Development of Cu Reinforced SiC Particulate Composites

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Abstract. This paper presents the results of Cu-SiCp composites developed by powder metallurgy route and an attempt has been made to make a comparison between the composites developed by using unmilled Cu powder and milled Cu powder. SiC particles as reinforcement was blended with unmilled and as-milled Cu powder with reinforcement contents of 10, 20, 30, 40 vol. % by powder metallurgy route. The mechanical properties of pure Cu and the composites developed were studied after sintering at 900°C for 1 h. Density of the sintered composites were found out based on the Archimedes’ principle. X-ray diffraction of all the composites was done in order to determine the various phases in the composites. Scanning electron microscopy (SEM) and EDS (electron diffraction x-ray spectroscopy) was carried out for the microstructural analysis of the composites. Vickers microhardness tester was used to find out the hardness of the samples. Wear properties of the developed composites were also studied.

1. Introduction
Composites materials offer several applications in the field of aerospace, automotive and ship building industry as it has different advantages over other conventional metals. Metal matrix composites (MMCs) combine both metallic properties such as toughness and ductility and ceramic properties such as modulus and high strength. They possess high shear strength and provide service at high temperatures. MMCs offer the possibility to tailor the properties of a metal by adding an appropriate reinforcement to develop materials having superior mechanical properties. Copper has high thermal conductivity and used as a structural material for cooling. In order to increase its high temperature properties different reinforcements are being used. The objective is to develop Cu based metal matrix composites by mechanical alloying (MA) route having high strength and microstructural stability at elevated temperatures [1-4].

Metal matrix composites are becoming an important structural material in engineering application. These composites find application in the area of aerospace, aircraft and automotive industries because of their excellent mechanical properties such as high specific strength, improved wear resistance and high specific modulus. Apart from this they also have very good thermophysical properties, such as low coefficient of thermal expansion and high thermal conductivity. Recently, metal-ceramic composites with high ceramic contents have become an area of focus for thermal management applications. Copper is widely used in thermal and electronic applications, due to the high electrical (5.96×10^7 S/m) and thermal conductivity (401 W/m K), good corrosion resistance and high melting point (1357.77 K). However, the low mechanical property of Cu at both room and high temperatures limits the extensive application of pure Cu. Discontinuously reinforced metal matrix composites are a class of materials that exhibit superior properties. In the present study, the focus was
towards development of Cu based metal matrix composites with SiCp reinforcement by powder metallurgy. It is well known that the particle reinforced metal matrix composites have excellent mechanical properties and light weight due to the addition of the high strength and high modulus particles like TiC, Al$_2$O$_3$, SiC, TiB$_2$ etc. Silicon carbide (SiC) is widely studied for its high temperature stability, high thermal conductivity, high hardness and high heat capacity. Its melting point is above 2600°C, and the thermal conductivity is 16.7 W/m K. These properties present SiC the possibility as potential additive to copper based metal matrix composites [5-8].

2. Experimental

Pure Cu powder procured form Loba Chemie India and SiC powder from Search Chem having 99% purity was used for the current research work. Initially Cu was milled for 20 h in a Fritsch P-5 planetary ball mill using hardened chrome steel vials and balls in order to synthesize nanostructured elemental Cu. Green pellets of unmilled Cu and as-milled Cu with different volume fractions of SiCp (10, 20, 30 and 40%) are formed by blending the constituents followed by cold compaction of the samples in an uniaxial compaction machine under a load of 665MPa. Sintering of the samples were done at 900°C for 1 h in Ar atmosphere. Vickers microhardness test was carried out over all the samples to determine the hardness. Densities of the prepared composites were also determined by Archimedes principle. Optical micrographs of the samples were taken using Carl Zeiss microscopes. A JEOL JSM-6480LV scanning electron microscope (SEM) equipped with an INCA PentaFET-x3 x-ray microanalysis system with a high-angle ultra-thin window detector and a 30 mm$^2$ Si (Li) crystal was used for microstructural characterization of the samples. A JEM - 2100 JEOL high resolution transmission electron microscope (HRTEM) with point to point resolution 0.194 nm was used for analysing the milled powder. A Phillips Pananalytical PW 3040/00 x-ray diffraction (XRD) was also used to characterize the milled Cu-powder and the various phases in the Cu-SiCp composites. Cu Kα radiation having $\lambda =1.5409$ Å was used for all x-ray diffraction analysis. A DUCOM ball on plate tribometer was used for study the wear characteristics of all the composites. Wear test were performed on 15 mm diameter samples of the various Cu-SiCp composites in a ball-on-plate wear tribometer having a diamond indenter under ambient environment. Dry sliding wear tests were performed on all the samples. A normal load of 20 N was applied for a period of 10 minutes.

3. Result and Discussion

The results for HRTEM analysis of 20 h milled powder is shown in figure 1(a), which indicates that the powder has been reduced to nanometric dimension after high energy milling for 20 h. Figure 1(a) is the bright field TEM image of the 20 h milled Cu sample. The SAD pattern in figure 1(b) shows complete ring pattern which suggest that the 20 h milled Cu powder has nanometric dimension. The ring patterns could be indexed to the various crystallographic planes of Cu.

![Figure 1](image_url)

Figure 1. (a) HRTEM analysis and (b) SAD pattern of 20 h milled Cu
The x-ray diffraction of Cu powder milled for various durations of time are shown in figure 2(a). The various peaks in the x-ray diffraction pattern could be indexed to the different crystallographic planes of Cu. No other peaks could be detected in the x-ray pattern suggesting that there is no contamination from the milling media. Voigt’s method was used for calculating the crystallite size of the milled Cu powder. After 20 h of milling the crystallite size of Cu was found to be 18 nm (figure 2(c)). There is a gradual drop in the crystallite size with milling time. From figure 2(c) it is evident that Cu could be reduced to nanometric dimension within 5 h of milling. Cold welding was also evident between 5 to 10 h of milling which led to the increase in crystallite size. There is a gradual increase in the lattice strain due to severe deformation of the milled powder and strain reaches a maximum value after 20 h of milling when the crystallite size is smallest (figure 2(d)). Lattice parameter of milled Cu was also determined using the Nelson-Riley function. The lattice parameter of Cu shows a slight increase during milling for 20 h [9-13].

Figure 2. (a, b) X -ray diffraction plots of Cu milled for various periods of time and variation of (c) crystallite size (d) r.m.s. strain and (e) lattice parameter of Cu with milling time.
The optical micrographs of various Cu-SiCp composites in figure 3 (a-d) shows that SiCp is uniformly distributed in the Cu matrix. The SiCp are found to be less than 100 µm in size. The particles are discontinuously dispersed in the Cu matrix. Figure 4 is the SEM image of the various Cu-SiC composites developed using for different vol. % of SiC particle reinforcement. From the microstructure it is clear that the SiC particulates are homogenously distributed over the Cu matrix.

Figure 3. (a-d) Optical micrographs of unmilled Cu- SiC composites (10, 20, 30 and 40 vol. % of SiC).

Figure 4. SEM images of unmilled Cu-SiC composites (a) 10 vol. %SiCp (b)20 vol. %SiCp(c) 30 vol. % SiCp and (d) 40 vol. %SiCp.
The EDS analysis in figure 5 suggests that a dark region in the SEM image corresponds to the SiC particles and light coloured region corresponds to the Cu matrix. The dark coloured SiCp are surrounded by the light coloured Cu rich region. EDX analysis shows the presence of oxygen in the sintered sample. This is due to the undesirable oxygen present during sintering in the argon atmosphere. The x-ray diffraction analysis shown in figure 7 confirmed the formation of Cu$_2$O phase.

The figure6(a) shows the density plot for unmilled Cu SiC composites for different vol. % of reinforcement. The density plots show the gradual decrease in relative density with increase in vol. % of SiCp reinforcement in Cu matrix. The hardness plot shows the comparison between the unmilled Cu-SiCp composites and as milled Cu-SiCp composites for different vol. % of reinforcement. The hardness increases with the increase in vol. % of reinforcement. It can be seen from the figure 6(b) that as milled Cu-SiCp composites shows better hardness than unmilled Cu-SiCp composites. Milled Cu
due to its smaller particle size leads to better sinterability and as a result gives higher hardness of the composites [14-16].

![XRD plots for unmilled Cu-SiCp composites.](image)

**Figure 7.** XRD plots for unmilled Cu-SiCp composites.

The figure 7 shows the x-ray diffraction and for unmilled Cu SiC composites for different vol. % of reinforcement. The higher content of SiCp in the composites leads to more intense x-ray diffraction peak corresponding to SiC. The x-ray diffraction shows peaks for Cu and SiC confirming the matrix and reinforcement material. The peaks confirm some formation of copper oxide (Cu₂O) layer in the composites.
Figure 8. (a) Wear Characteristic of unmilled Cu-SiC composites. SEM images of the wear track of (b) unmilled Cu (c) unmilled Cu-40 vol. % SiCp composite. (d-e) High magnification SEM images of the wear track of unmilled Cu-40 vol. % SiCp composite.

Figure 8 (a) shows the wear characteristic for unmilled Cu-SiC composites. The plot shows that the wear resistance of the Cu-SiCp composites are higher than native Cu. It can also be observed that as the vol. % of the SiC particles is increased the wear resistance of the Cu-SiCp is increased. Cu-40 vol. % SiCp shows the least wear depth (figure 8(a)). The increase in hardness due to the addition of higher vol. % of hard SiCp phase leads to the decrease in wear depth. The drastic reduction in wear rate may be attributed to the enhancement in hardness of the composite reinforced by SiC particles and greater reduction of direct load contact between the Cu-SiCp composite surface and ball in comparison with the pure Cu due to the load bearing component action of hard SiC particles. Figure 8(b) shows the SEM images for wear track of the pure Cu and unmilled Cu-40 vol. % SiCp composite. From the images it is evident that Cu-40 vol. % SiC composites show less width of wear track as compared to pure Cu [17-20].

Figure 8(a) shows the wear behaviour of pure Cu and Cu-SiCp composites. It was found that the hardness of Cu-SiCp composites increased with the addition of SiCp due to the presence of the harder ceramic particles of SiC. The hard SiC particles support the stresses between the contact surfaces preventing large plastic deformations and abrasions. This reduces the amount of worn material. The Cu-SiCp composites containing the hard SiC particles show better wear resistance due to the formation of a tribolayer at the interface. During wear rapid removal and regeneration of the tribolayer at the interface takes place. The interface temperature also increases during the wear test and this causes oxidation of the sample. The increase of interface temperature during the wear test significantly enhances the loss of mass by oxidation, matrix softening, cracking and delamination wear. In the initial stages of wear, fine particles are generated from the two surfaces in contact by the micro-cutting and rubbing effects. Sharp SiC particle edges protrude out of the Cu-SiCp composite surface. The wear particles entrapped by the contacting surfaces undergo a mechanical mixing process, which is very similar to the mechanical alloying (MA) process. During milling some original particles fracture further and expose atomically clean surfaces that come in contact with each other. With further mixing, cold welding and particle fracturing takes place which leads to a steady state particle size distribution in the mixture. Few fine particles are dislodged from the interface whereas some agglomerate and pile up. Due to the pressing and flattening effect of the normal load and frictional forces a compact mechanically mixed layer on the stationary and relatively soft composite surface is formed. This layer acts as a protective layer for the composite. It should be noted that due to the fine size of the debris particles and high temperature at the contact the metal components like Cu can be oxidized very rapidly [21-24].
Figure 9. (a-d) Optical micrographs of as-milled Cu-SiCp composites (10, 20, 30 and 40 vol% of SiCp) (e, f) Higher magnification optical micrographs of as-milled Cu-40 vol. % SiCp composites.
Figure 10. SEM image of as-milled Cu-SiCp composites (a) 10 vol. %SiCp (b) 20 vol. %SiCp (c) 30 vol. %SiCp and (d) 40 vol. %SiCp (e, f) Higher magnification SEM images of as-milled Cu-40 vol. %SiCp composites. The inset image in (e) shows the EDX analysis of SiC particle.

Figure 9 shows optical micrographs for as-milled Cu-SiCp composites for different vol. % of SiCp. From the micrographs it is evident that SiC particles are homogeneously distributed all over the matrix. The high magnification optical micrographs of as-milled Cu-40 vol. %SiCp composites in figure 9 (e, f) shows the interface between the SiC particle and the Cu matrix. Figure 10 shows SEM for as-milled Cu-SiCp composites for different vol. % of reinforcement respectively. The SEM images of the composites also show homogeneous dispersion of reinforcement over the Cu matrix. The scanning electron micrographs given in Figure 10 shows the typical microstructural features of a composite. In these micrographs of the various Cu-SiCp composites a range of SiC particulate sizes could be seen. Good interfacial integrity between the SiCp and the Cu matrix could also be observed. High magnification SEM images of as-milled Cu-40 vol. % SiCp composites in figure 10 (e, f) shows the interface between the SiC particle and the Cu matrix. EDX analysis inset in figure 10 (e) confirms that the dark particles are SiC. The SiC particles are embedded in the Cu matrix. The interface between the reinforcement and the matrix plays a crucial role in determining the mechanical properties of the composites. The SEM images the Cu-SiC interface suggests that the bonding between the Cu matrix and the SiC particles is very strong.

Figure 11 shows the density plots for as-milled Cu-SiCp composites for different vol. % of reinforcement. The relative density gradually decreases with the increase in the content of SiC as the incorporation of hard and brittle material in soft Cu matrix which provides void in the matrix. From the plot it is evident that as-milled Cu-SiCp composites shows better densifications values as compared to unmilled Cu-SiCp composites. Figure 12 shows the XRD plots for as-milled Cu-SiCp composites for different vol. % of SiC particles. Peak corresponding to Cu$_2$O could be detected in the x-ray diffraction plot.
Figure 13. (a) Wear Characteristic for as-milled Cu-SiCp composites. SEM images of the wear track of (b) as-milled Cu sample (c) as-milled Cu-40 vol. %SiCp sample (d, e) High magnification SEM images of the wear track of as-milled Cu-40 vol. %SiCp sample. Inset image in (e) shows the edge of the wear track of as-milled Cu-40 vol. %SiCp sample.

It is evident from figure 13(a) that there is a drastic reduction in wear rate with the addition of SiC particles to the Cu matrix. The dispersion of the SiC particles, as a hard ceramic phase in the Cu matrix, improves the wear resistance significantly. This can be attributed to the enhanced hardness of the composite reinforced by the SiC particles. It is known that improvement in hardness enhances wear resistance. The enhancement in the wear resistance of the composites can also be attributed to the good bonding between the Cu and the SiC particles. Bonding between the matrix and the reinforcement is known to play an important role in the wear resistance. Reduction of direct load at the contact between the Cu-SiCp composite surface and the ball due to load bearing component action of the hard SiC particles as compared to that of pure Cu also enhances the wear resistance of the Cu-SiCp composites.
To evaluate the wear resistance the as-milled Cu-SiCp composites were compared with pure Cu. It has been found that as-milled Cu-SiCp composites exhibits better wear behaviour in comparison to pure Cu. The enhancement of wear resistance is possibly due to the Orowan strengthening mechanism because of the fine dispersion of the SiC particles in the Cu matrix. The wear was found to be due to the combination of abrasion and delamination. From figure 6(b) it is evident that there is an enhancement of micro hardness due to the dispersion of SiC particles in the Cu matrix and this consequently improves the wear resistance of the composite. Figure 13 shows wear characteristics for as-milled Cu-SiCp composites. The plot between wear depth and time in figure 13(a) shows that as-milled Cu- 40 vol. % SiCp composites shows the lowest wear depth leading to higher wear resistance. Figure 13(b) shows the SEM images of wear tracks for as-milled Cu pellet and as-milled Cu- 40 vol.% SiCp reinforced composites [21-24].

![Figure 13(a)](image13a.png)  ![Figure 13(b)](image13b.png)

**Figure 13.** (a-b) SEM images of wear tracks for as-milled Cu pellet and as-milled Cu- 40 vol.% SiCp reinforced composites.

![Figure 14(a)](image14a.png)  ![Figure 14(b)](image14b.png)  ![Figure 14(c)](image14c.png)  ![Figure 14(d)](image14d.png)  ![Figure 14(e)](image14e.png)  ![Figure 14(f)](image14f.png)  ![Figure 14(g)](image14g.png)

**Figure 14.** (a-b) SEM images of wear debris from as-milled Cu-40 vol. %SiCp composite. (c) EDX analysis of the wear debris. (d) SEM image of the wear debris selected for elemental mapping. Elemental map of (e) Cu (f) Si (g) O. (h)

Figure 14 (a, b) are the SEM images of the wear debris from as-milled Cu-40 vol. %SiCp composite. The EDX analysis of the wear debris in figure 14(c) shows mainly the presence of Cu and very small amount of Si. This suggests that the wear debris consists mainly of Cu and has very small amount of SiC in it. The elemental map of Cu and Si in the selected area shown in the SEM image in figure 14(d) also suggest that the wear debris mainly consists of Cu and there is only a very small amount of SiC in it. The oxygen in the wear debris is possibly due to the oxidation of the sample by the unavoidable oxygen during sintering. Oxidation of the wear debris could also take place during the wear test [25-28].
4. Conclusion

1. Milling of elemental Cu has led to the formation of nanostructured Cu. There has been no trace of contamination from milling media. Oxidation of Cu was also not found during milling.

2. In all the composites developed a homogenous distribution of the SiCp reinforcement in the Cu matrix was observed.

3. As-milled Cu-SiCp composites show better densification than unmilled Cu-SiCp composites.

4. The hardness of the Cu-SiCp composite increases with the increase in the content of SiC particles. As-milled Cu-SiCp composites showed higher hardness as compared to unmilled Cu-SiCp composites.

5. Cu-SiCp composites containing higher vol. % of the SiCp shows better wear resistance. All the Cu-SiCp composites developed show better wear resistance than pure Cu.

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