively simple. The porosity was calculated from the total area of the black areas in the black and white binary images similar to Figure 3- 3(d). The porosity values obtained from each binary image can be used to represent the porosity at the middle point of the cross section where the SEM image was taken. The mean, standard deviation, coefficient of variation, minimum and maximum values of the 10 porosity values obtained for each sample were further calculated to compare the porosity and its variation among the 4 samples prepared with sintering times of 3, 5, 9 and 17 minutes.

In addition, the SEM images were also taken from the surface on the as-dried paste of Ag nanoparticles, and the pore size and porosity values were measured from these SEM images as the approximate values for sintering time of zero minutes.

3.2.3.2 Grain size

After sintering, the Fe foils were not bonded on the sintered Ag layers and were removed from the samples. Then the sintered Ag layers on the Ag foil substrates,

as well as the as-dried paste of Ag nanoparticles, were analyzed with X-ray diffraction (XRD).

XRD is based on constructive interference of monochromatic X-rays and a crystalline sample. XRD has been used for getting information about the crystal size and strain density of material, which is because widening of the XRD peaks can be used to measure the crystal sizes from approximately 2nm to 500nm and strain induced due to crystal imperfection and distortion. X-ray diffraction is most widely used for the identification of unknown crystalline materials.

The XRD data were obtained using a Siemens D500 X-ray diffractometer. The experimental conditions included a Cu target, operating at 40 kV and 30 mA, and a 0.15 ° receiving slit. The collected data angles (2θ) ranged from 35° to 120° with a step size of 0.01 ° and a counting time of 8s per step.

After obtaining the XRD data, a fundamental approach [66] was used to eliminate the machine-induced widening and calculate the sample-induced line widening at half the maximum intensity for all XRD peaks of Ag. This was done using the X-ray line profile fitting program, XFIT [66], and line profile Fourier analysis, FOURYA [67], in combination with the XRD spectrum of 300-mesh LaB₆ as standard sample.

The initial intention was to estimate the grain size values of the sintered Ag layers with the William-Hall equation as expressed as [68]:

$$\Delta K = 1/d + \alpha K^2 c + o(K^2 c) \quad 3-2$$

Where $\Delta K = 2 \cos \theta \Delta \theta / \lambda$ is the integral breadth of $K = 2 \sin \theta / \lambda$, θ is the diffraction angle, λ is the wavelength of X-ray, d is an apparent grain size, α is a constant, c is the average dislocation contrast factor, and o stands for higher order terms. However, the resulting data of ΔK and $Kc^{1/2}$ were not fitted to Equation 3.2 reasonably well. Thus, the Scherrer equation [69][70] as expressed in Equation 3.3 was used to estimate the grain size values of sintered Ag layers.

$$d = \beta \lambda / (\Delta \theta \cos \theta) \quad 3-3$$

Where β is a dimensionless shape factor close to 1 and $\Delta\theta$ is the line widening at half the maximum intensity. For each sample, the grain size is the average value of data calculated from the peaks observed in the XRD spectrum.

In order to evaluate the grain size values estimated with the XRD Scherrer method, the sintered Ag layers produced with sintering times of 5 and 17 minutes and the as-dried paste of Ag nanoparticles were also observed with a JEOL JEM-2000FX transmission electron microscope (TEM).

TEM is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

TEM sample preparation of small nanoparticles usually involves preparing a stable dispersion in a suitable liquid medium with the help of surface-active additives. Then a drop of the dispersion is transferred to a glassy carbon film mounted on a microscope grid.

Another method of TEM sample preparation is taking advantage of technology of FIB. The advantage of FIB sample preparation is that it is possible to prepare TEM specimens from precise locations in the sample.

In this work, the $15\ \mu\text{m} \times 5\ \mu\text{m} \times 0.2\ \mu\text{m}$ TEM samples were lifted out of the central areas in sintered Ag layers with a FEI Quanta 3D FIB-SEM machine. During this operation, the final accelerating voltage and current were 10 kV and 16 pA, respectively.

In addition, a few particles were obtained using a stainless steel knife to scratch the surface of the as-dried Ag nanoparticle paste which was then dispersed onto a thin carbon film fixed on a copper mesh for TEM observation.

3.3 Results

3.3.1 Thickness reduction during sintering process

SEM observation revealed that the microstructural features were not uniform along the polished and plasma-etched cross sections of all the sintered samples. Figure 3- 4 shows representative SEM images taken from the sample sintered at

240 °C and 5 MPa for 9 minutes. It can be seen that the sintered Ag layer is relatively thick and porous, and the bonding between the sintered Ag layer and both the Si IGBT and the brush-plated Ag layer on the Si₃N₄-based substrate is poor at the edge area. By contrast, the sintered Ag layer is relatively thin and dense, and the bonding between the sintered Ag layer and both the Si IGBT and the brush-plated Ag layer on the Si₃N₄-based substrate is quite good in the central area.

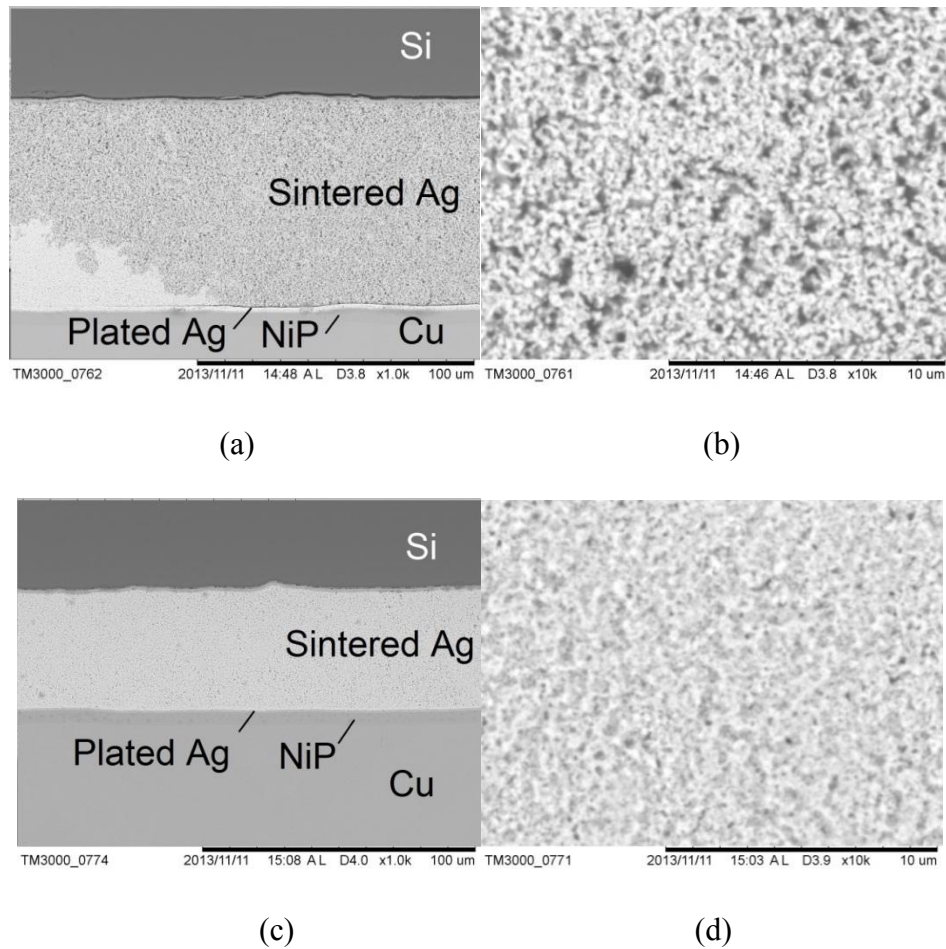


Figure 3- 4: SEM images taken from the polished and plasma-etched cross section of the sample of attaching one Si IGBT on the Si₃N₄-based substrate at 240 °C and 5 MPa for 9 minutes: (a) overview at edge area; (b) enlarged view at edged area; (c) overview in the cenrtal area; and (d) enlarged view in the central area.

Figure 3- 5 quantatively shows the variations in the thicknesses of the sintered

Ag joints along the cross-sectional positions in the four samples of attaching Si IGBTs on the Si_3N_4 -base substrates. The sintered Ag layers at one or both edge areas are significantly thicker than those in the central areas for all the four samples. In most cases, the maximum average thickness of 70 to 80 μm is thicker than two times of the minimum average thickness of 30 to 40 μm . Such a result suggests that there must be a certain amount of bending on the IGBTs after the sintering process.

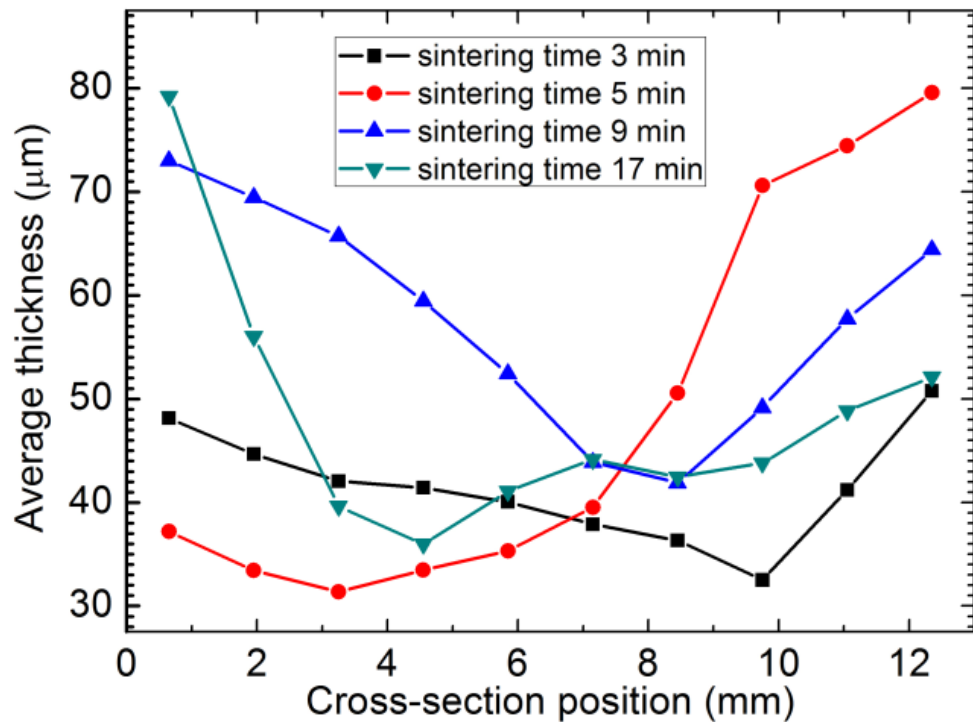


Figure 3- 5: Plots of thickness versus cross-sectional position for the four samples of attaching Si IGBTs on Si_3N_4 -based substrates.

Table 3- 1 lists the results of statistical analysis for the total thickness data series of the sintered Ag joints in the four samples. It can be seen that the average thickness of the four sintered Ag joints, 43.5, 50.6, 59.6 and 50.3 μm , fluctuate with the sintering time of 3, 5, 9 and 17 minutes. Such a fluctuation with the sintering time and the variations along the cross-sectional positions in the thickness can be attributed to the non-uniform thicknesses of the paste of Ag nanoparticles printed and dried on the substrates as evident in Figure 3- 6.

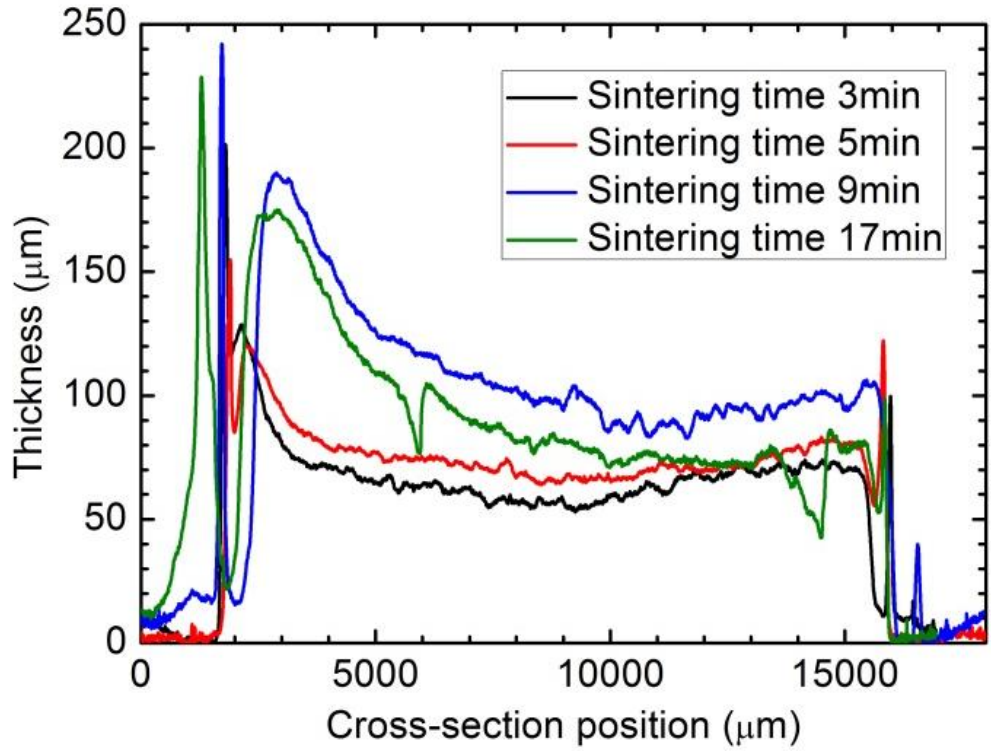


Figure 3- 6: Plots of thickness versus central cross-sectional position measured with a surface profiler for the four pads of paste of Ag nanoparticles printed on the Si_3N_4 -based substrates which were dried at $130\text{ }^\circ\text{C}$ for 30 min prior to attaching the Si IGBTs on them at $240\text{ }^\circ\text{C}$ and 5 MPa for 3 to 17 minutes.

Therefore, the evolution of the thickness during the sintering process was explored by plotting the percentage of thickness reduction versus sintering time:

$$P_{tr} = \frac{(h_0 - h)}{h_0} \times 100\% \quad 3-4$$

Where P_{tr} is the percentage of thickness reduction, h_0 is the mean of the total thickness series of the as-dried paste of Ag nanoparticles and h is the mean of the total thickness series of the sintered Ag joint. The results are presented in

Figure 3- 7 where log-log coordinates are employed. Here and in what follows, the R value stands for the coefficient of correlation for the linear data fitting. It can be seen that the percentage of thickness reduction increases, i.e the normalized thickness decreases with increasing the sintering time, and has a time dependence of the form $t^{1/n}$ with n close to 3.

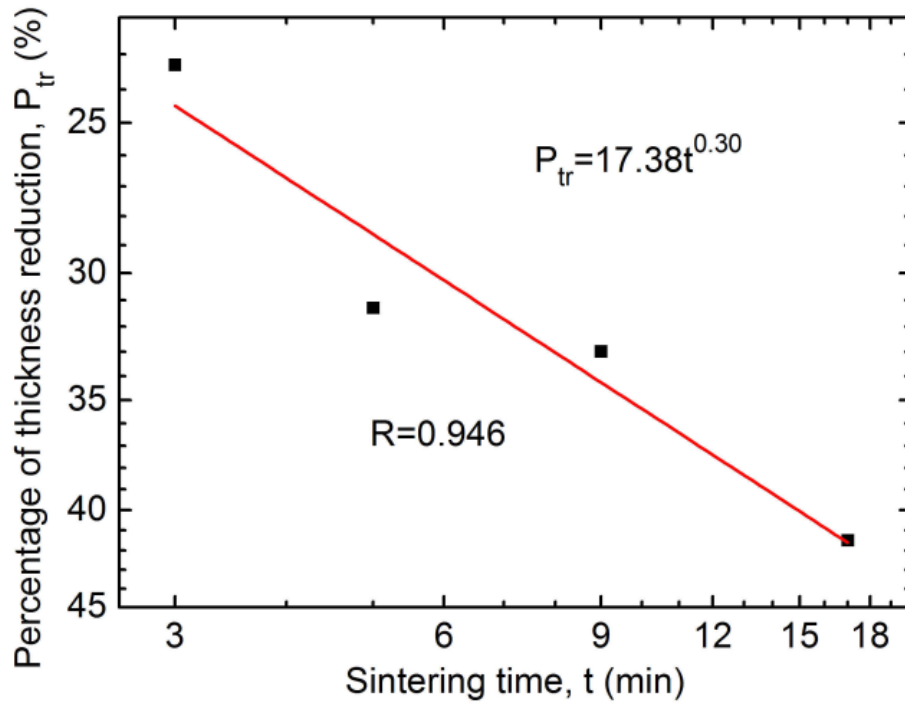


Figure 3- 7: Plot of percentage of thickness reduction versus sintering time on log-log coordinates.

3.3.2 Pore size and porosity evolution during sintering process

Figure 3- 8 and Figure 3- 9 quantitatively show the variations in the pore size and porosity of the sintered Ag joints along the cross-sectional positions in the four samples of attaching Si IGBTs on the Si₃N₄-base substrates. Despite fluctuation with the cross-sectional positions to some extent, both the average pore size and porosity at one or both edge areas are significantly higher than those in the central area for all the four samples. Similar to the variation in the average thickness, in most cases, the maximum average pore size of 0.19 to 0.24 μm and maximum porosity of 9.5% to 22.5% are close to or more than twice the

minimum average pore size of 0.11 to 0.13 μm and minimum porosity of 2.5% to 9.5%.

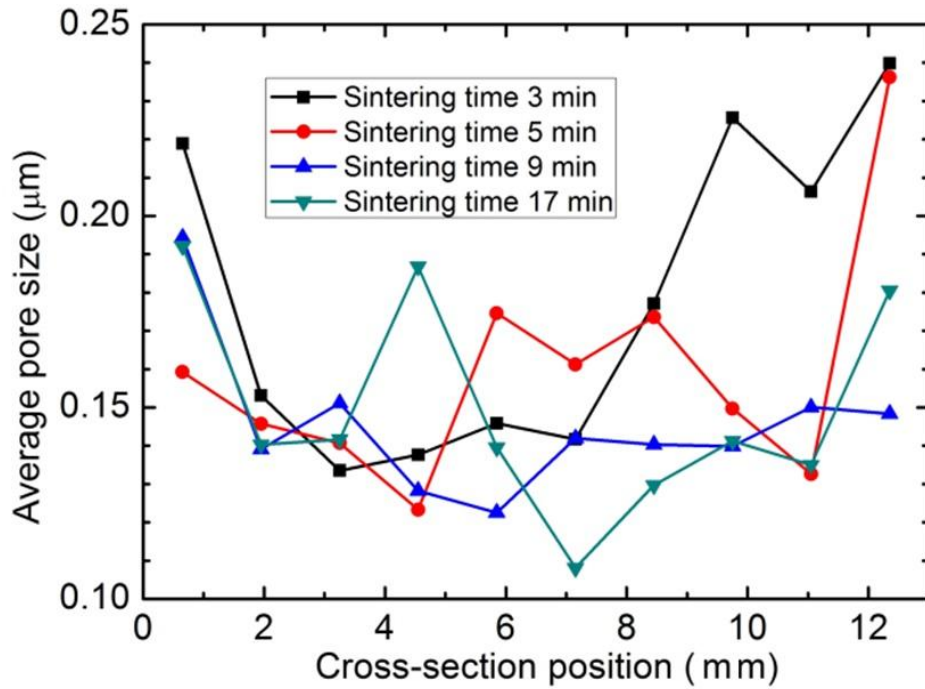


Figure 3- 8: Plots of average pore size versus cross-section position for the four samples of attaching Si IGBTs on Si_3N_4 -based substrates.

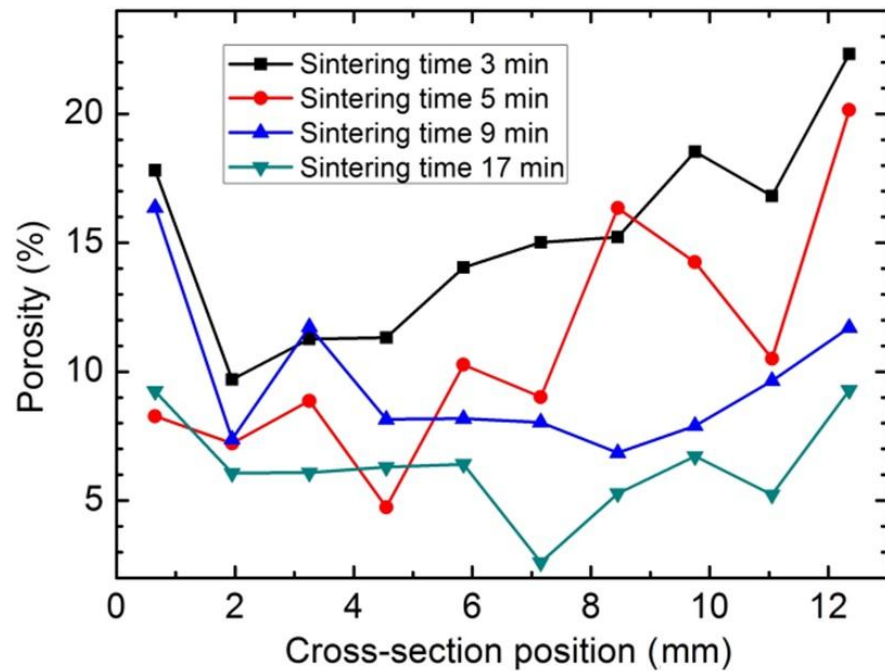


Figure 3- 9: Plots of porosity versus cross-section position for the four samples of attaching Si IGBTs on Si_3N_4 -based substrates.

Table 3-1 also lists the results of statistical analysis for the total pore size data series and the porosity data series of the sintered Ag joints in the four samples. The mean values of the pore size and porosity data both decrease with increasing the sintering time. The time dependence for the reductions in the pore size and porosity are plotted in Figure 3- 10. Here the $\bar{r}$ is the the mean of the total pore size data series, P is the mean of the porosity data series, $\bar{r}_0=0.17 \mu\text{m}$ and $P_0=26.6\%$ are the values of $\bar{r}$ and P obtained from the as-dried paste of Ag nanoparticles. The reductions in the pore size and porosity have time dependence of the form $t^{1/n}$ with n close to 2 and 3, respectively.

Table 3- 1: Results of statistical analysis for the thickness, pore size and the porosity of the sintered Ag samples

		Sintering time (min)			
		3	5	9	17
Thickness (μm)	Mean	43.51	50.55	59.59	50.33
	SD	5.19	18.08	10.50	11.77
	CV	0.12	0.36	0.18	0.23
	Min	33.33	32.40	41.96	36.52
	Max	55.78	82.87	77.16	83.53
Pore size (μm)	Mean	0.16	0.15	0.15	0.15
	SD	0.14	0.11	0.10	0.09
	CV	0.87	0.73	0.67	0.60
	Min	0.03	0.03	0.03	0.03
	Max	1.51	1.49	2.22	0.77
Porosity (%)	Mean	15.2	10.97	10.3	6.3
	SD	3.85	4.63	2.92	1.94
	CV	0.25	0.42	0.28	0.31
	Min	9.69	4.75	6.85	2.61
	Max	22.33	20.15	16.36	9.28

SD: standard deviation; CV: coefficient of variation

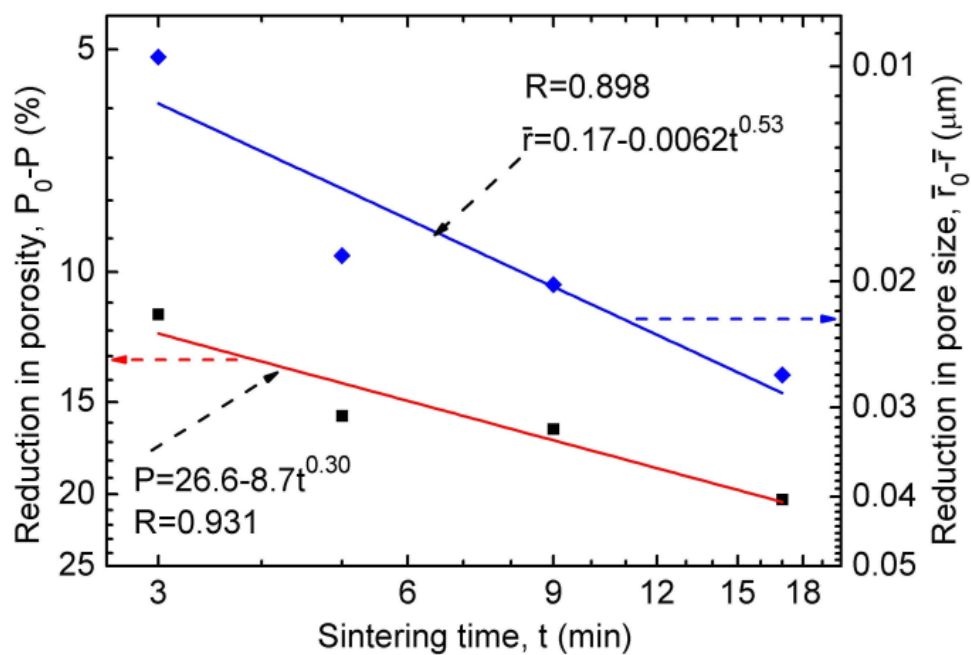


Figure 3- 10: Plots of reductions in pore size and porosity versus sintering time on log-log corridinates.

3.3.3 Grain growth during sintering process

There are 8 diffraction peaks of crystalized Ag grains which can be identified from the recorded XRD spectra of the as-dried paste of Ag nanoparticles and the sintered Ag samples, as Figure 3-11 shows.

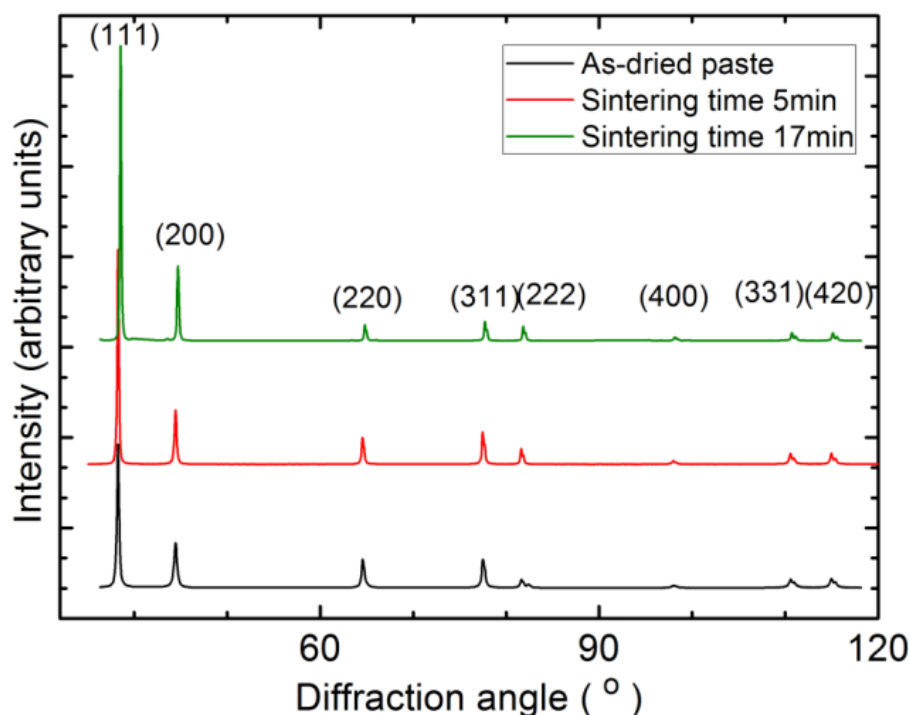
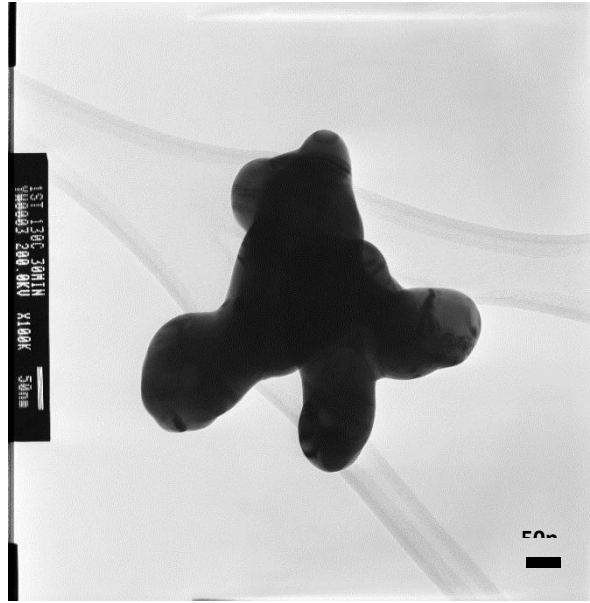
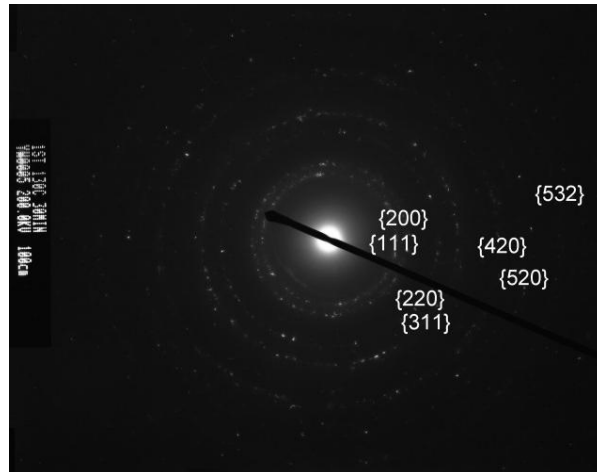


Figure 3- 11: XRD spectra of the as-dried paste of Ag nanoparticles and the samples sintered for 5 and 17 minutes.

Figure 3- 12 and Figure 3- 13 present the TEM results obtained from the as-dried paste of Ag nanoparticles and the samples sintered for 5 and 17 minutes. It was difficult to obtain selected area diffraction patterns of single Ag grains from these samples, and the diffraction rings shown in Figure 3- 12 (b) confirm that even single particles smaller than 100 nm shown in Figure 3- 12 (a) contain a number of Ag grains. Furthermore, coalescence of and formation of necks between particles can be observed in the as-dried Ag paste, and these processes continue during the sintering process. The coalescence of particles and formation of necks probably occurred along specific crystalline orientations. As a result, the preferred orientation of the Ag grains along the [111] direction was observed from the XRD spectra shown in Figure 3- 11.



(a)



(b)

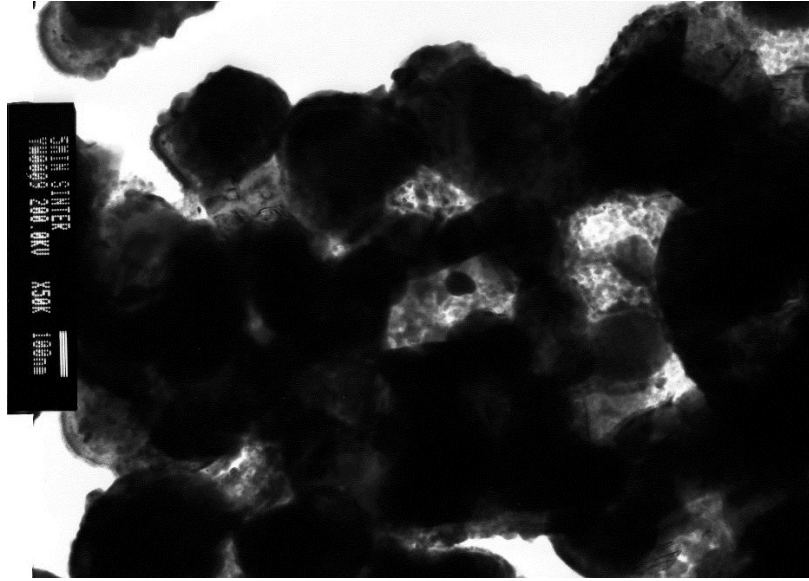
Figure 3- 12: TEM results of the as-dried paste of Ag nanoparticles: (a) one TEM image and (b) the corresponding electronic diffraction rings for multiple Ag grains.

Nevertheless, as shown in

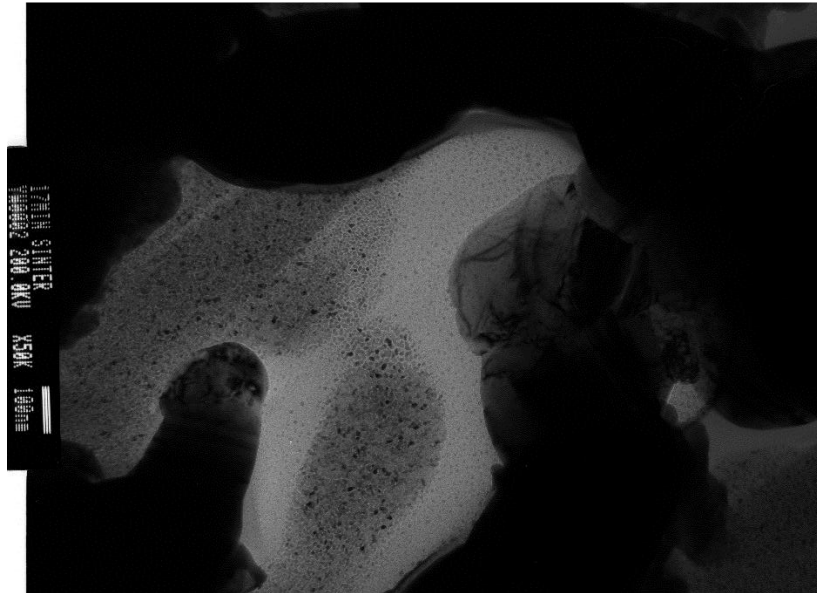
Figure 3- 14, the average grain size estimated using the Sherrer Equations from the 8 XRD peaks increases with increasing the sintering time. The kinetics of the grain growth can be further derived as the the following equation:

$$\bar{d}^{3.26} - \bar{d}_0^{3.26} = 4.75 \times 10^4 t \quad 3-5$$

Where $\bar{d}$ is average grain size, t is sintering time, and $\bar{d}_0$ is the value of $\bar{d}$ for the as-dried paste of Ag nanoparticles. If d_0 is assumed to be zero, a time dependence of the form $t^{1/n}$ with n close to 3 for the average grain growth can also be obtained.



(a)



(b)

Figure 3- 13: TEM images taken from the samples sintered for: (a) 5 min and (b) 17 min.

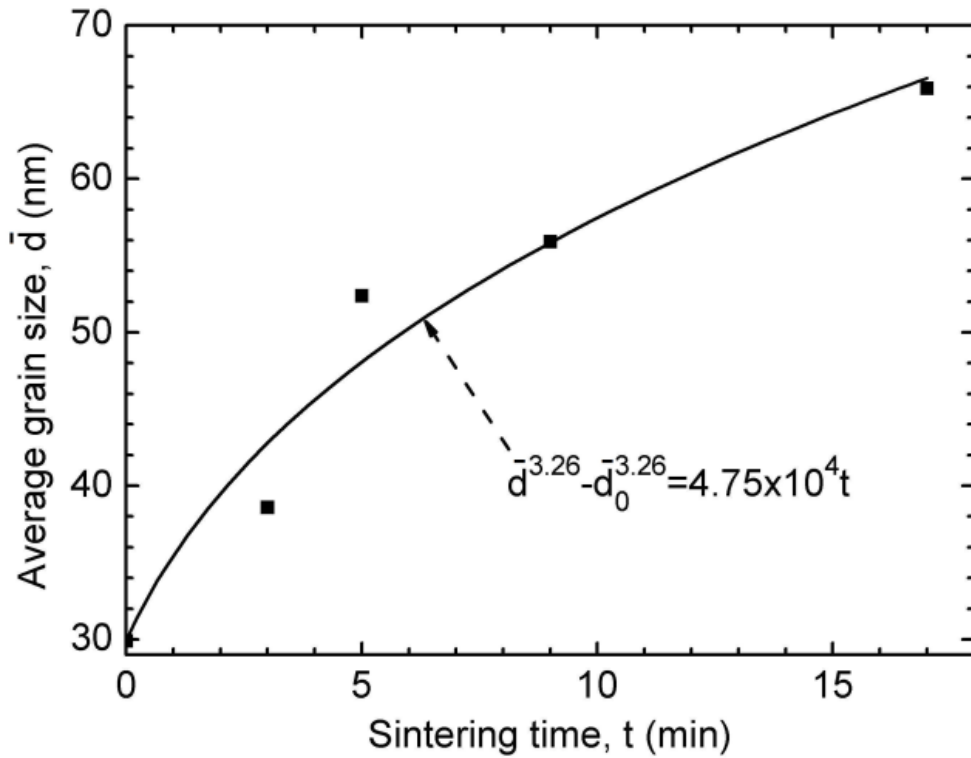


Figure 3- 14: Plot of average grain size versus sintering time on linear coordinate

3.4 Discussion

The non-uniform thicknesses and the spikes and valleys at the edges of the dried paste pads had already existed in the as-printed paste pads, and were caused by the pulling force due to the sticking of the wet paste to the side wall of the stainless steel stencil during the printing process. As reported in a previous work [72], there was no significant change in them after the drying stage. As schematically shown in Figure 3-1, the Si IGBT was reversely sited on 1 mm thick compliant silicone gel during the sintering stage. As a result, the non-uniformity of thicknesses and the existence of spikes and valleys at the edges of the dried paste pads would probably cause the Si IGBT to bend to some extent and relatively higher pressure applied on the Ag paste in the central areas.

Unlike solder reflowing where solder joints are formed through liquid wetting,

solid-liquid interfacial reaction and solidification, sintering is a process in which bonding is accomplished through atomic diffusion and particle consolidation. The Ag nanoparticle paste has been formulated for pressure-assisted sintering, and a higher level of pressure applied on the dried paste would promote the atomic diffusion and particle consolidation during the sintering stage. Therefore, for all the four samples, the sintered Ag layers in the middle areas were thinner, denser and bonded to the IGBTs and substrates better than at the edge areas.

Despite the variations in the thickness, pore size and porosity along the cross-sectional positions of the sintered Ag joints, the reductions in their average or mean values with increasing the sintering appear to have similar time exponents as shown in Figure 3- 7 and Figure 3- 10. This demonstrates that the present quantitative microstructure characterization is useful to investigate their kinetics, and the thinning of the sintered Ag joints was dominated by the densification of the Ag layers during the sintering stage.

In the theory of sintering of traditional powder particles, the kinetics is generally separated into three stages: the initial stage with rearrangement of particles and densification, the intermediate stage with further densification and grain growth, and the final stage with further grain growth only [73]. As aforementioned, the average size of the Ag nanoparticles in the as-received paste was about 20 nm, and that in the as-dried paste was 29.9 nm (

Figure 3- 14). This reveals that grain growth associated with the coalescence of and formation of necks between particles had already started during the drying stage (at 130 °C for 30 minutes). The time exponent of 3.26 describing the grain growth during sintering at 240°C and 5Mpa for 3 to 17 minutes is in a good agreement with those values close to 3 reported for grain growth during the intermediate stage of sintering of traditional powder particles [74]. Also, as shown in Figure 3- 10 and

Figure 3- 14, reduction in porosity and hence densification had been progressing continuously and simultaneously with grain growth. Therefore, in addition to lattice diffusion and diffusion from the surface (due to the extremely high surface area of Ag nanoparticles) , lattice diffusion from grain boundaries, grain boundary diffusion and plastic deformation were also important sintering mechanisms which occurred during the sintering stage. This is because the former

two are non-densifying mechanisms, and the latter three are common and possible densifying mechanisms for the present sintering of Ag nanoparticles.

From Figure 3- 10 and

Figure 3- 14, it can be further seen that the densification had not been completed and the Ag grains were still smaller than 100 nm in the sample sintered for 17 minutes. Therefore, when sintered Ag joints are used to assemble power electronic systems, further evolution of the microstructure is likely to occur, particularly during elevated application temperatures and should be taken into account for lifetime prediction and reliability analysis. Furthermore, the final densification that can be achieved for a sintered powder compact depends on the initial contact and arrangement of the powder particles. The purpose of the present quantitative microstructure characterization is to reveal the above problems.

3.5 Summary

From the above results and discussion for the quantitative microstructure characterization of the sintered Ag joints, the following conclusions can be drawn:

- (1) Thickness, pore size and porosity all vary considerably along the cross-sectional positions in the sintered Ag joints, which can be attributed to non-uniformity of the Ag nanoparticles pastes printed on the substrates;
- (2) In all the sintered Ag joints, the central areas with typical thicknesses of 30 to 40 μm and porosity values of 2.5% to 9.5% are thinner and denser than the two edge areas with typical thicknesses of 70 to 80 μm and porosity values of 9.5% to 22.5%;
- (3) There are reductions of 23.3% to 41.5% in the average thickness, 0.01 to 0.03 μm in average pore size and 11.4% to 20.3% in average porosity in the sintered Ag joints with increasing the sintering time from 3 to 17 minutes;
- (4) The average grain size in the as-dried Ag nanoparticles paste is 29.9 nm, and those in the sintered Ag layers are 38.6, 52.4, 55.9 and 65.9 nm for sintering times of 3, 5, 9 and 17 minutes respectively;
- (5) The reductions in average thickness, pore size and porosity and increase in grain size all exhibit similar a time dependence in the form $t^{1/n}$ with n close to 2 or 3.

- (6) For the sinterings of Ag nanoparticles at 240°C for 17 minutes, it is still in the intermediate stage, and both non-densifying and densifying mechanisms probably play important roles for the evolution of the microstructure during this stage.

CHAPTER 4 Microstructure evolution of sintered Ag joints during isothermal ageing

4.1 Introduction

Following the microstructure characterization of the as-sintered Ag joints carried out in the previous chapter, this chapter investigates the microstructure evolution of the sintered Ag joints to attach Si power dies subjected to high temperature storage. The samples have been prepared using the identical Si dies on the AlN-based substrates with four types of different finishes, and the samples of attaching Si dies have been stored at three temperatures for a number of different times. The microstructure characterization has been done using scanning electronic microscopy to observe and analyze the samples which were cross sectioned and polished after the high temperature storage.

The Si dies considered were 13 mm × 13 mm × 0.35 mm Si insulated gate bipolar transistors (IGBTs) with ~1/1 μm thick Ni/Ag metallization on their back sides. The four substrate finishes considered were bare Cu, 2 μm thick Ag, 5/2 μm thick NiP/Ag and 5/0.1 μm thick electroless NiP/Au on the AlN-based substrates. The isothermal ageing experiments were carried out at 150 °C, 200 °C and 250 °C for 4, 8, 16 and 32 days. The specific objectives of this work are: (i) to compare and explain the different patterns of the microstructure evolution of the sintered Ag joints observed with the four substrate finishes; and (ii) to use the present results to explain part of the degradation behaviors of the sintered Ag joints during thermal cycling tests which were reported in the reviewed literature [57][60] and have been carried out as presented in the next chapter.

The results obtained from the present work can directly be used to guide the selection of suitable substrate finish for the die attachments in high temperature power electronic systems. For instance, there is an increasing demand to develop power electronics modules which are reliable in continuous operation in an ambient temperature of 150 °C and above for periods of several years. Examples

includes aerospace where there is an increasing move to electronic rather than hydraulic or pneumatic systems, automotive under-hood applications in conventional, hybrid and electric drive systems and down-hole gas and oil field applications [32]. Furthermore, through analysis and comparison of the obtained microstructure features with those observed in the thermal cycling tests, they can also provide insight into the relevant degradation mechanisms of the sintered Ag joints occurring in those testes.

4.2 Materials and methods

4.2.1 Materials

The power dies considered, 13.5 mm × 13.5 mm × 0.35 mm Si IGBTs with ~1/1 µm thick Ni/Ag metallization, were obtained from Dynex Semiconductor Ltd (Lincoln, UK). Two types of pastes of Ag nanoparticles, Argomax 2020 and Argomax 5020 were used, and they were both obtained from Cookson Electronics (South Plainfield, NJ 07080, USA). They were formulated with appropriate organic dispersant, binder and thinner for sintering on the substrates with Ag and Au finishes (Argomax 2020) and bare Cu (Argomax 5020). The average size of the Ag nanoparticles in both pastes was ~20 nm.

The AlN-based substrates were custom manufactured by Remtec, Inc (Norwood, MA 02062, USA), and consisted of 1 mm thick AlN ceramic tiles sandwiched by 0.3 mm thick Cu directly bonded on both sides. The as-received substrates had three types of surface finishes, including bare Cu, 5 µm thick NiP, and 5 µm thick NiP followed by 0.1 µm thick Au on the top surfaces. The substrates with 2 µm thick Ag and 5/2 µm thick NiP/Ag finishes were prepared by further plating 2 µm thick Ag on the surfaces of the as-received substrates with bare Cu and 5 µm thick NiP, respectively. All the substrates were cut into 25 mm × 25 mm coupons prior to printing the pastes of Ag nanoparticles to prepare the samples of die attachments.

4.2.2 Sintering process

The sintered Ag samples of attaching the IGBTs on the substrates with the four types finishes were prepared using a home-made press. The Ag nanoparticle paste was first printed on all the substrates with 100 µm thick stainless steel

stencil, and the size of the printed paste was 16 mm × 16 mm on each of the substrates. Here Argomax 5020 paste was printed on the substrates with bare Cu, and Argomax 2020 paste was printed on the substrates with the other three surface finishes. The printed pastes on all substrates were placed in an oven to dry at 130 °C for 30 minutes.

Then one Si IGBT was positioned centrally on the dried paste on each substrate, and fixed in place with Kapton tape. The sample was turned upside down and placed on 1 mm thick silicone rubber situated on the cold plate of the press. The final sintering was performed at a temperature of 250 °C and pressure of 5 MPa for 5 minutes before releasing the pressure and cooling the sample down to room temperature within 3 minutes. Figure 4-1 shows the schematic sample geometry and temperature / pressure profile used to prepare these samples.

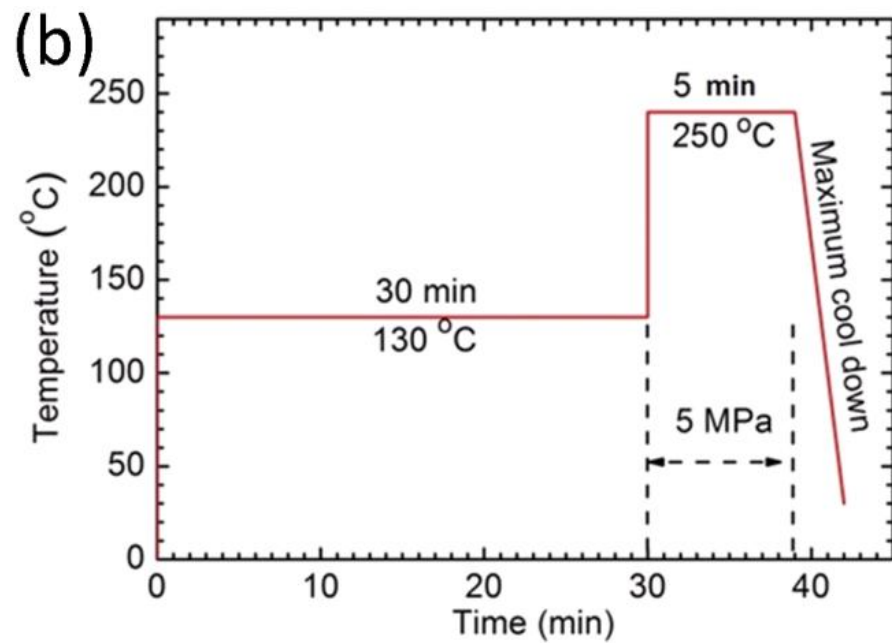
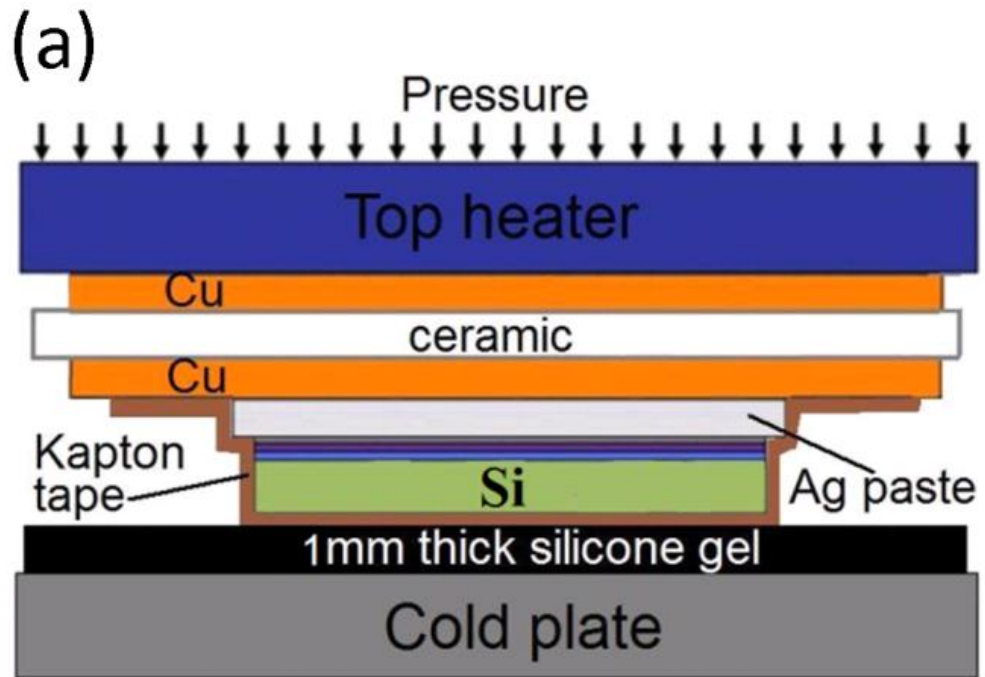


Figure 4- 1 Schematic diagrams of: (a) sample geometry and (b) temperature and pressure profile used during the sintering process. Note that the dimensions of sample geometry are not to scale.

The isothermal ageing experiments of the sintered Ag samples of attaching the IGBTs on the substrates with the four types of surface finishes were all carried out in air at temperatures of 150 °C, 200 °C and 250 °C for 4, 8, 16 and 32 days.

4.2.3 Microstructure characterization

The as-sintered samples and the samples after the isothermal ageing experiments were mounted in epoxy resin that was cured at room temperature for 24 hours. They were then cross-sectioned with a diamond saw and then successively ground with SiC papers and finally polished using diamond slurries of 3 µm and 1 µm. The polished samples were further etched with plasma cleaner to remove the polishing-induced deformation layers prior to microstructural observation. The microstructural observation and acquisition of images from all the samples were carried out with a Hitachi TM300 desktop scanning electronic microscope (SEM). After taking the SEM images, the pore size and porosity values of the sintered Ag joints, and the thicknesses of the characteristic layers formed at the interface between the sintered Ag joints and the substrates, including copper oxide and epitaxial layer of Ag on Au observed in part of the samples, were measured using image analysis method. The image analysis method for measuring similar pore size and porosity of a material and the thickness of a particular layer from the SEM images had been described in the previous chapter, and is not repeated here.

In the present work, the SEM images for measuring the pore size and porosity were 1280×960 pixels in resolution and 17 × 12.7 µm in size, and three representative images were taken from each of the sintered Ag joints. The pore size was expressed as “apparent” radius r and was calculated as:

$$r = \sqrt{S / \pi} \quad 4-1$$

Where S is the area of a pore measured from the SEM image. A data series for the pore size was obtained from the three SEM images for each sample, and those pores located at the four edges of the SEM images were excluded. The mean, standard deviation, coefficient of variation, minimum and maximum

values of the obtained pore size series were calculated to compare among the different samples. The measurement of porosity is relatively simple, and the porosity value of a sample was calculated as the percentage of the total area of all the pores observed in the three SEM images over the area of the three SEM images.

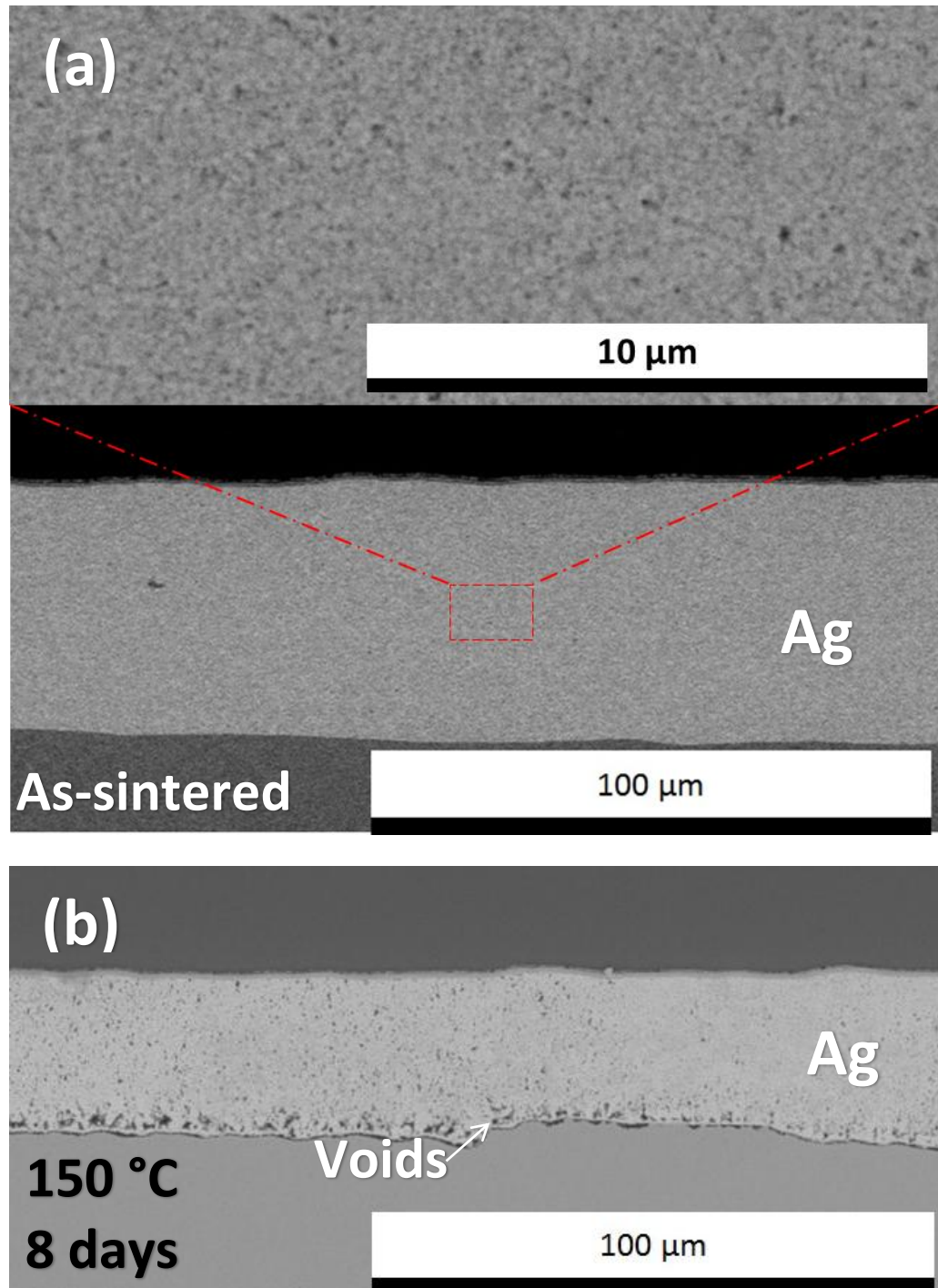
The SEM images for measuring the thicknesses of the copper oxide and epitaxial layer of Ag on Au were 1280×960 pixels in resolution and $17 \times 12.7 \mu\text{m}$ in size, and were three representative images taken at the interfaces between the sintered Ag joints and the substrates in the corresponding samples. A data series for the thickness of either the copper oxide or the epitaxial layer of Ag on Au was obtained from the corresponding three SEM images for each sample. The mean, standard deviation, coefficient of variation, minimum and maximum values of the obtained thickness series were also further calculated to compare among the different samples.

In addition, the microstructure at the interface between the sintered Ag joint and the substrate with Au/NiP finish in the sample aged at 250°C for 32 days was also observed with focused ion beam (FIB) ion channelling image. This was conducted using the FEI Quanta 200 3D DualBeam FIB / SEM to progressively mill the polished cross-sections, which provided grains and grain boundary contrast.

4.3. Results and discussion

4.3.1 The sintered Ag joints of attaching IGBTs on bare copper substrate

4.3.1.1 SEM images



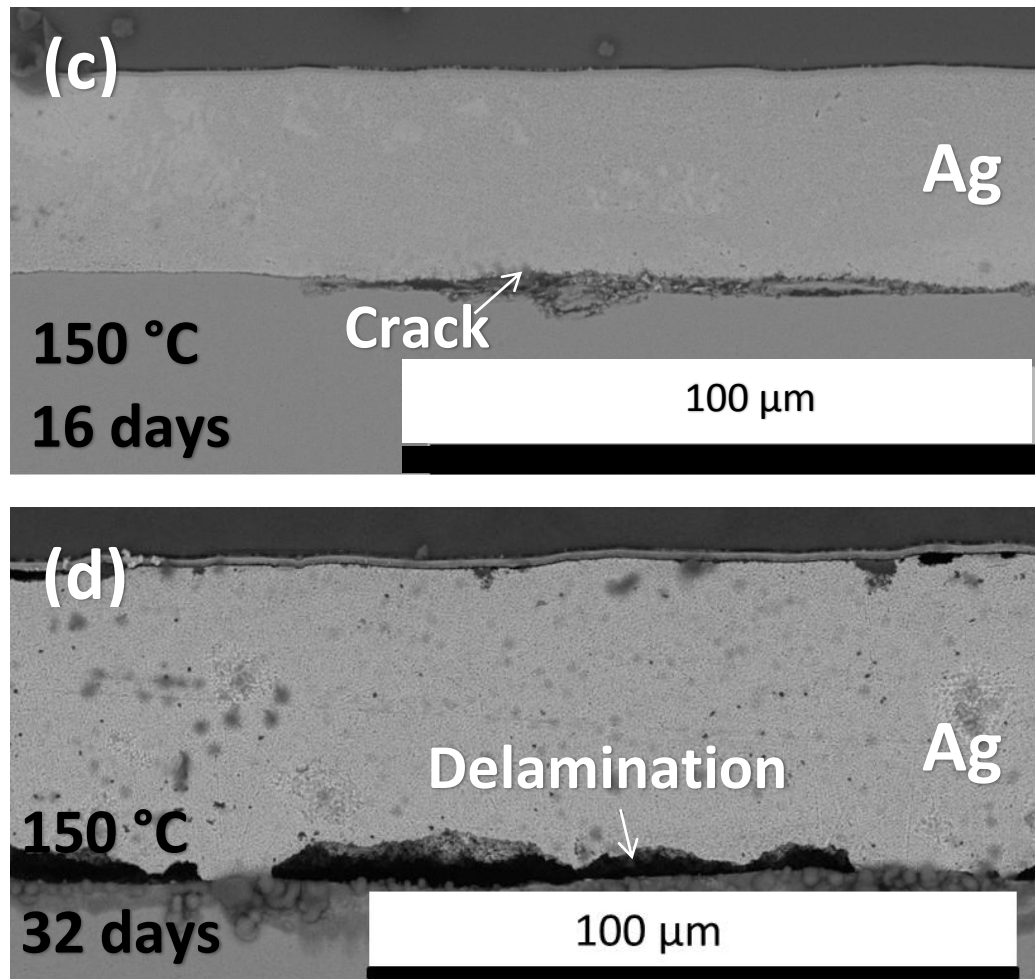


Figure 4- 2: Microstructure of sintered joints with DBC bare copper substrate after isothermal ageing at 150 °C

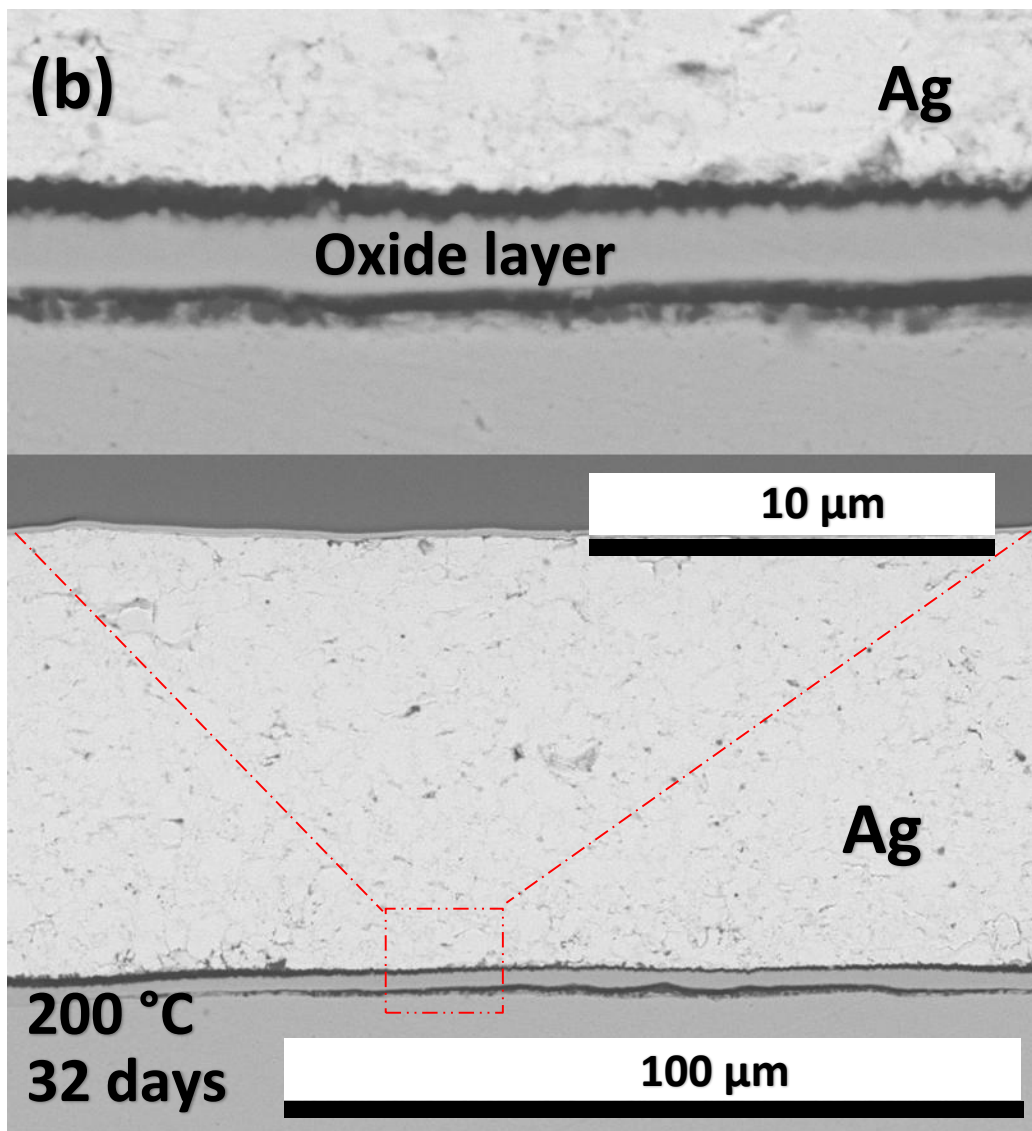
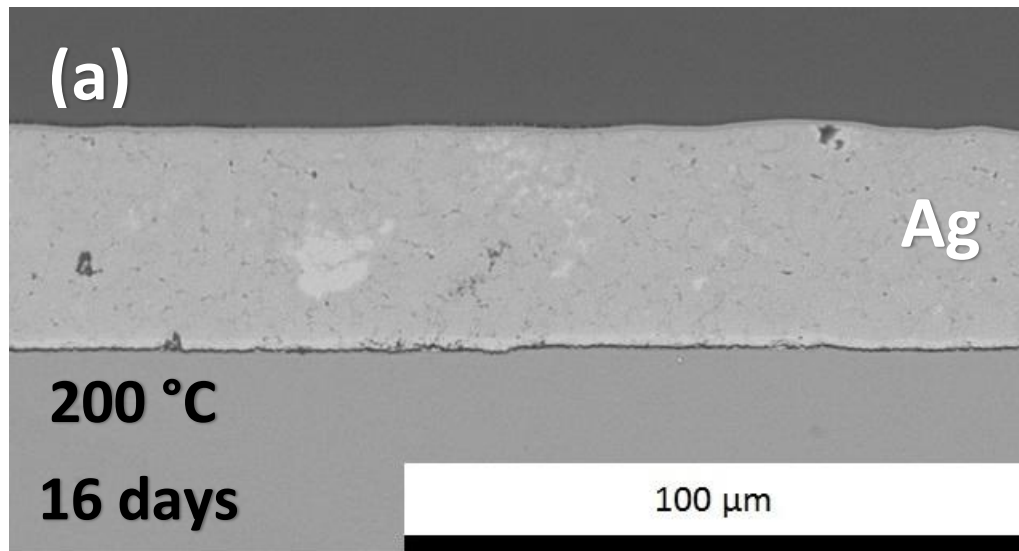


Figure 4- 3: Microstructure of sintered joints with DBC bare copper substrate after isothermal ageing at 200 °C

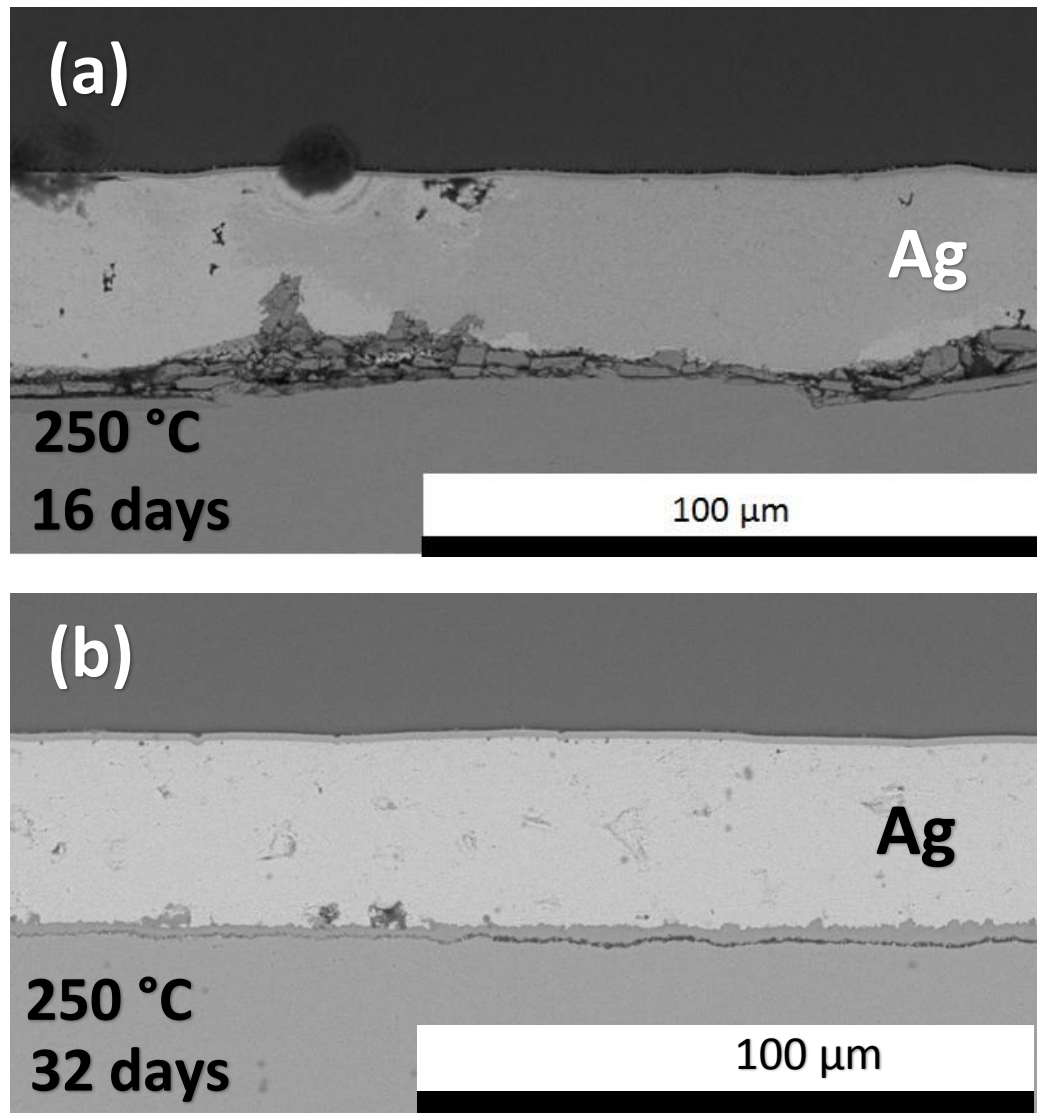


Figure 4- 4: Microstructure of sintered joints with DBC bare copper substrate after isothermal ageing at 250 °C

From SEM microstructure characterization, the as-sintered Ag joints with bare copper substrate showed a uniform sintered layer. After isothermal ageing for 8 days at 150 °C, voids showed up and mainly concentrated around the interface between sintered joints and substrate, as Figure 4- 2 (b) shows. With more isothermal ageing time up to 32 days at 150 °C, the cracks propagated along the interface, which might further cause interfacial delamination eventually, as Figure 4- 2 (c)-(d) show. At 200 °C and 250 °C, cracks were also occurred around the interface between substrate and sintered joint, as Figure 4-

3 and Figure 4- 4. With more ageing time and higher ageing temperature, sintered layer was separated from substrate and showed denser microstructure.

During isothermal ageing tests, as densification continues and grains grow, the volume of the whole sintered joint would be expected to shrink. However, the sintered joint in this work was bonded between a device and substrate, this kind of structure keeps the volume from shrinking. In this case, tensile stress develops along the interfaces and shear stress occurs on the substrate surface.

Because sintered Ag joint has a porous structure, air could easily react with Cu, and hence an oxide layer could be formed. With more ageing time, the thickness of the oxide layer increases. However, oxide layer formation and its thickness growth could reduce the interfacial bonding strength. As long as the shear stress exceeds the bonding strength, cracks could be initiated and propagated in the oxide layer, as Figure 4-5 shows.

If the sintered Ag layer separated from the substrate during isothermal ageing, the layer could probably densify freely without any constraint, so the sintered layer would present a much denser microstructure, and the Ag grain size would be larger. This would explain why, as Figure 4- 6 shows, porosity and pore size of sintered joints with bare copper substrates decreased during isothermal ageing.

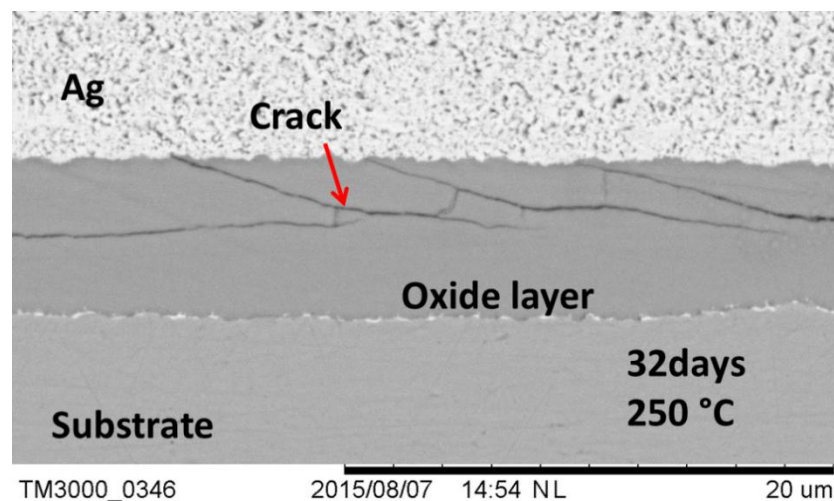


Figure 4- 5: Image of oxide layer on bare copper substrate after 32 days at 250 °C.

4.3.1.2 Pore size and porosity

Table 4- 1: Results of statistical analysis for the pore size and porosity of the sintered Ag samples with bare copper substrate

		Pore size				Porosity
	Aging time (day)	Mean	SD	Min	Max	%
		(μm)	(μm)	(μm)	(μm)	
150 °C	0	0.29	0.29	0.073	0.86	4.54
	4	0.19	0.035	0.073	0.27	3.09
	8	0.077	0.036	0.037	0.25	1.39
	16	0.082	0.04	0.037	0.31	1.49
	32	0.09	0.054	0.037	0.42	1.49
200 °C	4	0.14	0.19	0.073	0.86	1.78
	8	0.19	0.079	0.081	0.73	1.36
	16	0.08	0.079	0.073	0.50	1.21
	32	0.086	0.011	0.073	0.10	1.05
250 °C	4	0.13	0.048	0.073	0.32	2.07
	8	0.12	0.079	0.061	0.46	1.45
	16	0.041	0.079	0.037	0.35	1.32
	32	0.085	0.044	0.037	0.28	1.14

SD: standard deviation

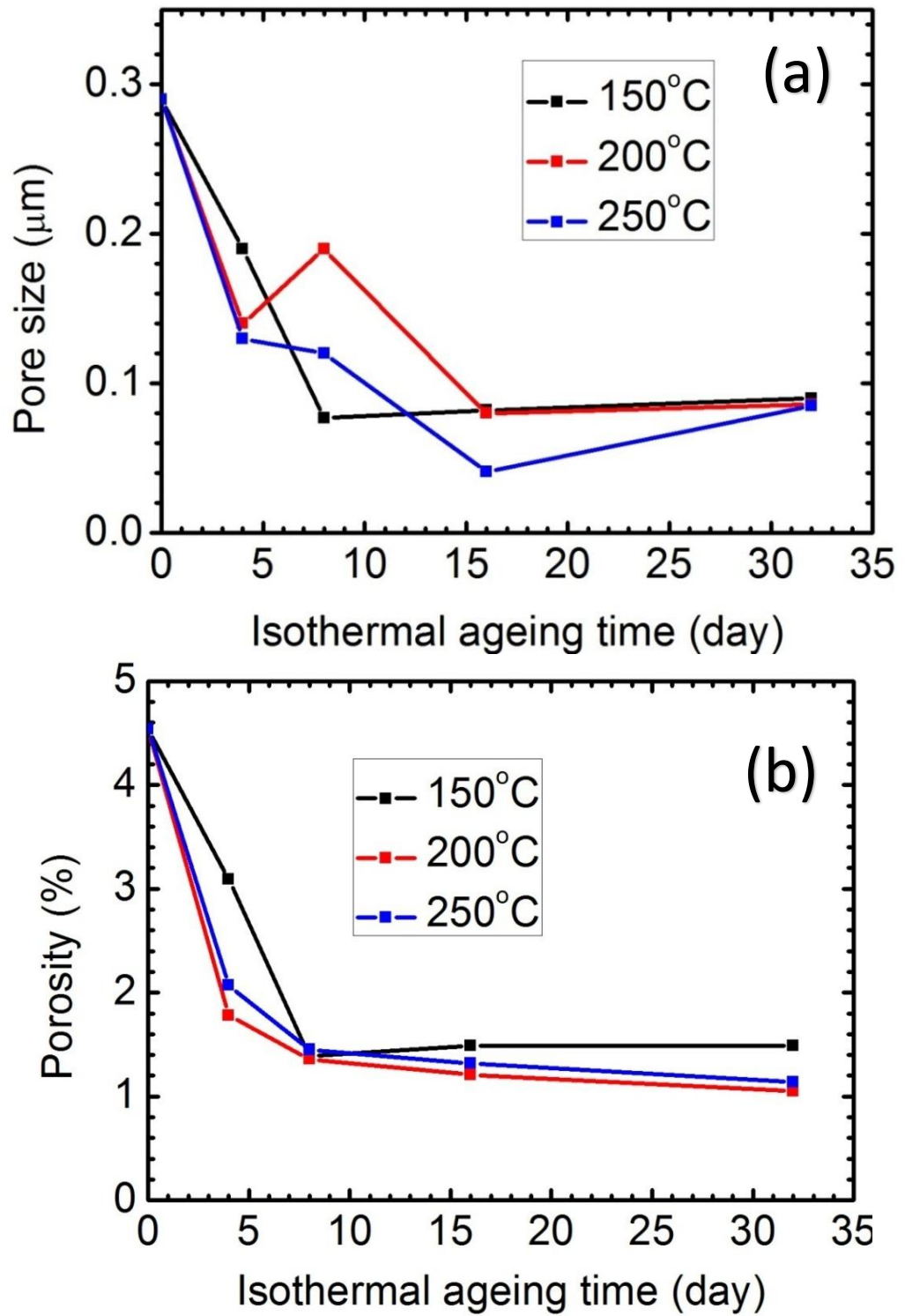


Figure 4- 6: Plots of mean pore size (a) and porosity (b) versus isothermal ageing time for the sintered joints with bare copper substrates.

Table 4-1 quantitatively shows the variations of pore size and porosity values of the sintered Ag layers. As Figure 4- 6 (a) and (b) show, the mean pore size and

porosity of sintered layers show a decreasing trend during isothermal ageing. At 150 °C, the porosity of sintered layer with bare copper substrate decreased from 4.54% for as-sintered to 1.49% for ageing 32 days at 150 °C while the pore size decreased from 0.29 µm for as-sintered to 0.09 µm for ageing 32 days.

At 200 °C and 250 °C, the porosity and pore size of sintered layers showed similar tendency as those of sintered joints at 150 °C. However, the value of mean pore size and porosity did not show much variation, which showed less relation to the isothermal ageing temperature. While with more ageing time, sintered layer presented denser microstructure.

4.3.1.4 Thickness of copper oxide

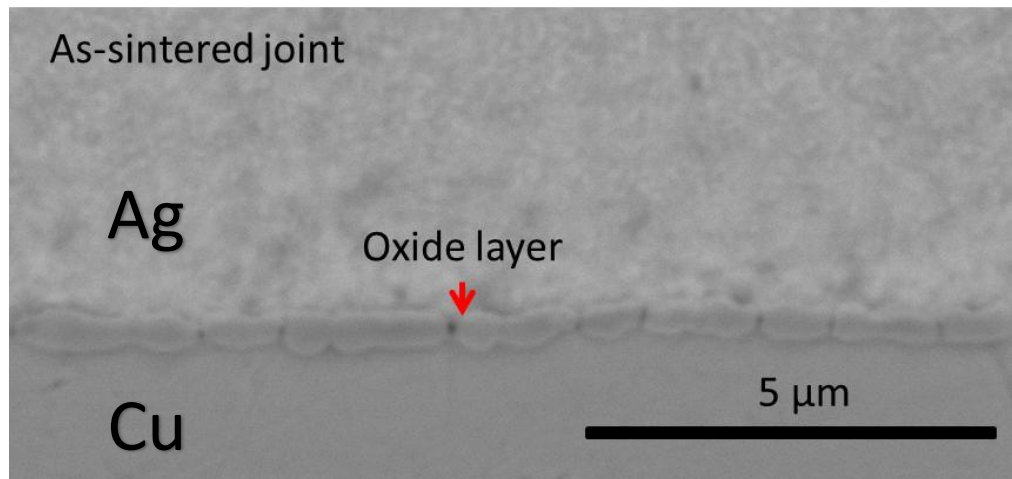


Figure 4- 7: Image of oxide layer on bare copper substrate

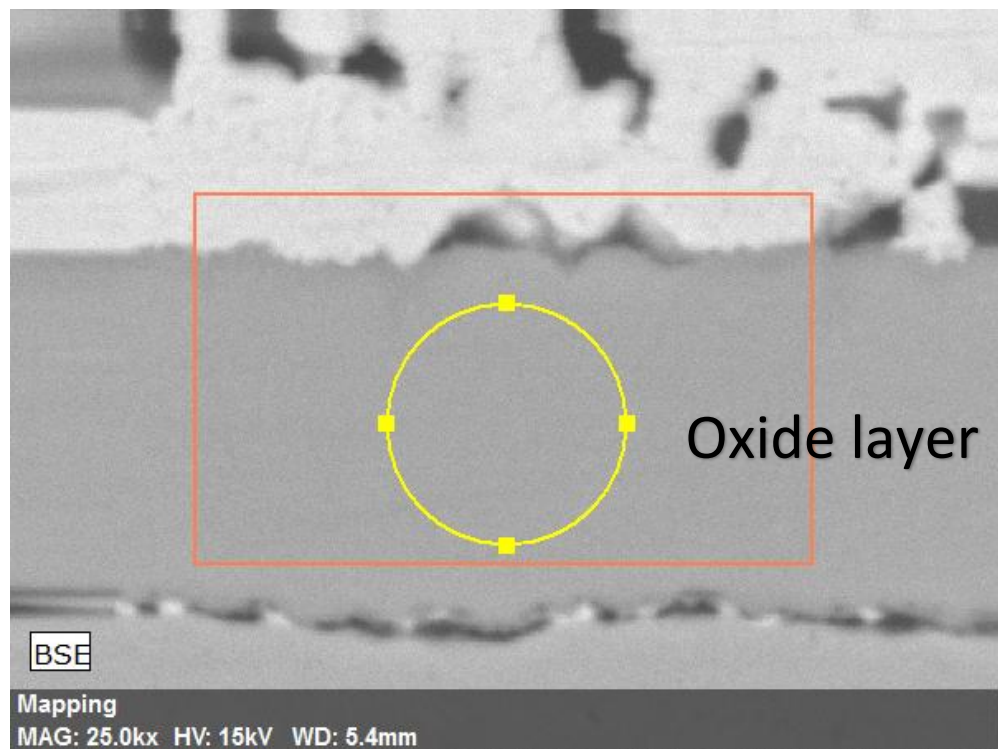


Figure 4- 8: EDX Image of oxide layer on bare copper substrate

Table 4- 2: EDX elemental analysis of oxide layer

Element	AN	series	[norm. at.%]	Error in %
Copper	29	K-series	73.9008033	2.452784178
Oxygen	8	K-series	26.0991967	2.036795028
			100	

Table 4- 3: Results of copper oxide thickness on bare copper substrate (μm)

	As-sintered	4	8	16	32
150 °C	0.38	0.9	1.03	0.61	3.61
200 °C	0.38	0.43	0.54	1.06	4.04
250 °C	0.38	1.37	2.62	4.14	6.6

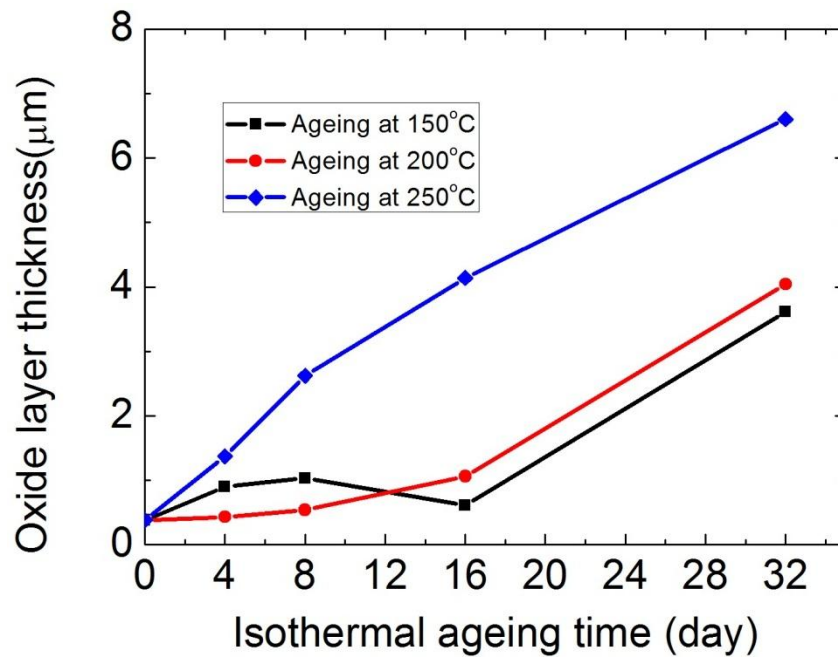


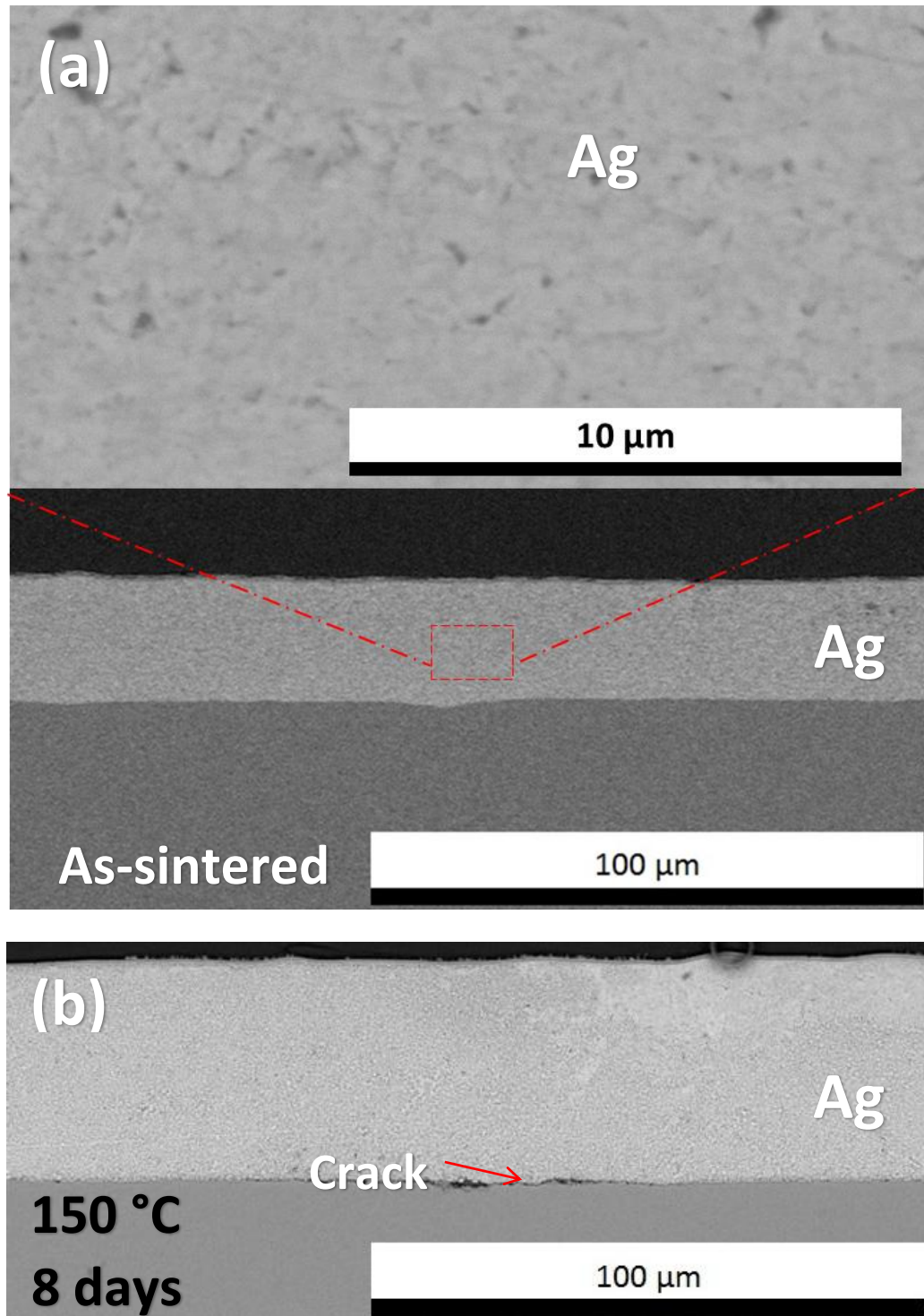
Figure 4- 9: Oxide layer thickness versus isothermal ageing time during thermal ageing for sintered joint with bare copper substrate

As Figure 4- 7 shows, an oxide layer exists on the bare copper substrate surface and is around 0.35 μm . The oxide layer became thicker with

increasing ageing time, as Table 4- 3. At 150 °C and 200 °C for up to 16 days, the oxide layer thickness did not go up fast, which were fluctuated from 0.43 µm to 1.61 µm. However, after 16 days both at 150 °C and 200 °C, the thickness increased quickly and reached 3.61 µm and 4.04 µm, respectively. At 250 °C, thickness of oxide layer grew much more quickly than those at 150 °C and 200 °C. As Figure 4- 9, the thickness of oxide lay grew from 1.37 µm after 4 days to 6.6 µm after 32 days.

4.3.2 The sintered Ag joints of attaching IGBTs on the substrate with Ag finish

4.3.2.1 SEM images



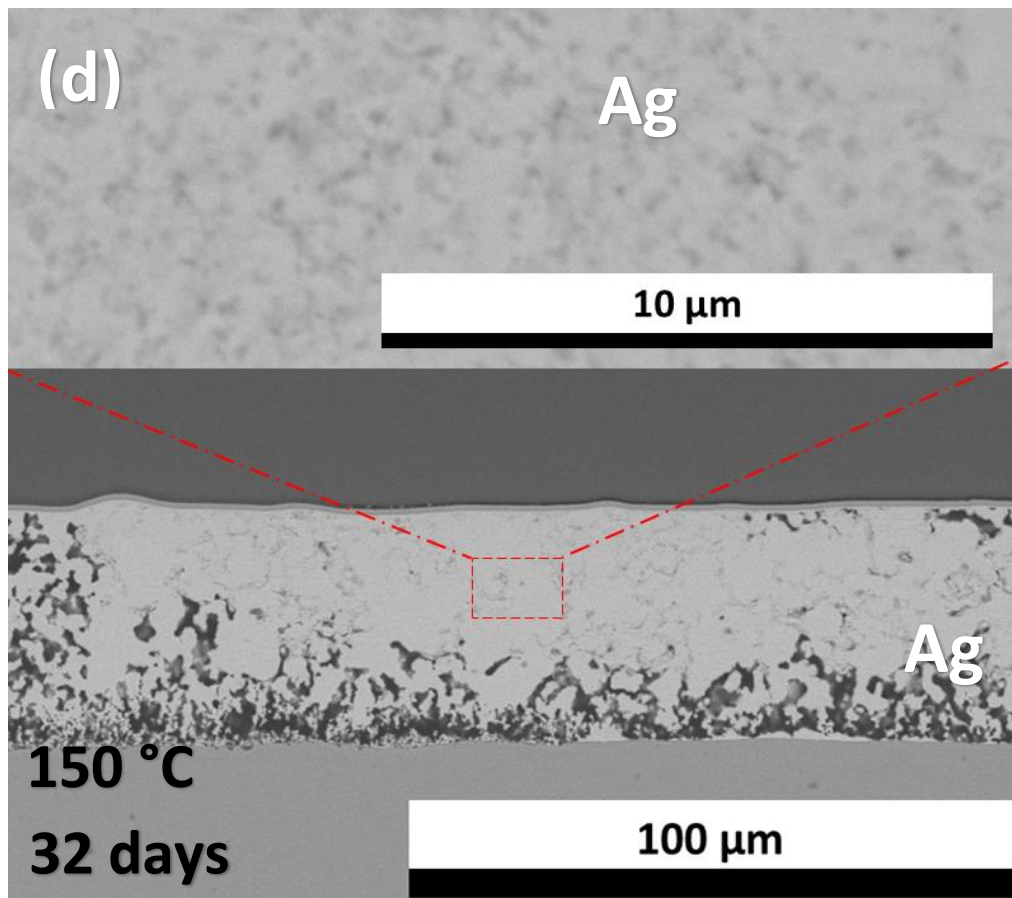
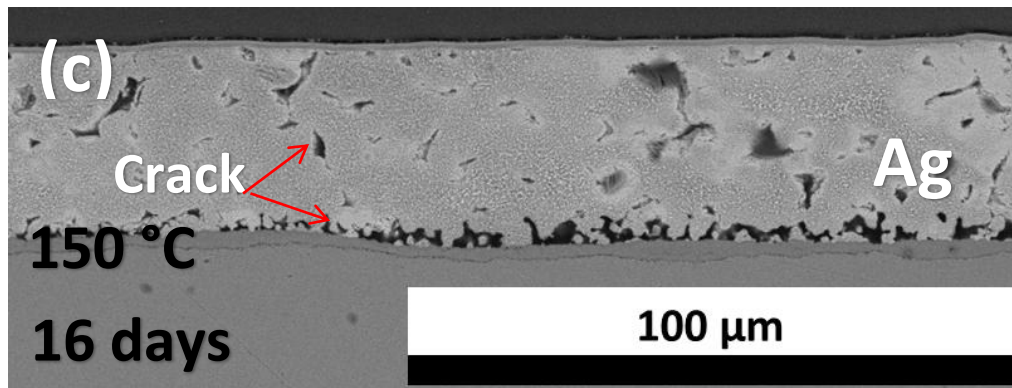


Figure 4- 10: Microstructure evolution of sintered joints with Ag finish substrate at 150 °C

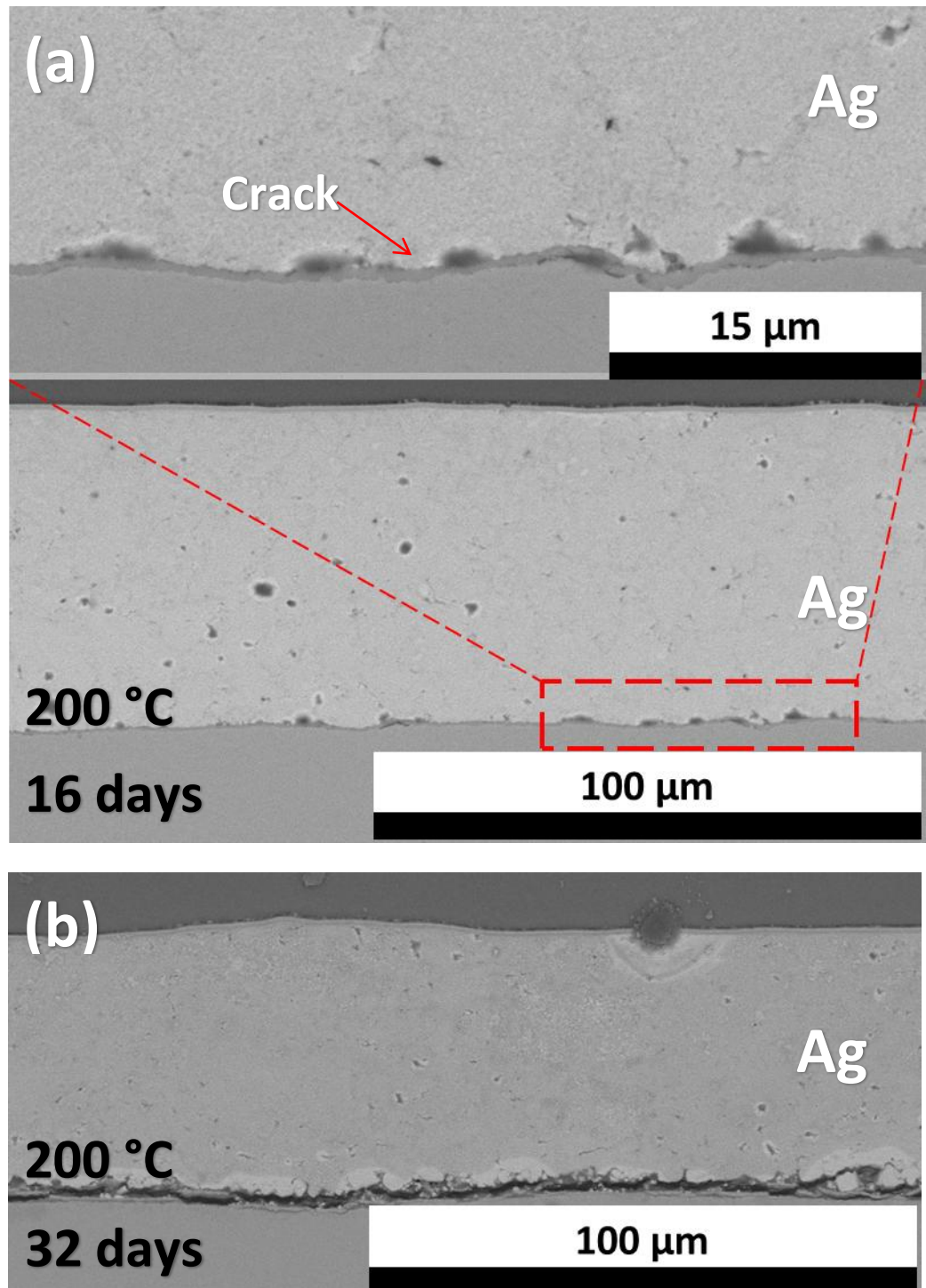


Figure 4- 11: Microstructure evolution of sintered joints with Ag finish substrate at 200 °C

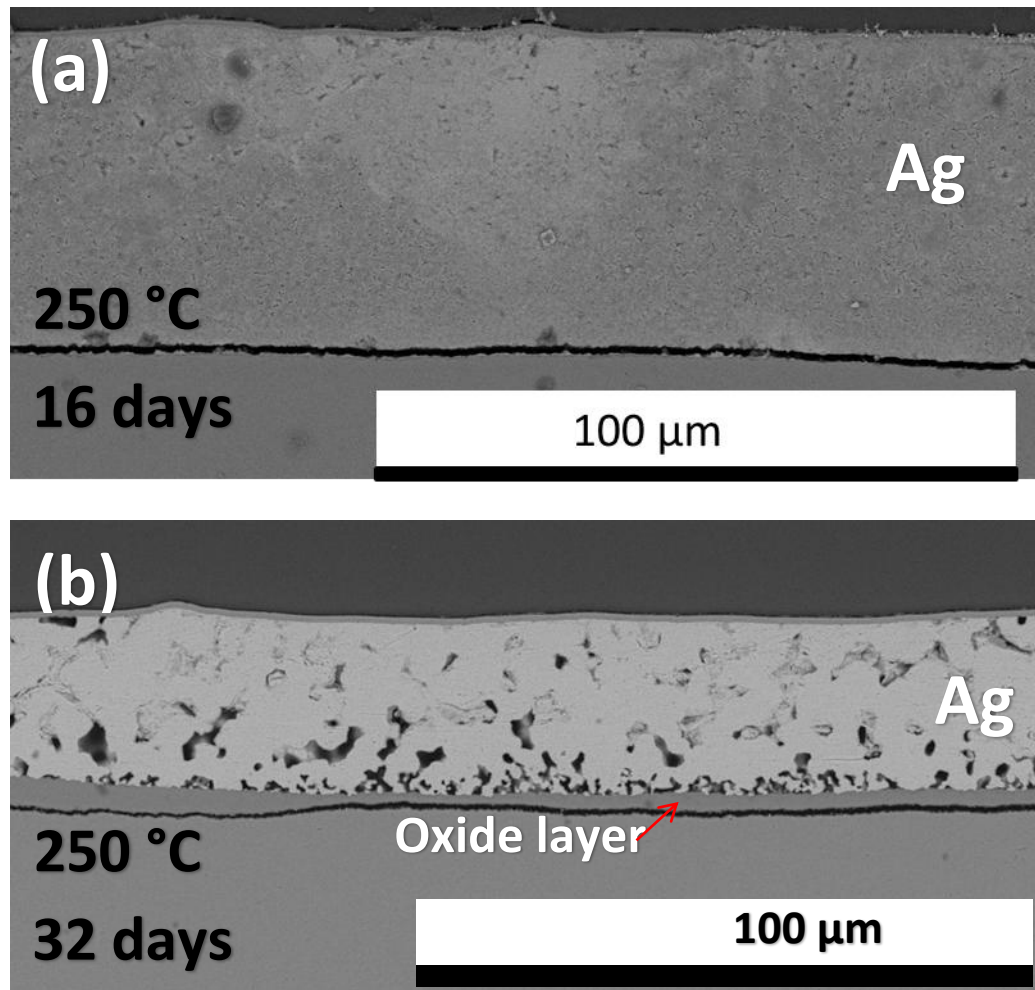


Figure 4- 12: SEM images of microstructure evolution of sintered joints with Ag finish substrate at 250 °C

At 150 °C for 8 days , fine cracks showed up along the interface between substrate and sintered joint, as Figure 4- 10 (b) shows. After ageing for 16 days, the cracks can be seen not only along the substrate surface, but also distributed in sintered joint randomly and separately, as Figure 4- 10 (c) shows. When ageing up to 32 days at 150 °C, microstructure of sintered joint became much denser and showed wider delamination than previous conditions, as Figure 4- 10 (d) shows.

At 200 °C and 250 °C, with more ageing time and higher ageing temperature, the sintered joints with Ag finish showed delamination around substrate interface and presented denser microstructure, as Figure 4- 11 and Figure 4- 12 show.

Comparing with sintered joint with bare copper substrate, those with Ag finish substrate showed less damage, and there were still some parts of sintered joint presented good bonding quality. Moreover, cracks in sintered joint not only occurred around the interface but also inside the sintered joint. It can be seen from SEM images that the oxide layers on Ag finish substrates were thinner than those on bare copper substrates.

Figure 4-13 is a SEM image of substrate with Ag finish. In this image, even though due to non-uniformity of the brush-plated Ag coating, some parts of substrate were not covered by Ag, which could be oxidized easily, some other parts of substrate with Ag finish were protected from oxidation, so the areas with Ag finish substrate showed a lower oxidation rate during isothermal ageing, and its thickness of oxide layer grew more slowly than that of bare copper substrate, as Figure 4- 16 shows. When oxide layer became thicker, the interfacial bonding strength could be reduced. As discussed previously, if shear stress exceeding bonding strength, cracks could be initiated and propagated along substrate surface, and sintered layer might separate from substrate eventually, which would result in much denser microstructure, and it then presented a similar microstructure evolution as sintered joint with bare copper substrate.

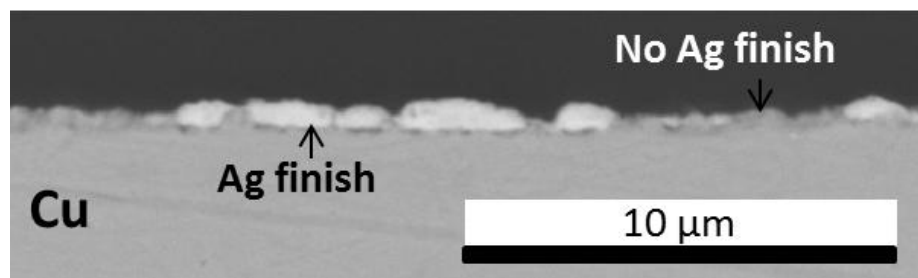


Figure 4- 13: Microstructure of substrate surface with Ag finish

In literature, Bai et al. [57] conducted thermal cycling tests from 50 °C to 250 °C, the bonding strength decreased with more thermal cycles. For sintered joints with Ag metallized copper substrate only failed at 500 cycles, which much less than those of sintered joints with Ag/Ni and Au/Ni substrate (4000 cycles and 6000 cycles, respectively). Bai et al. inferred that sintered joint with Ag metallized copper substrate was exposed to higher thermally-induced stress than

others. Actually, oxide layer growth has reduced the bonding strength might be another factor.

As mentioned, some parts of substrate surface have been well finished by Ag, and these parts presented good bonding quality during isothermal ageing tests. After 32 days at 150 °C, because of Ag finish protection, substrate surface has not been oxidized by air, and it did not show any degradation around the interface between substrate and sintered joint. From the following SEM image can be seen, the substrate surface wasn't covered by much oxide layer, which might be the reason for good bonding quality.

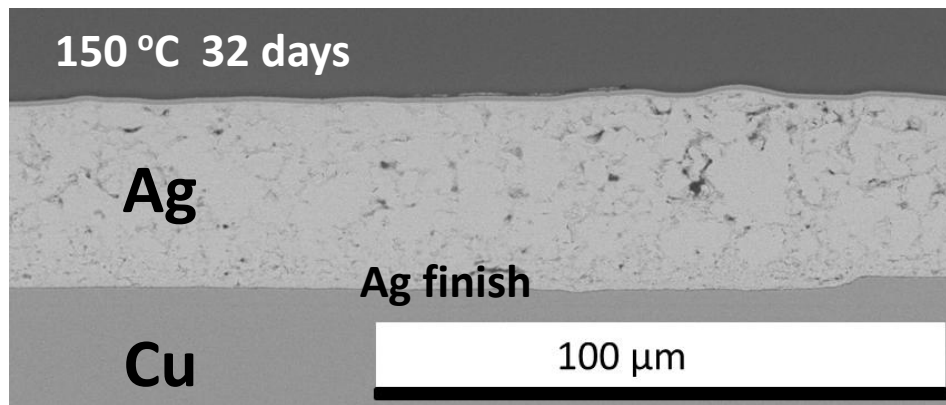


Figure 4- 14: SEM image of good bonding quality part in sintered joint with Ag finish substrate after 32 days at 150 °C

4.3.2.2 Pore size and porosity

Table 4- 4: The results of statistical analysis for the pore size and porosity of the sintered Ag samples with Ag finish substrate

	Aging time (day)	Pore size				Porosity
		Mean (μm)	SD (μm)	Min (μm)	Max (μm)	%
150 °C	0	0.25	0.15	0.092	0.72	4.09
	4	0.14	0.12	0.037	0.82	4.36
	8	0.15	0.079	0.061	0.80	3.23
	16	0.11	0.079	0.061	0.80	1.94
	32	0.10	0.048	0.037	0.42	2.73
200 °C	4	0.13	0.11	0.032	0.86	3.68
	8	0.15	0.138	0.073	1.45	2.38
	16	0.09	0.079	0.064	0.80	2.22
	32	0.12	0.072	0.073	0.60	1.56
250 °C	4	0.15	0.061	0.073	0.43	3.44
	8	0.13	0.079	0.052	0.56	1.05
	16	0.11	0.079	0.034	0.74	1.21
	32	0.063	0.031	0.037	0.54	1.43

SD: standard deviation

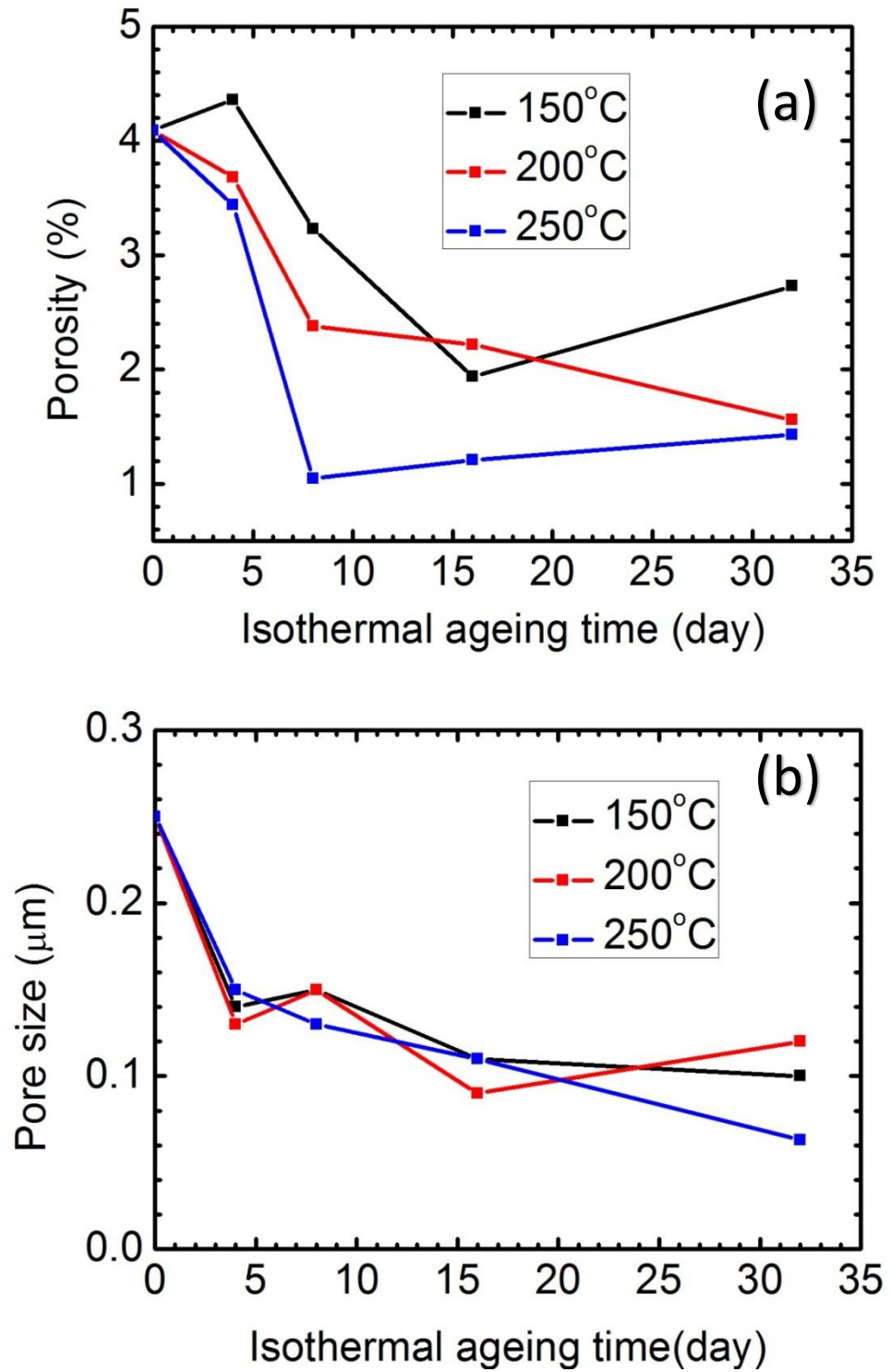


Figure 4- 15: Plots of pore size (a) and porosity (b) versus isothermal ageing time for the sintered joints with Ag finish substrate

The porosity and pore size of sintered layer with Ag finish substrate also presented decreasing trend, which showed similar tend as those with bare

copper substrate. However, the value of sintered joints pore size and porosity were slightly higher, because Ag finish might enhance the substrate interfacial bonding quality.

As Figure 4- 15 shows, isothermal ageing temperature has showed less effect on the porosity and mean pore size than isothermal ageing time. Especially, the values of pore size were quite close to each other with three different ageing temperatures.

4.3.2.4 Thickness of copper oxide

Table 4- 5: Results of copper oxide thickness on Ag finish substrate (μm)

	As-sintered	4 days	8 days	16 days	32 days
150 °C	0.34	0.33	0.63	0.36	1.01
200 °C	0.34	0.35	0.41	0.51	0.89
250 °C	0.34	0.95	1.57	1.89	2.16

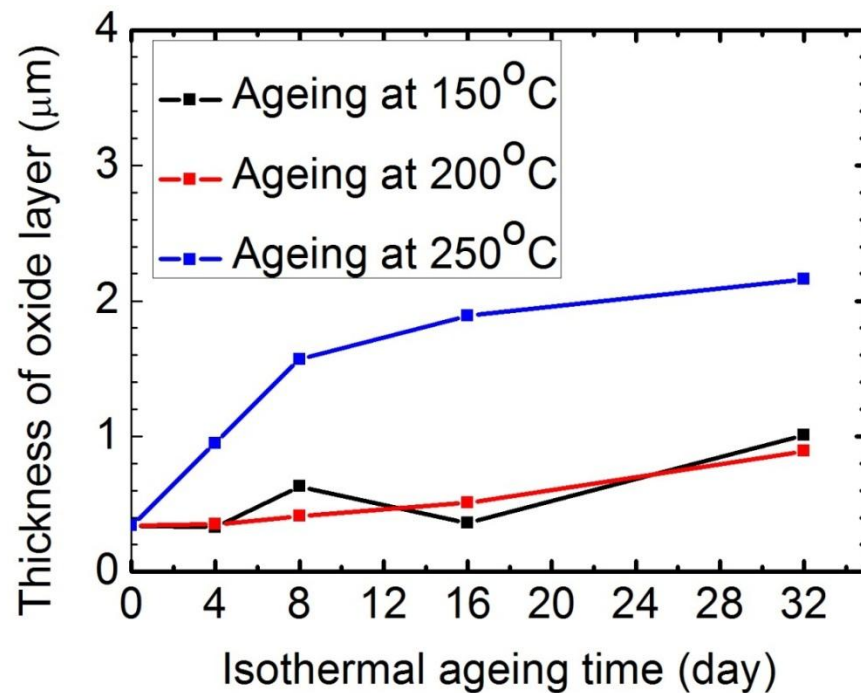


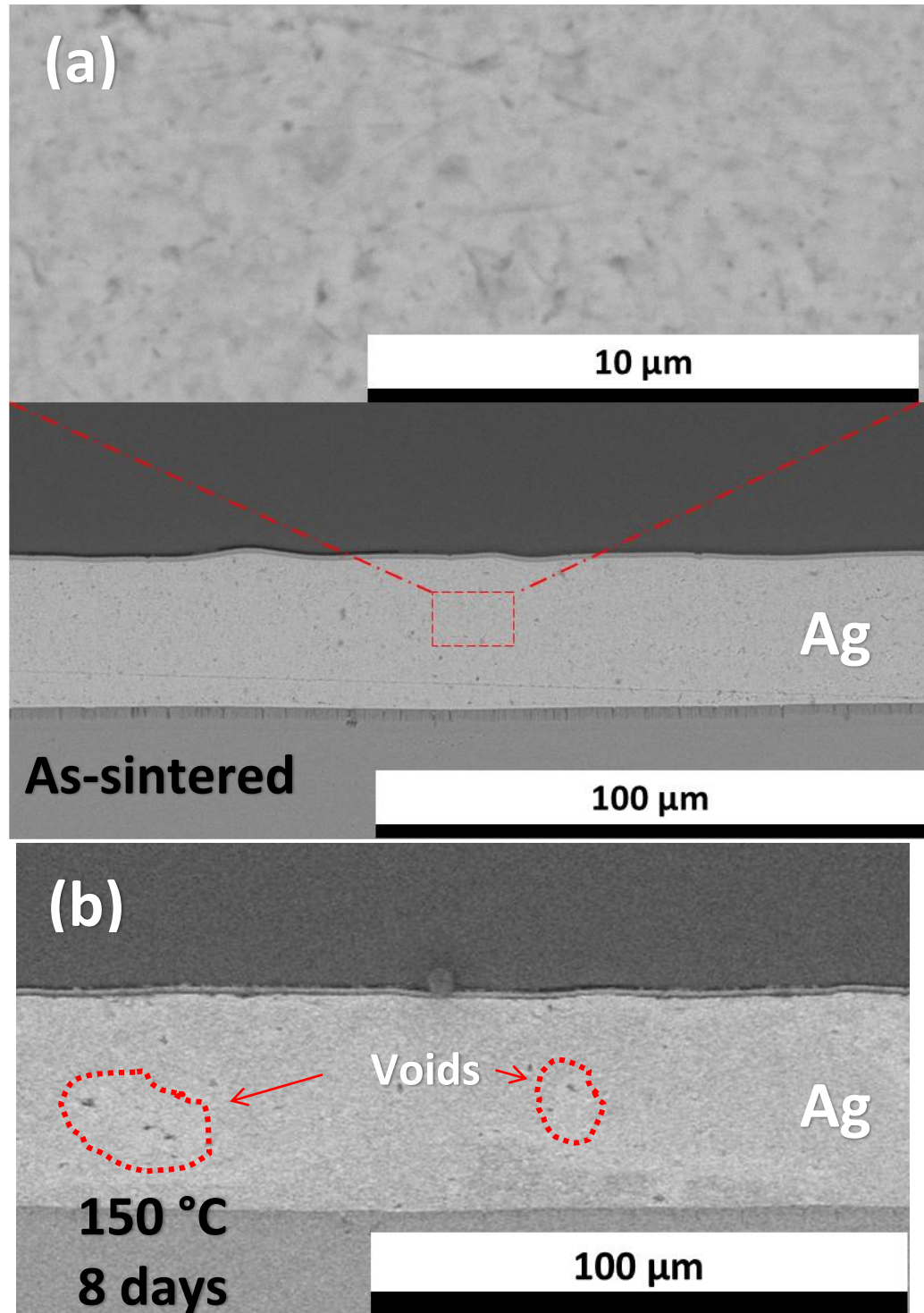
Figure 4- 16: Oxide layer thickness versus isothermal ageing time during thermal ageing for sintered joint with Ag finish substrate

As Figure 4- 16 shows, the thickness of oxide layer increased with more ageing time. Comparing with bare Cu substrate, the thickness of oxide layer on Ag finished substrate showed relatively lower value, because Ag finish might prevent parts of substrate surface from oxidation. At 150 °C and 200 °C, the thickness of oxide layer increased to 1.01 µm and 0.89 µm, respectively, which grew up much more slowly than that of oxide layer at 250 °C. At 250 °C, the thickness of oxide layer went up from 0.34 µm to 2.16 µm.

It has showed that isothermal ageing temperature has effects on the oxide layer thickness growth. At ageing temperature of 150 °C and 200 °C, the thickness kept at low growing rate. At 250 °C, the growing rate of oxide layer increased sharply and showed much higher value than those of oxide layers at 150 °C and 200 °C.

4.3.3 The sintered Ag joints of attaching IGBTs on the substrate with Ag/NiP finish

4.3.3.1 SEM images



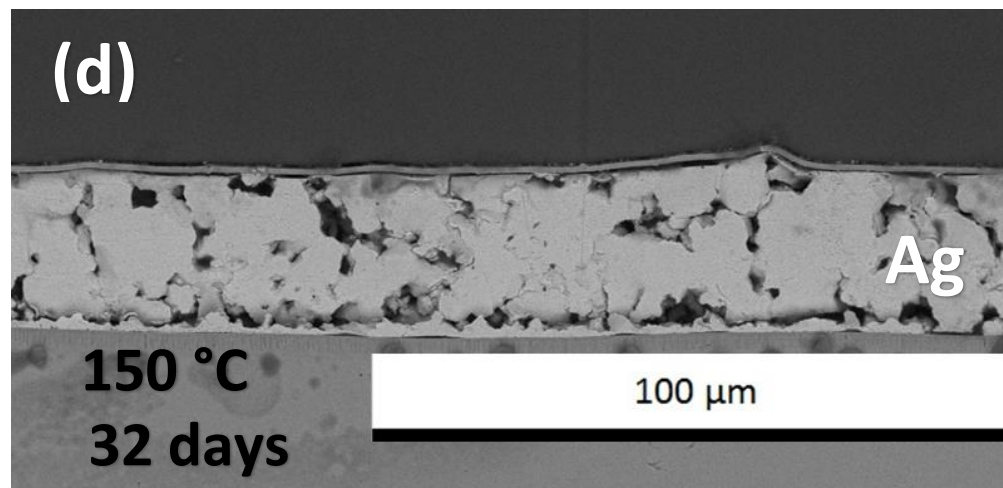
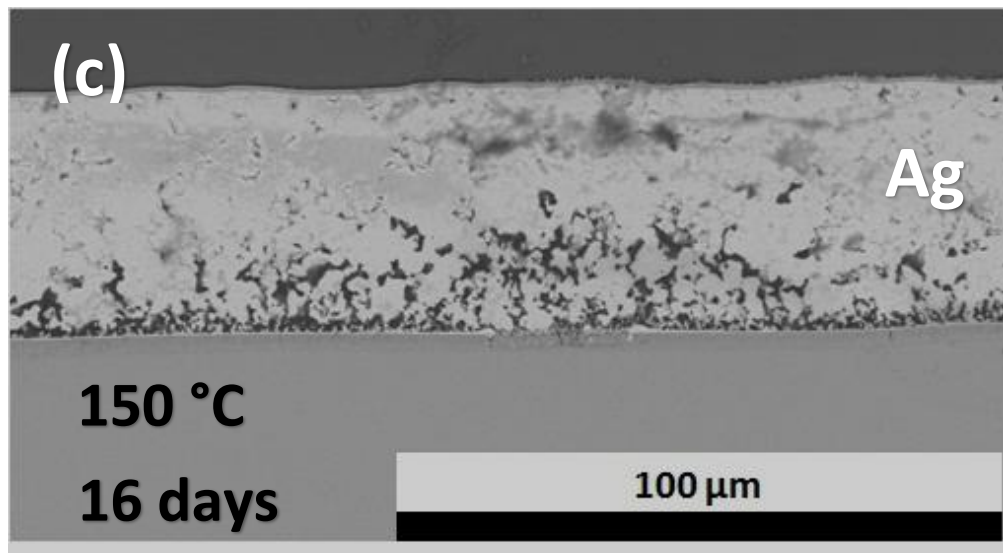


Figure 4- 17: Microstructure of sintered joints with Ag/NiP metallization substrate during isothermal ageing at 150 °C

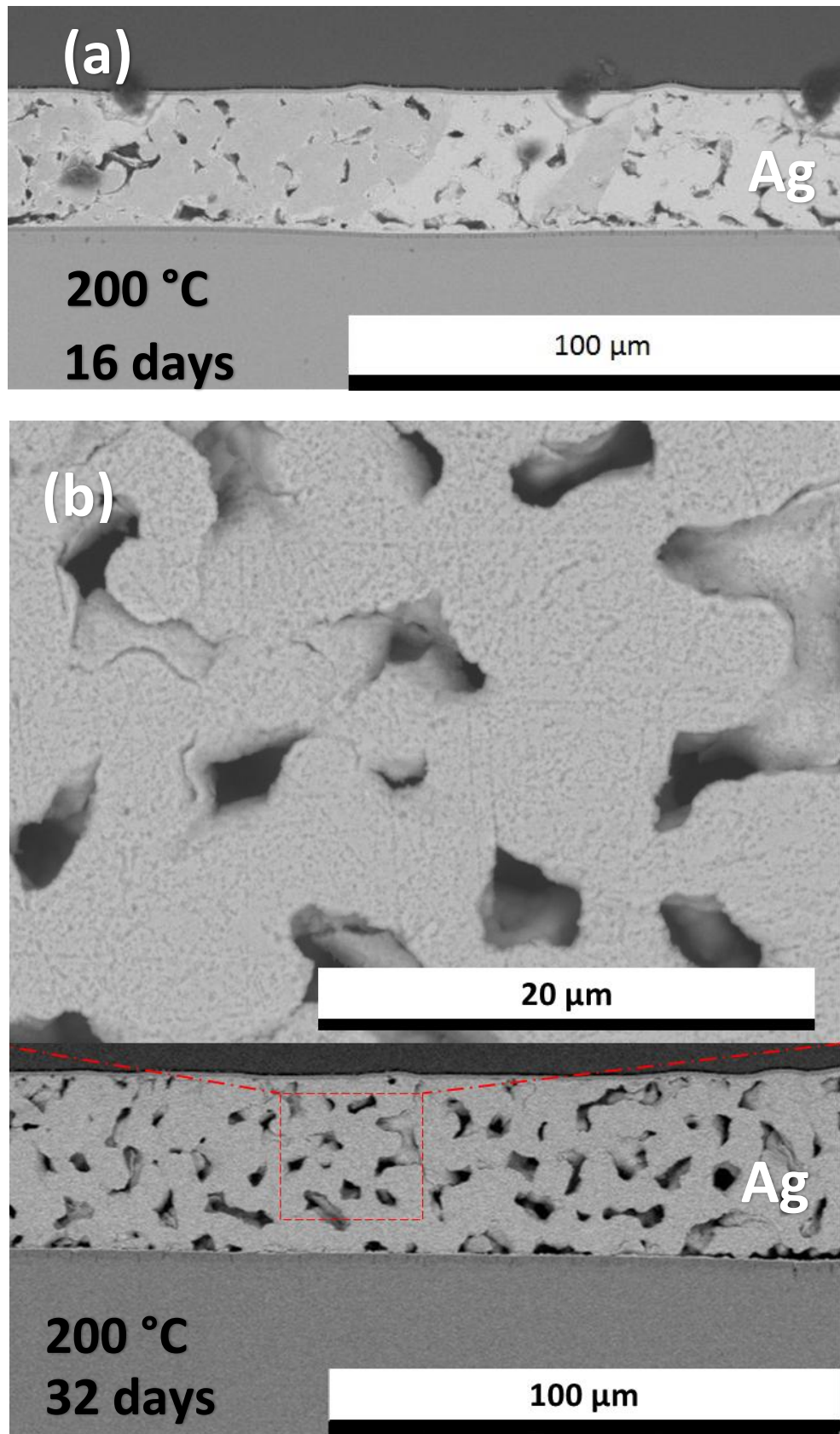


Figure 4- 18: Microstructure of sintered joints with Ag/NiP metallization substrate during isothermal ageing at 200 °C

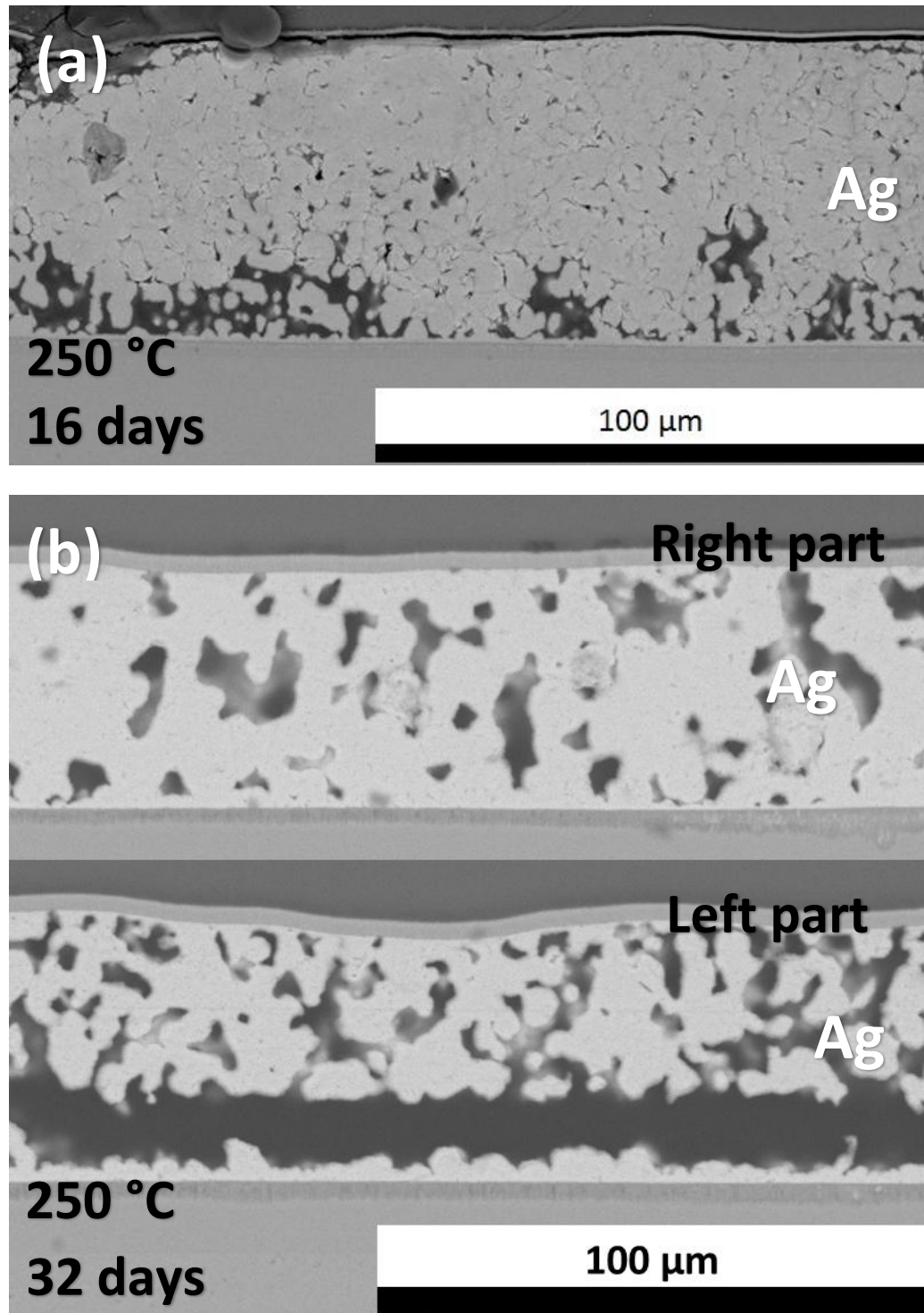


Figure 4- 19: Microstructure of sintered joints with Ag/NiP metallization substrate during isothermal ageing at 250 °C

In order to minimize the oxide formation, nickel was deposited on the surfaces of the substrates, which can be served as a barrier layer to prevent oxidation [58].

Because Ag/NiP metallized substrate in this work was not commercial available, Ag was further manually brush electroplating on top of as-received NiP metallization substrate. As the densification and grain growth occurring, the sandwich structure of sample constrains the volume of sintered joint from shrinking, so tensile stress developed in sintered joint during isothermal ageing. However, it was difficult to get very uniform metallization layer by manually electroplating, as Figure 4-20 (a) shows, some parts of substrate were non-uniform plated, while other parts were uniform plated. In area A, Ag metallization was little brush electroplated and the metallization layer was quite thin, which might further weaken the interfacial bonding strength. In area B, the Ag brush electroplating layer was not fully attached on the substrate. In this case, with more isothermal ageing time, the interface between substrate and sintered joint with non-uniform plated area might degrade, which would further cause interfacial delamination eventually. While some other well plated parts showed good interfacial bonding quality of sintered joints, as Figure 4-20 (b) shows. Therefore, with densification occurring and grain growing, Ag grain aggregated and the Ag particle size became bigger, so voids and pore were connected together. For sintered joints with non-uniform plated substrate, delamination showed up along the substrate surface, while sintered joints with uniform Ag plated substrate still bonded quite well after 32 days at 250 °C.

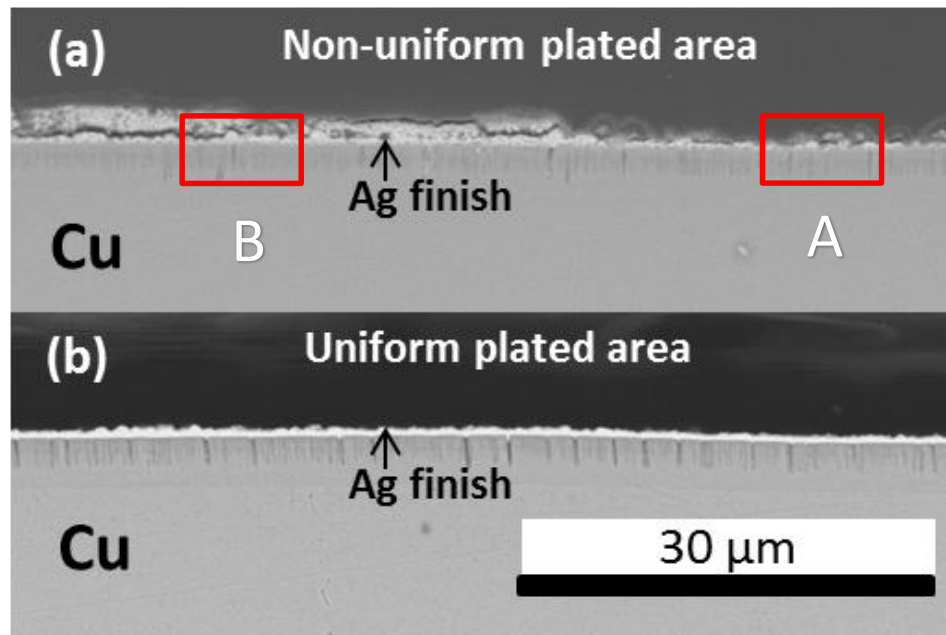


Figure 4- 20: Microstructure of substrate surface with Ag/NiP finish

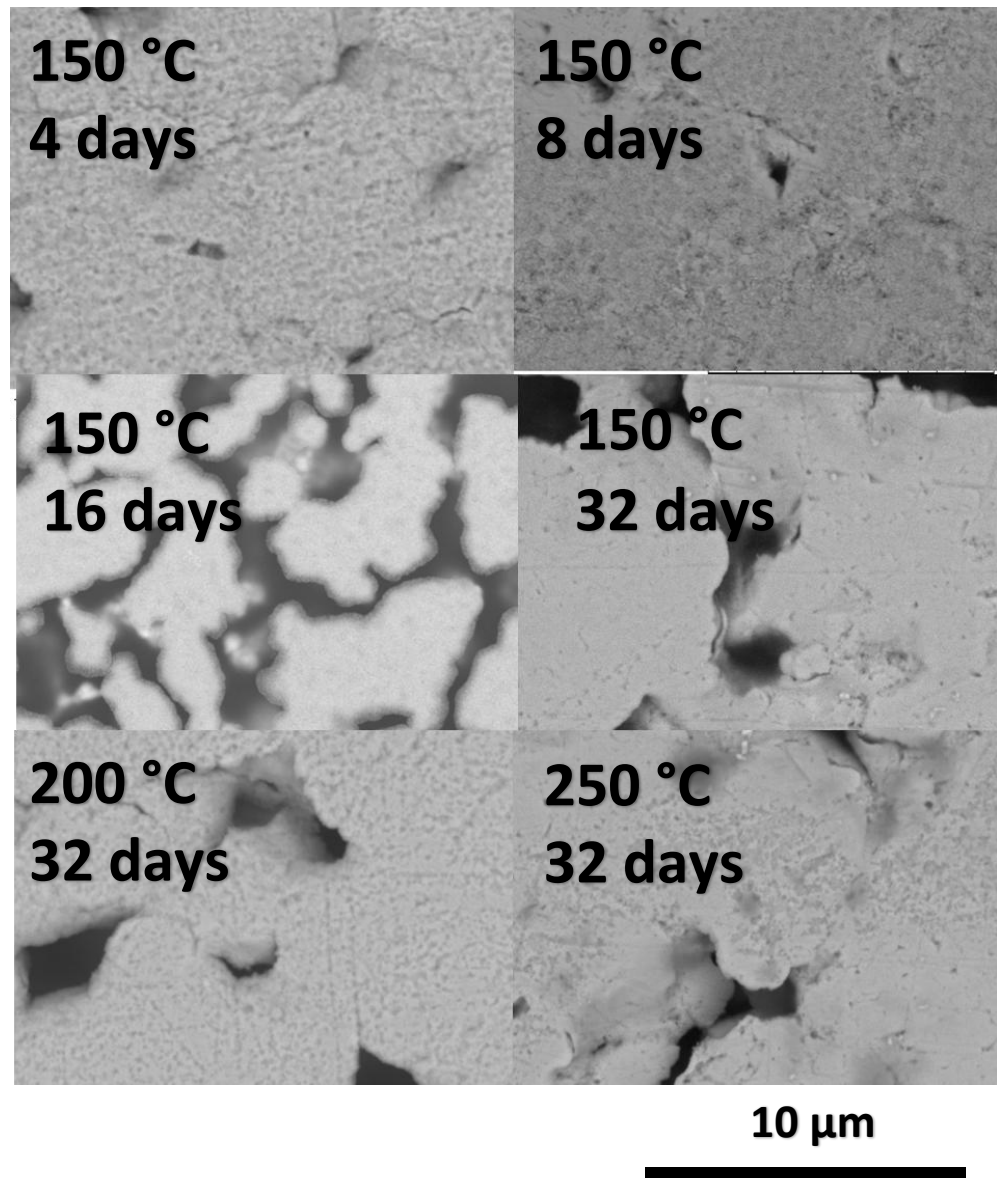


Figure 4- 21: Microstructure evolution of sintered joints with Ag/NiP metallization substrate during isothermal ageing

At 150 °C, after ageing for 8 days, the voids occurred and distributed separately in the sintered joints. After ageing for 16 days, the voids started concentrating around interface between substrate and sintered joint. After ageing for 32 days, cracks can be seen obviously in the sintered joint, some cracks have been connected together, as Figure 4- 17 (d) shows. Some cracks occurred along substrate surface, which would probably further reduce the interfacial bonding

strength, and eventually isolate the electrical and thermal conductivity in application.

At 200 °C, as Figure 4- 18 shows, voids and cracks showed randomly in the sintered joints. After ageing for 32 days, some cracks along the substrate interface occurred and grew longer and the wider.

At 250 °C, after ageing for 16 days, the sintered joint showed concentration of voids around the substrate interface and the middle area became much denser, as Figure 4- 19 (a) shows. After ageing for 32 days, the sintered layer was separated from the substrate in the left part of the sintered joints, but the right part of sintered joint was still well bonded, as Figure 4- 19 (b) shows.

In Figure 4- 21, with more ageing time, porosity of sintered joints increased and pore size of sintered joints also became bigger.

4.3.3.2 Pore size and porosity

Table 4- 6: The results of statistical analysis for the pore size and porosity of the sintered Ag samples with Ag/NiP finish substrates

		Pore size				Porosity
	Aging time (day)	Mean	SD	Min	Max	%
		(μm)	(μm)	(μm)	(μm)	
150 °C	0	0.11	0.047	0.06	0.35	4.99
	4	0.17	0.20	0.073	1.68	3.06
	8	0.097	0.089	0.037	1.011	5.02
	16	0.231	0.511	0.037	2.593	12.38
	32	0.441	0.398	0.037	2.048	15.94
200 °C	4	0.254	0.399	0.037	1.859	5.66
	8	0.259	0.324	0.037	1.398	9.31
	16	0.285	0.424	0.091	3.689	8.22
	32	0.536	0.936	0.073	4.747	13.53
250 °C	4	0.282	0.211	0.073	1.551	4.94
	8	0.221	0.5056	0.0367	3.755	5.42
	16	0.241	0.559	0.0367	2.566	12.24
	32	0.243	0.187	0.0367	1.392	9.61

SD: standard deviation

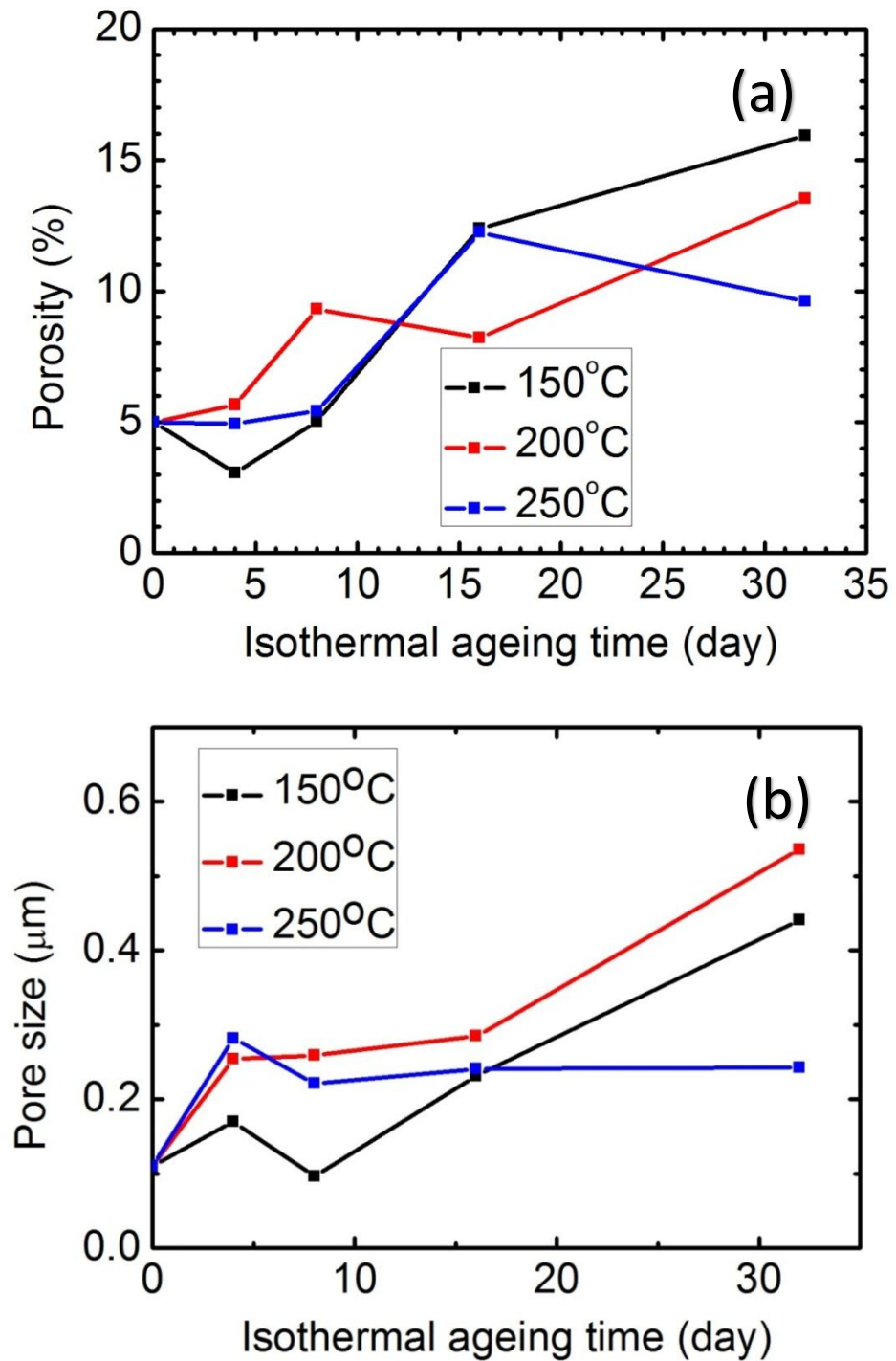


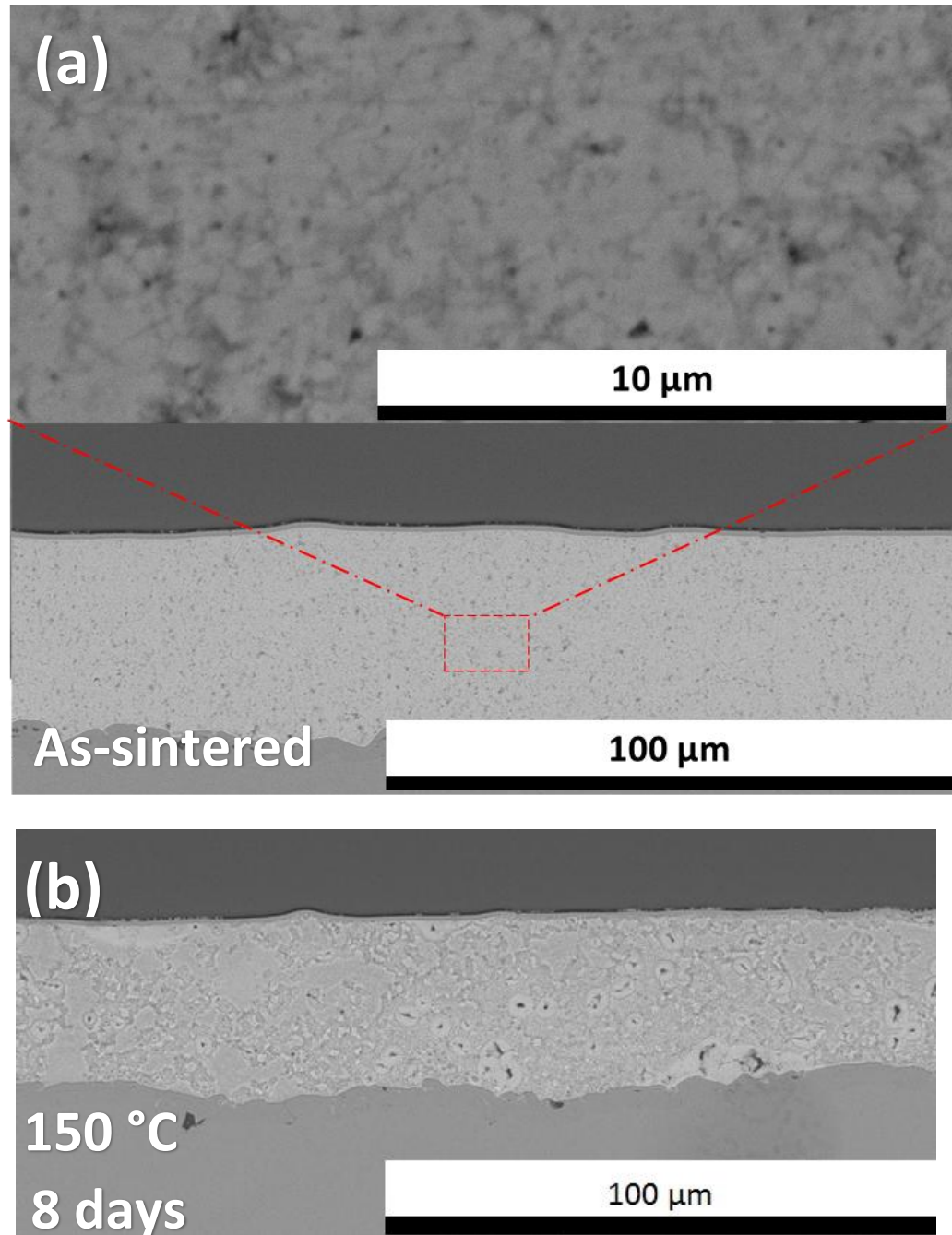
Figure 4- 22: Plots of porosity (a) and mean pore size (b) versus isothermal ageing time for the sintered joints with Ag/NiP finish substrates

At 250 °C, porosity of sintered joint first showed an As Figure 4- 22 shows, both porosity and mean pore size of the sintered joints with Ag/NiP metallization substrate showed an increasing trend for ageing up to 32 days. As

Table 4- 6 shows, porosity and mean pore size of as-sintered joint were around 4.99% and 0.11 μm , respectively. At 150 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$ with more ageing time, porosity of sintered joints increased from 3.06% to 15.44% and 5.66% to 13.53%, respectively. And mean pore sizes of sintered joints grew from 0.17 μm to 0.44 μm and 0.254 μm to 0.536 μm , respectively. These trends are different from those of sintered joints with bare copper substrate and Ag finish substrate. Because of porous property for sintered Ag joint, the microstructure of sintered joints with Ag/NiP became more porosity with more ageing time. At increase from 4.94% to 12.24% between ageing time 4 days and 32 days, then decreased to 9.61% after ageing for 32 days. The pore sizes of sintered joints showed relative stable values between 0.221 μm and 0.282 μm . At 250 $^{\circ}\text{C}$, the porosity and pore size did not grow as fast as those at 150 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$, especially after ageing for 16 days, because non-uniform metallized layer might cause cracks propagated along the substrate surface.

4.3.4 The sintered Ag joints of attaching IGBTs on the substrate with Au/NiP finish

4.3.4.1 SEM images



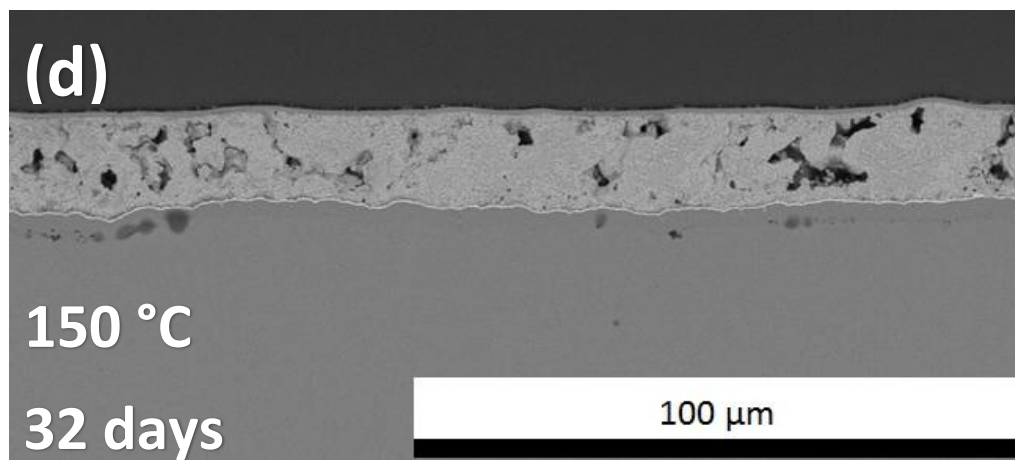
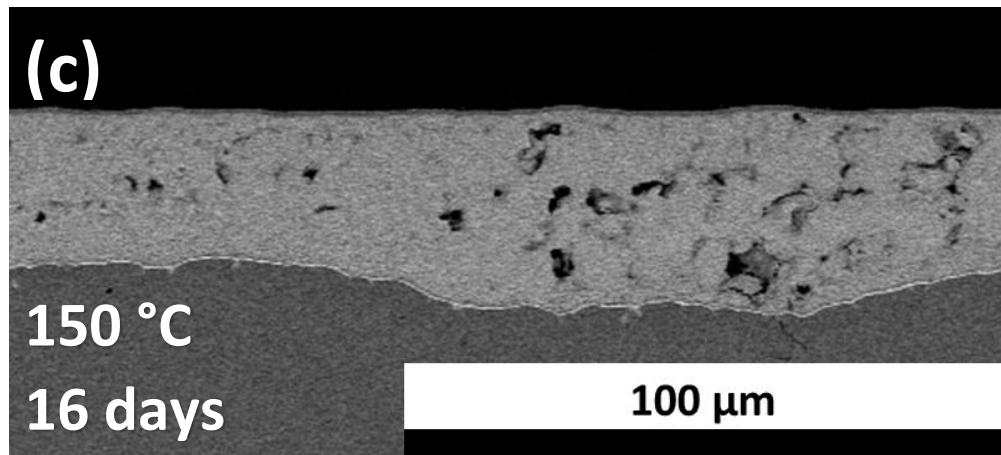


Figure 4- 23: Microstructure of sintered joints with Au/NiP metallization substrate during isothermal ageing at 150 °C

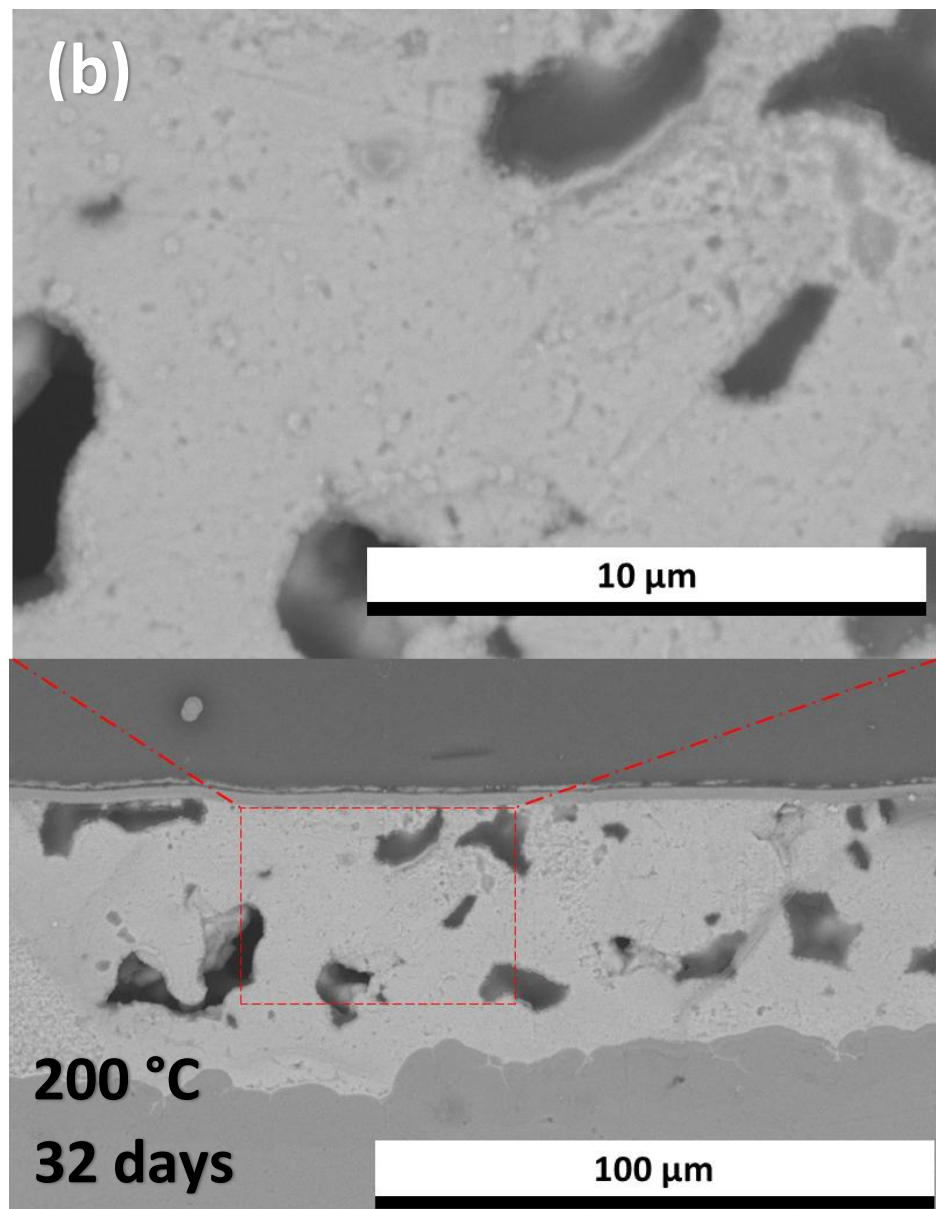
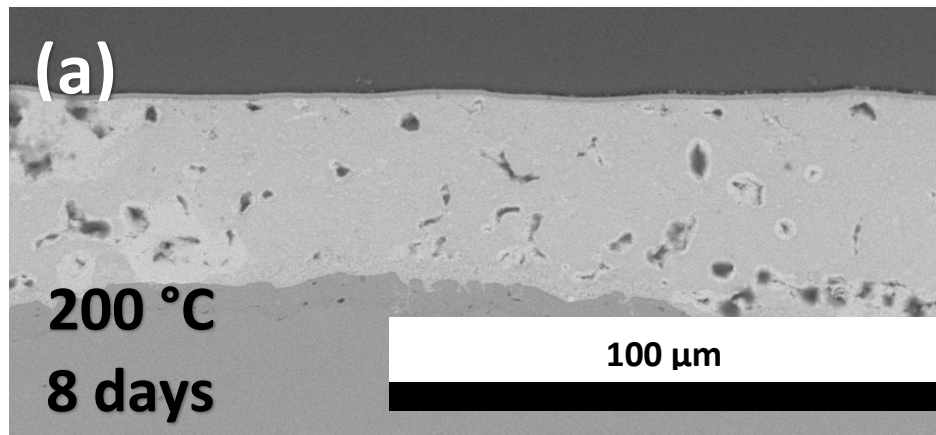


Figure 4- 24: Microstructure of sintered joints with Au/NiP metallization substrate during isothermal ageing at 200 °C

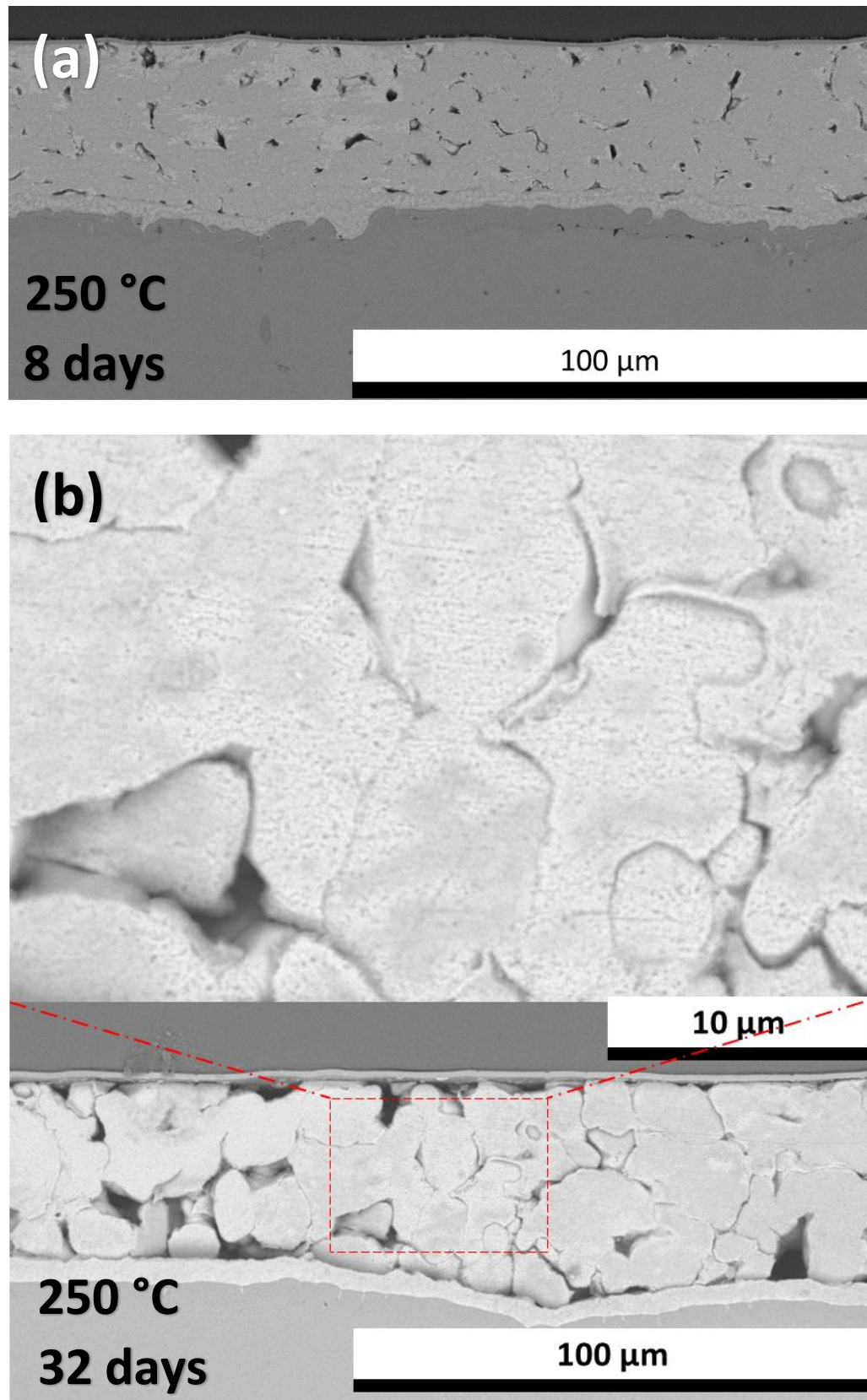


Figure 4- 25: Microstructure of sintered joints with Au/NiP metallization substrate during isothermal ageing at 250 °C

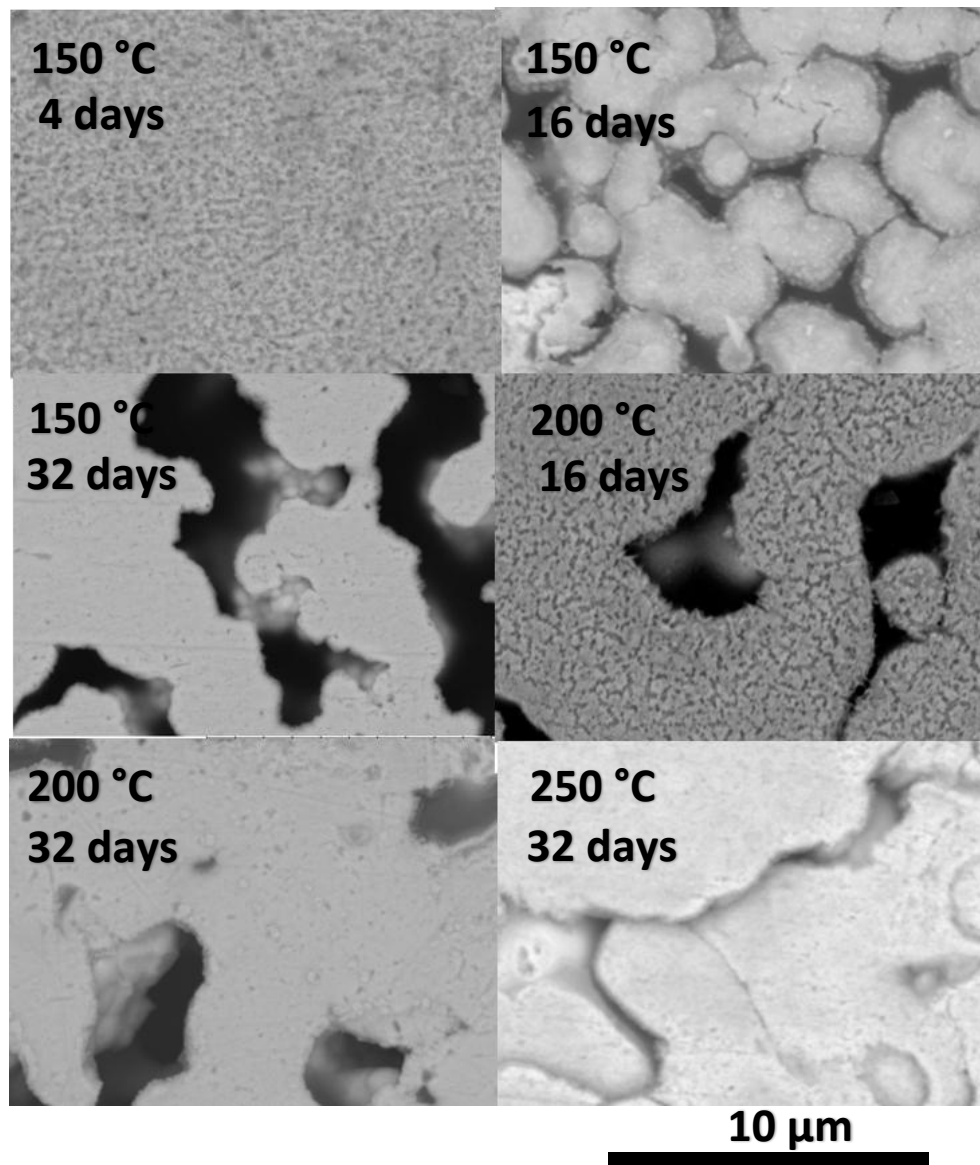


Figure 4- 26: Microstructure evolution of sintered joints with Au/NiP metallization substrate during isothermal ageing

At 150 °C for 8 days, the voids occurred separately in the sintered joint. After 16 days, the cracks initiated and propagated randomly in sintered joint, and Ag grain aggregated together, as Figure 4- 23 (c). After ageing for up to 32 days at 150 °C, the sintered joints still showed good bonding quality without any cracks or delamination around the interface.

At 200 °C, as Ag aggregation continued occurring, the sintered joints appeared more porosity. A layer without any voids or crack formed along the interface between substrate and sintered joint.

At 250 °C after ageing for 8 days, voids distributed randomly in the sintered joint. About 5 µm above the interface between sintered joints and substrates, crack along the substrates was formed in the void-free layer, and the grain boundary can be identified very clearly in the sintered joints.

Figure 4- 26 shows microstructure evolution of sintered Ag joints during isothermal ageing. From SEM images can be seen, with more ageing time and higher ageing temperature, the sintered joints showed more porosity microstructure and pore size increased.

From observation of SEM characterization, the Au metallization layer was very uniform, and the substrate surface was all covered by Au. For sintered joints with Au/NiP metallization substrate, with more isothermal ageing time, densification and grain growth could still continue. The sandwiched structure prevented the volume from shrinking, so the Ag grains in the sintered joint would further aggregate and grow. In the meanwhile, the voids and pores connected up and became bigger in size.

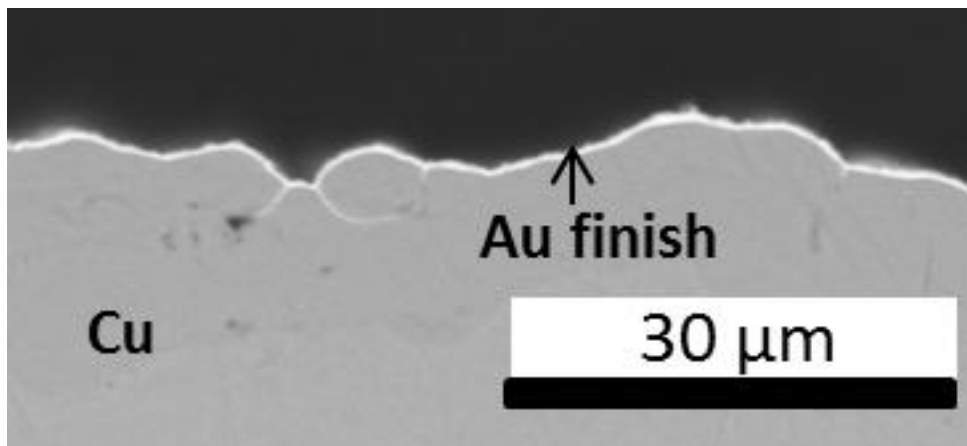


Figure 4- 27: Microstructure of substrate surface with Au/NiP finish

In literature, Paknejad et al. [57] showed the shear strength of sintered joints under thermal ageing at temperature of 300 °C. Four samples have been shear tested at each condition of 0 hour, 24 hours, 100 hours, and 500 hours. As their results show, as the samples the shear strength decreased with increasing

ageing time. It can be inferred that the bonding strength could be reduced during isothermal ageing. In order to investigate the cause of bonding strength reduction, samples which had been aged but not shear tested, were cross sectioned. With more ageing time, thicknesses of epitaxial layer increased quickly from 8 μm to 16 μm between 24 and 500 hours of ageing, and the epitaxial layer nearly covered half of the sintered joint after ageing for 500 hours. Paknejad et al. inferred that the increase of thickness of epitaxial layer was caused by migration of Ag atoms towards Au metallized layer and migration Au in the opposite direction.

Figure 4-28 illustrates process of formation and evolution for epitaxial layer growth. As Figure 4-28 (a) shows, during isothermal ageing, Ag atoms diffused along the grain boundary towards Au layer, and Au atoms also migrated in opposite direction, because the lattice constant of Ag is close to that of Au, then Ag atom reoriented to Au layer, and an epitaxial layer was formed. In the literature [57], diffusion coefficient (D) was estimated around 1.7×10^{-17} m/s. As shown in Figure 4- 32, the diffusion coefficient (D) in this work increased with higher isothermal temperature and is close to the value in literature, although a little lower. In literature [57], the Au metallized layer is 2 μm , much thicker than the 0.1 μm -thick Au metallized layer of the as-received substrate used in this work, and this might be the reason for the slower growth observed in this work. Furthermore, the isothermal ageing temperature was 300 $^{\circ}\text{C}$ in literature [57] , which is higher than temperature in this work, and this might be another factor for their faster epitaxial layer growth.

As the diffusion in sintered Ag is dominated by grain boundary diffusion, with increasing ageing time and more and more Ag and Au atom diffusing, the epitaxial layer became thicker, as Figure 4-28 (b) shows. As mentioned previously, the Au metallization layer in this work was very thin (0.1 μm), so it diffused out all the Au grains very quickly, and the diffusion flux would be imbalanced, these could have made voids concentrate in the epitaxial layer, so that the contact area between the Ag grain and Au layer deceased. With ageing temperature as high as 250 $^{\circ}\text{C}$, atoms diffused more quickly than those at 150 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$. At 250 $^{\circ}\text{C}$, cracks occurred in the epitaxial layer after 32

days, as Figure 4-29 shows, which might be a limitation for the further application of sintered joint at high temperature.

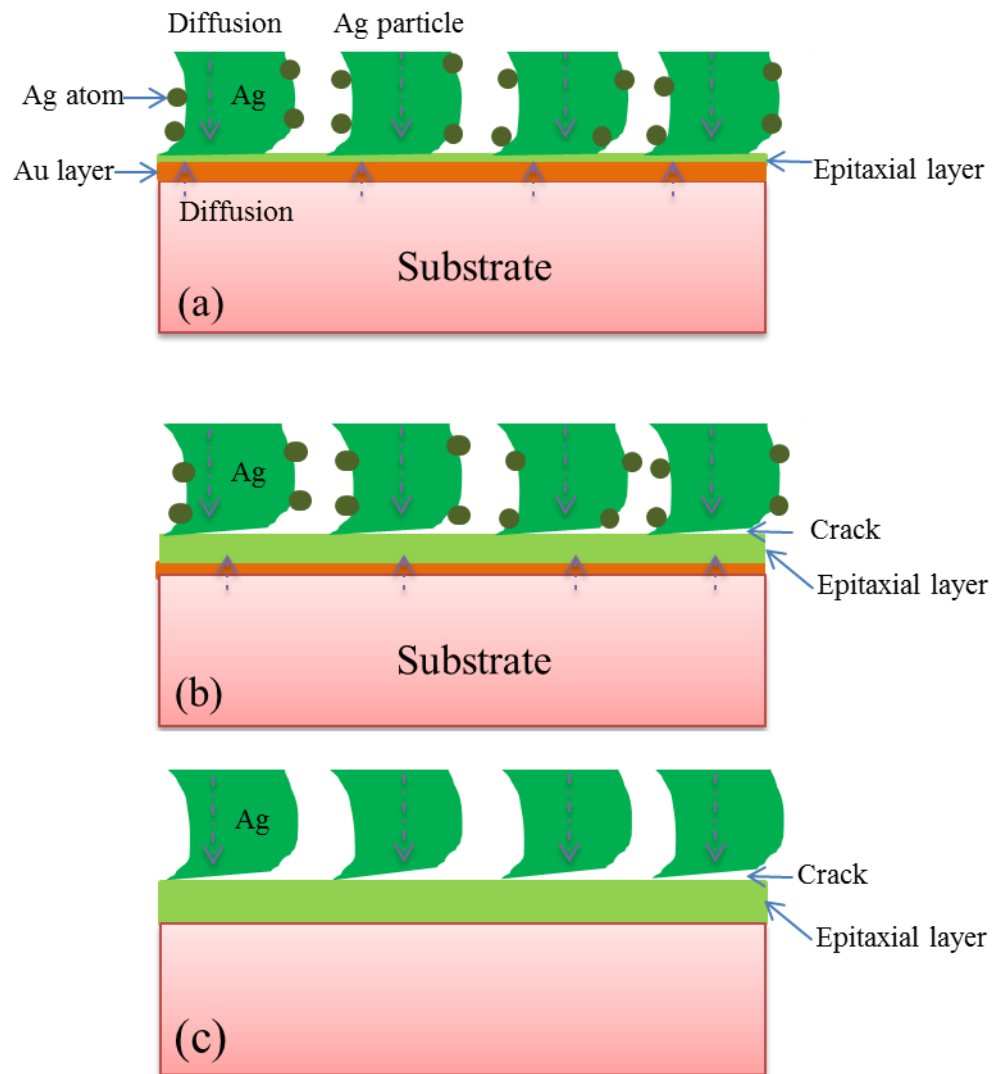


Figure 4- 28: An illustration of the epitaxial layer growth process during isothermal ageing

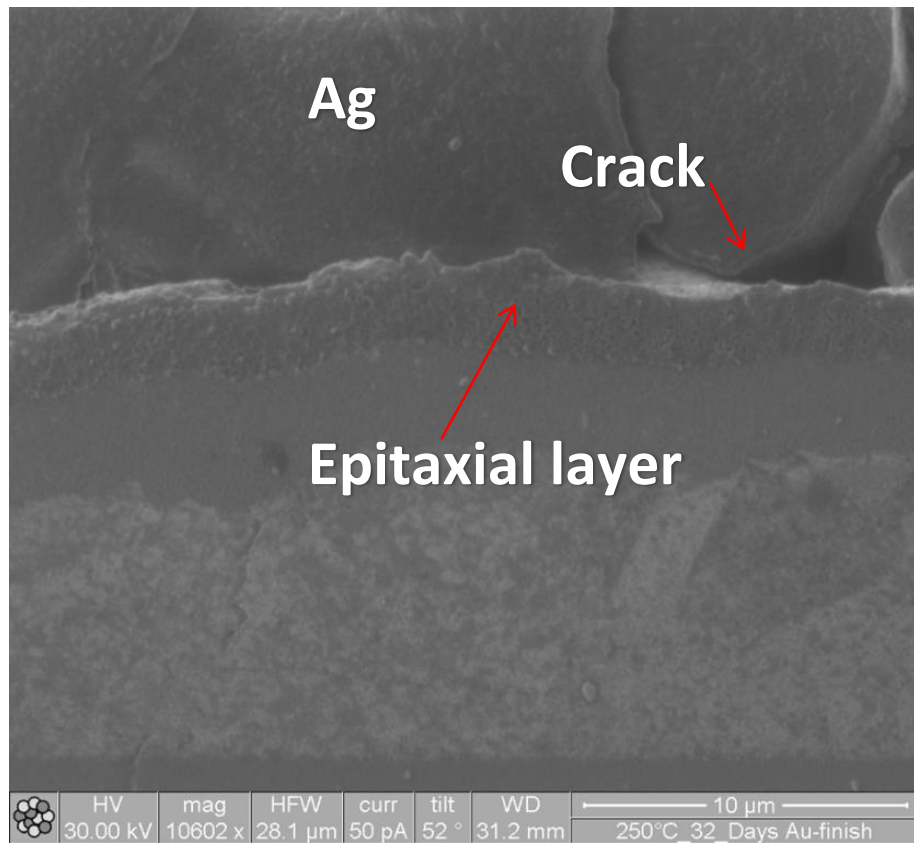


Figure 4- 29: FIB ion channelling image of epitaxial layer after 32 days ageing at 250 °C

4.3.4.2 Pore size and porosity

Table 4- 7: The results of statistical analysis for the pore size and porosity of the sintered Ag samples with Au/NiP finish substrate

	Aging time (day)	Pore size				Porosity
		Mean (μm)	SD (μm)	Min (μm)	Max (μm)	%
150 °C	0	0.15	0.06	0.073	0.46	4.25
	4	0.13	0.052	0.073	0.46	4.68
	8	0.136	0.154	0.036	1.259	3.03
	16	0.247	0.467	0.036	2.499	11.15
	32	0.43	0.892	0.036	2.99	16.51
200 °C	4	0.235	0.439	0.046	3.729	6.47
	8	0.311	0.853	0.061	4.473	21.46
	16	0.181	0.195	0.046	1.611	19.11
	32	0.237	0.589	0.036	4.890	20.4
250 °C	4	0.28	0.32	0.073	1.12	4.66
	8	0.431	0.635	0.091	4.295	5.47
	16	0.187	0.357	0.036	2.48	11.95
	32	0.151	0.249	0.036	2.708	10.24

SD: standard deviation

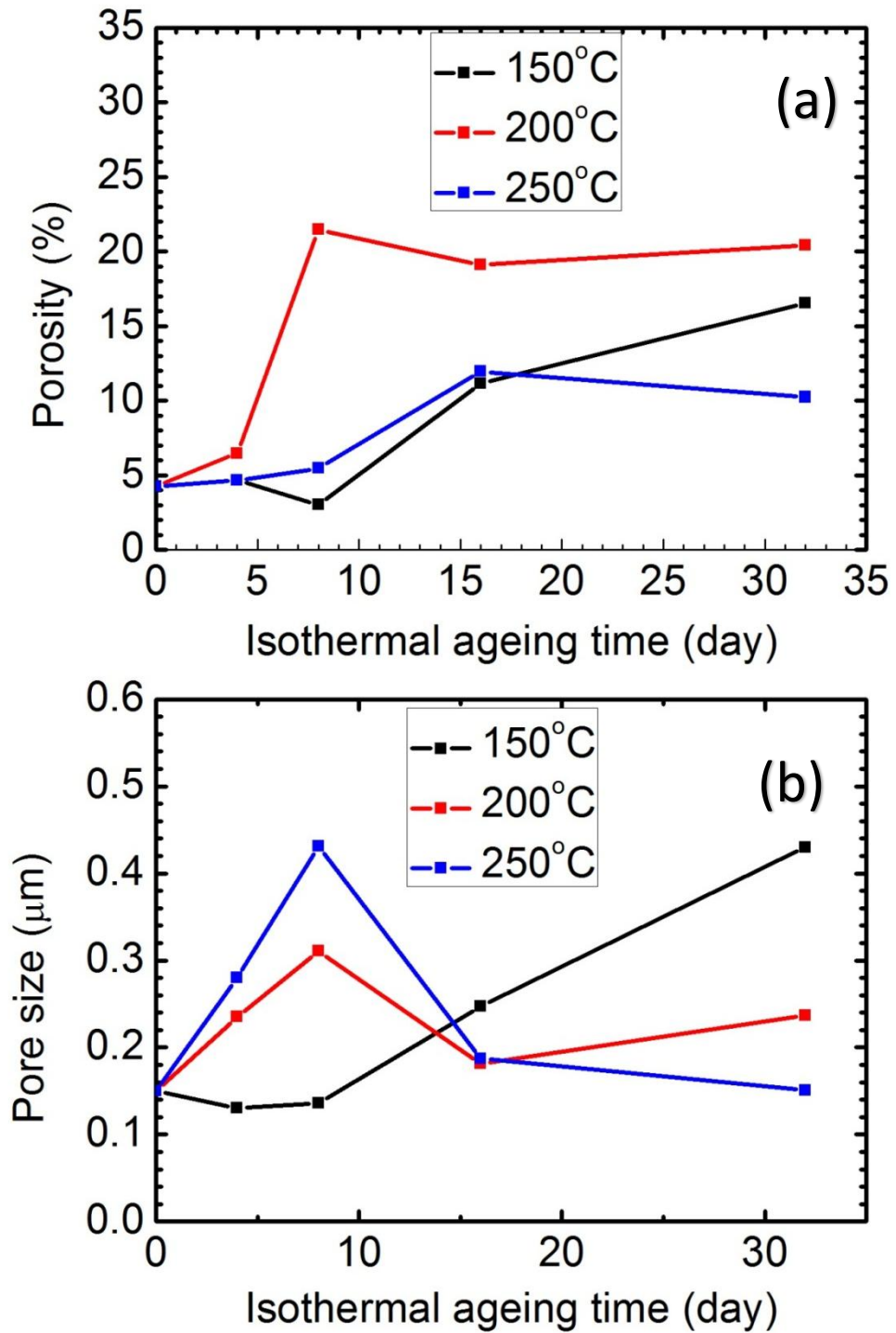


Figure 4- 30: Plots of mean pore size (a) and porosity (b) versus isothermal ageing time for the sintered joints with Au/NiP finish substrate

As Figure 4- 30 shows, the porosity of the as-sintered joints were around 4.25% after sintering process. At 150 °C, the porosity values of the sintered joints showed an increase trend with more ageing time, which increased as

high as 11.15% for 16 days. After ageing for 32 days, the porosities of sintered joints were 12.45%. The mean pore size showed the similar trend as porosity did at 150 °C, which increased from 0.13 µm to 0.43 µm from 4 days to 32 days.

At 200 °C after ageing for 4 days, the porosity of sintered joint increased rapidly, around 21.46%, 19.11% and 20.4% after ageing for 8 days, 16 days and 32 days, respectively. The mean pore size values fluctuated from 0.181 µm to 0.237 µm between ageing for 4 days and 32 days.

At 250 °C for up to 32 days, the porosity of sintered joints grew up from 4.66% to 10.24%, which shows lower value than those of sintered joints at 200 °C, the mean pore size grew up to 0.431 µm for ageing 8 days, and decreased to 0.151 µm for ageing 32 days.

4.3.4.3 Thickness of epitaxial layer of Ag on Au

Table 4- 8: Results of thickness of epitaxial layer (μm)

	Isothermal ageing time (days)			
	4	8	16	32
150 °C	0.44	0.62	0.62	1.01
200 °C	1.24	2.56	3.42	3.59
250 °C	1.86	3.69	4.17	4.16

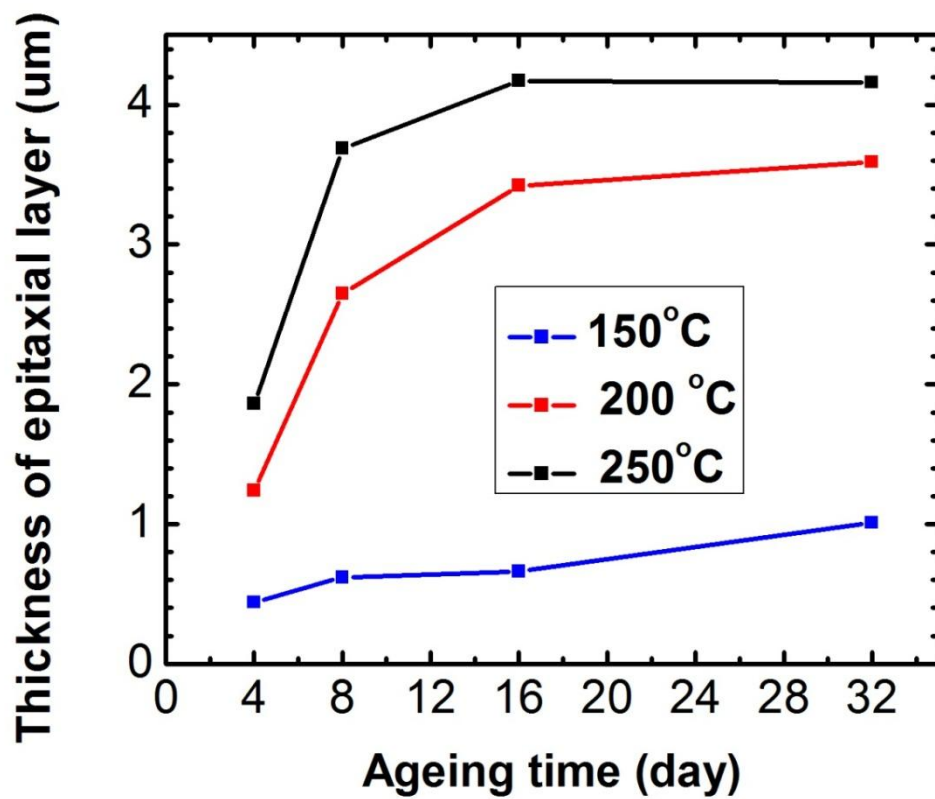


Figure 4- 31: Results of thicknesses of epitaxial layer versus ageing time during isothermal ageing

As Figure 4- 25 shows, there is a void-free layer on top of the substrate surface, and it grew thicker with higher ageing temperature and more ageing time. This void-free layer has been discussed and considered as epitaxial layer in literature [55][56][57].

In Figure 4- 31, the epitaxial layer thickness did not increase too much at 150 °C, and it went up from 0.44 µm (4 days) to 1.01 µm (32 days). However, at 200 °C and 250 °C, thickness of epitaxial layer grew up much more quickly. After 4 days, the thicknesses of epitaxial layer were 1.24 µm and 1.86 µm, respectively. After 32 days, thicknesses of epitaxial layers increased to 3.59 µm and 4.16 µm.

The increase of the epitaxial layer thickness during isothermal ageing tests indicates that the Ag atoms diffuse to Au layer and Au atoms diffuse to the opposite direction. This process could be quantitatively estimated by evaluation of diffusion coefficient (D) of Au into sintered Ag joint, and value of diffusion coefficient could further be used as determination of diffusion mechanism.

The epitaxial layer diffusion coefficient D could be calculated from following Equation 4-1:

$$\frac{dx}{dt} = \frac{D}{x} \quad 4-1$$

Where x_0 is the epitaxial layer thickness for as-sintered joint, which is 0 from SEM image.

$$\text{So,} \quad x = D^{1/2}T \quad (T = 1.4t^{1/2}) \quad 4-2$$

As Figure 4- 32 shows, D could get from the plot of epitaxial layer thickness versus isothermal ageing time. So D_1 is $1.93 \times 10^{-19} \text{ m}^2/\text{s}$ at 150 °C, D_2 is $3.17 \times 10^{-18} \text{ m}^2/\text{s}$ at 200 °C, D_3 is $7.12 \times 10^{-18} \text{ m}^2/\text{s}$ at 250 °C;

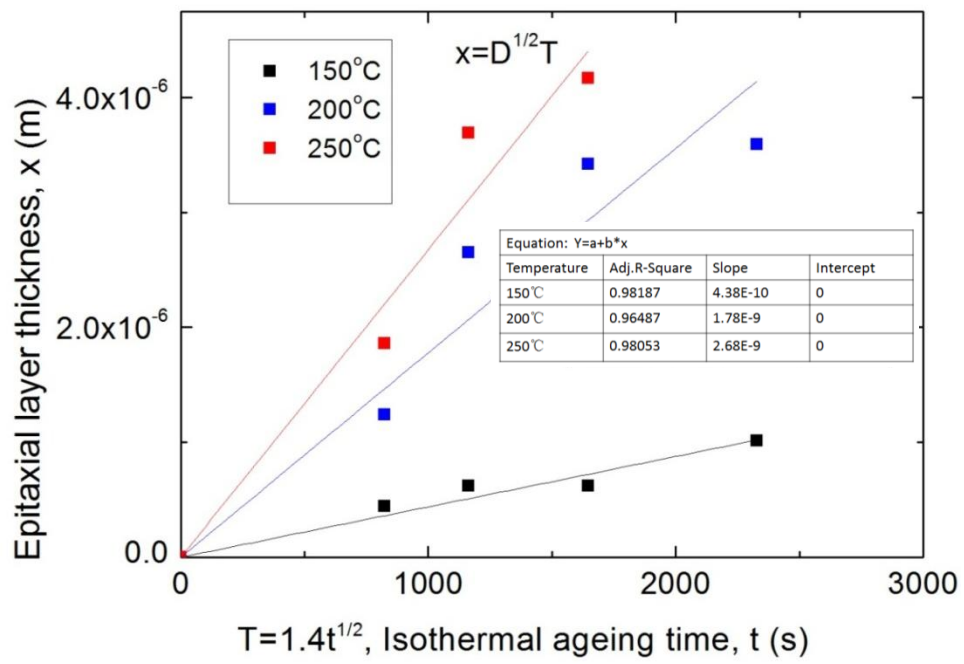


Figure 4- 32: Plot of epitaxial layer thickness versus isothermal ageing time

As the Arrhenius Equation 4-3 shows:

$$D = A \exp\left(-\frac{E}{RT}\right) \quad 4-3$$

Where D is the diffusion coefficient at temperature of T ; E is the activation energy; R is the energy constant which is 8.3145 J/mol*K; T is the Kelvin temperature and A is the collision frequency factor.

$$\ln D = \ln A - \frac{E}{RT} \quad 4-4$$

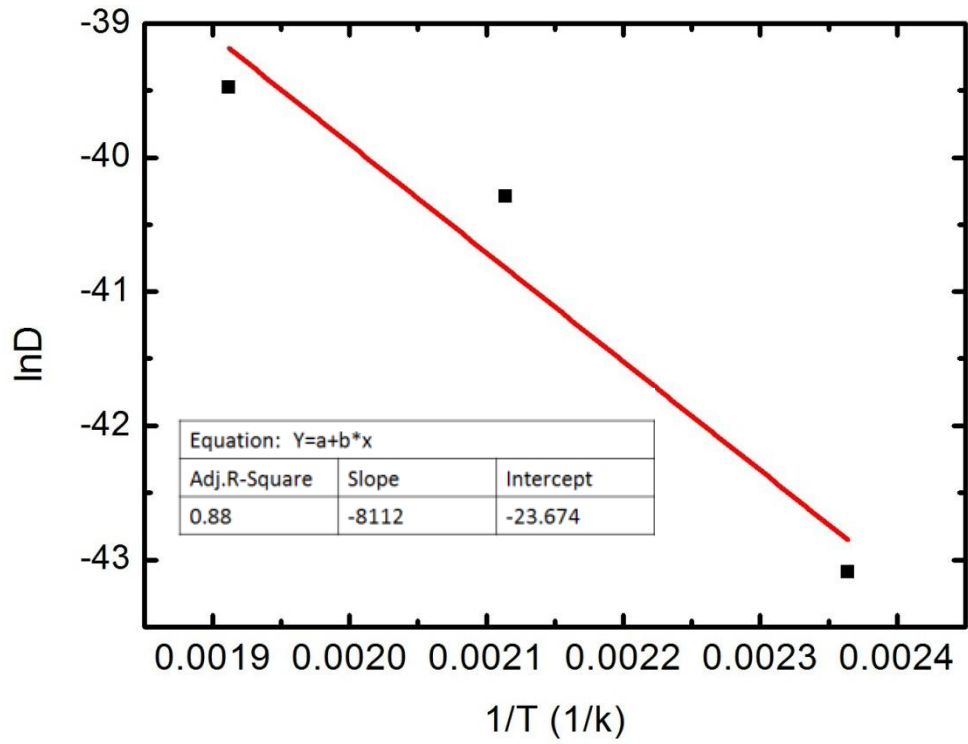


Figure 4- 33: Plot of $\ln D$ versus $1/T$ on linear coordinates

In this work, from Figure 4- 33 can be concluded, the diffusion coefficient D at isothermal ageing temperature of $300\text{ }^{\circ}\text{C}$ is $3.63 \times 10^{-17}\text{ m}^2/\text{s}$. Therefore, value of activation energy E could be got from Figure 4- 33, which is 67.4 KJ/mol .

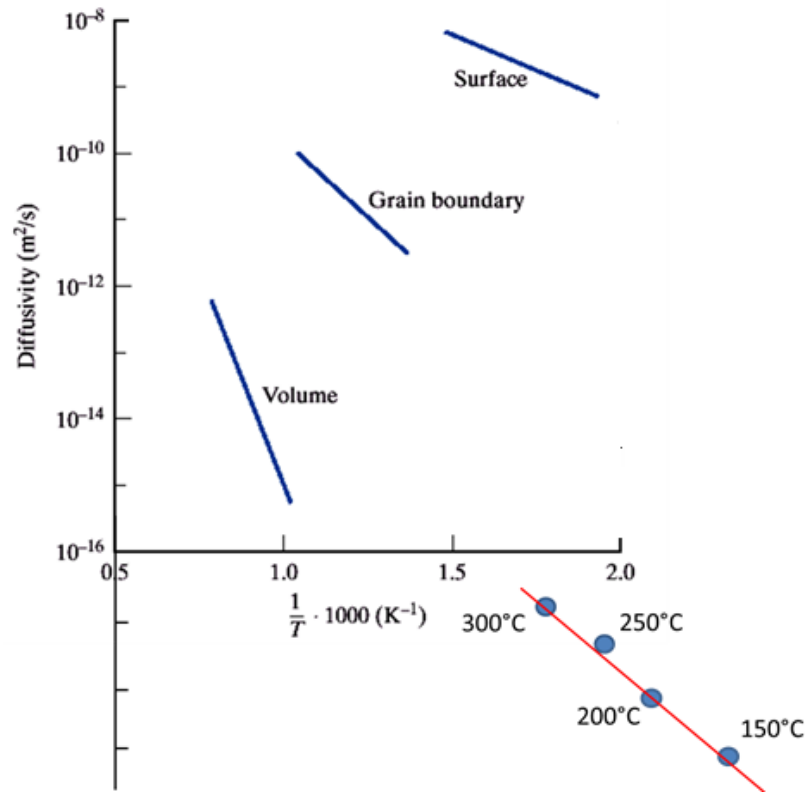


Figure 4- 34: Plot of comparison of estimated diffusion coefficients at relatively low temperatures with those reported in the literature for relatively high temperatures

In Figure 4- 34, three kinds of diffusion mechanism have been presented in literature [76], including volume diffusion, grain boundary diffusion and surface diffusion. According to previous results, the diffusion coefficients versus $1/T$ (where T is isothermal ageing temperature) can be plotted on coordinates, the results show the slope of grain boundary diffusion in the literature are the same as that of this work, hence it could be concluded that the grain boundary diffusion has had dominant role during epitaxial layer growth in this work.

4.4 Summary

In this chapter, sintered joints with four kinds of substrates finishes have been investigated during isothermal ageing at 150 °C, 200 °C and 250 °C. SEM images of microstructure evolution have presented and compared, and pore size and porosity have been calculated to reveal local densification variation.

(1) For the sintered Ag joints with only bare copper substrate, because of oxide on the surface of substrate, sintered joints has got poor bonding quality of interface between substrate and sintered layer, which could probably reduce bonding stress and cause crack propagation with more ageing time.

(2) For the sintered Ag joints with Ag finish substrate, as Ag finish could be a protection for substrate from oxide, the sintered Ag joints presented more porosity microstructure and bigger pore size in some local position, however, oxide layer still formed, which could be further reduce interfacial bonding quality.

(3) The sintered Ag joints with Ag/NiP finish substrate showed better bonding quality than those with bare copper substrate and Ag finish substrate. Because Ni could be served as a barrier layer to prevent oxide, sintered Ag joints continued occurring densification and cracks were showed randomly inside layer. But there was still some part of substrate lack of plated, so some sintered layer was separated from substrate during isothermal ageing tests.

(4) The sintered Ag joints with Au/NiP finish substrate showed the best bonding quality among those four kinds of substrate. An epitaxial layer was formed above the substrate surface, and its thickness was growing with more ageing time and higher isothermal ageing temperature. However, sintered layer would likely separated from epitaxial layer and crack formed at 250 °C.

CHAPTER 5 Reliability of sintered joints and solder joints under passive thermal cycling tests

5.1 Introduction

In this Chapter, in order to obtain information about the reliability of sintered joints and solder joints under passive thermal cycling tests, SAM and X-ray tomography have been employed as non-destructive characterization tools to observe the microstructure evolution of the samples. Moreover, sizes and temperature profiles effects of sintered joint on the thermomechanical reliability have been discussed, and soldered joints have been compared with sintered joints in terms of thermomechanical reliability and degradation. Ag nanoparticle film, which has more uniform structure and more even thickness, has been employed for thermal cycling tests to investigate the thermomechanical reliability and microstructure evolution of sintered Ag joint.

In the literature review, it was shown that degradation of sintered joints can be revealed by SAM images, however, the microstructural character of damage in sintered joints can not be identified due to limits of SAM resolution. A correlative approach combining SAM, X-ray tomography and SEM is used here as it allows us to interpret SAM images in microstructural terms.

As mentioned in Chapter 3, the as-sintered Ag nanoparticle is still intermediate stage. Therefore, under operation involving elevated temperatures, further evolution of the microstructure would occur and should be taken into account during reliability analysis.

5.2 Experiment procedure

5.2.1 Materials

In order to reduce thickness variation, the nanoparticles film to be sintering on Ag or Au finish was used for the thermal cycling tests. The film was obtained from Cookson Electronics (South Plainfield, NJ 07080, USA). The die attachment solders used in the comparative study were films of $\text{Pb}_{95}\text{Sn}_5$ and $\text{Sn}_{96.5}\text{Ag}_{3.5}$.

The Si devices were attached to Si_3N_4 substrates. The as-received substrates were cut into 25 mm $\times$ 25 mm coupons from 44 mm $\times$ 34 mm substrates which consist of 0.32 mm thick Si_3N_4 ceramic tiles sandwiched by 0.3 mm thick Cu actively brazed on both sides. The surface finish on the as-received substrates was 5 μm thick NiP. An additional Au layer of ~ 2 μm in thickness was deposited by eletroless plating onto the NiP finish. The Si devices attached on the Si_3N_4 -based substrates were 13 mm $\times$ 13 mm $\times$ 0.2 mm Si insulated gate bipolar transistors (IGBTs) with $\sim 1/1$ μm thick Ni/Ag metallization on their back sides.

5.2.2 Sample preparation

Samples were prepared with a number of dimensions and materials combinations. As mentioned previously, Silicon nitride was used as the base substrate material and silicon as the die material. The sizes of the die were 3 mm and 13 mm in length. All substrates and dies were bonded together by solder film or Ag nanoparticle film.

5.2.2.1 Electroless deposition of gold on as-received substrate

Gold electroless plating involves the immersion of as-received substrates in a plating bath and the consequent deposition of a layer of gold film on the base by means of chemical reaction and without the use of externally applied electrical energy. The plating process is illustrated below in Figure 5- 1:.

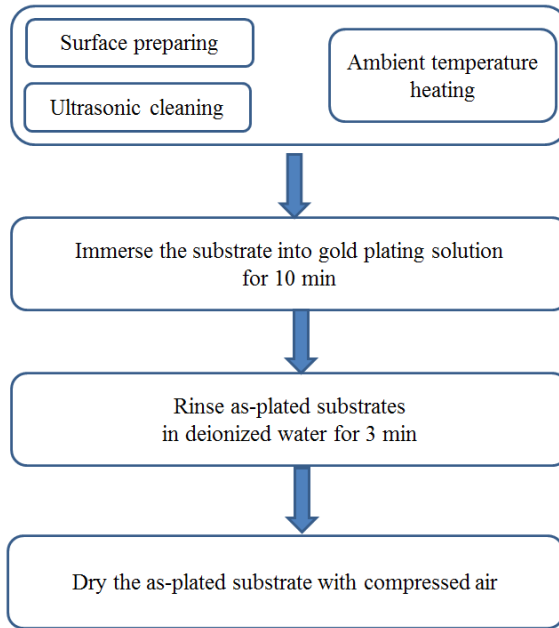


Figure 5- 1: Electroless deposition of gold on as-received substrate processes

The preparation of gold eletroless plating includes two main stages: sample cleaning and ambient temperature heating. The surfaces of as-received substrates initially were rubbed with MetaPrep Ultra (MPU) solution for 3 min, to remove oil and dirt. The substrates were then ultrasonically cleaned in deionized water for 3 minutes. A magnetic stirred water bath ensured temperature uniformity and stabilization (up to 0.1 °C). The gold-plating solution, also with a magnetic stirrer immersed was placed in a beaker in the stirred water bath. The water temperature stabilized at 90 °C.

After plating preparation, substrates were put into the beaker containing the gold plating solution for 10 minutes. They were then rinsed in deionized water for 3 minutes and dried with compressed air.

5.2.2.2 Sintering process

The sintering process of Ag nanoparticle film consists of two steps: (a) transferring the film and (b) sintering to form the attachment. First, the device was placed on top of a slice of Ag nanoparticle film; this assembly was then placed on 1mm thick silicone gel situated on a cold plate, as Figure 5-3 shows. The heating plate was then brought down onto the assembly and the transferring process was performed at 130 °C and under the pressure of 5 MPa

for 5 minutes, before releasing the pressure and cooling the assembly down to room temperature (within 3 minutes).

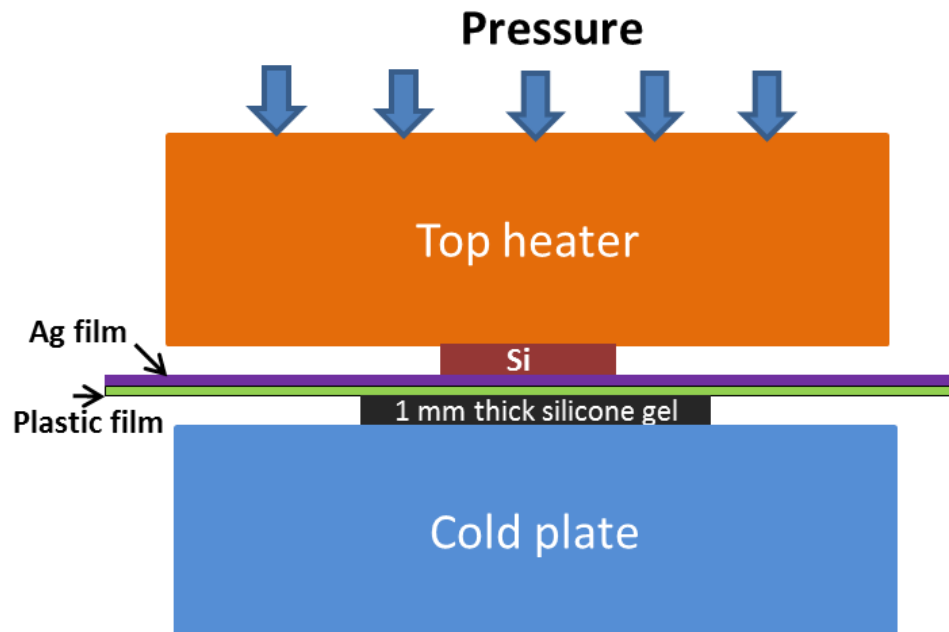


Figure 5- 2: Schematic sample geometry used to transfer Ag nanoparticle film. Note that the dimensions of sample geometry are not to scale.

After the transferring process, the device which now had the Ag nanoparticle film firmly attached was placed onto the substrate and fixed with Kapton tape. The sample was turned up-side down and put on the 1 mm thick silicone gel situated on the cold plate. Sintering was performed at 250 °C and 5 MPa for 5 minutes, before releasing the pressure and cooling to the room temperature (within 3 minutes), as Figure 5- 3 shows.

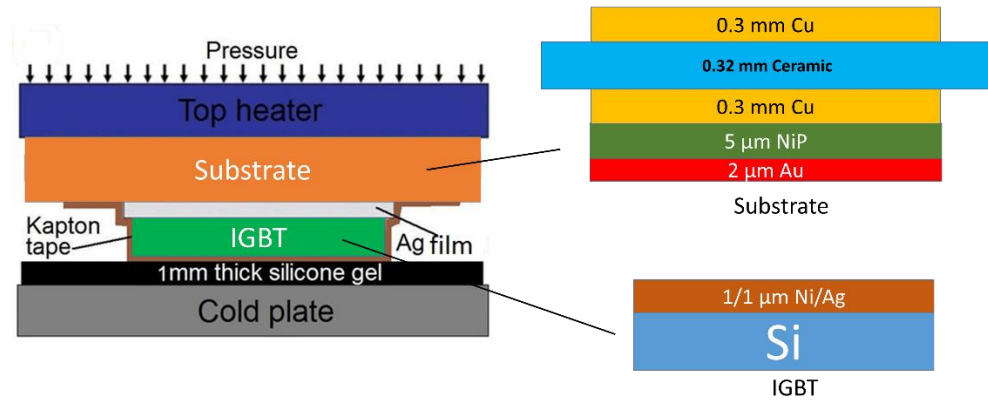


Figure 5- 3: Schematic diagrams of sample geometry used during the sintering process. Note that the dimensions of sample geometry are not to scale.

5.2.2.3 Soldering process

As mentioned previously, two solder alloys ($\text{Pb}_{95}\text{Sn}_5$ and $\text{Sn}_{96.5}\text{Ag}_{3.5}$) were studied side by side with the Ag sintered joint. For these alloys, there was sufficient solderability and wettability on the as-received Si_3N_4 -based substrates, therefore, the bonding process to attach the Si devices was relatively straightforward.

One piece of $\text{Pb}_{95}\text{Sn}_5$ solder preform was placed on Si_3N_4 -based substrate under one Si device, and put into a vacuum reflow oven pre-heated at 300 °C and evacuated below 5 mbar for 5 minutes, and then held at temperature and purged with 2% H_2 98% N_2 forming gas (330 L/h at 2bar) for 5 minutes. The reflow oven was further heated up to 375 °C and evacuated below 5 mbar for 3 minutes. The reflow process was held at 375 °C for 10 minutes, before being cooling down to room temperature (within 5 minutes).

Similarly, another piece of $\text{Sn}_{96.5}\text{Ag}_{3.5}$ solder preform was placed on Si_3N_4 -based substrate under one Si device, and put into a vacuum reflow oven pre-heated at 210 °C and evacuated below 5 mbar for 3 minutes, and then held at temperature and purged with 2% H_2 98% N_2 forming gas (330 L/h at 2bar) for 5 minutes. The reflow oven was further heated up to 275 °C and evacuated below 5 mbar for 3 minutes under a pure nitrogen gas flow of 330 L/h at 2 bar. The reflow process was held at 275 °C for 3 minutes, before being cooling down to room temperature (within 5 minutes).

5.2.3 Temperature cycling tests

In order to assess the thermomechanical reliability of the sintered Ag joints, thermal cycling tests were performed on sintered Ag samples as well as soldered samples. Two passive thermal cycling profiles were implemented in separate ESPEC thermal chambers.

One thermal cycling profile was designed to subject test samples to temperature cycling between -55 °C and 150 °C, which complete a full cycle every 15 minutes. The other thermal cycling profile was designed to subject test samples to temperature cycling between -55 °C and 125 °C, which complete a full cycle every 30 minutes, as Figure 5- 4 shows.

First, at temperatures above 125 °C, conventional Sn-based solder joints are generally weak points leading to failure of power electronics operated. Because the Sn-based solders are prone to creep at elevated temperatures and the accumulation of plastic work leads to crack initiation and propagation. Rapid growth of intermetallic compounds (IMCs) between the solders and the metallization on both the devices and the substrates may also take place above this temperature, resulting in brittle fracture of the joints.

Second, as literature shows [32], lots of power electronics applications require operation at high temperatures. Another temperature cycle between -55 °C and 150 °C has been extended to higher peak temperature especially for exploring the reliability for high temperature applications.

Therefore, for sintered Ag joints and solder joints, temperature of 125 °C and 150 °C were chosen as two peak temperatures for temperature cycling tests.

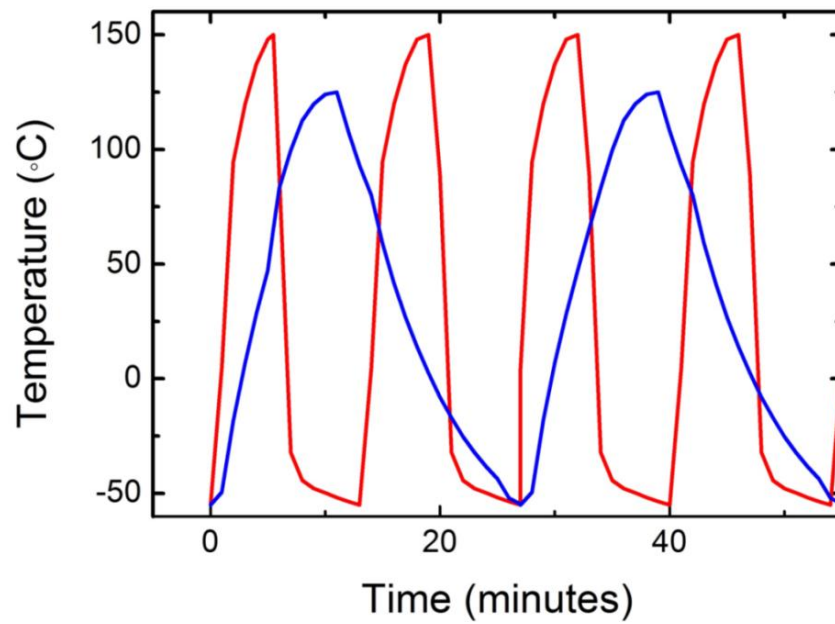


Figure 5- 4: Temperature profiles for thermal cycling tests between -55 °C to 125 °C and -55 °C to 150 °C

5.2.4 Microstructure characterization

5.2.4.1 X-ray tomography

X-ray computed tomography has been proved to be a reliable technique to obtain the 3D microstructure of materials to a satisfactory resolution.

Following image shows the process of X-ray tomography, which includes image acquisition and image reconstruction.

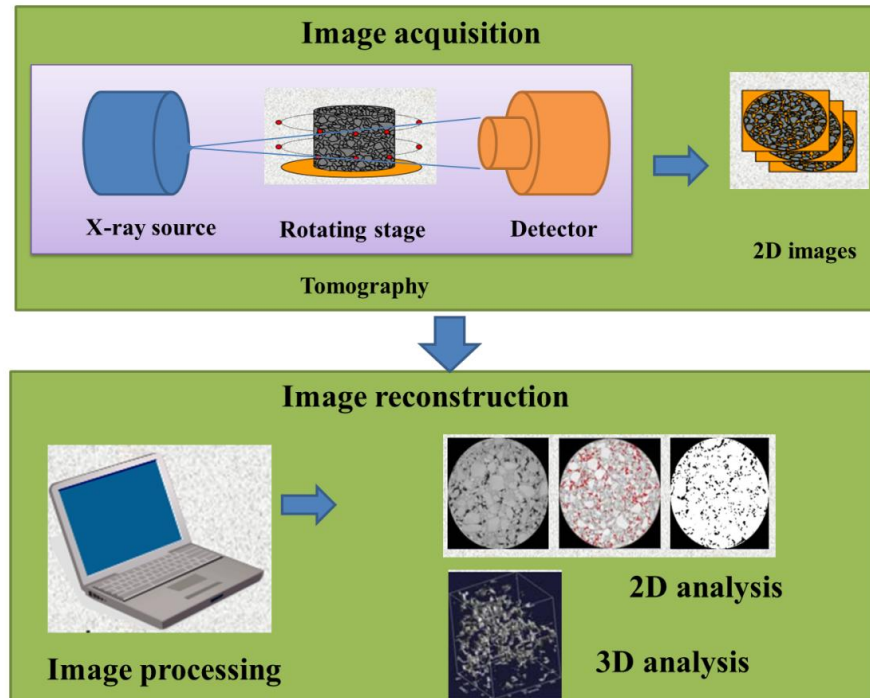


Figure 5- 5: X-ray tomography process during microstructure characterization

As Figure 5- 5 shows, during image acquisition, a rotating stage provides displacement in equally spaced angles, a detector collecting the 2D x-ray images at each angle. Then, all 2D images are mathematically superimposed and processed to obtain a 3D map of the sample to finish image reconstruction.

In this work, the same sintered joints were imaged after sintering process and then after every 1000 cycles. The distance between sample and source was 23 mm, while the distance between specimen and detector was 23.9 mm. A 160 kV source voltage and a 2×2 camera binning mode were used to capture the images at exposure time per projection 1 second, and pixel size of about 1.5 μm can be obtained, which is adequate for the resolution of cracks and delamination. A total of up to 1601 projections were acquired over a rotation span of 180 °for each specimen.

5.2.4.2 Scanning acoustic microscopy (SAM)

SAM is a non-destructive degradation analysis technique, which uses acoustic impedance ($AI = \text{density} \times \text{acoustic velocity}$) to produce images of interior

structure of a sample to detect defects, such as interfacial delamination, die tilt, etc. A SAM works on the principle of propagation and reflection of acoustic waves at interfaces where a change of acoustic impedance occurs.

In this work, acoustic data acquisition was performed using a scanning acoustic microscope (SAM 300, PVA TePla Analytical Systems GmbH, Germany) equipped with a 175 MHz transducer. During scanning, the samples were submerged in deionized water which acted as the coupling medium for the acoustic wave propagation.

5.2.4.3 Scanning electron microscope (SEM)

SEM has been carried out in previous chapters, and the process of SEM has been detailed. In this Chapter, after 4000 cycles between -55 °C to 150 °C, the samples (13mm×13mm in size) have been cross-sectioned, the cross-sectional direction as Figure 5- 6 shows.

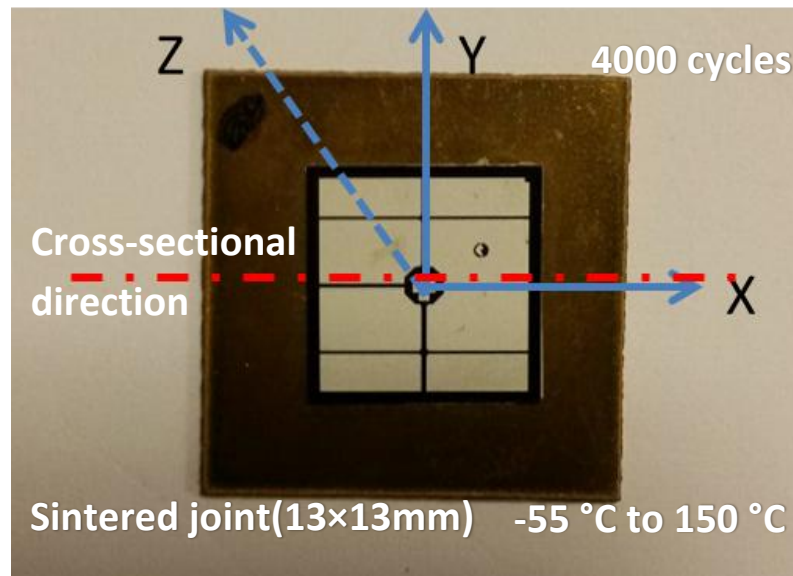


Figure 5- 6: Cross-sectional sintered Ag joint after 4000 cycles between -55 °C and 150 °C

5.3 Results

5.3.1 Sintered Ag joints

5.3.1.1 Thermal cycling between -55 °C and 150 °C

In order to investigate the degradation of sintered joints during thermal cycling tests between -55 °C to 150 °C, two sizes of die attachment (3 mm × 3 mm and 13 mm × 13 mm) have been studied.

(1) 3mm × 3mm sintered joints with dummy device

Two virtual cross-sections of the 3 mm × 3 mm sintered Ag joints A and B were cycled between -55 °C to 150 °C are shown in Figure 5- 7, Figure 5- 8 and Figure 5- 9.

In Figure 5- 7 (a), the as-sintered joints A exhibited uniform sintered layers, and no crack or voids can be detected in X-ray virtual cross-sectional tomography image. After 2000 thermal cycles as shown in Figure 5- 7 (b), the virtual cross-section of sintered joint A appeared slightly different from those of as-sintered joint, the area highlighted around the center are darker in colour than other areas. On a basic level, the existence of these patches indicates of differing levels of X-ray absorption in the different areas, and suggests non-uniform density was distributed in sintered Ag joint. As Figure 5- 7 (c) shows, the sintered joint after 3000 cycles showed some voids at the edges, the voids were about 0.5 μm in size and distributed randomly around the edges of sintered joint. After 4000 cycles of thermal cycling, there is a clear microstructural change which is the appearance of numerous cracks in the center of the sintered joint A, as Figure 5- 7 (d) shows. The shape and pattern of cracks are similar, several smaller cracks emanate from larger ones and interestingly, these occur in the previously mentioned dark areas. Figure 5- 7 (e) reveals even more cracks in the center of the sintered joint A after 6000 cycles. As can be seen from the image, the cracks are more clear, and the branches of the cracks have grown longer and thicker. Besides, some of the cracks had become connected. The final image of Figure 5- 7 (f) is the sintered attachments A after 8000 cycles, and shows yet more damage. The cracks are longer and have wider branches, which are nearly all connected to each other.

New fine cracks have also occurred in the center of the joint. By contrast to the center, the edges of sintered joint show only a few fine and long cracks with few or no visible branches. From Figure 5- 8 can be seen, when the sintered joints are visualised in the Y-Z planes, it can be seen that the quality is good and there is no delamination.

For another sintered Ag joint B, also 3 mm × 3 mm in size, X-ray image also exhibits uniform as-sintered layers, and no crack or voids can be detected.

After 2000 cycles, same dark areas showed up in sintered joint. One of these is highlighted in the X-ray tomography image, as Figure 5- 9 (b). After 4000 cycles, some fine cracks showed up within the dark areas, as Figure 5- 9 (c). After 8000 cycles, more cracks show up in the sintered joints, and the area covered by cracks distributed all over the whole sintered joint, as Figure 5- 9 (d).

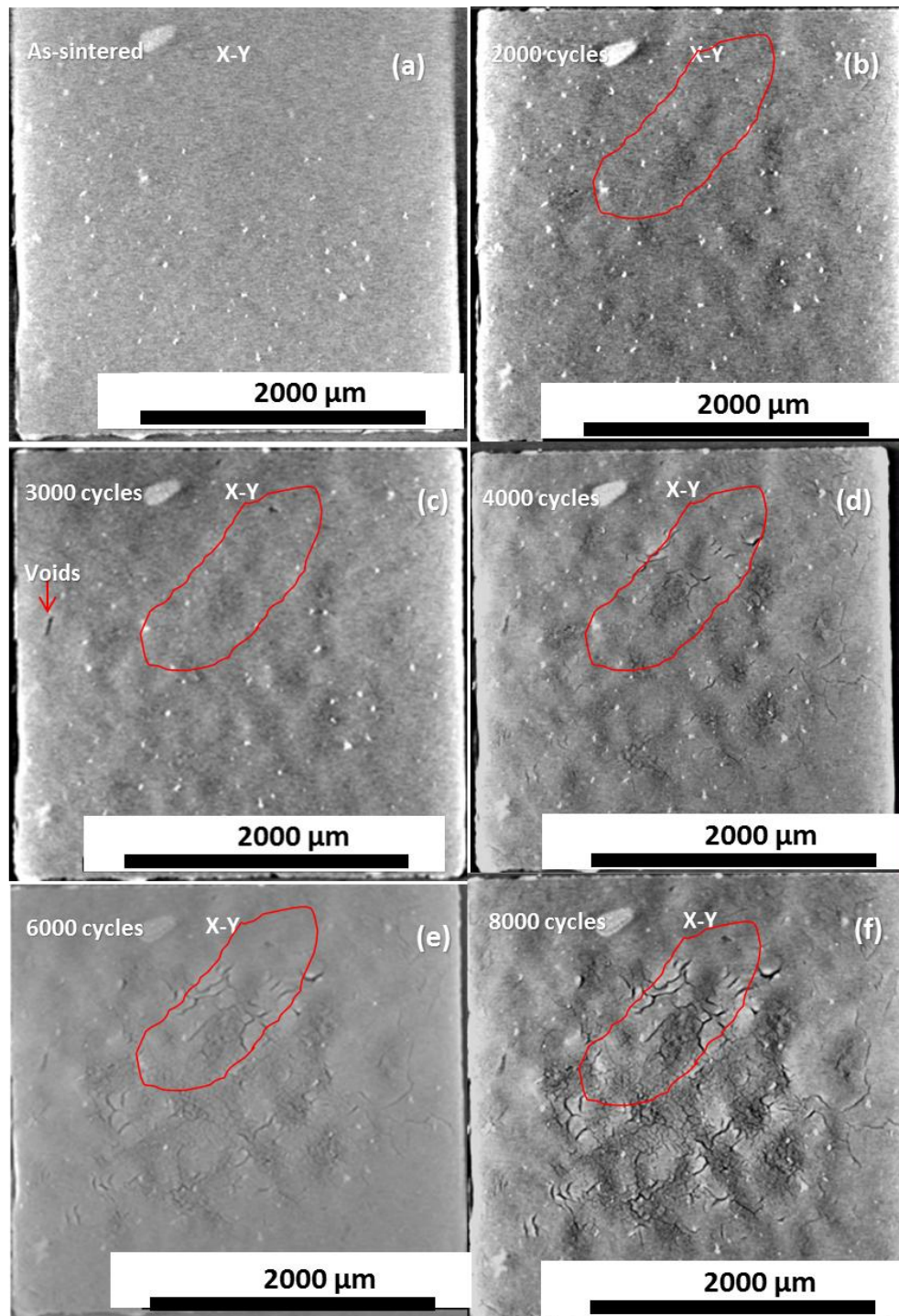


Figure 5- 7: X-ray tomography of sintered joints A (3mm × 3mm): (a) as-sintered; (b) 2000 cycles(c); 3000 cycles(d); 4000 cycles; (e) 6000 cycles; (f) 8000 cycles

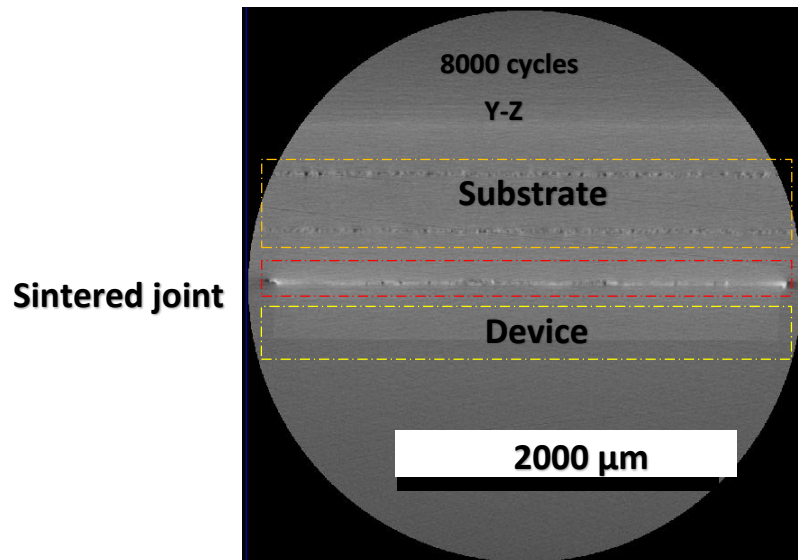


Figure 5- 8: X-ray tomography images of sintered joint A in Y-Z position

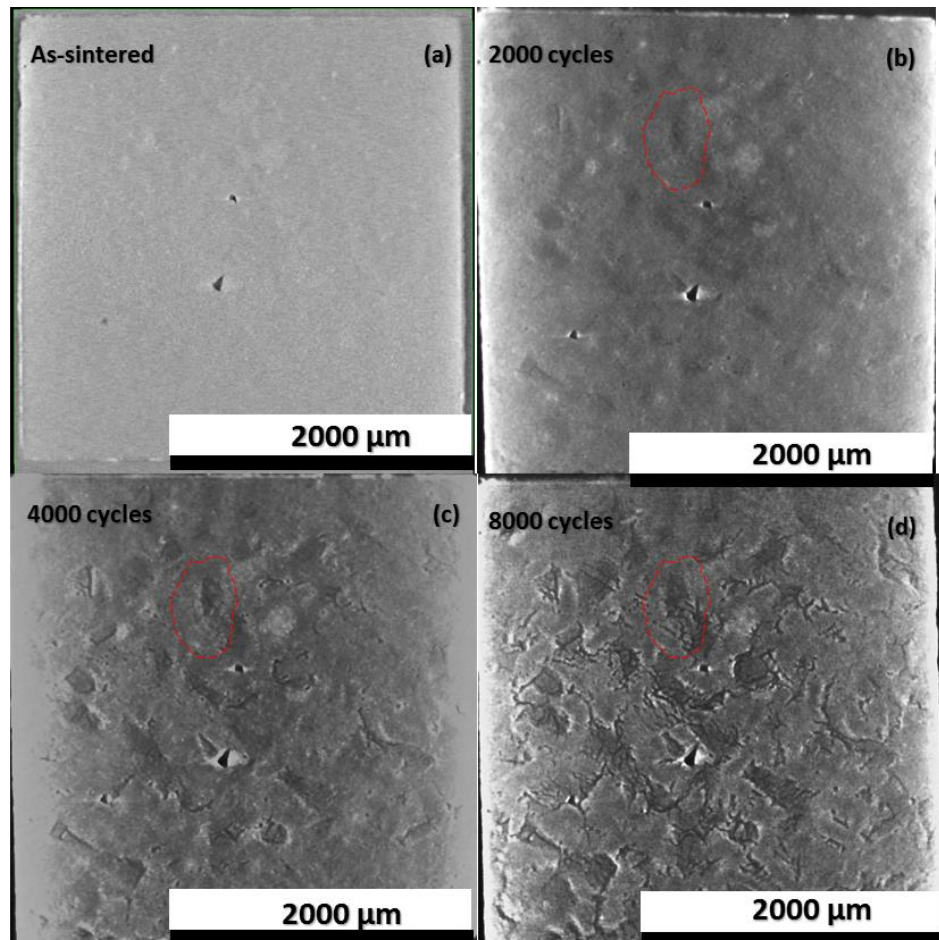


Figure 5- 9: X-ray tomography virtual cross-sectional images of sintered joints B (3mm × 3mm): (a) as-sintered; (b) 2000 cycles; (c) 4000 cycles; (d) 8000 cycles

Figure 5- 10 shows the 3D rendered images of sintered joints A after 8000 cycles between -55 °C to 150 °C. It can be seen that the top of slice near the sintered joint/die interface and bottom view of slice near the solder/substrate interface showed nearly the same degradation microstructure. Therefore, the corresponding black and white binary image could be used for measuring the percentage of damaged area including the observed voids and cracks.

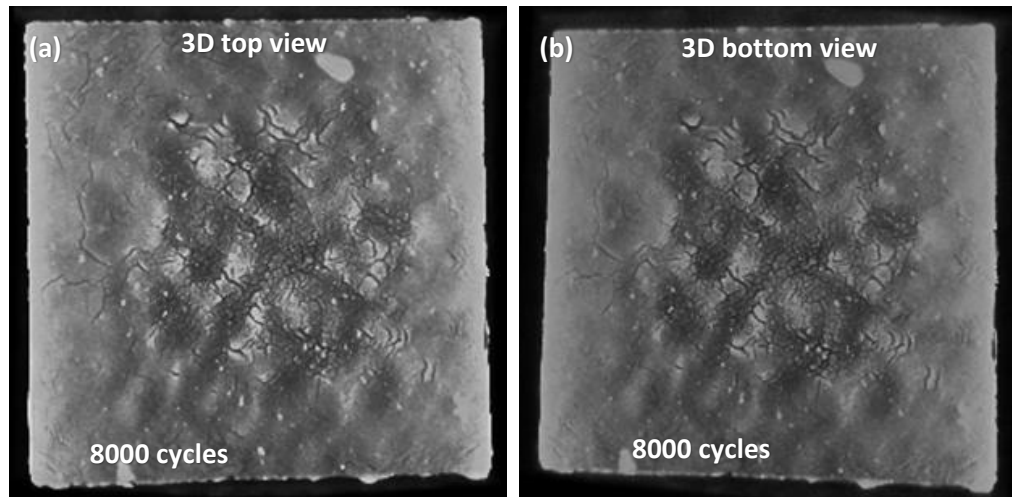


Figure 5- 10: 3D rendered images of sintered joints A after 8000 cycles between -55 °C to 150 °C: (a) 3D top view of slice near the sintered joint/die interface; (b) 3D bottom view of slice near the sintered joint/substrate interface

Figure 5- 11 shows one of representative X-ray tomography images and binary images used to measure the percentage of damaged area. As Table 5- 1 shows, damage area of sintered joint A and B have been quantitative characterized during thermal cycling up to 8000 cycles between -55 °C to 150 °C. Damage area of sintered joint A and sintered joint B shows an increased trend with more thermal cycles and reaches 4.18% and 4.91% respectively after 8000 cycles, as Figure 5- 12 shows.

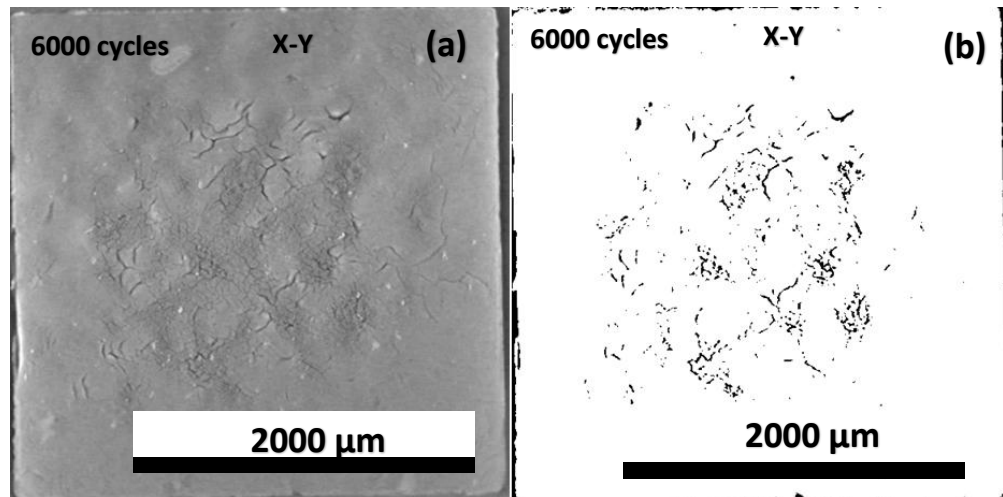


Figure 5- 11: (a) One representative X-ray image of sintered joint (3mm × 3mm) and (b) the corresponding black and white binary image

Table 5- 1 Different thermal cycles of sintered joints versus percentage of damaged area

Temperature cycles		Samples	
(cycles)	Sintered joint A	Sintered joint B	
0	0	0.1%	
3000	0.96%	1.23%	
6000	2.1%	2.49%	
8000	4.18%	4.97%	

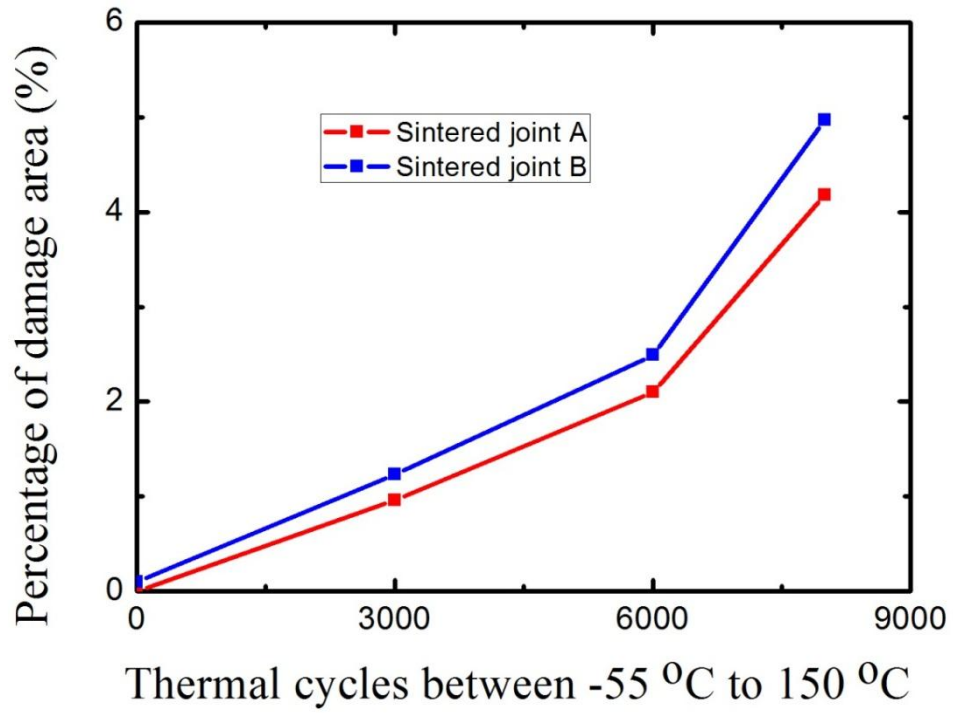


Figure 5- 12: Plots of sintered joints damage area percentage versus thermal cycles between -55 °C to 150 °C

For the die size of 3mm × 3mm, the sintered joint A showed more cracks around the center of the sintered joints than those near the edges of sintered joints, which can be correlated to its corresponding substrate surface profile image (Figure 5- 13). Here, the dark patches (i.e. less dense areas) in the cross-section correlate to local depressions in the substrate. From Figure 5- 13 we can see that after 4000 cycles of temperature cycling, cracks were most concentrated around the area F, which is also the lowest point on the substrate. After the sintering process, position F might have been the least densified part of the whole joint, and this may have led to it degrading faster than other parts of sintered joint A during the temperature cycling test.

Position E is the second lowest point of sintered joint A on the substrate, and also corresponds to a region of high density of damage after 8000 cycles.

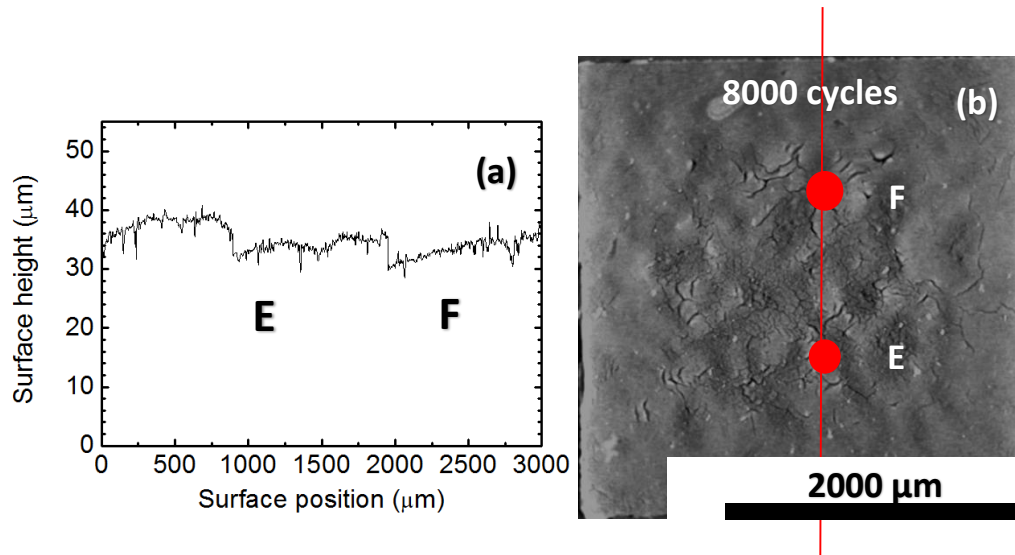


Figure 5- 13: (a) Substrate surface profile of sintered Ag joint A (3mm × 3mm) and (b) X-ray tomography image after 8000 cycles from -55 °C to 150 °C

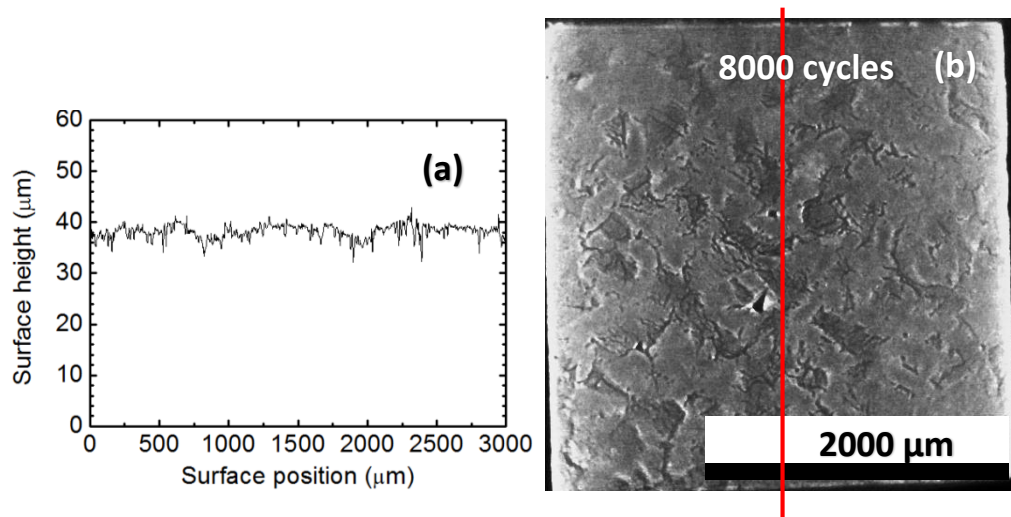
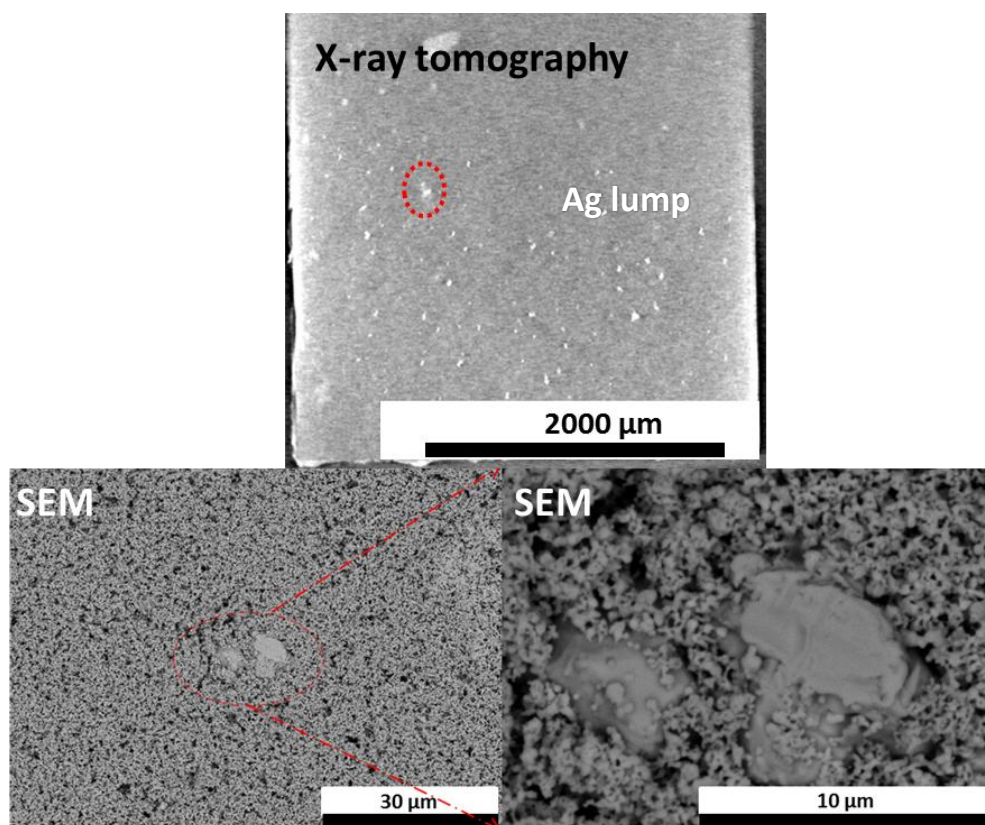


Figure 5- 14: Substrate surface profiles of sintered Ag joint B (3mm × 3mm) (a) and X-ray tomography image after 8000 cycles from -55 °C to 150 °C (b)

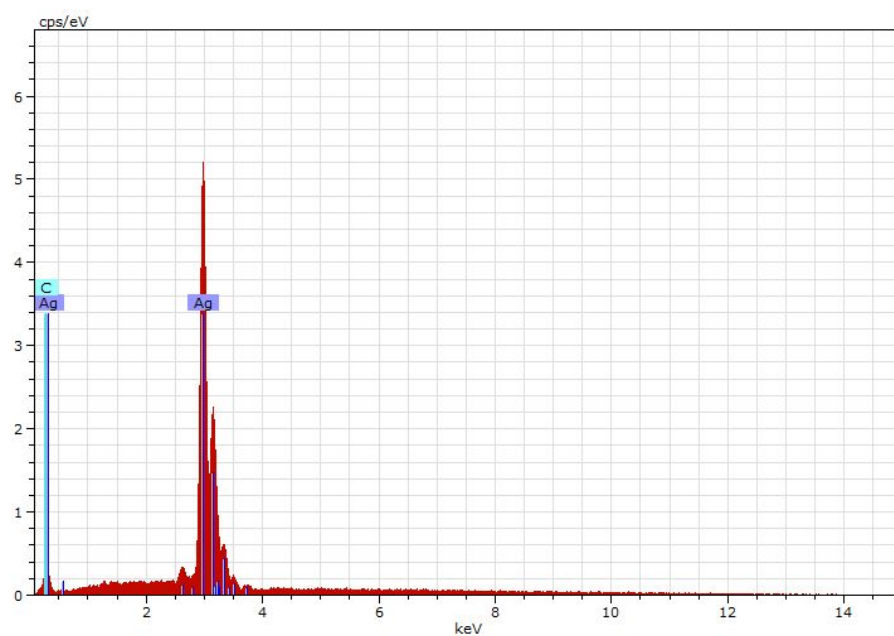
As Figure 5- 14 shows, sintered joint B substrate surface profile shows less roughness. It can be seen from X-ray tomography image, after thermal cycling for 8000 cycles, the sintered layer showed similar degradation microstructure as sintered joint A, the difference is all the whole sintered layer were covered by the dark patches, and fine cracks were distributed around those patches. This might also be caused by substrate roughness. Because the roughness is

lower than that of sintered joint A, the less crack concentration area can be developed during thermal cycling.

It can recall that there are some white spots and patches in the as-sintered joints which can be detected by X-ray tomography images. These are still visible after thermal cycling. To discover their origin, a sample of as-received film was investigated. As Figure 5- 15 shows, the randomly distributed coagulate lump has been conducted EDX test, it can be seen from EDX elemental analysis shows that the lumps was resulted by Ag nanoparticle paste non-uniform.



(a)



(b)

Figure 5- 15: Microstructure image of lump in nanoparticle Ag film (a) and EDX image of lump in nanoparticle Ag film (b)

Table 5- 2: EDX elemental analysis of lump in nanoparticle Ag film

Element	AN	series	[norm. at.%]	Error in %
Silver	47	L-series	87.038	3.30
Carbon	6	K-series	12.97	0.35
			100	

(2) Sintered joints with 13mm×13mm dummy device

Figure 5- 16 shows SAM images of the larger sintered joint (13mm × 13mm) investigated. As Figure 5- 16(a) shows, the as-sintered joint shows a uniform layer without any visible voids or delamination at the resolution of the SAM image. Like the X-ray images, the SAM image shows also regions of different degrees of densification, manifest as the relative dark area and relative light areas. After 1000 cycles, the darker areas showed a few voids around the bottom-right corner. After 3000 cycles, more voids in the right-bottom corner can be seen, and some white dots have shown up along the border line between relatively dark area and light area. After 4000 cycles, the voids increase further. For the relatively light area, the whole area has virtually turned white, and this enhances the contrast between these two areas. After 8000 cycles, the developing damage become even more noticeable in the SAM images, which shows more white spots appearing in the dark area and at the same time the light area becoming “whiter”. In order to help interpret the observed structures, the same sintered attachment specimen was imaged using X-ray tomography (after 8000 cycles), as Figure 5- 17 shows.

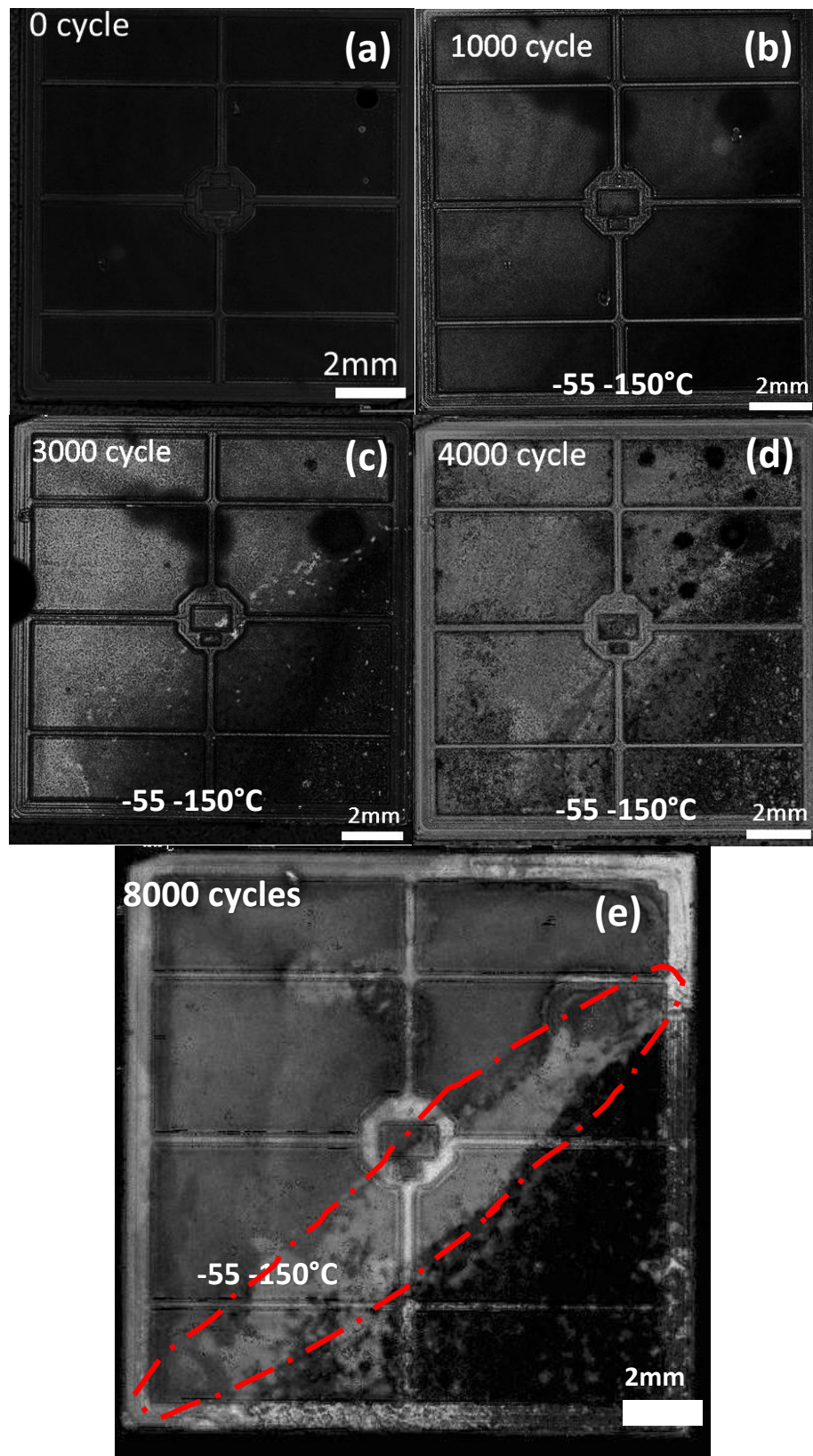


Figure 5- 16: SAM image of sintered joint of 13mm $\times$ 13mm between -55 $^{\circ}$ C to 150 $^{\circ}$ C: (a) as-sintered joint; (b) 1000 cycles; (c) 3000 cycles; (d) 4000 cycles; (e) 8000 cycles

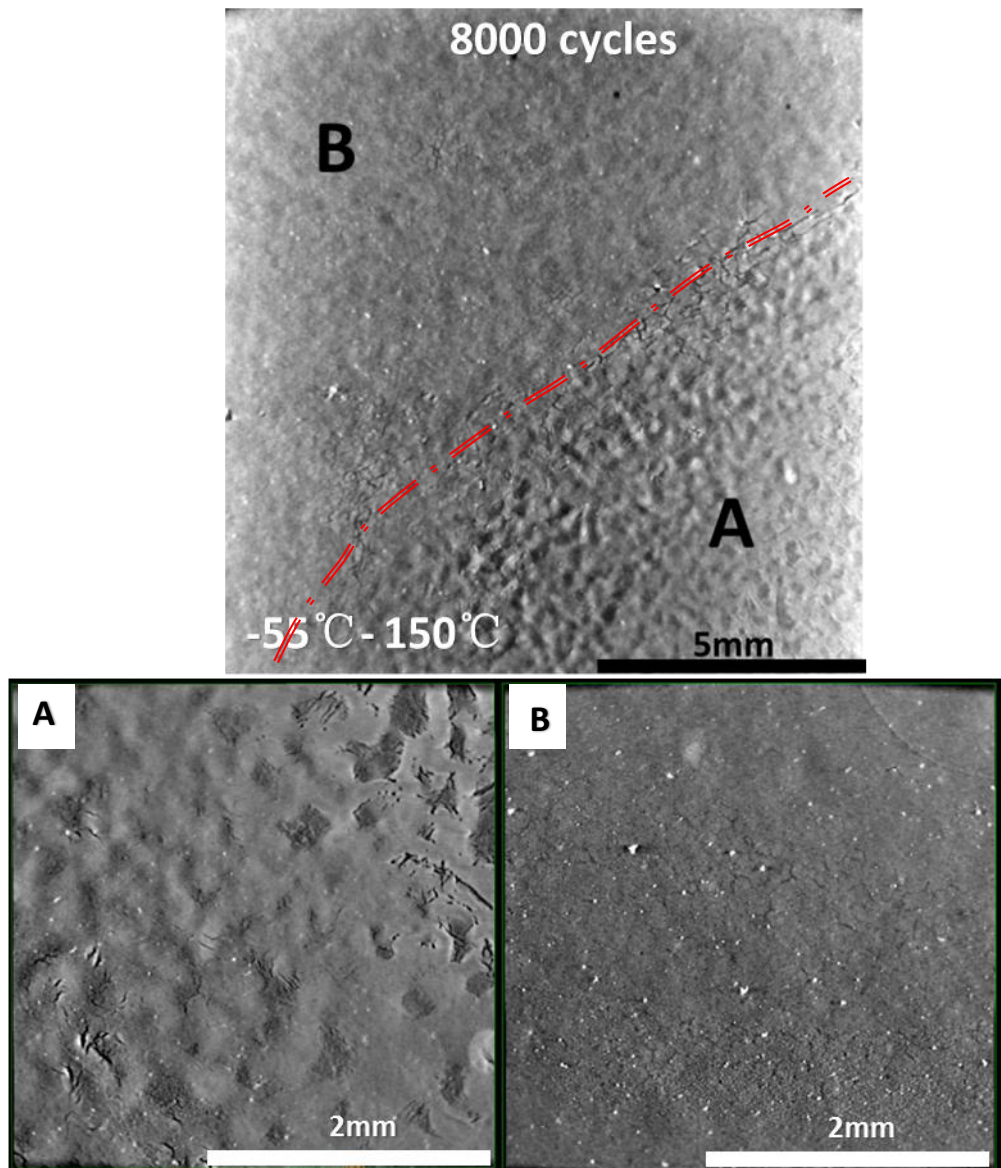


Figure 5- 17: X-ray tomography virtual 2D slices of sintered joints after 8000 cycles between -55 °C to 150 °C with dimension size of 13mm × 13mm

Figure 5- 17 shows X-ray tomography virtual 2D slices of sintered joints after 8000 cycles, which can further help to interpret the previous SAM results. Two different areas A and B in sintered joint have been investigated using X-ray tomography. As results show, the relative dark area in the SAM image can be detected some voids from X-ray image of area A, and the relative light area in the SAM image showed very fine cracks in X-ray image of area B, and the

area along the border shows branches of crack. These three degradation patterns occurred at the same time in the sintered joint, and seem to be related to the initial density of their respective regions. Therefore, the white spots in the dark areas of the SAM images correlate with voids. The relative dark area matches with fine, evenly distributed cracks. The boundary/interface which runs diagonally between the dark and light areas is clearly shown in the x-ray image as most ‘damaged’ and contains several interconnecting cracks.

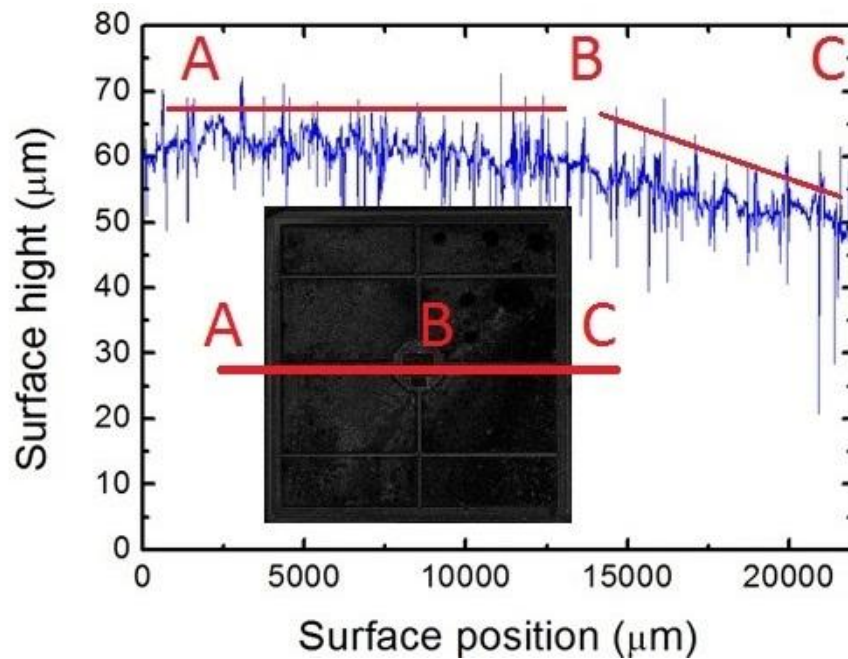


Figure 5- 18: Surface profiles of Au/NiP metallized substrate (13mm × 13mm)

Figure 5- 18 shows surface profiles of Au/NiP metallized substrate, the less dense B-C part of sintered joint firstly showed up voids. While the denser A-B part of sintered joint showed fine cracks degradation during thermal cycling. As Figure 5- 18 shows, substrate surface roughness bears relation to the degradation pattern of the sintered Ag joint. The substrates which were used as bonding materials were commercial available. However, after scanning with the surface profiler prior to sintering, fluctuations in height of surface can be seen. The surface profile for the substrate shows that the left A-B side of the

substrate is higher than the right B-C side. This difference in height may have resulted in the differences in densification observed in the sintered attachment, as the applied pressure during sintering would have been uneven over the entire die attachment area.

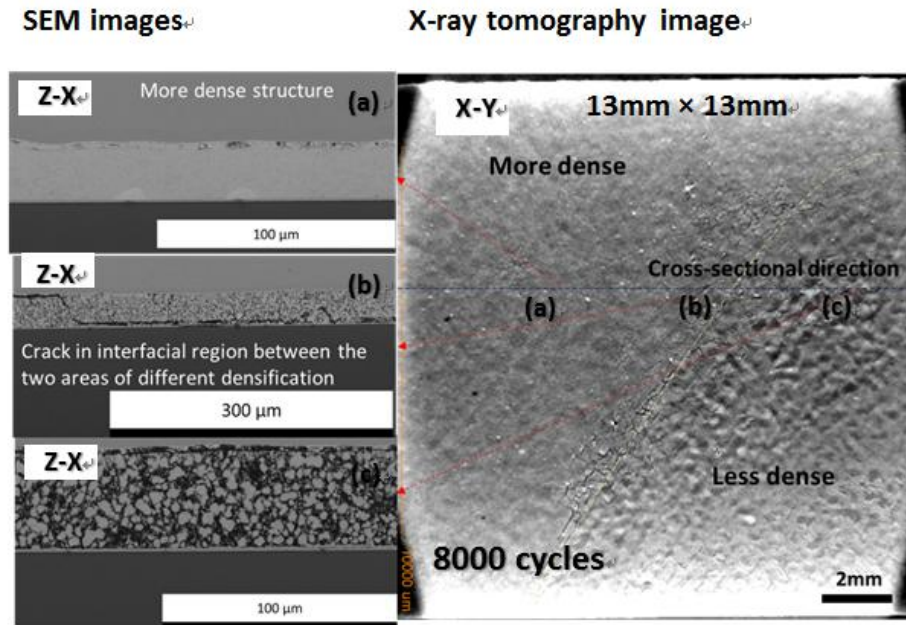


Figure 5- 19: Correlation of tomography with SEM cross-sections of sintered joint thermal cycled from -55 °C to 150 °C after 8000 cycles: (a) more dense structure part; (b) interfacial region between the two areas of different densification; (c) less dense structure part

A number of thermally cycled samples (separate from the ones in the ‘same sample’ study above) and 13mm × 13mm in size were cross-sectioned to shed more light on the relationship between the damage observed and their respective microstructures.

Three SEM images are presented in Figure 5- 19, thermal cycled between - 55 °C to 150 °C and show different regions within the same joint presenting different forms of degradation. Interestingly, these can be related to degradation patterns observed in the SAM image subjected to the same thermal cycling regime. For the less densely compacted regions of the sintered joint, voids can be seen very obviously in Figure 5- 19 (c), while in the more dense

parts, there are cracks initiating from the interface between substrate and sintered joint as Figure 5- 19 (a) shows. Figure 5- 19 (b) presents the region where the less dense area meets the more dense part, which shows large cracks and delamination having occurred at both interfaces (top and bottom) of sintered joint. Again, this concurs with what was observed in the X-ray tomography image, which also showed extensive cracking running diagonally where the two areas of different densities meet.

5.3.1.2 Thermal cycling between -55 °C and 125 °C

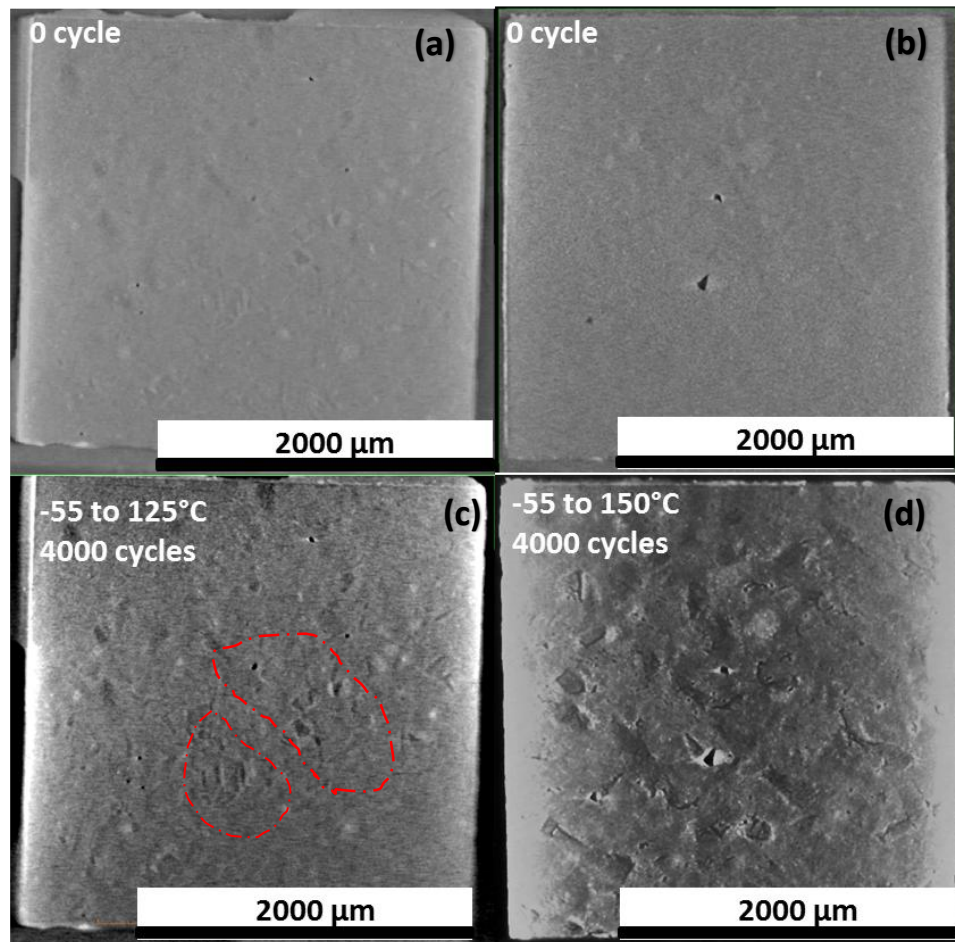


Figure 5- 20: X-ray tomography virtual cross-sectional images of sintered joints with dimension size of 3mm × 3mm thermal cycled between -55 °C to 150 °C and -55 °C to 125 °C

In order to investigate the influence of ΔT and peak temperature on degradation, sintered joints were also conducted in the thermal cycling

chamber between -55 °C to 125 °C with lower ramp rate. X-ray tomography images of sintered joints thermal cycled between -55 °C to 125 °C showed some differences from those cycled between -55 °C to 150 °C after the same number cycles. After 4000 cycles cycled between -55 °C to 125 °C, there were fewer voids and cracks than those after 4000 cycles between -55 °C to 150 °C. For sintered joint cycled between -55 °C to 125 °C, only few voids and very fine crack concentrate around some centre area, as the highlighted area. But for sintered joints cycled between -55 °C to 150 °C, cracks already occurred all over the sintered joint.

5.3.2 Sn_{96.5}Ag_{3.5} solder joints

In order to compare the reliability of sintered Ag die attachments with that of conventional solder attachments, solder Sn_{96.5}Ag_{3.5} joints have been subjected to the same thermal cycling regimes.

5.3.2.1 Thermal cycling between -55 °C and 150 °C

(1) Solder joints with 3mm × 3mm dummy device

Two solder Sn_{96.5}Ag_{3.5} joints A and B (3mm×3mm) were examined by X-ray tomography and show degradation microstructure, as Figure 5-21 and Figure 5-22 shows.

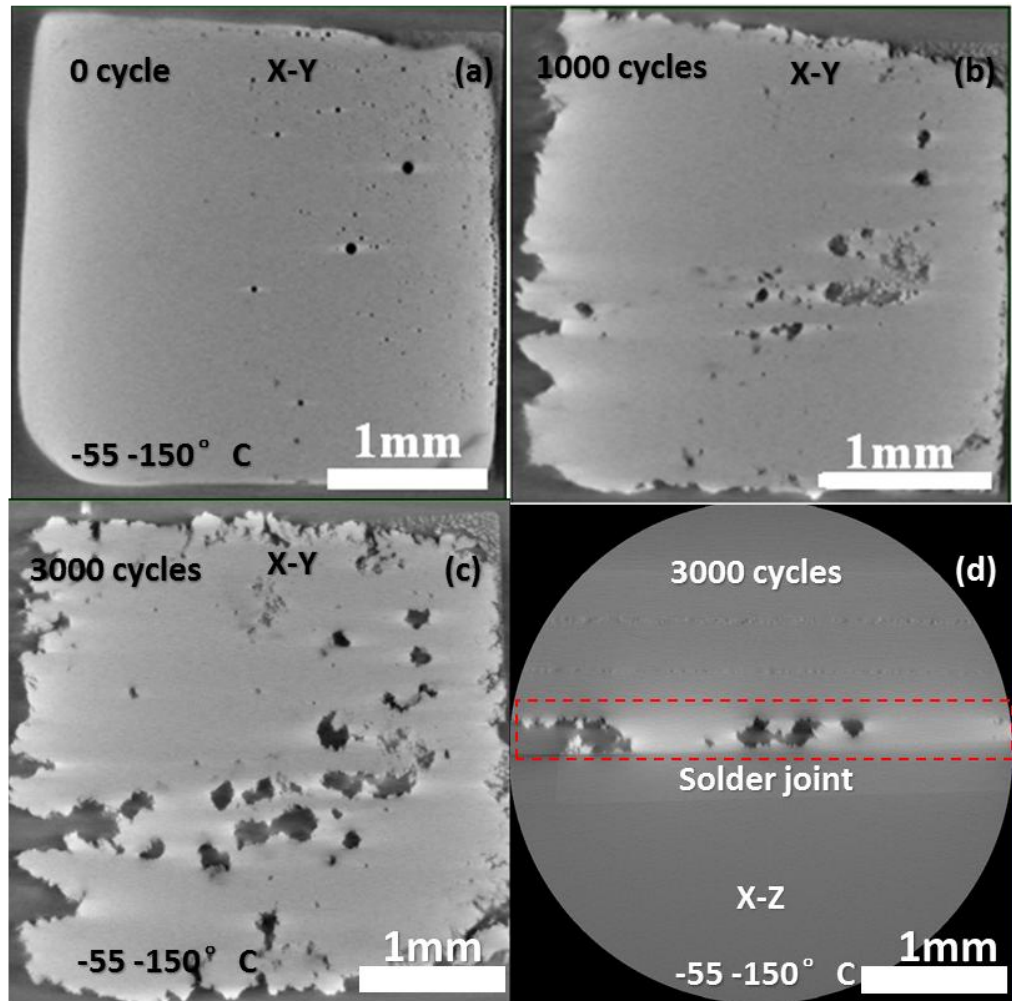


Figure 5-21: X-ray tomography images of solder $\text{Sn}_{96.5}\text{Ag}_{3.5}$ joints A (3mm×3mm): (a) 0 cycle; (b) 1000 cycles; (c) 3000 cycles; (d) 3000 cycles on X-Z position

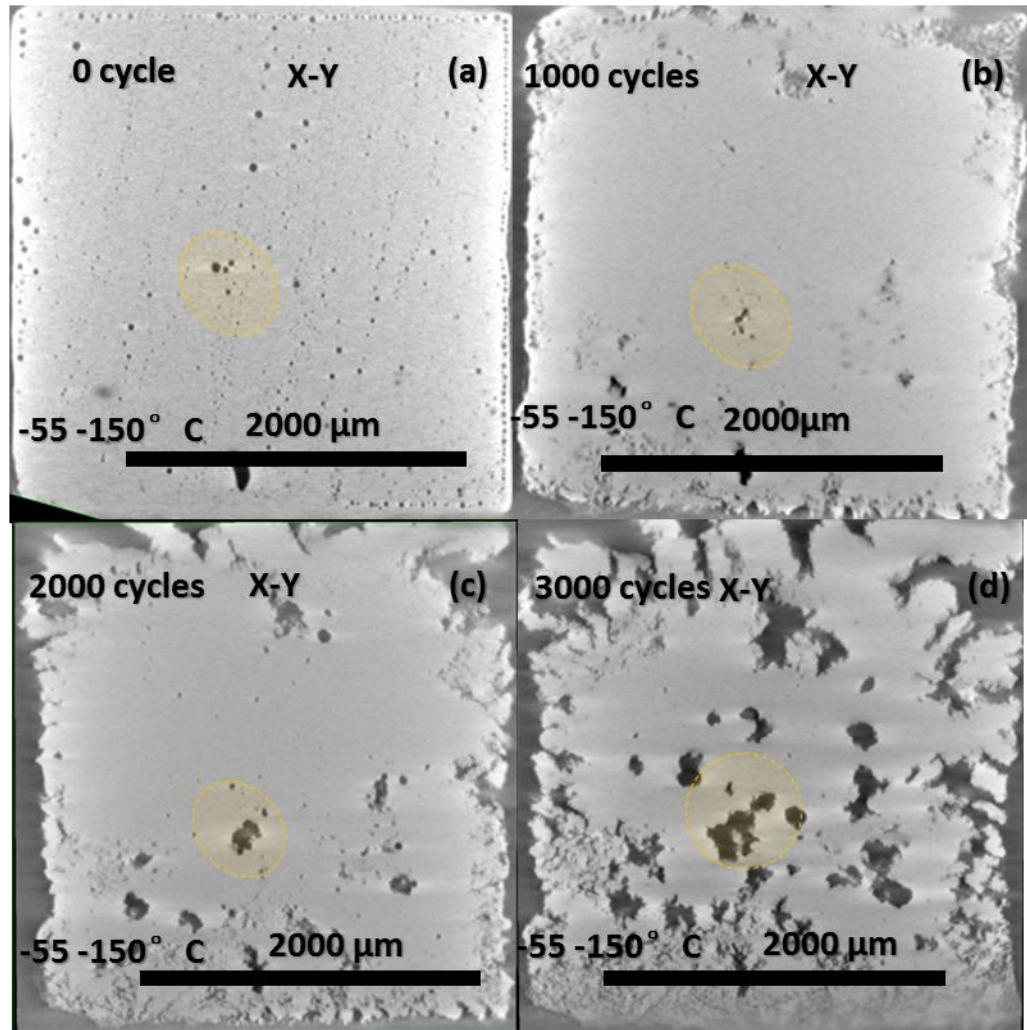


Figure 5- 22: X-ray tomography images of solder $\text{Sn}_{96.5}\text{Ag}_{3.5}$ joints B ($3\text{mm} \times 3\text{mm}$): (a) 0 cycle; (b) 1000 cycles; (c) 2000 cycles; (d) 3000 cycles

$\text{Sn}_{96.5}\text{Ag}_{3.5}$ solder attachments ($3\text{mm} \times 3\text{mm}$) were investigated under thermal cycling between $-55\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$. A lot of flux fumes are produced during reflow soldering due to thermal decomposition. Some gases might be entrapped between the flat surfaces of substrate and solder film, and pore and voids can be formed during that process [77], so there were some voids in the as-soldered joint. As showed in literature [16], some voids in as-soldered joint also can be identified in X-ray projection images. After 1000 cycles, degradation occurred from the edges of the soldered joint; besides, more cracks and voids showed up around the previous damaged area. After 3000 cycles, the

size of the voids grew significantly larger in the centre of the joint. Furthermore, the degradation rate of sintered joint and soldered joint is different from area to area. The edges of soldered joint showed more damage area and fracture degradation, which presented different crack morphologies from those in the centre.

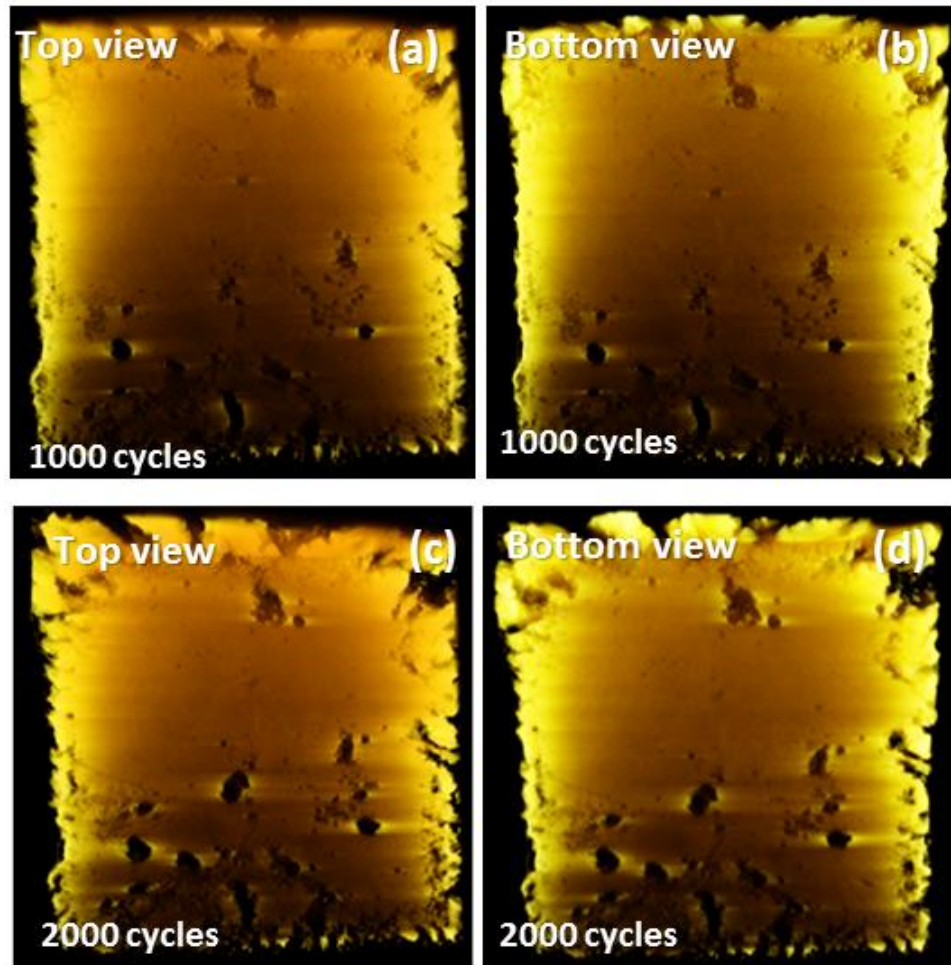


Figure 5- 23: 3D X-ray images of solder $\text{Sn}_{96.5}\text{Ag}_{3.5}$ joints B ($3\text{mm} \times 3\text{mm}$) damage evolution between $-55\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ for 1000 cycles and 2000 cycles: the top view of slice near the solder/die interface (a) and (c); the bottom view of slice near the solder/substrate interface (b) and (d)

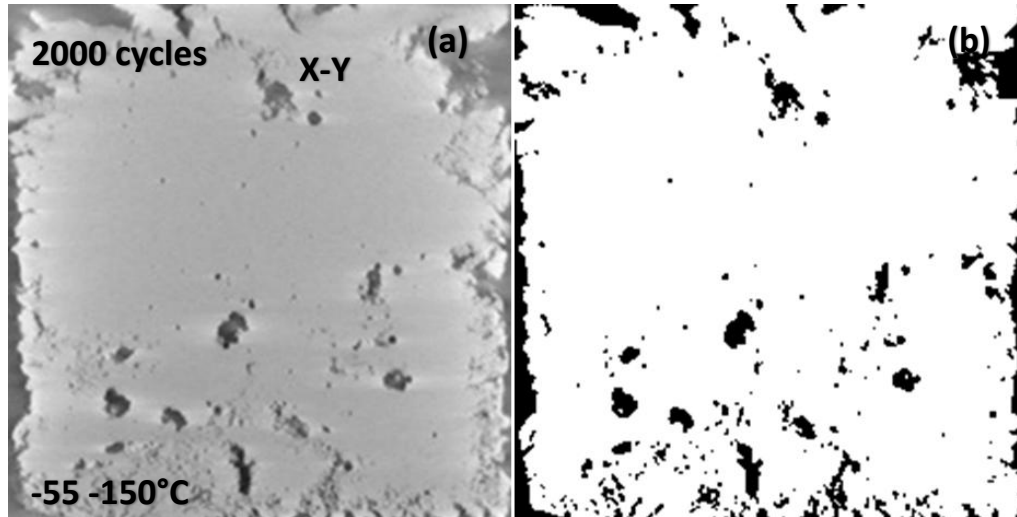


Figure 5- 24: (a) One representative X-ray image of solder $\text{Sn}_{96.5}\text{Ag}_{3.5}$ joint (3mm × 3mm); (b) the corresponding black and white binary image

Because the solder layer was quite thin, after the same thermal cycles, solder joint showed almost the same degradation on both slices, as Figure 5- 23 shows. Therefore, black and white binary image analysis could be used for measuring the damaged area percentage of solder joints during thermal cycling. Damage area of solder joints A and B have been quantitative characterized up to 3000 cycles between -55 °C to 150 °C, as Table 5- 3 shows. The damage area increased much more quickly than that of sintered joint, as Figure 5- 25 shows. After 3000 cycles, the damage areas of solder joints A and B have reached as high as 19.83% and 25.34%, respectively.

Table 5- 3: Different thermal cycles of solder $\text{Sn}_{96.5}\text{Ag}_{3.5}$ joints versus percentage of damaged area

Temperature cycles		Samples	
(cycles)		Solder joint A (%)	Solder joint B (%)
0		3.14	4.19
1000		7.82	11.09
3000		19.83	25.34

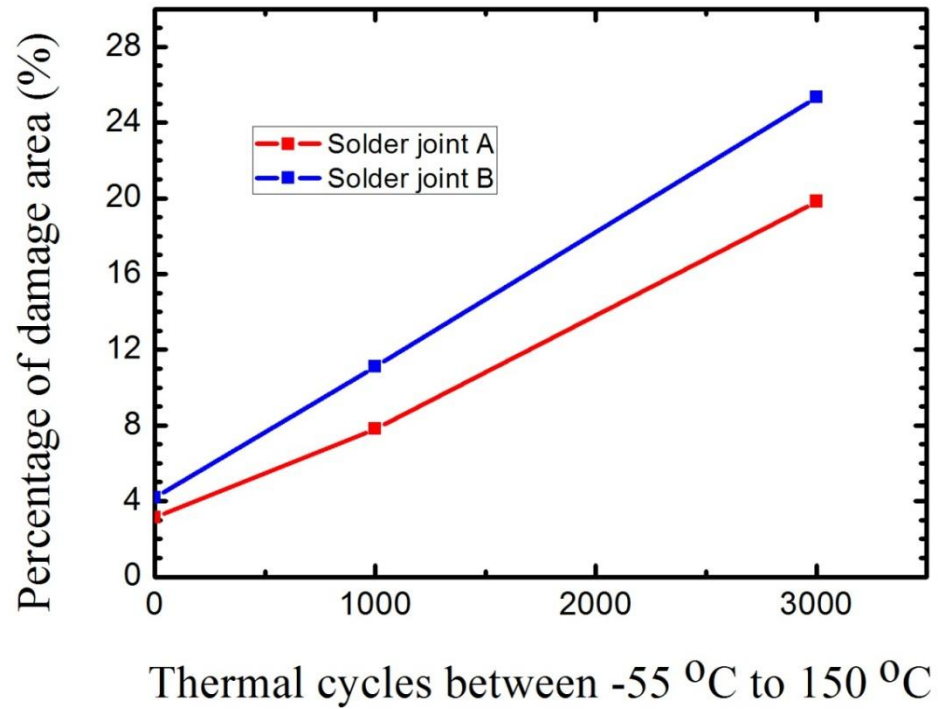


Figure 5- 25: Plots of two solder $\text{Sn}_{96.5}\text{Ag}_{3.5}$ joints damage area percentage versus thermal cycles between $-55\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$

(2) Solder joints with 13mm×13mm dummy device

As can be seen from Figure 5- 26 (a), the SAM image of as-soldered $\text{Sn}_{96.5}\text{Ag}_{3.5}$ joint showed some delamination not only in the centre but also at edges of the joint. After 1000 cycles between $-55\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$, a few voids occurred randomly in solder joint, as Figure 5- 26 (b). However, after 2000 cycles, significant change has occurred in the solder joints, that is, the white, unattached area extends and covers over half of entire attachment area, as Figure 5- 26 (c). After 3000 cycles, nearly all the soldered joint has turned white, which indicates that the soldered layer might nearly separate from substrate, as Figure 5- 26 (d) shows.

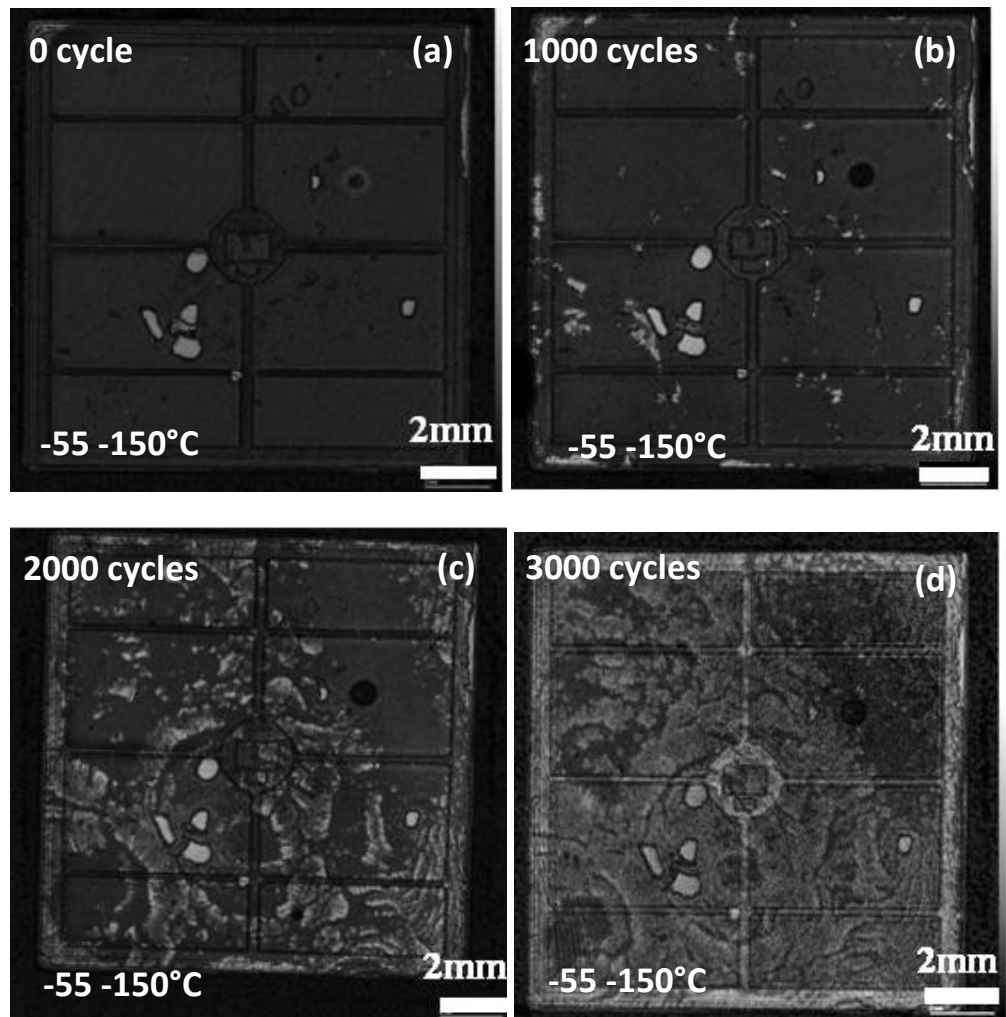


Figure 5- 26: SAM images of solder $\text{Sn}_{96.5}\text{Ag}_{3.5}$ joints with size of 13mm $\times$ 13mm between -55 $^{\circ}\text{C}$ to 150 $^{\circ}\text{C}$: (a) 0 cycle; (b) 1000 cycles; (c) 2000 cycles; (d) 3000 cycles



Figure 5- 27: Images of real $\text{Sn}_{96.5}\text{Ag}_{3.5}$ solder joint after thermal cycling for 3000 cycles from $-55\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$

As the side-view in photograph of Figure 5- 27 shows, the solder joint is almost completely detached from the substrate, which is in agreement with the SAM image of solder $\text{Sn}_{96.5}\text{Ag}_{3.5}$ joint thermal cycling after 3000 cycles.

5.3.2.2 Thermal cycling between $-55\text{ }^{\circ}\text{C}$ to $125\text{ }^{\circ}\text{C}$

In order to investigate the influence of ΔT and peak temperature on degradation, solder $\text{Sn}_{96.5}\text{Ag}_{3.5}$ joints and solder $\text{Pb}_{95}\text{Sn}_5$ joints with dimension size of $3\text{mm} \times 3\text{mm}$ were also conducted in the thermal cycling chamber between -55 to $125\text{ }^{\circ}\text{C}$ with lower ramp rate.

For soldered $\text{Sn}_{96.5}\text{Ag}_{3.5}$ joints, X-ray tomography images of sintered joints cycled between -55 to $125\text{ }^{\circ}\text{C}$ showed similar degradation microstructure as those cycled between -55 to $150\text{ }^{\circ}\text{C}$. However, because of the smaller temperature range and lower peak temperature during thermal cycling, as Figure 5- 28 shows, after 4000 cycles in the attachment cycled between -55 to $125\text{ }^{\circ}\text{C}$, there are fewer voids around the centre and edges of the sintered joint.

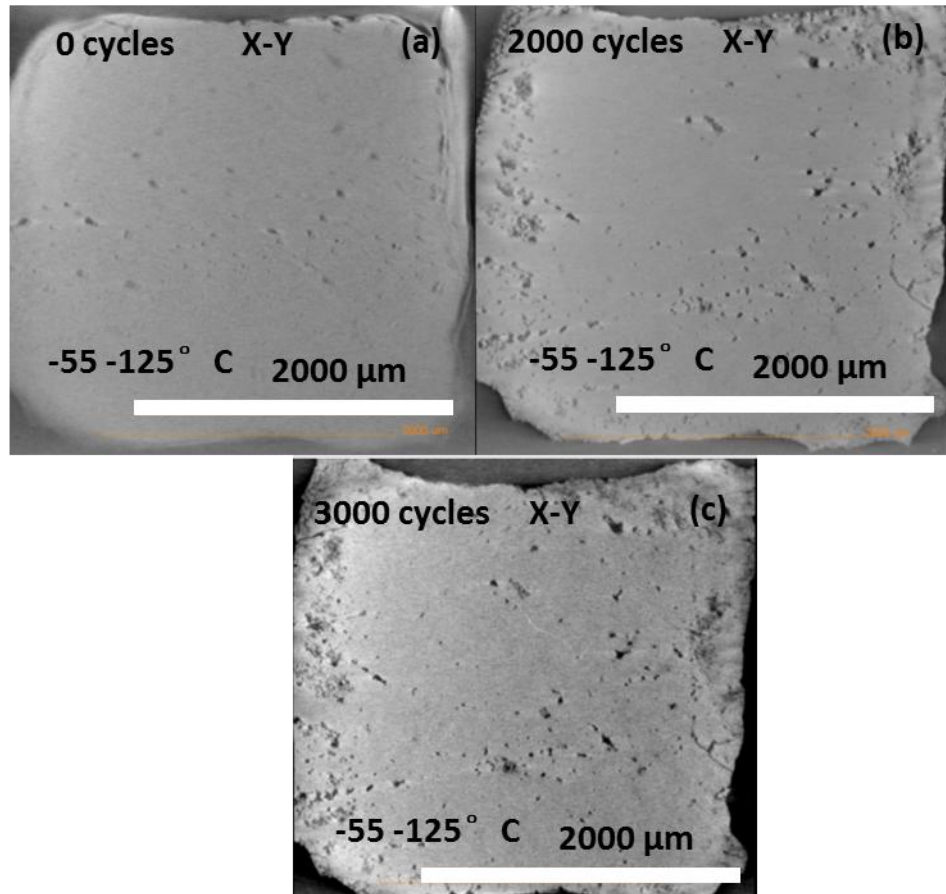


Figure 5- 28: X-ray tomography virtual cross-sectional images of solder joints ($\text{Sn}_{96.5}\text{Ag}_{3.5}$) with dimension size of $3\text{mm} \times 3\text{mm}$ under temperature cycling between $-55\text{ }^{\circ}\text{C}$ to $125\text{ }^{\circ}\text{C}$: (a) 0 cycle; (b) 2000 cycles; (c) 3000 cycles

5.3.3 Pb₉₅Sn₅ solder joints

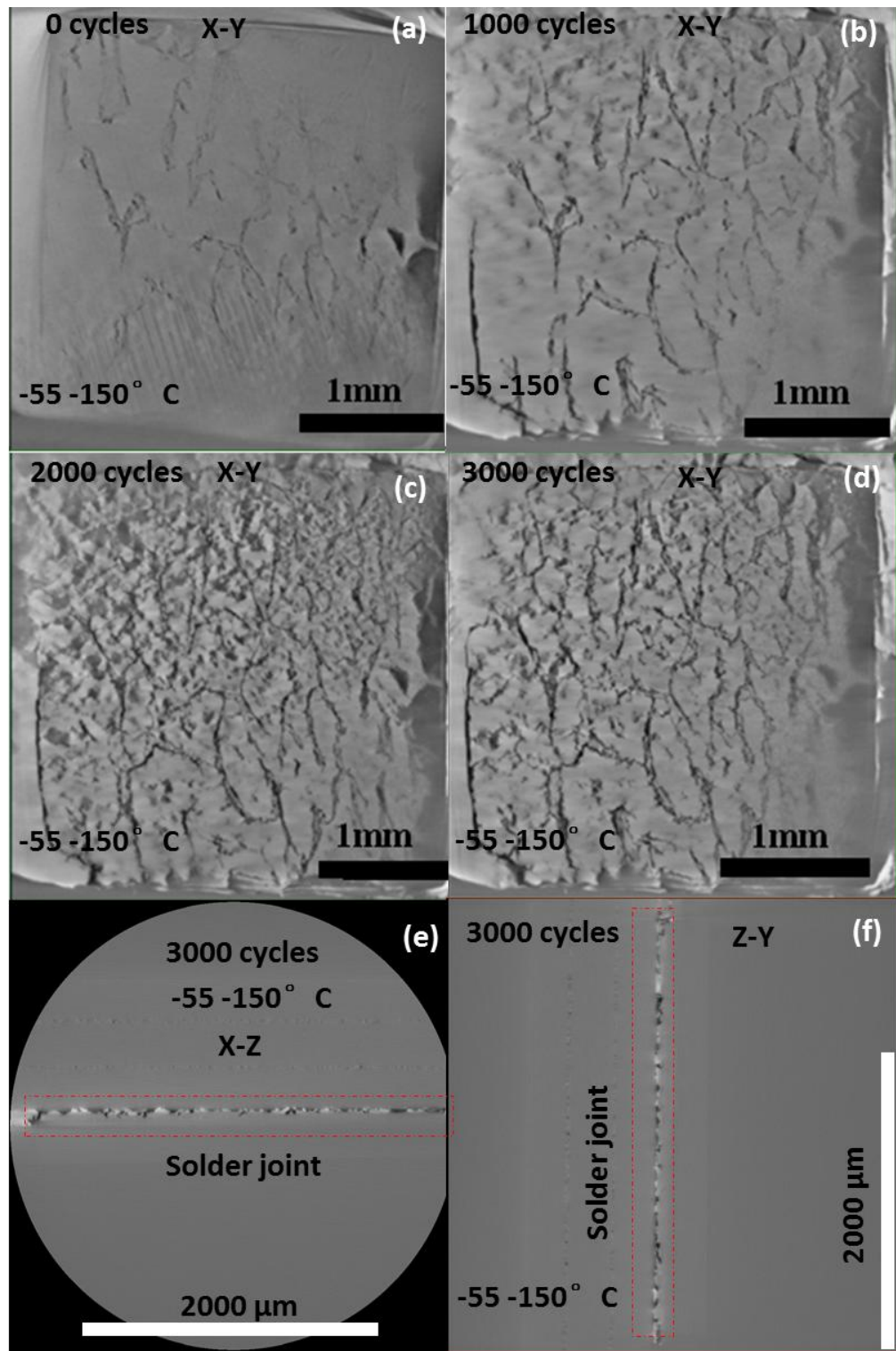


Figure 5- 29: X-ray tomography virtual cross-sectional images of soldered Pb₉₅Sn₅ joints with dimension size of 3mm × 3mm between -55 °C to 150 °C: (a) 0 cycle; (b) 1000 cycles; (c) 2000 cycles; (d) 3000 cycles; (e) 3000 cycles on Z-Y position; (f) 3000 cycles on X-Z position

The response of another kind of solder joint ($\text{Pb}_{95}\text{Sn}_5$) to thermal cycling between $-55\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ has also been investigated. The X-ray virtual cross-sectional tomography results seemed to show different degradation characteristics from the $\text{Sn}_{96.5}\text{Ag}_{3.5}$ solder attachments. The X-ray tomography images show that most of the damage is in the form of cracks with similar vertical directions in the view of the XY plane. After 3000 cycles, the cracks in $\text{Pb}_{95}\text{Sn}_5$ solder joint became wider and longer. From X-Z plane and Z-Y plane can be seen, the solder joint has already damaged very seriously after 3000 temperature cycles, and some parts of $\text{Pb}_{95}\text{Sn}_5$ solder joint has been delaminated from the substrate.

As all the virtual cross-sections images presented, it is clear to see that degradation during thermal cycling between $-55\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ was far more extensive within both two kinds of solder alloy materials than sintered Ag joints.

5.4 Discussion

5.4.1 Sintered Ag joints

5.4.1.1 Non-uniform degradation

As Figure 5- 13 shows, surface roughness has relation to the degradation pattern of sintered Ag joint. The substrates which were used as bonding materials are all commercial available. After scanning with a surface profiler, fluctuations in roughness of surface could be seen, and the difference in height may have resulted in the differences in densification observed in the sintered attachment, as the applied pressure during sintering would have been uneven over the entire die attachment area, which could result in different degradation microstructure areas in sintered layer.

As results show, there are some non-uniform lumps in Ag nanoparticles film, which showed white spots in X-ray tomography images and might further cause different density of sintered joints, and probably lead to cracks propagation around those denser parts because of different densification.

Therefore, it can be concluded that the degree of densification of the sintered Ag joint impacts on the type and extent of degradation. In the application of sintering technology, surface roughness of the substrate surface needs to be carefully considered during the selection of substrates.

Navarro et al. [58] investigated the effect of surface roughness of as-sintered joints on the mean value of the shear strength. The results showed shear strengths increased with lower values of roughness.

In this work, for the sintered joints with Au/NiP metallization substrate, microstructure evolution of sintered joint was evaluated by non-destructive methods of X-ray tomography and SAM. The results show that the microstructure evolution of sintered Ag joint can be influenced by substrate surface roughness, which would further have effect on degradation of sintered joint.

5.4.1.2 Effect of device size on degradation

Two dimension sizes of sintered Ag joints ($13\text{ mm} \times 13\text{ mm}$ and $3\text{ mm} \times 3\text{ mm}$) have been tested to investigate the size effect on the degradation of sintered Ag joints during temperature cycling.

With dimension size of $3\text{ mm} \times 3\text{ mm}$, the sintered Ag joints showed cracks propagation and crack growth from the series of X-ray tomography images. As discussed before, the degradation pattern is related to the surface roughness of the substrate. The surface of the small substrate ($3\text{ mm} \times 3\text{ mm}$) showed less fluctuation (about $20\text{ }\mu\text{m}$) than the large substrate ($13\text{ mm} \times 13\text{ mm}$) (about $50\text{ }\mu\text{m}$). It therefore makes sense that the sintered layer of the small die attachment would be more uniform compared to the large one. For the small size of sintered joint after 8000 cycles, only no more than 5% of the whole area was covered by damage, which was far less than that of large one.

In the literature, Panaccione et al. [78] discussed the effect of dimension of bonding area on the shear strength. With bonding area increased from 3.9 mm^2 to 5.4 mm^2 , the shear strength decreased as much as 30%. However, the reason for the differences of shear strength has not been discussed.

Although the above authors did not present the microstructure evolution of two sizes of sintered joints, the results from literature coincide with previous explanations of device size effect on degradation. In this research, microstructure evolution in different sizes of sintered Ag joints has been observed by non-destructive technology. Damage evolution in the same specimen has been tracked over 8000 cycles. As results show, larger substrates might present more roughness, which probably leads to less reliability during thermal cycling.

5.4.1.3 Effect of temperature swing on degradation

Two temperature profiles (-55 °C to 150 °C and -55 °C to 125 °C) have been applied on sintered Ag joints during thermal cycling tests to reveal the influences of temperature swing on the degradation of sintered Ag joints. As results show, the sintered joints under temperature cycling between -55 °C to 150 °C showed more damage and quicker degradation rate than those cycled between -55 °C to 125 °C.

Temperature swing between -55 °C to 150 °C is higher than that between -55 °C to 125 °C, sintered joint might not perceive the temperature in most part of the joint because of relevant quick temperature change. Therefore, tensile stress on the sintered joint thermal cycled between -55 °C to 150 °C with higher ramp rate will show more significant effects than those cycled between -55 °C to 125 °C with low ramp rate.

Besides, thermal cycling between -55 °C to 150 °C has higher peak temperature and larger temperature swing than those cycled between -55 °C to 125 °C. Therefore, sintered joints during the thermal cycling between -55 °C to 150 °C have showed more degradation than those between -55 °C to 125 °C.

5.4.2 Comparison of sintered Ag joints with solder joints

As can be seen from Figure 5- 30, unlike solder reflowing, sintering is an atomic diffusion processing where the bonding is accomplished through atomic diffusion and particle consolidation. Therefore, the microstructural features of the sintered Ag joints are different from those of the reflowed solder joints, and there are re-arrangement of Ag nanoparticles, densification

and grain growth occurring during the sintering process. These microstructural features in the sintered Ag joints depend on both the formulation of the paste and the sintering parameters such as heating rate, sintering temperature, pressure and time, and have effects on the thermal and electrical performance and thermomechanical reliability of the sintered Ag joints in service. As discussed in Chapter 3, the sintered Ag joint has the porous microstructure and the sintering kinetics is still in intermediate stage after sintering process, so further densification and grain growth would occur. As previous X-ray virtual cross sectional tomography images show, during thermal cycling tests, voids first occurred and distributed randomly, then cracks formed and propagated separately in sintered joints. For the solder joints, rapid growth of intermetallic compounds (IMCs) between the solders and the metallization on both the devices and the substrates might cause brittle fracture, which could probably prohibit electrical and thermal conductivity.

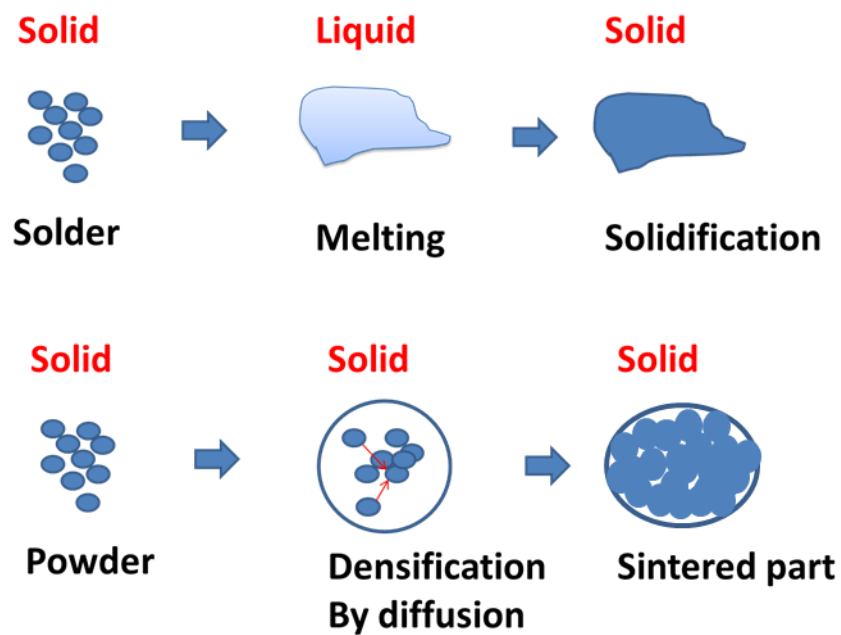


Figure 5- 30: Illustration on reflow solder process and sintering process mechanisms

For the $\text{Sn}_{96.5}\text{Ag}_{3.5}$ solder joint with the size of $3\text{mm} \times 3\text{mm}$, there were two kinds of degradation microstructure which could be seen from the series of X-

ray images. Around the edges of soldered joint, degradation features appeared after 1000 cycles. As Figure 5-21 shows, the left side of solder joint showed much more damaged than right side, which means the degradation rate of solder joint was different from the edge to edge during temperature cycling. In the centre of solder joint, degradation microstructure with a different character was observed. In this area, there were some voids and pores in the centre of as-soldered joint. As Figure 5-21 and Figure 5-22 show, pores became bigger holes in the solder layer with more temperature cycles.

For the $\text{Pb}_{95}\text{Sn}_5$ solder joints with the size of $3\text{mm} \times 3\text{mm}$, there were also two kinds of degradation microstructures in the soldered joints. One is fracture degradation near the edges of soldered joint. The other is new cracks initiating around the existing cracks which occurred during reflow soldering. Therefore, both $\text{Pb}_{95}\text{Sn}_5$ and $\text{Sn}_{96.5}\text{Ag}_{3.5}$ solder joints were investigated by X-ray tomography, however, they have shown different kinds of degradation microstructure during thermal cycling tests, especially in the centre of solder joints, the hole of degradation for $\text{Sn}_{96.5}\text{Ag}_{3.5}$ and the cracks branches of degradation for $\text{Pb}_{95}\text{Sn}_5$. With non-destructive tool of X-ray tomography, the degradation microstructure showed more planes of microstructure features and could present the whole 3D microstructure during thermal cycling.

For sintered Ag joints with the size of $3\text{mm} \times 3\text{mm}$, as discussed in Chapter 3, because sintered Ag joint has a porous structure of and sintering kinetics is still in the intermediate stage after sintering process, Ag grain would continue growing and densification would continue occurring during thermal cycling, so the volume of sintered joint tends to be shrinking. However, the sintered joint was bonded between substrate and device, the sandwiched structure prevents the sinter joint from further shrinking, so tensile stress would occur in the sintered joint. Because of good bonding quality of interfaces, the Ag aggregated with size of Ag gain increased, and tiny voids or pores were connected each other and presented bigger size in the sintered joint during thermal cycling, as Figure 5-31 shows.

For sintered Ag joint with the size of $13\text{mm} \times 13\text{mm}$, after temperature cycling for 3000 cycles, the whole sintered joint showed degradation, however, the

microstructures of degradation were different depending on their original as-sintered densities. In the less dense area, because of further densification and Ag grain growth, Ag grain presented bigger size and this area showed high porosity microstructure with more temperature cycles. In dense area, because of tensile stress, Ag grain aggregated together and voids connected each other, which were characterized fine cracks during thermal cycling. As the X-ray tomography images shows, the border of these two parts with different densification is characterized by a high concentration of cracks. As showed in Figure 5- 13, Figure 5- 14 and Figure 5- 18, different surface roughness caused the variation in densification, so thermomechanical properties of two parts might be different, which could cause different degradation microstructure, even in the same sintered joint. Therefore, the mismatch in thermomechanical property probably is the reason why the border of two parts has a high concentration of cracks.

Sintered Ag joints with size of 3 mm × 3 mm have been cross-sectioned both after sintering process and after 4000 thermal cycling, as Figure 5- 31 shows. For as-sintered joint, the SEM images of cross-sectional sample show uniform and porous microstructure, as Figure 5- 31 (a) and (b) show. As discussed in Chapter 3, further densification and grain growth would occur after sintering process. Therefore, after 4000 cycles between -55 °C to 150 °C, as can be seen from SEM images in Figure 5- 31(d), the Ag grains aggregated together and grain sizes showed much bigger than those in as-sintered joint. As Figure 5- 31 (c) shows, because of good bonding quality of interfaces, device and substrate prevent the sintered joint from shrinking and crack occurred and propagated in the sintered joint. As Figure 5- 31 shows, during both isothermal ageing and thermal cycling tests, degradation of sintered joints with Au/NiP metallization substrate presented similar microstructure evolution. In Figure 5- 31, because of porous structure, the cracks distributed randomly inside the sintered joint, these kind of microstructure evolution might prolong the sample's lifetime, as there is less thermal or electrical insulation around interfaces.

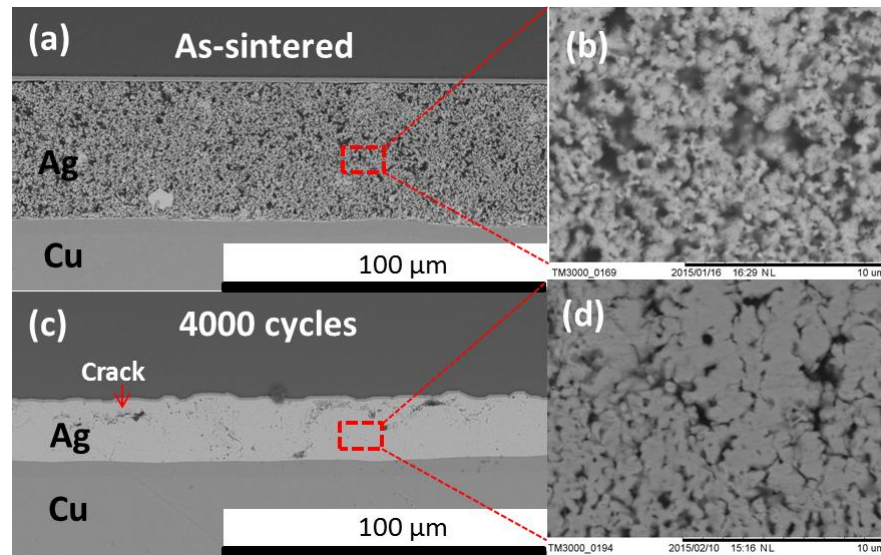


Figure 5- 31: SEM images taken from the cross section of sintered joints (3mm ×3 mm) between -55 °C to 150 °C: (a) as-sintered joint; (b) enlarged view of as-sintered joint; (c) sintered joint after 4000 cycles; and (d) enlarged view of sintered joint after 4000 cycles.

From literature can be known, mechanical test commonly applied for revealing the reliability of sintered joint. In literature [17], shear tests have been conducted during thermal cycling. As Figure 5-32 shows, the bonding strength has been decreased from around 40 MPa to around 20 MPa after 4000 cycles. As SEM images of Figure 5-33 shows, microstructure of sintered joints has changed significantly. Before thermal cycling test, there is few and small voids distributed in sintered joints. With more temperature cycles, a large number of voids and cavities have formed in sintered joints. After temperature cycling of 4000 cycles, the voids and cavities showed much more and the size was over 2 μm, and the strength of sintered joint has decreased as much as 50% of as-sintered joints.

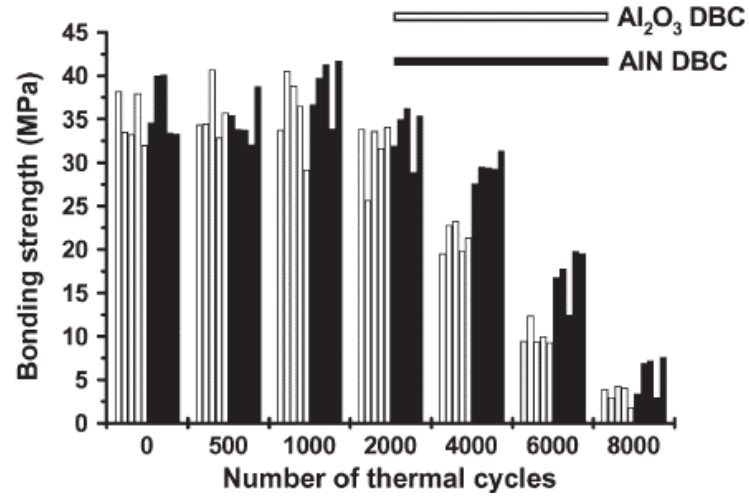


Figure 5- 32: Bonding strength changes of the silver die attachment during the 50 °C–250 °C thermal cycling test [17]

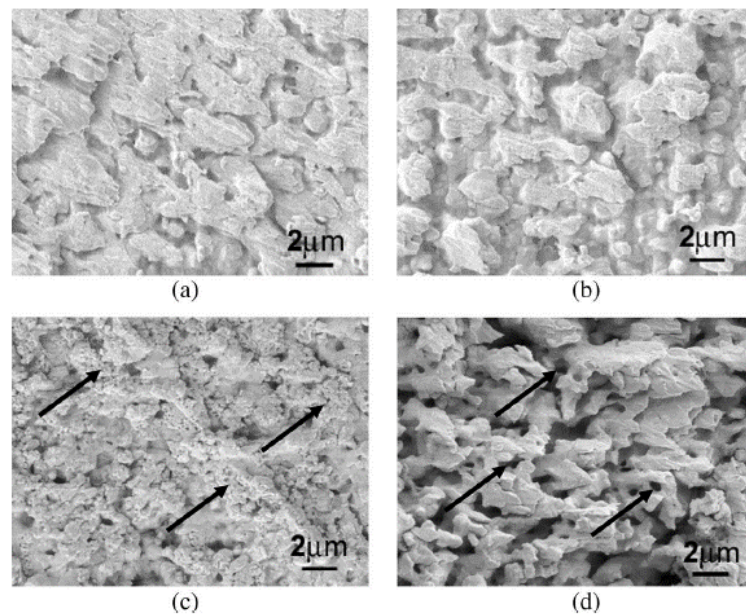


Figure 5- 33: Microstructure of the sheared-off silver die attachment after (a) 0, (b) 2000, (c) 4000, and (d) 6000 cycles. [17]

Those SEM images reveal microstructure of sintered joints, which has a limitation of the observation area, moreover, the failure mechanism or microstructure evolution of the whole sintered joint or solder joint cannot be determined straightforward. Furthermore, the specimen has to be cut and

destroyed, which cannot be further conducted in the later tests. In this case, the crack or delamination in one sample cannot be traceable throughout the whole test.

In the literature, Heuck et al. [80] presented the SAM images of sintered Ag joints after power cycling of 600000 cycles and soldered Cu-Sn joints after power cycling of one million cycles. From the images, only white spots could be identified in the SAM images of sintered joints and soldered joints, and no further details of degradation could be inferred. Boettge [63] et al. also presented the SAM results of sintered Ag joints. In order to confirm the degradation details, the cross-sectional images were further applied on sintered joints. In the literature, the delamination of interface between substrate and sintered joint was found in SEM images, and Boettge has discussed the root cause of delamination was still not completely understood and might be the issues of substrate metallization, not optimized sintering parameters or compatibility problems in terms of Ag particle paste and the metallization.

Combination of destructive characterization with non-destructive characterization probably could identify more information of microstructure evolution for sintered joint during thermal cycling test. In this work, with non-destructive characterization, sintered joint A and sintered joint B showed different degradation microstructure evolution during thermal cycling from -55 °C to 150 °C. Because of substrate roughness effects, degradation of sintered joint A mainly concentrated around the area with larger roughness value, while sintered joint B presented degradation all over the whole joint without much crack concentration because the substrate got low roughness value. If these samples have been cross-sectioned, SEM images could not demonstrate those different microstructure evolutions and degradation patterns.

5.5 Summary

In this chapter, sintered joints with two sizes of 3 mm × 3 mm and 13 mm × 13 mm have been conducted by thermal cycling tests between -55 °C to 125 °C and -55 °C to 150 °C. In order to compare with solder joints in terms of reliability during thermal cycling, Pb₉₅Sn₅ and Sn_{96.5}Ag_{3.5} solder joints have

been applied. Non-destructive and destructive methods have been used as microstructure characterization tools to reveal the degradation of both sintered joints and solder joints during thermal cycling.

(1) Surface roughness of substrate has showed effects on densification of sintered joints, which could cause sintered layer densification variation. For small size of sintered joints (3 mm × 3 mm), degradation pattern during thermal cycling can be influenced by surface roughness. The area with higher value of surface roughness might cause more damage concentration. As the microstructure images of Ag nanoparticle film shows, the non-uniform of as-received nanoparticle film might be another possible cause to the crack initiation and propagation during thermal cycling. Randomly distributed coagulate lumps is detected, which would further lead to degradation around the lumps area. For large size of 13 mm×13 mm sintered joints, different roughness of substrate surface also showed different kinds of degradation microstructure. Because of different thermomechanical properties in different dense level parts of sintered joints, the border of two parts degraded the most quickly.

(2) Size of die attachment and temperature swing also presented effects on the degradation of sintered Ag joints. Small size of die attachment might have lower surface roughness, which could reduce degradation concentration. Sintered joint thermally cycled between lower temperature swings showed better reliability.

(3) Non-destructive tools including X-ray tomography and SAM have been applied for microstructure characterization, which could show the microstructure evolution of sintered joints and solder joints during thermal cycling.

Degradation microstructure differences between sintered joints and solder joints could be identified with non-destructive characterization, which showed that the sintered joints had much better bonding quality and reliability than solder joints. With X-ray tomography characterization, the differences of degradation microstructure between two sintered joints (3mm×3mm) with

different surface roughness substrates could also be identified, which showed that sintered joint with higher value of surface roughness substrate presented more damage concentration.

CHAPTER 6 Conclusions and Future Work

6.1 Conclusions

There is an increasing challenge in sufficient reliability for the conventional solder alloys and conductive adhesives to be used in power die attachments and interconnects for developing high power density and high performance power electronic systems. To address this challenge, sintering of nanoparticles has been investigated in this work as alternative high performance die attachment and interconnect material and technology.

Characterization of as-sintered joint microstructure with SEM, TEM and XRD is necessary to obtain the information about the densification, uniformity, grain size and voids/defects, which are necessary for investigating the effects of the sintered parameters on the quality of the sintered joint. In theory for the sintering of traditional powder particles, sintering kinetics is still in intermediate stage with further densification and grain growth. Therefore, when the sintered Ag joints are used to assemble power electronic systems, further evolution of the microstructure subjected to elevated application temperatures would occur and should be taken into account for lifetime prediction and reliability analysis.

Sintered joints with four kinds of substrates were carried out isothermal ageing tests at 150 °C, 200 °C and 250 °C. The four substrate finishes considered were bare Cu, 2 µm thick Ag, 5/2 µm thick NiP/Ag and 5/0.1 µm thick electroless NiP/Au on the AlN-based substrates. Microstructure evolution of the sintered Ag joints during the isothermal ageing was presented in forms of SEM images. For the sintered joints with Ag finish and bare copper substrate, oxide layer was formed on the substrate surfaces, and it further reduced the bonding strength and caused the delamination of interface of substrate surfaces. For the sintered joints with Ag/NiP finish substrates, because of brush electroplating Ag on the substrate surface, there is non-uniform plating

layering, which cause some parts of substrate surface lack of metallization and showed weak bonding strength. So crack and delamination occurred eventually. For the sintered joints with Au/NiP metallization substrates, the sintered joints showed good bonding quality. There is an epitaxial layer on the substrate surface, and it was growing with more ageing time. However, at 250 °C, the epitaxial layer showed crack propagation along the substrate surface, which showed a limitation of sintered Ag joints applied as die attach in high temperature power electronic systems. With comparing and explaining the different patterns of the microstructure observed, the results further guided the selection of suitable substrate finish for the die attachments in following thermal cycling tests.

Two sizes of sintered Ag joints (3mm ×3mm and 13mm ×13mm) have been carried out thermal cycling tests from -55 °C -150 °C and -55 °C -125 °C. In order to make comparison of reliability with solder joints, two kinds of solder joints (Pb95Sn5 and Sn96.5Ag3.5) have been applied for the same conditions as sintered joints. Both non-destructive methods and destructive methods have been used as microstructure characterization tools to reveal the microstructure evolution and degradation during thermal cycling. From the results can be seen, surface roughness showed significant effects on the densification of sintered Ag joints, and further caused different degradation microstructure in the sintered joints, because different densification presents different thermomechanical properties. For small size (3mm ×3mm) of sintered joints, cracks initiated and propagated from less dense parts of sintered joints and non-uniform spots in the as-received film. For large size (13mm ×13mm) of sintered joints, cracks not only initiated and propagated from less dense parts of sintered joints, but also showed up more and thicker around border of two densification parts. After comparing with reliability of two kinds of solder joints, sintered Ag joints showed better bonding quality and reliability during thermal cycling tests.

In literature, reliability results of sintered joints were normally evaluated by bonding strength by shear tests and characterized by cross-sectional SEM images. In this work, with microstructure features of sintered joints observed

from X-ray tomography and SAM, because a specific specimen can be evaluated over its lifetime, a true image of microstructure evolution of damage during operation can be obtained, and crack and degradation can be observed three-dimensionally, which showed advantage of this non-destructive methods for degradation analysis.

6.2 Future work

Ag sintering has been under intensive investigation and is promising as alternative high performance die-attach material/technique. However, there is still a lack of data for properties and reliability of sintered Ag joints which can be used to optimize the design and predict the lifetime of the power conversation systems.

To extend this work, Lifetime model of sintered silver joints can be established through combination of the results of the experimental reliability tests and the thermomechanical modelling and simulation, this model is expected to predict the lifetimes and optimize the designs of a range of high performance and highly reliable power switch modules.

(1) FEA modelling.

With the thermomechanical properties as materials parameters, FEA model can be developed with the commercial software ABAQUS and its graphic user interface CAE to simulate the stress-strain development in the samples during the thermal cycling test, as well as the stress-strain development in the samples during the sintering processes.

(2) Simulation of stress-strain development

With the developed previous FEA model, the stress-strain development in different samples can be simulated and analyzed. These results will help to find the sites of non-elastic strain accumulation.

(3) Combination of results from experiments and thermomechanical simulation.

The agreement between degradation from thermal cycling test results and weak point from simulation results can be compared, which is expected to use for selecting of stress-strain criterion to establish lifetime model of sintered Ag joints.

(4) Establishment and refinement of lifetime model of sintered silver joints.

The relationship between the results of thermal cycling test and stress-strain criterion will be established by fitting them to equation somewhat similar to those for describe the lifetime of conventional solder joints.

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