

The Effects of Sintering Parameter to the Microstructure and Thermal Properties of CuSiC Composite for Electronic Packaging Application

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Abstract: Microelectronics and nano-electronics play a prominent role in current technologies and will do so to a greater extent in the future. The availability of suitable new materials for the electronic packaging is critical to the continuing advancement (miniaturisation and integration) of electronic components. As matter of fact, a plethora of new products/processes have been brought-in over the last few years. Much of the materials and microstructure research related to packaging has involved investigation toward better thermal management. Miniaturisation of electronic chips which have increasing functionality within the same package size has induced significant increases in requirements for extraction of heat from the integrated circuit (IC). Packaging materials therefore have to be capable to conduct heat efficiently and at the same time have low coefficient of thermal expansion (CTE) to minimize the thermal stress and warping. Since copper (Cu) is a better thermal conductor than aluminium (Al), therefore, copper should be the best candidate as thermal material. With the presence of silicon carbide (SiC) as reinforcement, copper silicon carbide (CuSiC) metal matrix composite (MMC) should be able to perform better as a heat spreader or a heat sink than aluminium silicon carbide (AlSiC) metal matrix composite. In the present study, the focus was toward development of light weight metal matrix composite with high ceramic contents, good thermal dissipation and easy of processability. Copper silicon carbide was chosen as the material basis for focused investigation to solve thermal management problems presented by current IC systems. Powder metallurgy routes were chosen to fabricate the MMC based on this materials system. Copper and silicon carbide powders were mixed together in a planetary ball mill, and the green articles were then compacted and sintered to produce the final product of CuSiC. The effects of sintering parameters were investigated for their effects towards the produced composite density, porosity and specific heat capacity. Sintering parameters investigated included temperature, heating duration and the gaseous environment. Upon sintering, the CuSiC particle bond to one another giving a higher strength and a possibility in attaining desirable density. The higher in density and the lower in porosity of the CuSiC composite, will create a low specific heat capacity characteristic which is closer to the specific heat capacity of pure copper (Cu). Thus to achieve the lower specific heat capacity, the amount of porosity in the CuSiC composite must be minimized through the optimization of the sintering parameters. Finally in a nutshell, in order to boost the specific heat capacity of the CuSiC, the recommended sintering parameter suggests that the CuSiC composite should be sintered at 950°C for seven hours in nitrogen gas.

Keywords: Microelectronics, nano-electronics, electronic packaging, electronics component, thermal management, integrated circuit, packaging materials, coefficient of thermal expansion, copper, aluminium, silicon carbide, aluminium silicon carbide, copper silicon carbide, metal matrix composite, powder metallurgy, sintering, specific heat capacity.

INTRODUCTION

Nowadays consumers demand smaller, slimmer and reliable electronics. As a result, to meet these demands, manufacturers have been pushed to the limit in developing enhanced and improved electronic packages. Improvements have related to aspects of high density packaging, miniaturisation of the electronic chips with increasing speed, enhanced thermal properties and increased reliability which have resulted in the scenario of severe thermal management issues. In the aspect of thermal management, the primary driver of today's integrated circuit technology is shrinking feature size and increasing functionality on-chip with their associated high heat flux and large temperature gradient. Due to these problems, electronics packaging designers and engineers have to work hard to design the universal thermal materials that are able to conduct heat efficiently and at the same time have low coefficient of thermal expansion (CTE) to minimize the thermal stress and warping.

In the past decade, Metal Matrix Composites (MMC's) have come into prominence by offering significant improvements over their polymer matrix counterparts due to increase in tolerance of high temperature, transverse strength, chemical stability, hardness and wear resistance, with significantly greater toughness and ductility than ceramic matrix composites. In addition, MMCs are rapidly becoming prime candidates as structural material in engineering application. For example, aluminium reinforced by Al_2O_3 and SiO_2 is used in the aerospace, aircraft and automotive industries because of its excellent thermo-physical properties such as low coefficient of thermal expansion (CTE), lower thermal capacity, and improved mechanical properties such as higher specific strength, better wear resistance, and specific modulus. Recently, metal/ceramic composites with high ceramic contents have become another focus for thermal management applications such as electronic packaging. The widespread use of these composites requires a deep understanding of their thermal expansion and some relative properties. For instance, the packaging materials in microelectronics should have low thermal capacity which inversely proportional to thermal conductivity in dissipating the heat, and low CTE to decrease the thermal expansion mismatch among the devices. Low and suitable CTE, together with lower specific heat capacity, can be achieved by blending appropriate metallic and ceramic phases to form a composite.

Despite many theoretical and experimental studies having been carried out on the subject of CTE of particle-reinforced MMC, few of them are directed toward the effect of particle surface coating on the thermal expansion behaviour and other characteristics of these composites. It was thus considered worthwhile to fabricate the copper-based ceramic-reinforced composites and to study their thermal capacity and thermal expansion characteristics. Copper silicon carbide (CuSiC) metal matrix composites have been widely

studied for their excellent electrical conductivity, thermal conductivity, specific heat capacity and frictional properties; and these composites were mainly prepared by powder metallurgy routes which sintering was the dominant process. Typically, surface energy is accessed by the surface area. Smaller particles have high surface areas and more energy per unit volume which promotes faster sintering. With particles, there is an inherent driving force for mass flow, and the smaller particle size, the greater the driving force. The sintering stress is high with small powders, but sintering requires mass flow to respond to the inherent stress. When the temperature is raised and held for longer time, the atoms move faster and the stress direct to the flow. Similarly, two factors are important to mass transport in sintering which are stress (or force) and mobility.

The sintering stress is larger with smaller particles and higher surface areas, and the mobility increases with higher temperatures and longer duration. Heat provides the atomic motion that allows sintering in response to the sintering stress applied. It allows transport by plastic flow or viscous flow. Moreover, the sintering process of CuSiC is thermally activated, meaning that input energy is necessary for mass flow. Sintering is faster at higher temperature with longer sintering time because of the increased number of activated atoms and available sites. Thus, proven by the results, sintering temperature and time are dominant parameters in defining a sintering cycle of CuSiC composite. Besides, the sintering atmosphere influences sinter bonding and compact composition of CuSiC composite. Many materials including CuSiC prove unstable with high vapour pressure during sintering, so a protective atmosphere is selected to inhibit volatilization and loss of composition. During heating, the first task of sintering atmosphere is to assist in extracting surface contaminants and processing organics. The use of nitrogen and argon gases is keys to ensure proper sintered properties of CuSiC composite. Nitrogen is neutral in many situations. It is a very active agent in the sintering, because of its role in preserving the compound stoichiometry. Nitrogen is the major constituent of air and leads to nitrogen absorption at high temperatures. Argon, on the other hand, is an inert gas which is useful in sintering since it reduces evaporation and can be purified to high levels and results in some oxide reduction.

MATERIALS AND METHODS

The sintering parameters investigated included temperature, heating duration and the gaseous environment towards the microstructure and thermal properties of the composite, in which the main goal is to produce composite with good density, low porosity and low specific heat capacity.

Raw Materials:

The constituent materials used in this study were in powder forms which are the copper and silicon carbide. The copper powder used (has a colour tone of light reddish brown) was in spheroidal shape and has particle size of <10 micron. The density of the copper powder used was 8.94 g/cm³, whilst the silicon carbide powder used (in pale grey colour) has mesh size up to 320 with density of 3.217 g/cm³.

Powder Preparation:

The composite to be prepared should comprise of 90 volume % of copper and 10 volume % of silicon carbide (90% Cu - 10% SiC). A correct portion of copper (Cu) and silicon carbide (SiC) powder has to be mixed, prior to the next processes, in order to ensure the right composition been achieved. Since SiC was known as a material with higher hardness, therefore 90% Cu 10% SiC is the most suitable combination because the higher SiC content, the harder the samples would be. Besides, high content of SiC would reduce the machinability during the powder pressing and would cause the mould to be easily damaged.

Table 1: Weight proportion for Cu and SiC powder

	Cu	SiC
% Volume	0.9	0.1
Volume [cm ³]	1.08	0.12
Weight [g]	9.655	0.386
Total weight [g]	10.041	

To mix the powder of copper and silicon carbide, the desired dimension and/or the volume of the pellet should be decided. The weight proportion for Cu and SiC powder is shown in Table 1. In this study, a pellet with 1.5 cm diameter and 0.55 cm thickness is targeted. This makes a total volume of a pellet become 0.972 cm³ which is near to 1 cm³ as the volume formulation of a cylindrical pellet.

Procedures:

In this study, the CuSiC composite is produced solely by powder metallurgy method. The sequences of steps in the experiments were indicated in the flow diagram shown in Fig. 1.

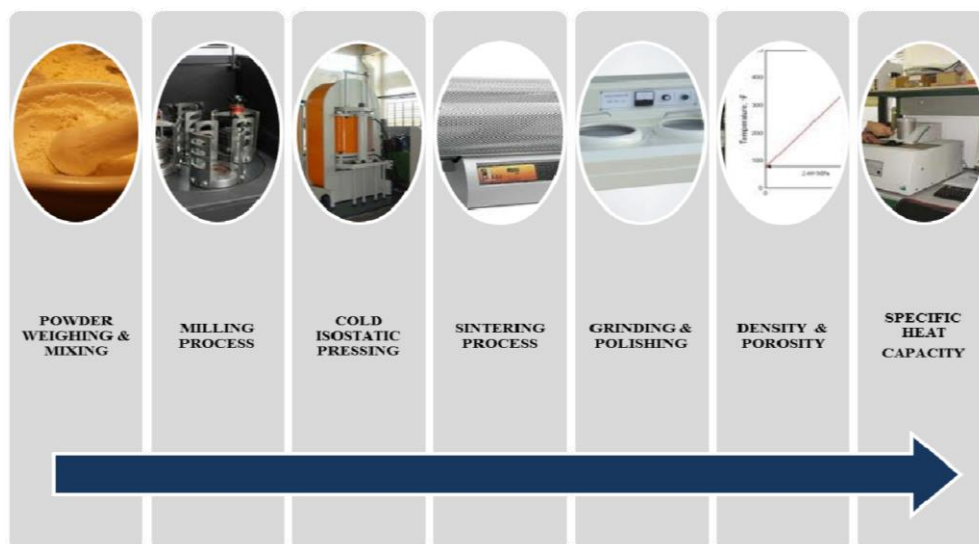


Fig. 1: The sequence of steps utilised in the powder metallurgy process of CuSiC metal matrix composite (MMC) production

Milling Process:

Based on the weight proportion for Cu and SiC as shown in Table 1, Twenty-four (24) samples were prepared and been divided into 8 batches where each batch contained of 3 samples named as A, B, and C. This is shown in Table 2 below.

Table 2: 24 samples of copper and silicon carbide prepared

90%Cu10%SiC	Per sample [g]	24 samples [g]
Weight of copper (Cu)	9.655	231.720
Weight of silicon carbide (SiC)	0.386	9.264
Total weight	10.041	240.984

Each batch was calculated to have 28.965g of copper silicon carbide (CuSiC) powder. Prior to the milling process, 100g of zirconia balls were milled in the jar together with sand at the speed of 450 rpm, for a duration time of 30 minutes. This was then followed by a water cleansing and later on followed by acetone rinsing, in order to remove any impurity that may be collected. The final step taken was the drying process of the balls and jar by using air gun. Once these control measures were accomplished, then only the copper (Cu) and SiC powders that were weighted, been poured into the milling jar. Each batch of copper silicon carbide (CuSiC) powder was then proceed with milling process using high-energy planetaryball-mill for 2 hours and 40 minutes

with an interval of 30 minutes plus break after 10 minutes of each rotation. The speed for milling was set at 200 rpm. This parameter was selected according to the design of experiment (DOE) result which indicated that this parameter had been providing the best uniformity in term of mixing copper (Cu) and silicon carbide (SiC) particles.

Cold Isostatic Pressing:

Before the compaction process taken place, the mould and the plunger must be cleaned from any contamination. Appropriate weight of milled CuSiC powder is weighted and poured into the mould. At this stage, the loss of powder through the milling process has caused the targeted pellet thickness, varying from 0.40cm to0.55cm. In view of this scenario, the weight of CuSiC composite which needed to be pressed (for1pellet), must be calculated. Once the total volume of 1 pellet of compaction was known, then the weight of CuSiC can be calculated as per the method used during powder preparation step. Details weight proportion of CuSiC powder is shown in Table 3.

Table 3: Weight Proportion of CuSiC powder for 1 pellet

	Cu	SiC
% Volume	0.9	0.1
Volume [cm ³]	0.6362	0.0707
Weight [g]	5.688	0.227
Totalweight [g]	5.915	

To simplify this, 6gm of CuSiC were measured and poured into the mould. The milled powders were then pressed into green shape through cold isostatic pressing method. The CuSiC powder was pressed consecutively for 2 minutes at 4 tones which created 3 stages of powder pressing parameters (4 tones for 2 minutes (with release load); 8 tones for 2 minutes (with release load) and 12 tones for 2 minutes (with load held)). These powder pressing parameters were performed as regards to the design of experiment (DOE) results which indicated the better compaction of powder. Theoretically, the higher load, the better compaction will be acquaintance. Finally, after the final stage of pressing been achieved, the pellet was then removed from the mould. The weight of the pellet was taken using weighing machine, the thickness was measured using thickness gauge meter and the diameter of the pellet were measured by using vernier-calliper and these measurements were noted as “before-sintered data”.

Sintering Process:

Sintering process had been noted as the most prominent part of the powder metallurgy routes as well as in the whole procedures of this study, since the main goal here is to study the effects of sintering parameters to microstructure and thermal conductivity of CuSiC. In theory, the process of sintering should be performed at the temperature lower than the melting temperature of the chosen materials. Since the melting temperature of CuSiC is about 1250°C, the best range of the sintering temperatures should be within 850°C to 950°C. In addition, the different atmospheres will also result in different sintering effects. Based on the verification of the sintering parameters and conditions per the researches that had been conducted and been reported by Randall M German, thus the sintering parameters chosen for copper silicon carbide (CuSiC) were shown in Table 4.

The sintering processes were conducted in a tube furnace in which the flow of nitrogen or argon gas can be provided. The sintering were performed 8 times (as shown in Table 4), with different parameters as indicated above. The ramp-up rate of the heating is set to be 5°C/minute and so as the ramp-down rate. Nitrogen or Argon gas flow rate is set to be around 1 litre/minute. After the sintering process completed, the weight, diameter and thickness of the pellet were measured. The measurement taken was noted as “after-sintered data” which will be compared later on with the “before-sintered data”.

Density and Porosity Measurement:

The density changes that taken place before and after the sintering processes, including the weight, thickness, and diameter of each of the twenty-four (24) CuSiC samples were recorded before and after sintering. The true density and porosity of the CuSiC, is determined by Archimedes method (using Shimadzu BX 4200H weight balance). As of the porosity and density, the samples were first weight in the air to determine W_1 (weight in air), then the samples were immersed into the water for 30 minutes to determine W_2 (weight in water). After 30 minutes, the samples were taken out from the water and dry-up and been weighted again in air for W_3 (weight after immersed). With the obtained data, the density of the CuSiC can be calculated as follow:

$$\%porosity = (W_3 - W_1 / W_3 - W_2) \times 100\%$$

Table 4: Sintering parameters for copper silicon carbide (CuSiC)

Sample ID	Temperature [°C]	Soaking Hour [hrs]	Gas Type	Ramp Up [°C/min]	Ramp Down [°C/min]
1A	850	3	Nitrogen	5	5
1B					
1C					
2A	850	7			
2B					
2C					
3A	950	3			
3B					
3C					
4A	950	7			
4B					
4C					
5A	850	3	Argon	5	5
5B					
5C					
6A	850	7			
6B					
6C					
7A	950	3			
7B					
7C					
8A	950	7			
8B					
8C					

Grinding, Polishing and Metallographic Analysis:

During sintering processes, some samples were cracked due to the effects of powder press and dimensional shrinkage. As a result, only one sample out three from each of the batch (with less or no defect at all) was chosen to undergo the metallography analysis as well as the specific heat capacity test. These samples were grinded with 80-grit silicon carbide (SiC) sand paper, by using Buehler Phoenix Beta grinder/polisher machine. The grinding and polishing processes are prominent in revealing the microstructure of the produced CuSiC. The minimal thickness susceptible for testing is around 0.40cm and when the thickness of every sample had reached 0.42cm, these samples were then grinded with silicon carbide (SiC) sand paper with grit sizes of 120, 240, 320, 400, 600, 800, 1000 and 1200 for about half-an-hour until all scratches and defects were fully eliminated. Finally, when the pellet thickness reached around 0.40cm, the pellets were then subjected to polishing process using polishing paste of 6micron.

Subsequently to the grinding and polishing processes, the samples with lowest and highest sintering parameters (of nitrogen and argon atmospheres) were undergone metallographic analysis through JOEL JSM6460LA SEM/EDS and Nikon ME600 Light Microscope Image Analyser. The chosen set of samples for the metallographic analysis was sample no. 1, no. 4, no. 5 and no. 8. The reason behind for this selection was to observe and compare the effects of lowest and highest parameters of sintering in term of the distribution of CuSiC particles, presence of porosity, cracks and other defects, effect of using nitrogen and argon gas, as well as the existence of interface reaction zone between Cu and SiC particles. As regards to image analyser, the samples were examined under 3 different magnifications that were 50X, 100X and 200X. The observation focused on the surface conditions of the samples. On the contrary, observations that were conducted under the scanning electron microscope (SEM) were under 4 different magnifications that were 500X, 2000X, 5000X and 10000X. The observations focused on the aspect of particles distribution, porosity and the search for interface reaction zone. Through these observations, the microstructures obtained can be related to their physical and electrical properties.

Heat Capacity Characterization:

Heat capacity often simply called specific heat, or thermal capacity, is the heat capacity per unit mass of a material. Occasionally, in engineering contexts, the volumetric heat capacity is used. Heat capacity is the measurable physical quantity that specifies the amount of heat required to change the temperature of an object or body by a given amount. The SI unit of heat capacity is joule per kelvin, J/K. Heat capacity is an extensive property of matter, meaning it is proportional to the size of the system. When expressing the same phenomenon as an intensive property, the heat capacity is divided by the amount of substance, mass, or volume, so that the quantity is independent of the size or extent of the sample.

Temperature reflects the average randomized kinetic energy of particles in matter, while heat is the transfer of thermal energy across a system boundary into the body or from the body to the environment. Translation, rotation, and a combination of the two types of energy in vibration (kinetic and potential) of atoms represent the degrees of freedom of motion which classically contribute to the heat capacity of matter, but loosely bound electrons may also participate. On a microscopic scale, each system particle absorbs thermal energy among the few degrees of freedom available to it, and at sufficient temperatures, this process contributes to the specific heat capacity.

Fig. 2 illustrates the Phyme-Palmer specific heat capacity measurement equipment used in this study. A piece of tin (Sn) plate was heated in the fire bricks using a heating element coil at 6V. The steady state temperature of the heated tin plate was recorded as T_1 . The sample of CuSiC composite was then placed in contact with the heated tin plate and another piece of tin plate was placed on top of the CuSiC, in order to create a "sandwich" of Sn-CuSiC-Sn. At this stage, T_2 was recorded once the temperature reaches its steady state. After T_2 has been recorded, the heating voltage was doubled to 12V and the Sn-CuSiC-Sn was heated-up to $T_2 + 50^\circ\text{C}$. Once the heating process completed, the CuSiC sample (with the top cover of tin) were taken out from the fire brick, to let it cool. The cooling temperature of the CuSiC with tin plate was recorded over time.

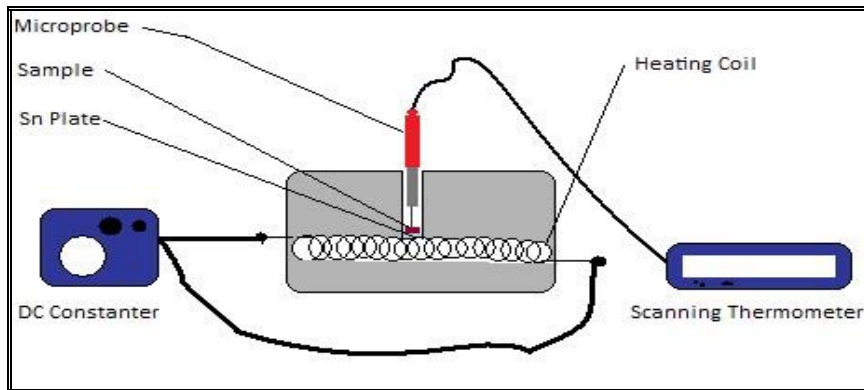


Fig. 2: Illustrates the Phyme-Palmer specific heat capacity measurement equipment

Log cooling temperature over time will be plotted and dT/dt at T_2 was calculated from the plotted graph. At T_2 , the cooling rate of the tin plate is equal to the heating rate of CuSiC.

The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius. The relationship between heat and temperature change is usually expressed in the form shown below where c is the specific heat. The relationship does not apply if a phase change is encountered, because the heat added or removed during a phase change does not change the temperature.

$$Q = cm\Delta T \text{ where;}$$

Q = heat added

c = heat capacity

m = mass

ΔT = change in temperature

RESULTS AND DISCUSSIONS

Particle Size:

Normally surface energy is accessed by the surface area of the samples, in which it meant that, smaller particles will have higher surface area and more energy per unit volume, which able to promote faster sintering. The size of copper (Cu) and silicon carbide (SiC) powders used were $100\mu\text{m}$ and $150\mu\text{m}$ respectively. The selection of these particle sizes was meant to enhance the role of surface area in optimizing the properties of CuSiC during sintering process. Fig. 3 below showed the SEM images of copper (Cu) and silicon carbide (SiC) particles in powder form at the magnification of 500X, whilst Fig. 4 showing the results of the particle size distribution analysis by using Malvern Mastersizer2000.

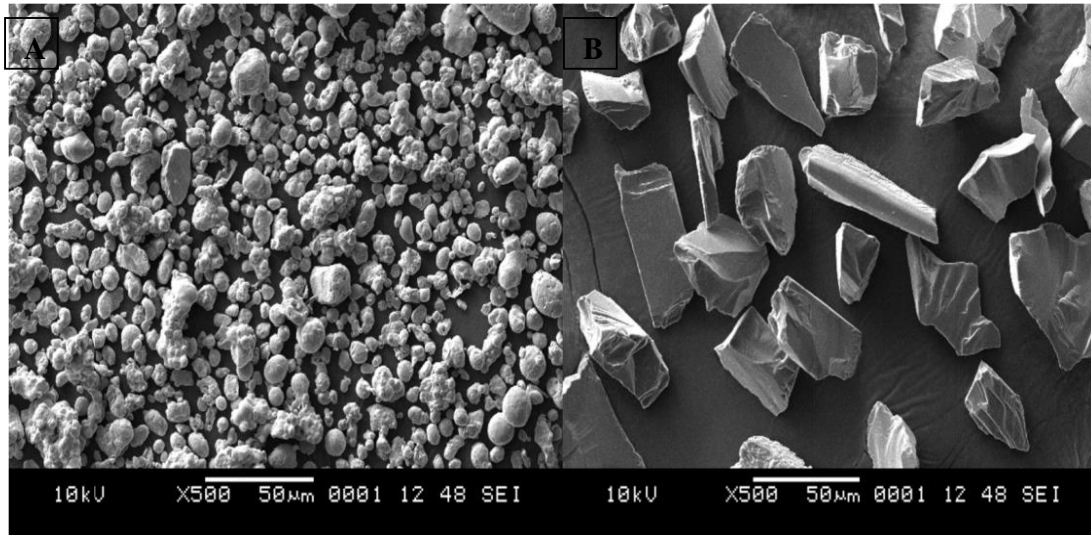


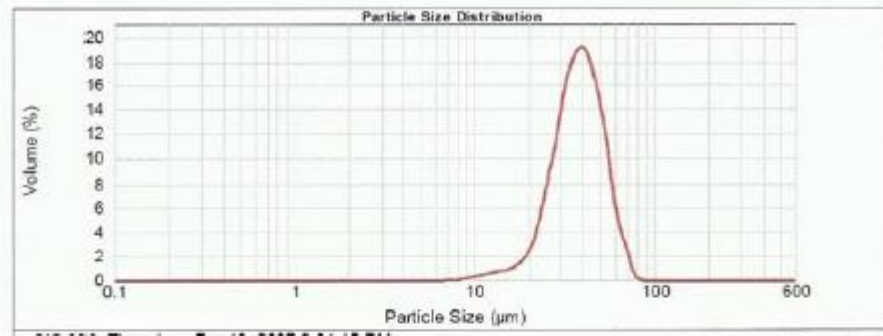
Fig. 3: SEM image of Cu and SiC particles in powder form at magnification of 500X. (A) Image of copper (Cu) particles with smaller size and round shape (B) Image of silicon carbide (SiC) particles with larger size and angular shape.

Since the shape of Cu and SiC are round and cylindrical, their combinations will promote a system with concave and convex surfaces. The use of particles of elliptical shape does not appear to reduce the porosity, but cylindrical or angular-shaped particles, if properly arranged, would reduce the porosity below that possible with spheres. In a system consisting of mixed concave and convex surfaces, there are further energy gradients in the microstructure that drive mass transport. One of the important factors to mass transport in sintering is stress or force. The sintering stress is larger with smaller particles and higher surface area. Small particles are more energetic. With the said particles, there is an inherent driving force for mass transport, and with the smaller particle size, the greater the driving force will be.

In consequence, there are other influences affected by particle size. Embedded in the neck growth for each transport mechanism is particle size dependence. Surface diffusion and grain boundary diffusion are very sensitive to particle size. These interfacial diffusion processes are favoured at the smaller particle sizes because of the high interface content per unit volume.

Porosity:

Pores were the inherited part of sintering process. They were presented in the powder compact as inter particle voids. During sintering, pores can form from uneven phase distribution, unbalanced diffusion events, reaction with the atmosphere, and capillary spreading of a liquid upon melting. In this study, the percentages of porosity of all the CuSiC samples was shown in Fig. 5. It can clearly be seen that sample number 4, indicated the lowest average porosity percentages as compare to other samples. On the contrary, sample number 5, shown the highest percentages of porosity. The dissimilarity pattern was definitely influenced by the sintering parameters which were temperature, soaking hour and gas type.



Size (µm)	Volume In %	Size (µm)	Volume In %
1.096	0.00	11.482	0.58
1.259	0.00	13.183	0.73
1.445	0.00	15.136	0.94
1.660	0.00	17.378	1.61
1.905	0.00	19.953	3.14
2.188	0.00	22.909	6.41
2.512	0.00	26.303	10.07
2.884	0.00	30.200	14.76
3.311	0.00	34.674	17.17
3.802	0.00	39.811	16.86
4.365	0.00	45.709	13.50
5.012	0.00	52.481	8.69
5.754	0.00	60.256	3.74
6.607	0.01	69.183	1.13
7.586	0.08	79.433	0.00
8.710	0.21	91.201	0.00
10.000	0.39	104.713	0.00
11.482		120.226	0.00

Fig. 4: Particle size distribution analysis

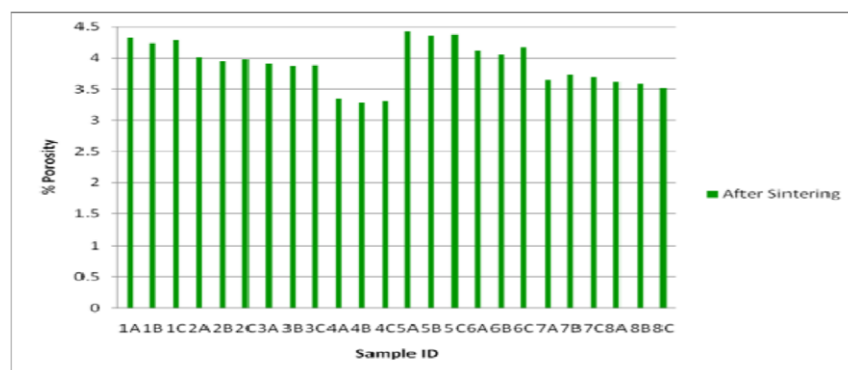


Fig. 5: The percentage of porosity in CuSiC samples

Although it was known that the gas type that had been used which were nitrogen and argon did not bring in a big influence to porosity, but it does aids in oxide and contaminant reduction which contribute to pores elimination. During sintering, sample number 4 had undergone the use of nitrogen gas at 950oC for 7 hours of soaking time, whilst samples number 5 had undergone the use of argon gas at 850oC for 3 hours of

soaking time. Theoretically, the higher temperature and longer soaking hour will drive to faster mass transport which will eventually reduce pores and remove oxide and contaminants.

As such, in order to examine the microstructure of the pores during sintering process, 4 samples were selected for comparison purpose at two different extremes which are as follow:

- a) Sample number 1: undergone the sintering process at the temperature of 850°C for 3 hours of soaking time in nitrogen gas environment;
- b) Sample number 4: undergone the sintering process at the temperature of 950°C for 7 hours of soaking time in nitrogen gas environment
- c) Sample number 5: undergone the sintering process at the temperature of 850°C for 3 hours of soaking time in argon gas environment and;
- d) Sample number 8: undergone the sintering process at the temperature of 950°C for 7 hours of soaking time in argon gas environment.

The SEM micrographs of sample number 1 and sample number 4 are shown in Fig. 6 and Fig. 7, respectively.

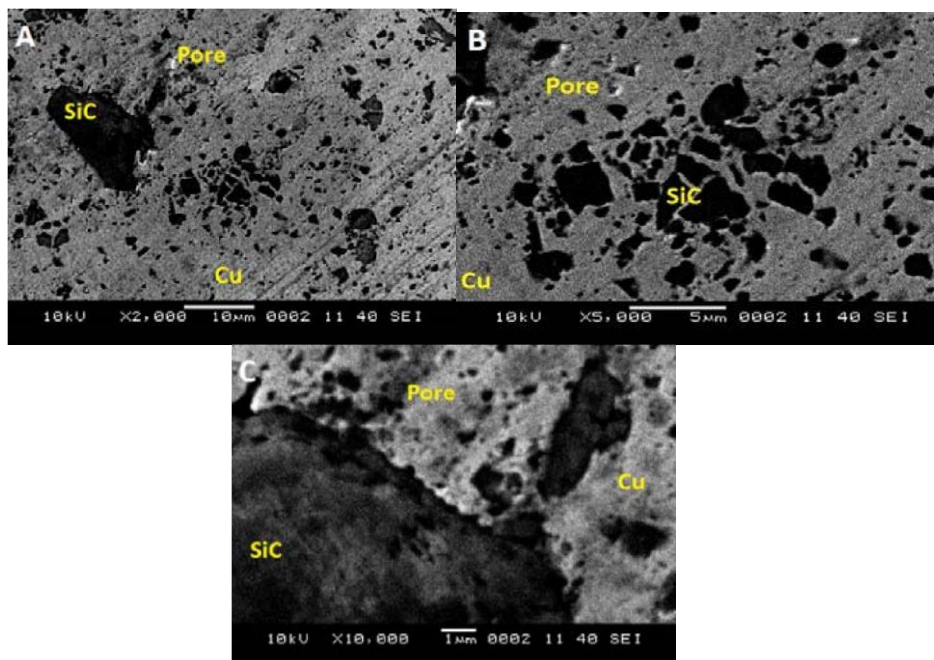


Fig. 6: Microstructure of sample number 1 (at different magnifications) which had undergone the sintering temperature of 850°C for 3 hours of soaking time in nitrogen gas environment (A) 2000X magnification (B) 5000X magnification (C) 10000X magnification

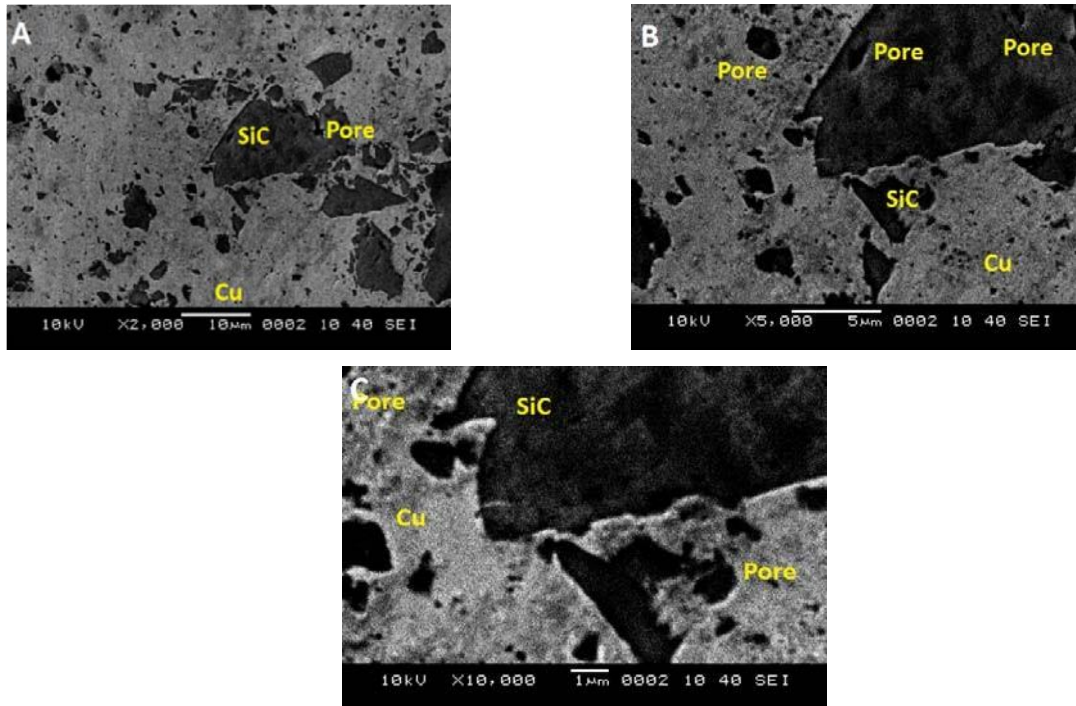


Fig. 7: Microstructure of sample number 4 (at different magnifications) which had undergone the sintering temperature of 950°C for 7 hours of soaking time in nitrogen gas environment (A) 2000X magnification (B) 5000X magnification (C) 10000X magnification

In Fig.6, it can obviously be seen that the distribution of SiC particles were scattered around the CuSiC surfaces. At higher magnification of 5000X and 10000X, it can be seen that the pores were relatively in large quantity. This was dissimilar with what could be seen in Fig. 7 which shows smaller quantity of pores. This is due to the different sintering parameters between the two samples (in the same nitrogen gas environment) which proved that at higher temperature and longer soaking time, the higher rate of pores could be eliminated. Pore size, shape and connectivity were the typical concerned during sintering. The size and shape of the pores vary during sintering.

The initial stage of sintering was characterized by rapid growth of the inter-particle neck. In the intermediate stage, the pore structure becomes smoother and has an interconnected with cylindrical nature as the compact properties were developed. It is common for grain growth to occur in the later portion of the intermediate stage of sintering, giving a larger average grain size with fewer grain. That is accompanied by possible pore isolation and a slower sintering rate. The open pore becomes geometrically unstable when the porosity has shrunk to approximately 8% (92% of theoretical density). At that point, the cylindrical pores collapse into spherical pores, which are not as effective in slowing grain growth. The appearance of isolated pores indicates the final stage of sintering and slow densification. Gas in the pores will limit the end-point density; accordingly vacuum sintering can produce high final densities as long as the metal does not evaporate. No clear distinctions exist between the sintering stages. The initial stage generally corresponds to a microstructure with a large curvature gradients. Both the neck size ratio and shrinkage are small and the grain size is no longer than the initial particle size. In the intermediate stage, the pores are smoother and the

density is between 70 and 92% of theoretical. By the final stage of sintering, the pores are spherical and closed, and the grain size is evident.

On the other hand, the SEM micrographs of sample number 5 and sample number 8 were shown in Fig. 8

and Fig. 9 below, respectively.

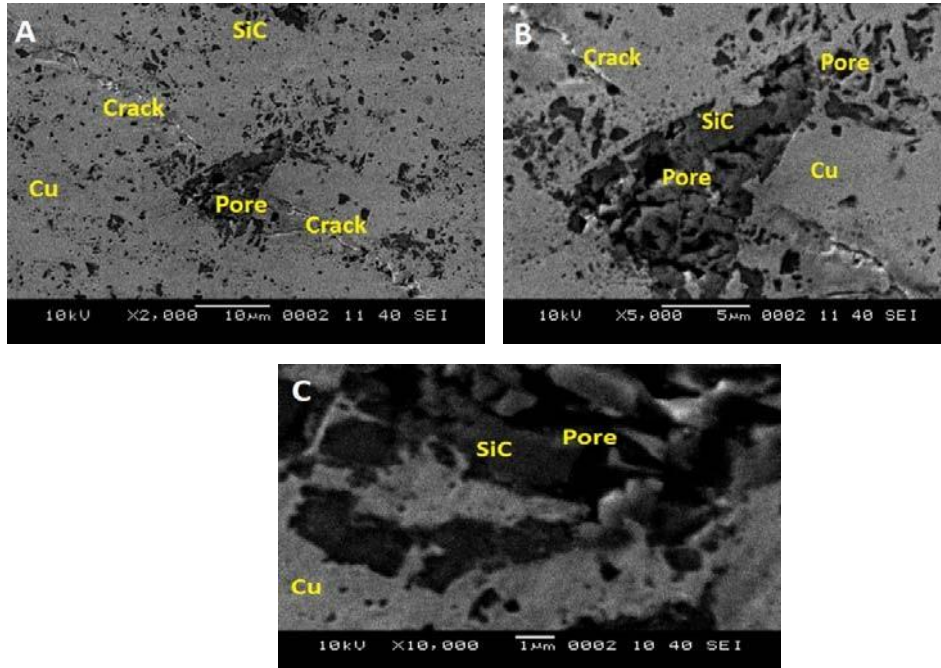


Fig. 8: Microstructure of sample 5 (at different magnifications) which had undergone the sintering temperature of 850°C for 3 hours of soaking time in argon gas environment
(A) 2000X magnification **(B)** 5000X magnification **(C)** 10000X magnification

Fig. 8 and Fig. 9 above show the microstructure in opposition mode as compared to Fig. 6 and Fig. 7. As refers to Fig. 8, it can be obviously seen that the distribution of SiC particles is still scattered around the CuSiC surface and at higher magnification of 5000X and 10000X, the pores are relatively in smaller quantity with smaller size compared to Fig. 9. This was opposing the theory of the higher temperature and the longer soaking time, which could produce high rate of pores elimination.

Further to this, one-way ANOVA analysis of the percentages of porosity had been conducted in order to ensure that the obtained data were statistically sound. The summarized paired t-test were shown in Fig. 10. Based on the paired t-test which means to determine the significance of a difference in terms of porosity between all the samples, it can be concluded that sample number 4 shows the highest difference as regards to porosity since its paired ring locates at the bottom of the analysis and away from the rest of the samples. As regards to other samples, it can be noted that there are slight differences in terms of porosity between other samples, since the rings do not stack on each other. This condition was statistically proven by the positive values achieved. Referring to the mean values (in Fig. 10), it can be seen that sample number 4 which had undergone the sintering temperature of 950°C for 7 hours of soaking time in nitrogen gas environment, has the lowest percentage of porosity of 3.317% whilst sample number 5 which had undergone the sintering temperature of 850°C for

3 hours of soaking time in argon gas environment, has the highest percentages of porosity of 4.38%.

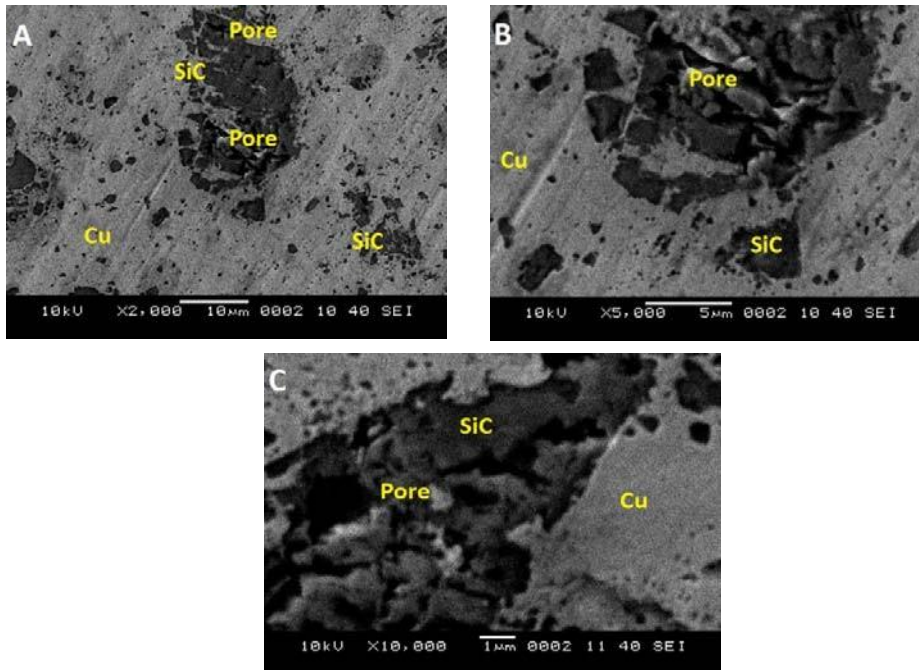


Fig. 9: Microstructure of sample 8 (at different magnifications) which had undergone the sintering temperature of 950°C for 7 hours of soaking time in argon gas environment
(A) 2000X magnification **(B)** 5000X magnification **(C)** 10000X magnification

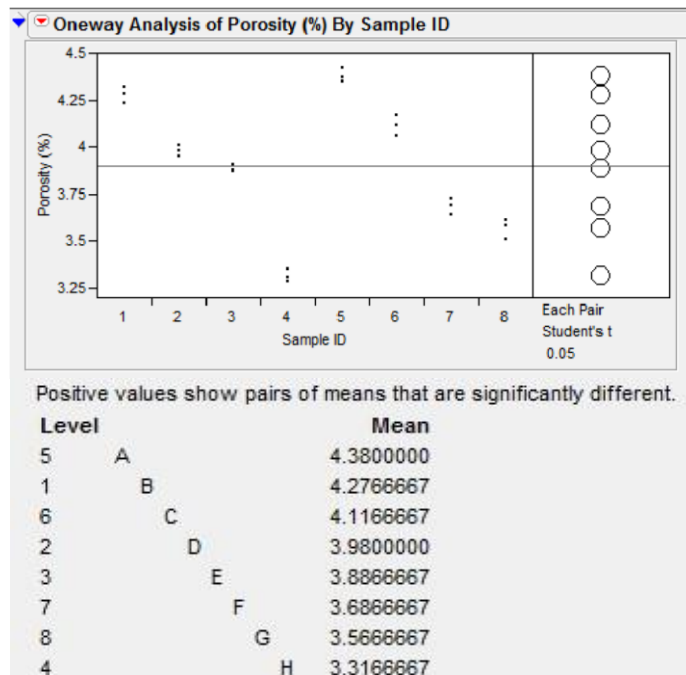


Fig. 10: One-way ANOVA analysis of porosity percentages

In a typical system when one constituent melts or reacts, it will generate an increase in porosity during the heating stage to the sintering temperature. Besides, the entrapped gas in closed pores will also increase the possibility of porosity due to an internal gas pressure. In addition, sample preparation and etching could also influence the presence of porosity. Etching will usually enlarge pores, leading to an overestimate of the porosity.

The best microstructure preservation will occur by repeatedly polishing and etching the samples, impregnating epoxy into the polished surface, and then repolishing and then repolishing after the epoxy becomes rigid. This procedure allows final polishing without disturbing the fragile pore structure.

Density:

Density is the most widely reported property in sintering. It is defined as the mass per unit volume. Unlike the absolute density which depends on composition, the fractional or percentage density gives evidence of fundamental events occurring during sintering, independent of the material. The change in density due to sintering is termed as densification. Even inter-particle neck growth, with a loss of surface area, occurs in some powder compacts without a density change, densification is a useful concept especially when comparing systems of differing theoretical densities or initial porosities. Densification, final density, neck size, surface area, and shrinkage are related measures of pore elimination during sintering

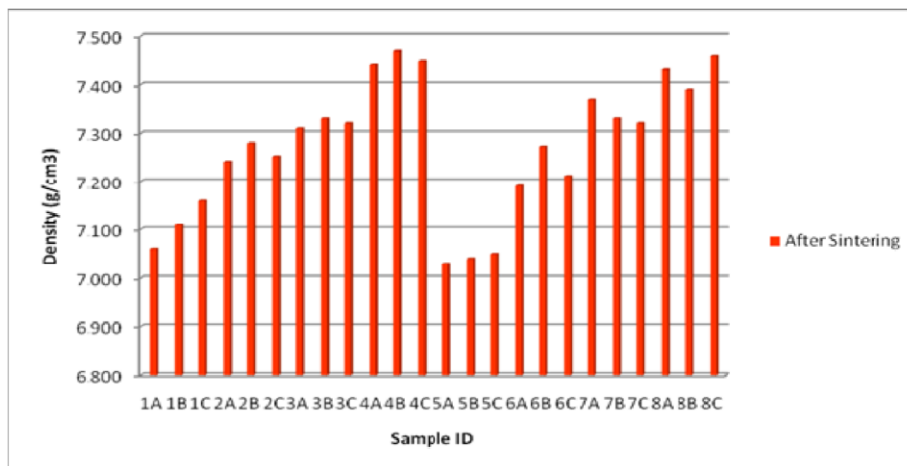


Fig. 11: Density of CuSiC samples determined by Archimedes technique.

The density of all the samples in g/cm^3 were shown in Fig. 11. For sample number 1 to number 4 which were sintered in nitrogen gas environment, an incremental trend can be observed as the temperature getting higher (from 850°C to 950°C) and the duration getting longer (from 3 hours to 7 hours). Thus, this trends is abiding to the theory of porosity which states that the lower porosity percentage, the better density would be. As per ASTM B311 - 08, density alone cannot be used for evaluating the degree of densification because chemical composition and heat treatment affect the pore-free density. On the other hand, for sample number 5 to number 8, which were sintered in argon gas environment, it has shown the similar trend as the nitrogen atmosphere's samples. As a result, this trend still act in

accordance with the theory of porosity, which states that the lower porosity percentage, the better density would be. In fact, the increment in temperature (from 850°C to 950°C) and its duration (from 3 hours to 7 hours), helped to remove the gas that has been trapped within the closed pores of CuSiC during sintering. The trapped gas will lead to higher porosity which eventually reduce the density.

One-way ANOVA analysis of density had been conducted and the summarize paired t-test data were shown in Fig. 12. Based on the paired t-test which mean to determine the significance of a difference in term of density between all the samples, it can be concluded that there were coupled happened between the tabulated data, in which sample number 4 was coupled to sample number 8 (sintered at 950°C for 7 hours), sample number 7 was coupled to sample number 3 (sintered at 950°C for 3 hours), sample number 2 was coupled to sample number 6 (sintered at 850°C for 7 hours) and finally sample number 1 was coupled to sample number 5 (sintered at 850°C for 3 hours). These coupling indicated that the samples which were sintered with similar temperature and duration would not have a significant difference with the effect of gas environment. Thus, this verifies that the use of gas (either nitrogen or argon) in sintering process, does not affect the final density value of the samples cause the prime effect will only be the temperature and the duration of sintering.

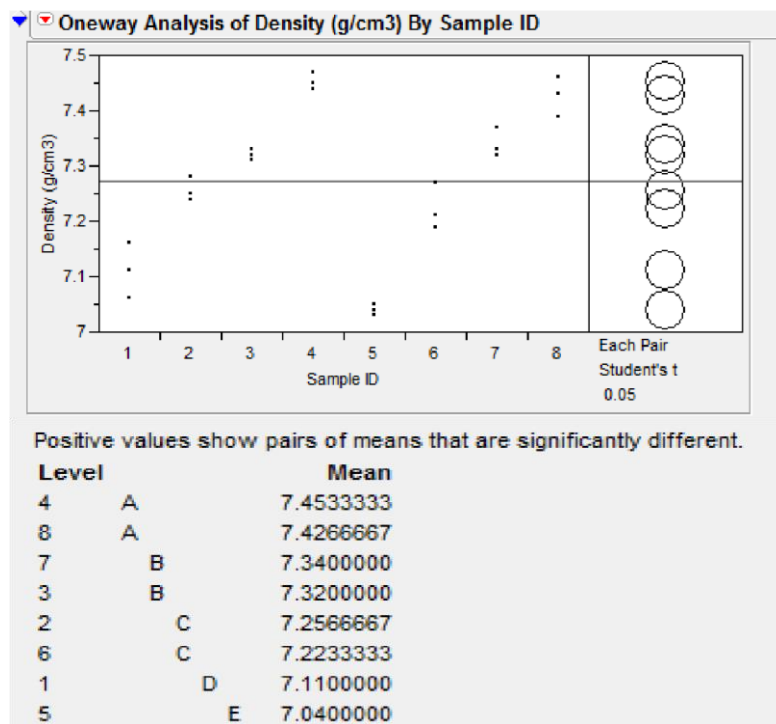


Fig. 12: One-way ANOVA analysis of density

Referring to the mean values (in Fig.12), it can be noted that sample number 4 has the highest density value of 7.45 g/cm³, followed by its couple, that was sample number 8 with 7.43 g/cm³. Meanwhile, sample number 5 has the lowest density of 7.04 g/cm³, which followed by its couple, that was sample number 1, with density value of 7.11 g/cm³.

Heat Capacity:

Thermal conductivity and specific heat capacity are inversely proportional for most materials at normal temperatures. This is due to the fact that both thermal conductivity and specific heat capacity have their origin in molecular vibrations. Thermal conductivity is the rate at which a material conducts heat away. It depends on how easily the electrons can move inside the material, whereas specific heat has to do with how much energy is needed to raise an object's temperature, which has to do with the amount of freedom the atoms have in the material.

The specific heat capacity values (in kJ/kg.K) of all samples are shown in Fig. 13. From the bar graphs, it can be seen that sample number 4 has the highest specific heat capacity value of 1.032 kJ/kg.K, followed by sample number 8 with 1.004 kJ/kg.K (these samples were sintered at 950°C for 7 hours). On the other hand, sample number 5 has recorded the lowest value of specific heat of 0.856 kJ/kg.K, followed by sample number 1 which had been sintered at 850°C for 3 hours.

Based on the trend shown, it can be concluded that the specific heat capacity of CuSiC sample is directly proportional to the density and reversely proportional to the porosity. The higher density and lower porosity of CuSiC composite will lead to better specific heat capacity that close to the specific heat of pure copper.

The specific heat values obtained were further subjected for Bivariate analysis which able to show the relationship between two continuous variables. The Bivariate platform analysis results appear in a scatterplot as shown in Fig. 14. By using the Fit Mean command, a horizontal line can be added to the scatterplot which represents the mean of the Y response variable. As refers to the Fit Mean Report in Fig. 14, the mean of the response variable (which actually the specific heat of the CuSiC composite) is recorded as 0.9355 kJ/kg.K.

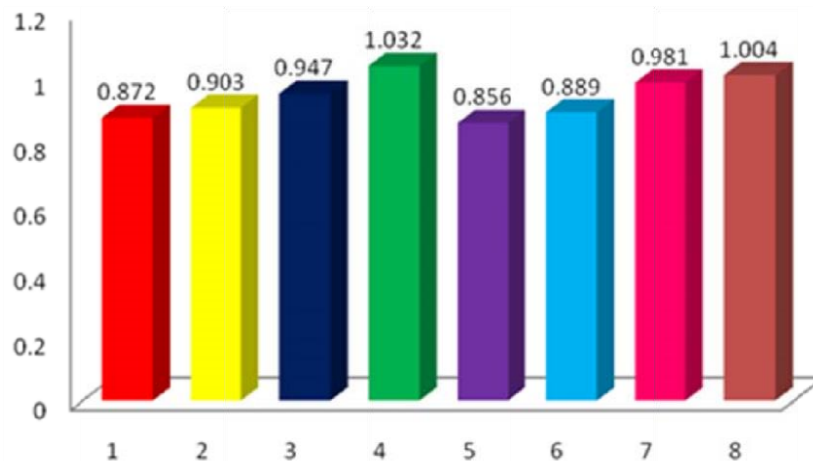


Fig. 13: Specific heat capacity (in kJ/kg.K) of each sample

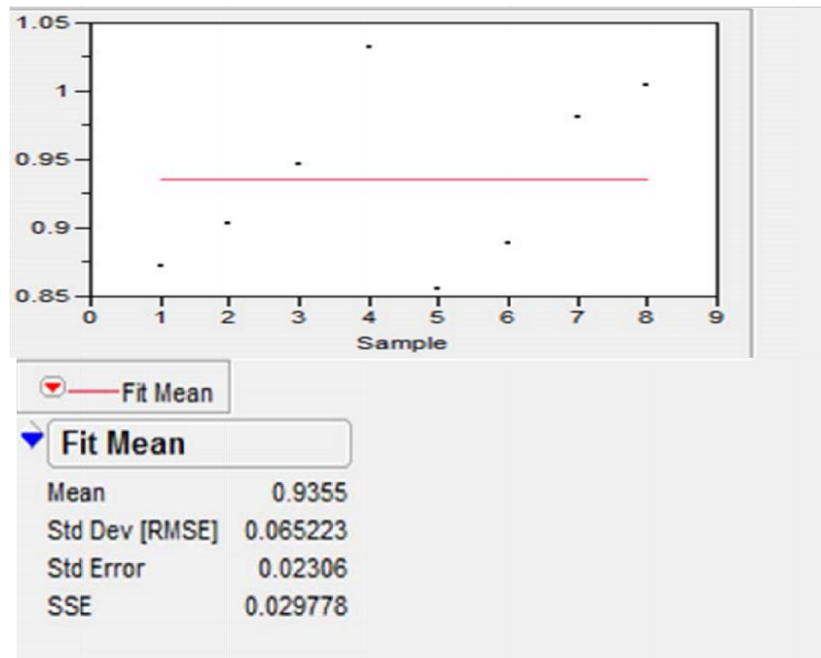


Fig. 14: Bivariate fit of specific heat of each of the CuSiC composite with fit mean

The standard deviation of the response variable that obtained from Fit Mean Analysis is 0.065223, whilst the standard deviation of the response mean is 0.02306. As such, the mean value of the specific heat from the Bivariate Fit Analysis is 0.9355 kJ/kg.K, which is slightly lower as compared to the theoretical value for pure copper (Cu) which is 1.156 kJ/kg.K. This value is acceptable since the test sample is MMCs of copper silicon carbide (CuSiC). Theoretically, in the copper matrix composite reinforced with SiC, an interfacial transition layer between SiC ceramic and Cu may be formed, which may help to reduce the residual stresses and at the same time, help to increase the mechanical strength. But with less control, it will reduce the thermal properties of copper.

Prediction Profile of Best Sintering Parameter:

Basically, in accordance with the study on the effects of sintering parameter to microstructure and thermal properties of CuSiC composite, there are few criteria available in order to enhance the thermal properties of CuSiC composite in terms of specific heat. Less percentage of porosity and higher density of CuSiC composite will be the best. Higher density of CuSiC will provide better specific heat for CuSiC. Thus, to achieve the better specific heat capacity, the porosity percentage of the samples must be minimized in order to optimize its density.

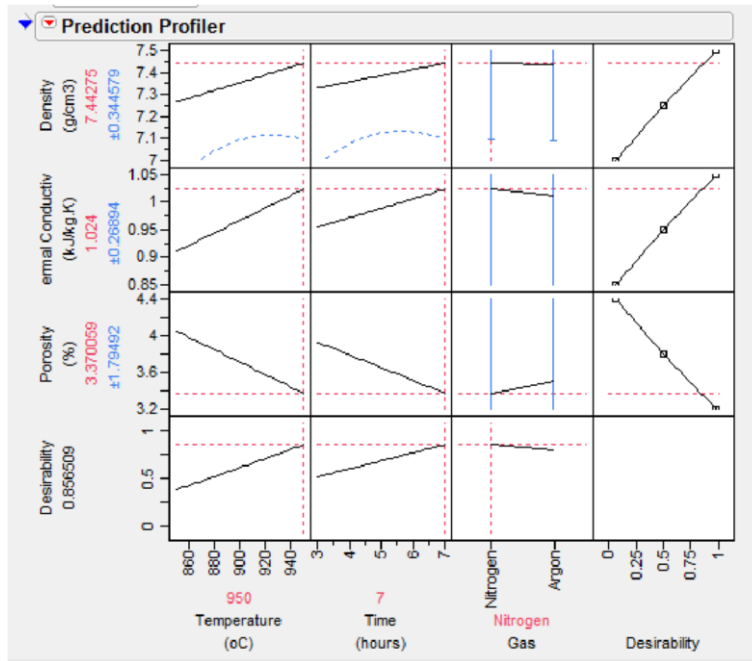


Fig. 15: The prediction profiler for maximum desirability of properties of CuSiC

Based on Fig. 15, the bottom part of the figure (noted with red colour) shows the best sintering parameter which can be used to boost the best specific heat of CuSiC. The recommended sintering parameter suggests that the CuSiC samples should be sintered at 950°C for seven hours in nitrogen gas. With the sintering parameter, the percentage of porosity in CuSiC can be decreased to 3.37% and the density of CuSiC can be increased up to 7.443 g/cm³. By having those values of porosity percentage and density, it is expected that the specific heat capacity of CuSiC will be closed to the value of 1.024 kJ/kg.K.

Summary:

Customer's demands of electronic devices to have features like 'shrinking in size plus increasing in functionality' had actually created serious 'thermal management' problem to all electronics manufacturers. The millennium discovery of 'new highly potential thermal management material' like CuSiC metal matrix composite, to be used as heatsink or heat spreader in electronic packages, would be very promising since it has good specific heat capacity, light weight and easy-to-process characteristics. In a nutshell, in order to boost the best specific heat capacity of CuSiC, the recommended sintering parameter suggests that the CuSiC samples should be sintered at 950°C for seven hours in nitrogen gas. With the sintering parameter, the percentage of porosity in CuSiC can be decreased to 3.37% and the density of CuSiC can be increased up to 7.443 g/cm³. By having those values of porosity percentage and density, it is expected that the specific heat capacity of CuSiC will be closed to the value of 1.024 kJ/kg.K. This parameter obey the theory of sintering which states that the lesser percentage of porosity in CuSiC composite, the higher the density of CuSiC will be. Higher density of CuSiC will provide better specific heat for CuSiC. Thus, to achieve the better specific heat capacity, the porosity percentage of the samples must be minimized in order to optimize its density.

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