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Effect of Percentage Alumina on the Growth Kinetics of Copper and Hardness of Cu-Al_2O_3 Composite

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ABSTRACT

In this paper, the effect of the amount of alumina reinforcement on the growth kinetics of copper grains during the early stages of sintering and hardness of the composite was investigated. Samples were obtained by mixing the powders of copper and alumina of different compositions (5% and 10%wt alumina) and compacting at 3,000 psi. Sintering is done using a tube furnace in a nitrogen atmosphere for varying times (10, 20, 40, 80, 160 minutes) and temperatures (750°C, 850°C, 950°C). Afterwards, the samples were prepared for metallographic examination and the average grain size of copper was measured. Photomicrographs showed an increase in copper grain size and decrease in porosity with increasing temperatures. From the kinetic study, the following grain growth equations for 5% alumina and 10% alumina copper-matrix composite were obtianed. Hardness measurements were performed using the Vickers Hardness Tester. Higher hardness of the composite was attained at increased temperatures and % alumina.

1. INTRODUCTION

1.1. Background of the Study

Metal matrix composites (MMCs) are considered as important engineering materials with potential applications in a variety of fields. MMCs possess superior mechanical properties such as increased stiffness, higher strength, improved wear resistance, and low coefficient of thermal expansion [1]-[3]. The popularity of copper in the industry is mainly due to its high electrical and thermal conductivities. These, aside from its excellent corrosion resistance and ease in fabrication make copper suitable for wide variety of applications. Copper alloys are used as resistance welding electrodes, seam welding wheels, incandescent lamp leads, x-ray tube components, relay blades and contact supports, targets for neutron source, integrated circuit lead frames, and hybrid circuit packages, among others [4]. The mechanical properties of copper can be improved by alloying. However, alloying results to a considerable loss in conductivity. To remedy this, composite materials were developed. These are produced by incorporating

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fine second phase particles in the metal matrix to improve its mechanical properties while preserving the material's conductive properties. The strengthening phase can be in the form of fibers, particulates of whiskers. Powder strengtheners, however, are more advantageous as far as economic considerations are concerned [5]. Ceramics, such as alumina, are good choice for the second phase owing to its high hardness and wear resistance. Since alumina is insoluble in the copper matrix, its original particle size nor spacing is neither altered even at high temperatures. This characteristic of alumina makes the strength and conductivity of the resulting composite stable even at elevated temperatures [6]. Equally important as the choice of reinforcement is the choice of the matrix. The matrix is the continuous constituent and is often (but not always) present in greater amount. The matrix is responsible for taking up external loads and distributing them over the composite volume [7]. The properties of the composite mainly depend on the individual properties and relative amounts of the matrix and the reinforcement [9]. MMCs can be fabricated economically by Powder Metallurgy (P/M) process. P/M is comprised of three important steps: (1) metal powder fabrication, (2) blending and compaction, and (3) sintering. Sintering is the process of heating compacted powders to high temperatures (usually below the melting temperature of the matrix) to create interparticle welds, thus improving the strength of the compact [10]. The sintering process in P/M strengthens a powder metal compact by broadening the bonds among the particles resulting to "'neck-formation"' [11]. Grain growth kinetics is vital in sintering studies. Kinetics basically gives the rate at which the reaction proceeds to the right direction or how fast it produces the desired products [12]. Understanding the process that lead to grain growth is very important since grain size is a major factor in determining many electrical, magnetic, optical and mechanical properties [13].

1.2. Objectives of the Study

The purpose of this research is to determine the effect % alumina on the growth kinetics of copper grains and the hardness of the composites during the early stages of sintering. The kinetic parameters such as the grain growth exponent (n), the activation energy (Q) and the constant of equality (K_o), in the grain growth equation [10]

$$G^n - G_o^n \sum K_o texp\left(-\frac{Q}{RT}\right) \tag{1}$$

where G is the average grain size (diameter) at time t, G_o is the initial grain size, R is the universal gas constant and T is the absolute temperature, will be evaluated.

2. METHODOLOGY

Alumina-reinforced copper-matrix composites (5%wt and 10%wt alumina) were produced by powder metallurgy route. Weighed powders of copper (about 9μm) and alumina (about 1μm), were mixed in a rotary mill with methanol for 24 hours. After that, the powder mixtures were dried and compacted in a hydraulic press at a pressure of 3,000 psi. Next, the samples were sintered at varying temperatures (750, 850, 950°C) in a tube furnace purged with nitrogen gas. The experimental settings used in the study is given in Table I.

After sintering, the samples were cold-mounted, ground and polished and later etched. Photomicrographs of the samples were obtained using the scanning electron microscope

Variables	Settings
%wt Alumina	5, 10
Temperature (°C)	750, 850, 950
Time (mins)	10, 20, 40, 80, 160

Table I. Variable settings used in the study.

(SEM) and surface Morphology Apparatus (SMA). The average grain sizes of copper were measured using lineal analysis. Finally, hardness measurements were performed using the Vickers Hardness Tester. The choice of the hardness test is limited by the small size of the samples. Presence of pores in the samples makes hardness measurements difficult to measure accurately.

3. RESULTS AND DISCUSSION

3.1. Microstructure of sintered Copper-Alumina Composite

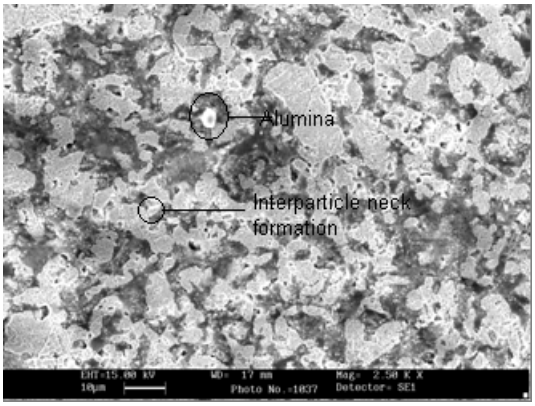
Figure 1 shows the microstructure of samples sintered for 80 minutes at different temperatures (750, 850 and 950°C). Inter-particle neck formation between copper grains can be observed in the micrographs. Etching the polished specimens revealed the copper grain boundaries. Alumina particles can be seen in the micrographs. However, some alumina particles were dislodged during sample preparation. This could be due to the poor adhesion between the particles of alumina and copper grains. The microstructures show porosities and gaps between alumina and copper. This observation is in agreement with a study by Moustafa et. al [3]. They further explained that because of the lack of both wettability and solubility of alumina with copper, the composite is characterized by solid-state sintering between the copper grains which result in a copper skeletal structure. In their study, good adhesion between alumina and copper was achieved when alumina powder was first coated with nickel using an electroless plating process prior to mixing with copper powder.

Coarser grains with lesser % porosity were obtained with higher sintering temperatures. It can be observed from the micrographs that pores form a continuous network. This pore structure characterizes the intermediate sintering stage. In other systems, this continuous pore structure has been observed to collapse into spherical pores in the final stage of sintering. Long sintering times or very high temperatures would be necessary to reach the final stage [10]. In Figure 1(a), some copper grains are larger than those seen in Figures 1(b) and 1(c). This could be due to the large initial size of some of these powders.

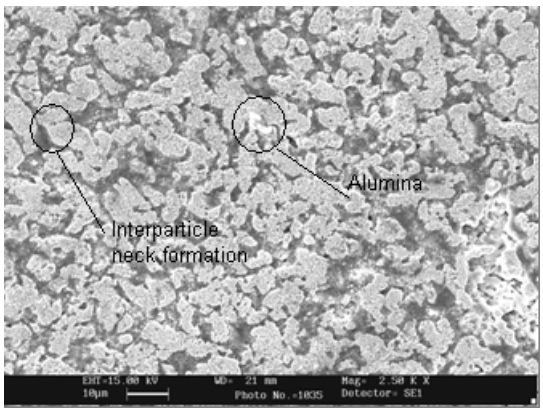
3.2. Grain Growth Kinetics

A plot of copper grain size versus time for two compositions ($Cu{-}5\%\mathrm{Al_2O_3} and Cu{-}10\%\mathrm{Al_2O_3}$) sintered at different temperatures(750, 850 and 950°C)is shown in Figure 2.

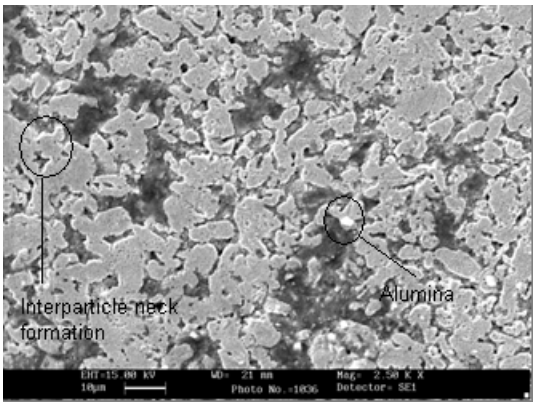
The average copper grain size of the green compact is around 10μm. The grain size increases with increasing temperature and time sintering. For the same temperature and time of sintering, finer grain sizes were obtained for the composite with higher alumina content. This could be due to the decrease in Cu/Cu contact with increasing alumina content [3]. By taking



(a) 750°C, % porosity = 28.81



(b) 850°C, % porosity = 25.54



(c) 950950°C, % porosity = 23.92

Figure 1. SEM micrograph of Cu-10%Al_2O_3 composite sintered for 80 minutes

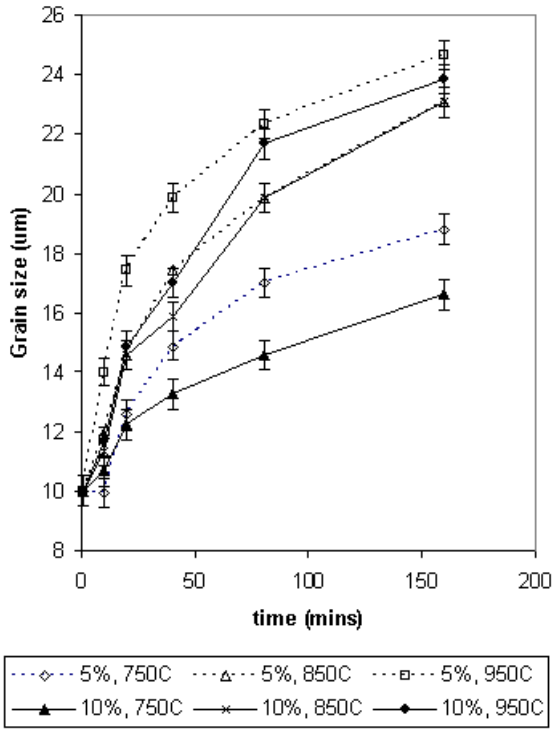


Figure 2. Plot of copper grain size vs. sintering time for two compositions (5% and 10% alumina) at different temperatures (750, 850 and 950°C).

the logarithm of both sides, Equation (1) becomes

$$log(G^n - G_0^n) = logK_0 + \log t - \frac{0.434Q}{RT} \tag{2}$$

Consider a constant temperature (T), then let the G=G1 at t=t1 and G=G2 at t=t2. Substituting these values into Equation (2) gives

$$log(G_1^n - G_0^n) = logK_0 + logt_1 - \frac{0.434Q}{RT} \tag{3}$$

$$log(G_2^n - G_0^n) = logK_0 + logt_2 - \frac{0.434Q}{RT} \tag{4}$$

Subtracting Equations (3) and (4) yields

$$\log\left(\frac{G_1^n - G_0^n}{G_2^n - G_0^n}\right) = \log\left(\frac{t_1}{t_2}\right) \tag{5}$$

where G_1 and G_2 are the grain sizes of Cu at time t_1 and t_2 respectively, and G_0 is the initial grain size. Equation (5) can be simplified to

$$\left(\frac{G_1^n - G_0^n}{G_2^n - G_0^n}\right) = \left(\frac{t_1}{t_2}\right) \tag{6}$$

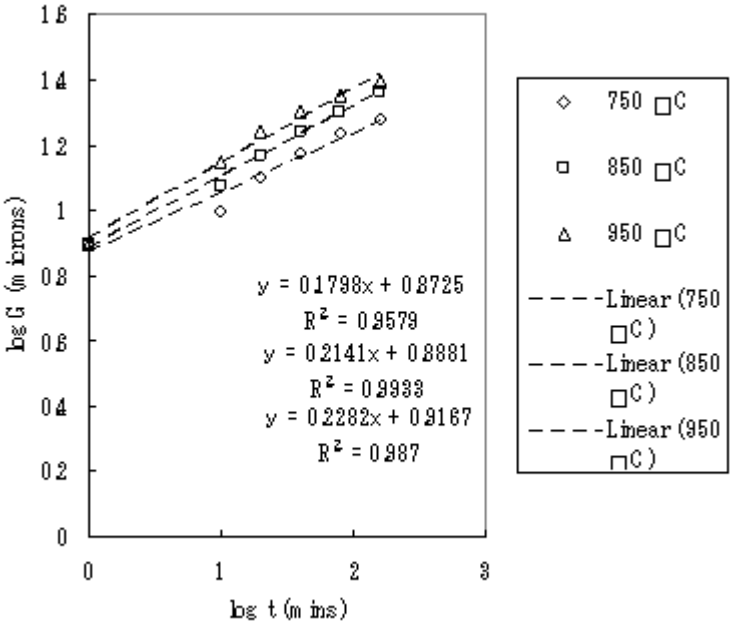


Figure 3. $\log G$ versus $\log t$ for copper-5% alumina.

In order to determine the grain growth exponent n, first, $\log G$ versus $\log t$ plots (Figures 3 and 4) were constructed. From the equation of the lines, the values of G_1 and G_2 corresponding to times t_1 and t_2 respectively were calculated. Then the values were plugged into Equation (6) and n was computed by iterative method using MS Excel. The values of the grain growth exponent n were determined to be equal to 4.55 ± 0.34 for copper-5% alumina and 4.89 ± 0.91 for copper-10% alumina composite (Table II). A higher n value means a lower rate of growth of copper grains. Based on the results of Table II, the grain growth exponents at 750°Cdiffer quite appreciably and are higher than those obtained at 850 and 950°C. The difference in the growth exponent could possibly be due to a shift in the material transport mechanism as temperature is increased. The dominant transport mechanisms at low sintering temperatures requiring lesser energy for activation are surface diffusion and grain boundary diffusion. At high temperatures the dominant mechanism is volume diffusion [13]. Each of these mechanisms would have a different time and temperature dependence. More studies would be needed to investigate this possible difference in growth mechanisms. The effect of increasing % alumina on the growth exponent is more pronounced at 750°C. At this temperature, the increase in % alumina from 5 to 10% resulted to an increase in n from 5.05 to 6.25. At higher temperatures of 850 and 950°C, n is hardly affected by the increase in % alumina. A possible explanation is that at 750°C, surface diffusion and grain boundary diffusion are the dominant transport mechanisms, and that the presence of more alumina particles at the copper-copper interface hinders to a greater extent material transport. It is therefore recommended that sintering be

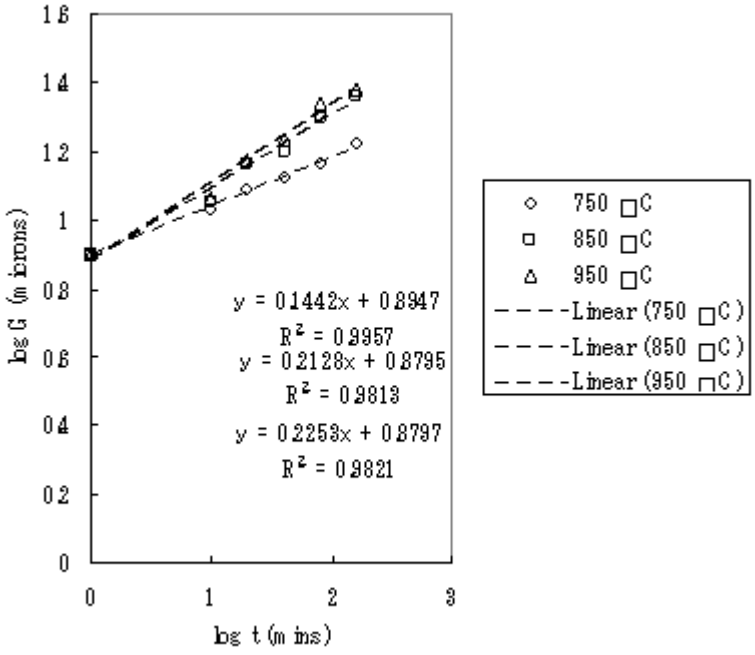


Figure 4. $\log G$ versus $\log t$ for copper-10% alumina.

	Cu-5% Al_2O_3	Cu-10% Al_2O_3
Temp, (°C)	n	n
750°	5.05	6.25
850°	4.34	4.25
950°	4.25	4.17
AVE	4.55	4.89
AVEDEV	0.34	0.91

Table II. Calculated n values.

done at temperatures higher than 850°C, where the dominant transport mechanism is possibly volume diffusion, thereby avoiding or minimizing the hindering effects of alumina.

Equation (1) can be rewritten in the form:

$$\log\left(\frac{G^n - G_0^n}{t}\right) \sum -0.434\frac{Q1}{RT} + logK_o \tag{7}$$

A plot of $\log\left(\frac{G^n - G_o^n}{t}\right)$ vs. $\frac{1}{T}$ was constructed (Figure 5 in order to determine the activation energy for copper grain growth. In this plot different n values are used for Cu-5%Al_2O_3 (n=4.55) and Cu-10% Al_2O_3 (n=4.89). Calculated values of K_0 and Q are summarized in

% Alumina	Q, KJ/mole	K_o
5	84.12	7.2×10^7
10	100.12	7.6×10^8

Table III. Computed values of Q and Ko.

Table III. The activation energy determined from experiment increased with the amount of the ceramic phase from 84.12 KJ/mol to 100.12 KJ/mol for 5 and 10 wt% Al_2O_3 respectively. A similar observation was made by other researchers [14] on the Al/AlN system. They also found that the increase in the ceramic phase affects the diffusion mechanisms. It is possible that the observed difference in the activation energy may be related to the effect on the diffusion mechanisms of increasing the ceramic phase content. By using the constants calculated, a generalized grain growth equation for the composite was obtained. These equations predict the grain size of copper given the sintering time and temperature. For the Cu-5% Al_2O_3 the grain growth equation is given by:

$$G^4.55 - G_o^{4.55} = 7.2 \times 10^7 t \exp\left(-\frac{84.12}{RT}\right) \tag{8}$$

for the $Cu - 10\%Al_2O_3$ system, the grain growth equation is:

$$G^4.89 - G_o^{4.89} = 7.6 \times 10^8 t \exp\left(-\frac{100.12}{RT}\right) \tag{9}$$

3.3. Effect of % Alumina and temperature on Composite Hardness

Figure 6 shows the Vicker's hardness of $Cu - Al_2O_3$ composite as a function of %alumina and temperature of sintering. The hardness was observed to increase with increase in %alumina and sintering temperature. The obtained hardness values of the sintered composites are higher than that of pure copper which is around VHN 37.6 [16].

For alumina the Vickers hardness number is usually above 1200 [16]. For a two component composite, assuming the Law of Mixtures applies, the average hardness of a composite may be estimated using the relation [8]

$$H_c = H_m f_m + H_r f_r \tag{10}$$

where H_c = composite hardness,
H_m, H_r = hardness of the matrix and the reinforcing particle respectively,
F_m, f_r = volume fraction of the matrix and the reinforcing particle respectively. Using equation 7 to estimate the average hardness of copper-10%alumina composite and assuming that the sintered composite contains no porosities, Vickers hardness number close to 300 can be obtained. Taking into account the presence of porosities, and assuming a porosity of say 20%, the hardness would still be greater than VHN 200. However, the experimental hardness values only reached a maximum of about VHN 77. One reason for this is that full densification was not achieved since sintering was not carried out until the final stage. Another is that composite hardness may depend on other factors such as matrix and pore structure, distribution and ceramic phase, strength of the copper/alumina inter-phase, among others. Further studies

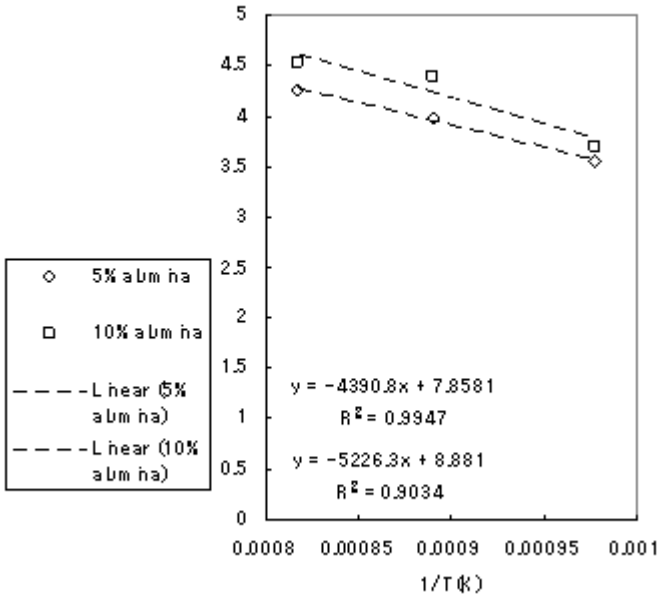


Figure 5. $\frac{1}{T}$ versus $\log\left(\frac{G^n - G_o^n}{t}\right)$ for Cu-5% Al_2O_3

would be needed investigate the effect of these factors. The effect of composite hardness of increasing the temperature from 850 to 950°Cis greater than increasing temperature from 750°Cto 850°C. This could be due to the exponential dependence of the sintering process on temperature [10], [14]. Since the rate of copper agglomeration and pore elimination would be faster at higher temperatures, higher hardness of the compact could be attained at a shorter time.

4. CONCLUSION

The grain growth kinetics of copper in a copper-alumina metal-matrix composite during the early stages of sintering was studied. For compositions considered, the following relations were obtained:

$$Cu - 5\%Al_2O_3 G^4.55 - G_o^{4.55} = 7.2 \times 10^7 t \exp\left(-\frac{84.12}{RT}\right) Cu - 10\%Al_2O_3$$

$$G^4.89 - G_o^{4.89} = 7.6 \times 10\% t \exp\left(-\frac{100.12}{RT}\right)$$

Higher growth rates were obtained with higher sintering temperatures and lower % alumina. The effect of % alumina in decreasing copper growth rate is more pronounced at lower tempera-

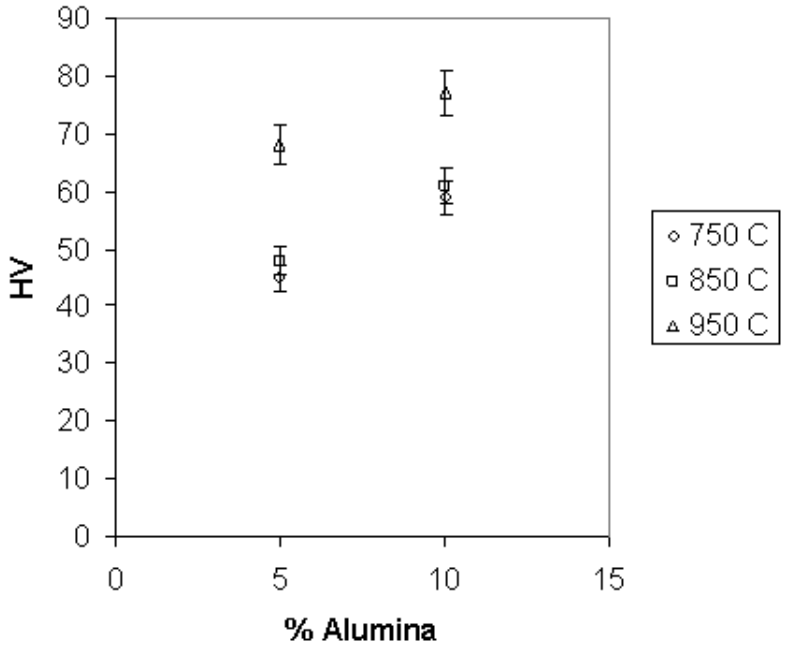


Figure 6. Hardness of composite sintered at different temperatures for 160minutes.

tures. Increased in % alumina and sintering temperature resulted to higher composite hardness.

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