The Effects of The Electroless Copper Coating to The Thermal Expansion Behaviors of Silicon Carbide Particles Reinforced Copper Matrix Composites for The Electronic Packaging Applications.

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LIST OF ABBREVIATION

CTE	Coefficient of thermal expansion
PMCs	Polymer matrix composites
CCCs	Carbon/carbon composites
MMCs	Metal matrix composites
Al-SiC	Silicon carbide particle-reinforced aluminum
Cu-SiC_p	Silicon carbide particles reinforced copper matrix
Cu-C_f	Carbon fiber reinforced copper
SiC	Silicon carbide
XRD	X-ray diffraction
SEM	Scanning electron microscope
EDX	Energy dispersive x-ray
CVD	Chemical vapor deposition
PVD	Physical vapor deposition
SiC_p	Silicon carbide particles
HOPG	Highly ordered pyrolytic graphite
CMC	Ceramic matrix composites
E_g	Energy band gap
PM	Powder metallurgy
Cu-C_f	Carbon fiber reinforced copper matrix

VLSI	Very large scale integration
ULSI	Ultra large scale integration
DMAB	Dimethylamine borane
EDTA	Ethylene diamine tetra acetic acid
TEA	Triethanol amine
2-MBT	2-Mercaptobenzothiazole
RDS	Rate determining step
ICP-AES	Inductively coupled plasma-atomic emission spectroscopy
TEM	Transmission electron microscope
FESEM	Field emission scanning electron microscope
ROM	Rule of mixtures
D[4,3]	Volume mean diameter
SEI	Secondary electron imaging
$Cu\text{-}SiC_{p'}$	Copper coated $Cu\text{-}SiC_p$
LVDT	Linear variable differential transformer
DMA	Dynamic mechanical analysis
D[4,3]	Volume mean diameter
FCC	Face centered cubic
TDC	Three-dimensional crystallites
rpm	Revolution per minute

LIST OF SYMBOLS

X_c	Property of the composite
X_m	Property of the matrix
X_r	Property of the reinforcement
v_m	Volume fraction of the matrix
v_r	Volume fraction of the reinforcement
E_{eq}	Equilibrium potential
E	Potential
E^o	Standard potential
α	Coefficient of thermal expansion (CTE)
L_o	Original length
ΔL	Change in length
ΔT	Change in temperature
v_p	Volume fraction of particle
α_m	CTE of the matrix
α_p	CTE of the particles
K	Bulk modulus
K_m	Bulk modulus of the matrix
K_p	Bulk modulus of the particles
G	Shear modulus
G_m	Shear modulus of the matrix
G_p	Shear modulus of the particles
ρ	Density
M_i	Mass of the copper coated SiC_p
M_{fp}	Mass of the filter paper
M_f	Final mass of the filter papers and the copper coated SiC_p
$m_{Cu\prime}$	Mass fraction of copper deposit on the SiC_p
$v_{Cu\prime}$	Volume fraction of copper deposit on the SiC_p
ρ_{Cu}	Theoretical density of copper
ρ_{SiC_p}	Theoretical density of SiC_p
v_{SiC_p}	Volume fractions of SiC_p

V_{CuSiC_p}	Volume of Cu-SiC_p composite
V_{Cu}	Volume of copper powder
m_{SiC_p}	Mass fraction of SiC_p
M_{SiC_p}	Mass of SiC_p
M_{CuSiC_p}	Mass of Cu-SiC_p composite
ρ_{SiC_p}	Density of SiC_p
ρ_{CuSiC_p}	Density of Cu-SiC_p
m_{Cu}	Mass fraction of copper powder
M_{Cu}	Mass of copper powder
$V_{Cu'}$	Volume of the electroless copper deposit on the SiC_p
$m_{Cu'}$	Mass fraction of copper in the SiC_p
M_y	Required mass of copper coated SiC_p
M_x	Required mass of copper powder
ρ_B	Bulk density
D	Mass of the sample in air
W	Mass of the sample in water
D_w	Density of water
ρ_o	Theoretical density of the composites
ρ_{Cu}	True density of the copper powder
ρ_{SiC_p}	True density of the SiC_p
E	Young's modulus
E'	Storage modulus
E''	Loss modulus
v	Poisson's ratio
$E^o{}_{ox}$	Standard oxidation potential
$E^o{}_{red}$	Standard reduction potential
ρ_B	Bulk density
ρ_A	Absolute density
P	Apparent porosity
ρ_f	Pore volume fraction
$\Delta\rho_B$	Difference in bulk density
$\%\Delta\alpha$	Percent change in CTE

Kesan Salutan Kuprum Tanpa Elektrik Terhadap Perlakuan Pengembangan Haba Komposit Matriks Kuprum Diperkuat Zarah Karbida Silikon Untuk Aplikasi Pembungkusan Elektronik.

ABSTRAK

Permintaan terhadap bahan-bahan pengurusan haba termaju dengan sifat keberkondakan haba yang tinggi dan pekali pengembangan haba (CTE) yang rendah dijangka meningkat disebabkan oleh kemajuan teknologi dalam perkakasan pengurusan haba. Komposit matriks kuprum diperkuat zarah karbida silikon (Cu-SiC_p) sangat berpotensi sebagai bahan pengurusan haba disebabkan keberkondakan haba yang tinggi dan sifat CTE yang rendah. Tetapi komposit Cu-SiC_p yang diperbuat melalui kaedah metalurgi serbuk konvensional mempunyai sifat-sifat termofizikal yang rendah disebabkan ketiadaan ikatan antara matriks kuprum dan tetulang zarah karbida silikon (SiC_p). Dalam usaha untuk meningkatkan ikatan di antara kedua-dua juzuk, SiC_p telah disalut dengan kuprum melalui proses salutan tanpa elektrik. Proses salutan tanpa elektrik tersebut terdiri daripada proses-proses pembersihan permukaan, pemekaan, pengaktifan dan pemendapan kuprum. Di antara proses-proses tersebut, zarah seramik telah dibilas dengan air ternyahion untuk meminimumkan pencemaran. Berdasarkan kepada keputusan dan dapatan eksperimen, pemendapan kuprum berterusan pada SiC_p telah diperolehi melalui proses salutan tanpa elektrik. Ketulenan filem kuprum yang diperolehi adalah tinggi dan disalut secara sekata ke atas permukaan SiC_p. Ketebalan lapisan kuprum bersalut dianggarkan kurang daripada 1μm. Lapisan kuprum bersalut pada SiC_p juga didapati meningkatkan ikatan antara matriks kuprum dan tetulang SiC_p. Lapisan kuprum bersalut meningkatkan kekuatan hijau komposit itu untuk membenarkan pecahan isipadu SiC_p yang tinggi dimasukkan ke dalam matriks kuprum. Nilai-nilai CTE komposit Cu-SiC_p bersalut kuprum adalah jauh lebih rendah daripada komposit Cu-SiC_p yang tidak bersalut. CTE komposit Cu-SiC_p bersalut adalah sejajar dengan model Kernel. Pemeriksaan mikrostruktur komposit juga menyokong keputusan CTE. Hubungan baik antara matriks kuprum dan tetulang SiC_p wujud dalam komposit Cu-SiC_p bersalut kuprum. Di dalam komposit Cu-SiC_p tidak bersalut pula, lompang submikron telah terhasil antara matriks kuprum dan tetulang SiC_p. Ini mungkin punca di sebalik nilai CTE yang lebih tinggi berbanding komposit Cu-SiC_p bersalut kuprum.

The Effects of The Electroless Copper Coating to The Thermal Expansion Behaviors of Silicon Carbide Particles Reinforced Copper Matrix Composites for The Electronic Packaging Applications.

ABSTRACT

The demands for advanced thermal management materials with high thermal conductivity and low coefficient of thermal expansion (CTE) are expected to increase due to the technological progress in the thermal management hardware. Silicon carbide reinforced copper matrix (Cu-SiC_p) composites are highly rated as thermal management materials due to the high thermal conductivity and low CTE properties. But the Cu-SiC_p composites fabricated via the conventional powder metallurgy methods have inferior thermophysical properties due to the absence of bonding between the copper matrix and the SiC_p reinforcement. In order to improve the bonding between the two constituents, the SiC_p were copper coated via electroless coating process. The electroless plating process consisted of surface cleaning, sensitization, activation and copper deposition processes. In between the processes, the ceramic particles were rinsed thoroughly with deionized water to minimize contamination. Based on the experimental results and findings, a continuous copper deposition on the SiC_p was obtained via the electroless plating process. The copper film was found to be high in purity and homogeneously deposited on the SiC_p surfaces. The thickness of the coated copper layer was roughly estimated to be less than 1μm. The copper coated layer on the SiC_p also improved the bonding between the copper matrix and SiC_p reinforcement. The copper coated layer improved the green strength of the composites thus allowed a high volume fraction of SiC_p to be incorporated into the copper matrix. The CTE values of the copper coated Cu-SiC_p composites were significantly lower than those of the uncoated Cu-SiC_p composites. The CTE of the coated Cu-SiC_p composites were in agreement with Kernel's model. The microstructure examination of the composites also supports the CTE results. A good bonding between the copper matrix and the SiC_p reinforcement exists in the copper coated Cu-SiC_p composites. Where else in the non-coated Cu-SiC_p composites, submicron gaps were observed between the copper matrix and the SiC_p reinforcement. This could be the reasons behind the higher CTE values as compared to copper coated Cu-SiC_p composites.

CHAPTER I

INTRODUCTION

1.1 Research Background

For the past few decades, there has been a tremendous market demand for electronic devices and systems. According to a published report by *BCC Research* on September 2011, the thermal management market is expected to grow from $6.7 billion in 2011 to $9.1 billion by 2016. More than 80% of the total thermal management market is dominated by the thermal management hardware such as heat sinks, fans and blowers. Hence, the technological progress in the thermal management hardware is also expected to grow due to the demands in increased functionality and miniaturization of electronic devices (Zweben, 2002). Thus new advanced thermal management materials with high thermal conductivity and low coefficient of thermal expansion (CTE) are highly needed to effectively dissipate heat from the electronic devices.

The amount of heat dissipation in electronic devices has been increased tremendously as depicted by Fig. 1.1. These have caused critical design issues related to the requirements of thermal management, reliability, weight and cost of the electronics packaging (Zweben, 2005). These complex design requirements translate into a set of material requirements which cannot be fulfilled by the conventional packaging materials. A high increase in the power consumption and heat dissipation also leads to the high failure rate in electronic packaging. 55% of the failures in electronics packaging come from temperature dependent fault (Neubauer, Angerer, & Korb, 2005). These failures are caused by the high temperature and the thermal expansion mismatch between the board and chip (Kowbel, Champion, Withers, & Shih, 2000).

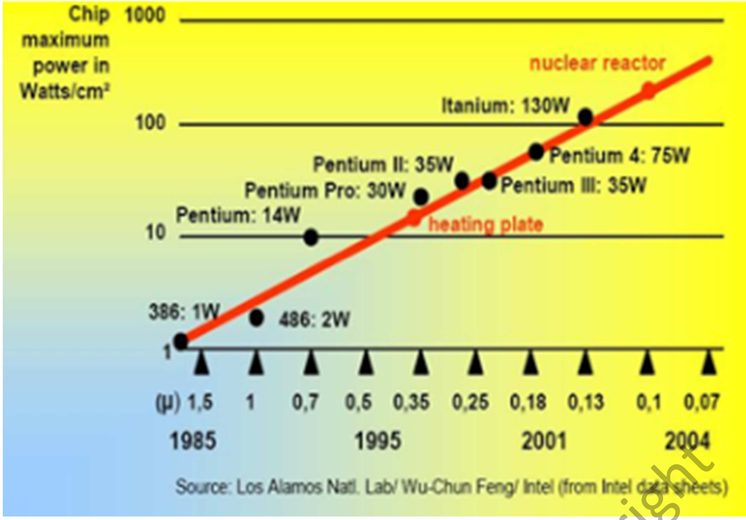

Figure 1.1: The increases in the power consumption of Intel's microprocessors (Krieg, 2004).

In order to tackle these issues, numerous advanced packaging materials have been developed. The thermophysical properties of these materials are shown in Fig. 1.2. The most important types of packaging materials are the composites (Chung, 2000). These packaging composites can be categorized into three main groups; polymer matrix composites (PMCs), carbon/carbon composites (CCCs) and metal matrix composites (MMCs) (Zweben, 2001). The main reinforcements of these composites are continuous and discontinuous thermal conductive carbon fibers and thermal conductive ceramics particles such as silicon carbide and beryllium oxide. Many of the composites, especially those reinforced with fibers, are strongly anisotropic. Where else, particle reinforced composites are usually isotropic.

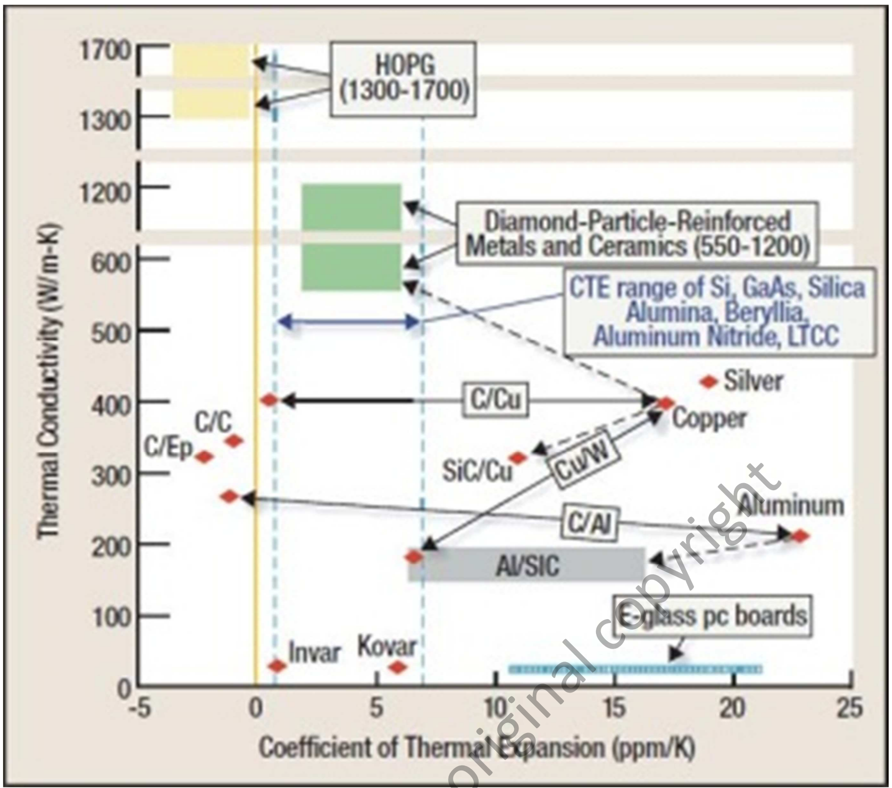

Figure 1.2: Thermophysical properties of advanced packaging materials as illustrated by Zweben (2005).

Among the composite groups, metal matrix composites (MMCs) have tremendous potentials as packaging materials because the properties of MMCs can be engineered to meet the critical design needs. By controlling the percentages of each constituent in the composites, the CTE of the MMCs can be tailored to match the CTE of semiconductors, ceramics substrates and optical fibers. Thus the thermal stresses and warpage issues can be minimized at the same time. At the time being, the MMC of greatest interest is silicon carbide particle-reinforced aluminum or Al-SiC. It is not only very cost effective thermal management material for electronics packaging (Occhionero, Hay, Adams, & Fennessy, 1999) but also performs better than copper metal (Romero, Fusaro, & Martinez, 1995). The CTE of Al-SiC can be tailored between 6.2 and 23 ppm/K but its thermal conductivity is limited to 220 W/m.K. Therefore, for heat sinks which require materials with higher thermal conductivity, silicon carbide particle reinforced copper matrix composites has a greater potential than Al-SiC. This is due to the fact that copper has almost double the thermal conductivity of aluminum. Among numerous copper based MMCs, silicon carbide particles reinforced copper (Cu-SiC_p) and carbon fiber reinforced copper (Cu-C_f) composites are the greatest interests in packaging materials industry (Neubauer et al., 2005).

The Cu-SiC_p composites seem to have more potential as packaging materials as compared to Cu-C_f due to the anisotropic behavior of the carbon fiber. But due to the absence of bonding between the copper matrix and silicon carbide (SiC) reinforcement, especially for Cu-SiC_p composites fabricated via powder metallurgy method, the Cu-SiC_p composites also have a disadvantage. One of the methods to improve the bonding between the two constituents is by coating the SiC reinforcement with a metal film. Coated reinforcement can produce more than 20% increase in the thermal diffusivity of the composites as compared to the non-coated composites (Neubauer et al., 2005). Significant improvements in thermal conductivity and CTE of Cu-SiC_p composites as compared to the non-coated Cu-SiC_p composites were also observed by Shu and Tu (2003) and Schubert et al. (2007 & 2008).

There are numerous methods available to coat the surface of the nonmetallic reinforcements, such as sputter coating (Köck, Brendel, & Bolt, 2007; Schubert et al., 2008), chemical vapor deposition (CVD) (Brendel, Popescu, Köck, & Bolt, 2007; Brendel, Popescu, Schurmann, & Bolt, 2005), physical vapor deposition (PVD) (Navinsek, Panjan, & Milosev, 1999), sol-gel coating (Torres, Campo, Ureña, & Rams, 2007) and electroless plating (T.-Y. Chan & Lin, 1999; Han et al., 2006; L. B. Li, An, & Wu, 2005; Sard, 1970; Sharma, Agarwala, & Agarwala, 2006). Among all these methods, electroless plating is the least expensive, simple and able to provide copper deposits with excellent physical and metallurgical features (Deckert, 1994). Moreover, a homogeneous copper film on the silicon carbide particles (SiC_p) can be obtained via electroless coating process to promote bonding between copper matrix and SiC_p reinforcement (Shu & Tu, 2003). The improved bonding between the coated SiC_p reinforcement and copper matrix allowed applied load to be transferred more efficiently and contributed to large strain-to-failure figures (Davidson & Regener, 2000). Furthermore, these composites have relatively higher density, lower porosity and mechanically more superior than those fabricated from uncoated powders (Moustafa, Abdel-Hamid, & Abd-Elhay, 2002). Keeping all these potentials in mind, it is therefore worthwhile to study the effects of electroless coating of SiC_p on the CTE and microstructure of SiC_p reinforced copper matrix composites.

1.2 Problem statement

Cu-SiC_p composites fabricated via powder metallurgy methods have inferior thermophysical properties due to the absence of bonding between the copper matrix and the SiC_p reinforcement (Davidson & Regener, 2000; Neubauer et al., 2005). In order to improve the thermophysical properties of the Cu-SiC_p composites, the bonding between the copper matrix and the SiC_p reinforcement must be improved (Pelleg, Ruhr, & Ganor, 1996; Shu & Tu, 2003). One of the methods to improve the bonding is by coating the SiC_p particles with a homogeneous copper film via electroless coating process (Chang, Lin, Lin, & Kattamis, 1999; Chang & Lin, 1996; Han et al., 2006). Numerous studies showed that a continuous copper film can be developed on the surface of SiC_p but, only a few were directly studying the effects of the electroless copper coating on the thermal expansion of the Cu-SiC_p composites (Shu & Tu, 2003). Therefore, it was substantial to fabricate the Cu-SiC_p composites by means of electroless copper coating. Furthermore, the potential of these particular Cu-SiC_p

composites as thermal management materials can be evaluated by comparing their thermal expansion characteristics and microstructures to those made from the uncoated SiC_p.

1.3 Research objectives

The thermophysical properties of Cu-SiC_p composites can be optimized by improving the bonding between the copper matrix and SiC_p reinforcement. This can be done via an electroless coating process. With these considerations in mind and the statements made in the preceding introduction, the present work is aimed for the following objectives:

i. To develop surface treatment and electroless copper coating processes in order to achieve homogenous and high purity copper deposit on the SiC_p.
ii. To study the effects of copper coated SiC_p particles on the physical and thermal properties of the Cu-SiC_p composites with different volume fraction of SiC_p.
iii. To analyze which model can best describes the thermal expansion behavior of the Cu-SiC_p composites.

1.4 Scope of works

The scope of this research is quite narrow. Only a few key items are covered which are the electroless copper coating process of SiC_p and the fabrication process of Cu-SiC_p composites via a conventional powder metallurgical methodology. The electroless coating process was not new but rather a reproduced process which was published by numerous researchers. Nevertheless, a few modifications were made in the coating process to improve the quality of the electroless copper deposit. XRD and

SEM/EDX analysis were performed to determine the homogeneity and purity of the copper film on the SiC_p. Then, the powder metallurgical methodology was used to fabricate the Cu-SiC_p composites at different volume fractions of SiC_p. The fabrication techniques involved the conventional uniaxial powder pressing and sintering processes. The experimental data were analyzed to determine the effects of volume fraction of SiC_p on the density, porosity and thermal expansion of the Cu-SiC_p composites. At the same time, these results were correlated to the microstructure of the Cu-SiC_p composites and compared to the experimental results of other researchers.

1.5 Thesis outline

This thesis reports the research activities and study done on the effects of electroless copper coating of SiC_p on the microstructure and CTE of Cu-SiC_p composites fabricated via powder metallurgy method. This report is divided into five main chapters.

Chapter 1 covers a short introduction on the thermal management materials in electronic packaging and the prospects of Cu-SiC_p composite as thermal management materials. This chapter also discloses a few experimental results published by the previous researchers. The objectives and scope of the research are also included in this chapter.

Chapter 2 consists of the details of literature studies for this research. Basically, there are seven main topics which are the advanced packaging materials, metal matrix composites (MMCs), fabrication of copper MMCs via powder metallurgical approach, thermal expansion of particles reinforced MMCs, electroless metal coating process, pretreatments of nonmetallic substrates and electroless copper deposition on SiC_p.

Chapter 3 describes the experimental procedures and process flow involved in the research. These include step-by-step procedures in electroless copper coating process, compaction of the green body, sintering process, density and porosity measurements, CTE measurement and samples preparation for microstructure examination.

Chapter 4 reports the experimental results and discussions. The correlations between the studied factors and experimental responses are analyzed by comparing them to theoretical data and the results reported by previous researchers.

Chapter 5 provides the conclusions of the research study based on the experimental results and findings. Conclusions are made based on the interpretation of the experimental results and by stressing the significance, limitation and implications of experimental findings. In addition, recommendations for future projects are also included.