INFLUENCE OF BORON CARBIDE ADDITION ON PARTICLE SIZE OF COPPER ZINC ALLOYS SYNTHESIZED BY POWDER METALLURGY

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Abstract. Material systems with the combination of metals and non-metals forming an alloy systems has numerous advantages when compared with the monolithic materials. Synthesizing such materials systems can easily be done by many solid state processing methods. Copper Zinc (Cu-Zn) forms a ductile material system finding its applications in various conductive and tribological applications. Nano composites finds lot more applications due to the high specific area occupied by the particles. Focus of the current project is on the study of influence of Boron Carbide (B₄C) powders addition into the Cu-Zn matrix while synthesizing them through high energy ball milling. B₄C powders are added to the matrix at 10 % by volume. Particle size of the powder are determined by Scherer and Williamson-Hall synthesis methods after characterizing the milled powders by X-Ray diffraction (XRD). As the B₄C powders are brittle, maximum volume fraction of these powders are expected to influence particle size of Cu-Zn alloy powders. Powder morphology is analysed by scanning electron microscopy (SEM). Influence of B₄C powder particles upon grain size of Cu-Zn alloy powder blends was very minimum due to the tendency of particles to get saturated with respect to particle size after repeated milling.

Keywords: Ball milling, XRD, SEM, particle size

1. INTRODUCTION

Metal matrix composites (MMCs) are constitutive materials comprising of more than one material whose properties can be customized as per the requirements by making suitable modifications in the content of constituents [1]. MMCs can be claimed to be reliable only when there is a reasonable return of performance for the cost incurred in processing of the material. Tailorable properties are readily achieved only by the use of such composite materials and it has been in the limelight for the past few decades [2, 3]. Copper, Aluminium and Magnesium are the most commonly used base metals as far as MMCs are concerned. Copper is majorly used due to its meritorious characteristics like better electrical and thermal conductivity and enhanced ductility [4]. Boron Carbide (B₄C) is one among the hardest...
material and ranks between 9 and 10 in Mohr’s scale of hardness. It is characterized by better chemical and thermal stability [5]. As boron carbide possess inherent hardness and better mechanical properties, it could be positively used in various punitive industry applications including wear resistant components, vehicles and body armors in military vehicles and elevated temperature nozzles. Usage of boron carbide is supplemented by many other better characteristics such as low specific gravity and elevated melting point [6-9].

The technology of manufacturing MMCs is in competition with other modern material technologies, for example powder metallurgy [10]. Powder metallurgy (P/M) technique is a solid state processing method of composite materials mainly used to manufacture the particulate reinforced composites [11]. Various classical components with intricate shapes and medium sizes can be fabricated through this technique easily [12-14]. Common methodology of powder metallurgy involves three steps: first is blending and synthesis of precursor powder particles known as mechanical alloying, second is to densify the alloyed powders by applying pressure over them when placed inside a closed die called compaction and the third is to consolidate them by reducing their density further through heating called sintering [15]. Mechanical alloying is carried out by ball milling, densification process in a die and plunger and sintering is done in a muffle furnace. PM technique renders numerous merits when compared to the typical material processing methods including accommodation of shape complexity, better dimensional stability, less energy consumption during manufacturing and optimum material usage [16, 20-22]. As the PM manufactured components were greatly influenced by the compaction and densification, particle size of the precursor powders play a salient role in the powders compressibility [17-19]. Due to this fact, the mechanical alloying of the powder particles were carried out using a high energy ball mill. Unlike normal particle reduction methods such as pulverization, ball milling utilizes the enormous energy from the steel balls generated due to their impacts with the powder particles which results in a large scale forging thus minimizing the powder particle size [23, 24]. Here XRD is utilized to assess the various constituents present within the milled powders with the help of the diffraction spectra obtained by passing X-rays through them and could also be used in determination of particle size based on the peak properties. SEM is a widely used microscopic imaging method that renders a high quality image through the sputtering of electrons that were focused over the surface to be examined and is used to reveals the internal characteristics of blend powders in micro level [25].

In the current work copper and zinc powders were blended with various weight fractions of boron carbide powders and were mechanically alloyed for various milling durations. Influence of addition of a hard ceramic particle in a ductile-ductile system is analyzed with respect to the particle size of the blended composite powders. After milling, the particle size of the milled powders was calculated by XRD and the dominant process responsible for the variation of particle size was determined by SEM.

2. EXPERIMENTAL DATA

2.1. Materials
Copper, Zinc and Boron Carbide are purchased from Coimbatore metal ltd, Coimbatore, with standard particle size of 325 mesh. The manufacturing of Copper, Zinc, Boron Carbide composites by means of mechanical alloying in a high energy ball mill. Copper is mixed with the Zinc (Cu - 90%, Zn -10%), then Copper-Zinc is reinforced with Boron Carbide in 10 % by weight.

Table 1. Material properties

| PROPERTIES             | COPPER | ZINC | BORON CARBIDE |
|------------------------|--------|------|---------------|
| Poisson ratio          | 0.34   | 0.25 | 0.20          |
| Young's modulus (GPa)  | 120    | 108  | 450           |
| Shear modulus (GPa)    | 48     | 43   | 180           |
| Melting point (°C) | 1085 | 420 | 2350 |
|-------------------|------|-----|------|
| Mohr’s hardness    | 9.0  | 2.5 | 3.0  |

The materials are added to the vial of ball milling setup with the ratio between balls and powders (BPR) as 10:1. Toluene is used as the process control agent (PCA) as per the requirement. The speed ratio of sun and the planet wheels, to which the vial is attached, were set as 1:4. The planetary gears rotate in self-contradicting direction within a regular interval of time of 15 seconds between each change in rotation direction. The speed of rotation of the vials were maintained at 120 rpm [26]. These process standards were maintained for various milling durations of 10, 20 and 30 hours. In order to dissipate the heat from the vials generated due to friction, they were set to be idle for 10 minutes after a continuous run for 75 minutes.

2.2. Characterization by XRD and SEM

The main objective of the XRD technique is to characterize the powders for their particle size based on the peaks obtained. In the current work a total of ten samples were characterized by XRD, which were collected at various milling time periods, like 10, 20 and 30 hours. Usual procedures were adopted to carry out XRD analysis. About 60 gm of powders were taken from every sample and evaluated. The powders were closely packed in a glass slit of size 12 mm × 12 mm × 2 mm. The measurements of XRD were carried out using Schimadu XRD machine with Kα value of 0.154 nm.

The SEM produces images from the samples through scanning the specimen with the support of a focused electron beam. The milled powders were evaluated using a FE-SEM model Carl Zeiss Microscope to identify the prevailing particle size variation phenomenon after each milling cycle. Current study helps to converge to a result that the particle size cannot be downsized beyond steady state.

2.3. Analysis of particle size by Williamson-Hall synthesis

The values obtained from the XRD analyses were used to calculate the particle size and strain induced on the surface of the powders. The calculations were based on the Williamson-Hall equation, as given in Equation (1).

\[
\beta \cos \theta = \frac{k\lambda}{t} + 4\varepsilon \sin \theta
\]  

where \( k \) is the shape factor (value = 0.5), \( \lambda \) is the wavelength of the X-rays (value 0.154 nm). A plot between \( \beta \cos \theta \) (y-axis) and \( 4\sin \theta \) (x-axis) would render a straight-line equation in which the slope (m) could be equated to the lattice strain directly and the intercept (c) could be used to calculate the particle size (t) by using the following relation: \( c = k\lambda/t \).

2.4. Analysis of particle size by Scherer Equation

Similar to the Williamson-Hall synthesis, the particle size (t) of the powders were evaluated from the X-ray peak broadening data in orthogonal direction to the powder surface by using Scherer equation. It is given by:

\[
t = \frac{0.9\lambda}{\beta \cos \theta}
\]  

where \( \theta \) is the Bragg angle, \( \lambda \) is the wavelength of X-ray radiation (1.54 Å), and \( \beta \) is the full width at half maximum of the considered X-ray peak (FWHM) in radians. Since Scherer’s equation gives only the particle size of the powder and neglects the lattice strain induced during variation of particle size, it is less sensitive when compared with other synthesis equations [27].
3. RESULTS AND DISCUSSION

3.1. Particle Size reduction
Generally copper is a ductile metal while zinc is partially brittle in nature up to certain temperature. When these elements were combined to form an alloy system they were expected to behave more like a brittle system. Due to X-ray peak broadening there is a raise in powder deformation as the milling hours increase thereby increasing the strain induced on the surface responsible for the reduction of particle size of the powders. Purchased copper and zinc particles were observed to have micron sized particles which got reduced directly to nano scale after a long milling cycle of 10 hours. This is due to the fact that the powder particles were imparted with defects in larger magnitudes over their surface which shifted the particle size to even lower values. From the figures, it could be observed that the X-ray peaks experienced a mild shift towards their right which was solely because of the homogenous suspension of zinc atoms into the abundant copper matrix. Yet this phenomenon has to be verified by taking XRD of purchased zinc powder. When the unreinforced copper-zinc powders were milled for various durations, it could be observed that there is a continuous reduction in particle size due to the presence of partially brittle zinc. Minimum particle size was obtained during the highest duration of milling of 30 hours. Figure 1 shows the XRD peaks of copper-zinc alloys for various milling durations.

![Figure 1 XRD peaks of Cu-Zn alloy for various milling duration (h) – a) 10h b) 20h c) 30h](image)

On contrary, when 10 % B<sub>4</sub>C particles were reinforced to Cu-Zn system, the behaviour of composite powders was slightly different. The particle size of the powders decrease at 30 hours after increasing during 20 hours of milling. This could be attributed to the higher hardness of the B<sub>4</sub>C powders which could have acted as additional milling agent for reducing the powder particle size but due to higher amount of surface defects the particles developed a tendency to
stick to each other thereby increasing the average particle size of the composite powders. This is the reason for higher particle size of B₄C reinforced composites when compared with unreinforced alloy [27]. Yet the tendency of particles to undergo further reduction could be studied by possibly increasing the volume fraction of B₄C powders. Table 2 shows the variation of particle sizes after various milling durations calculated by Williamson-Hall synthesis and Scherer’s equation.

| Milling duration (hours) | Particle size by Williamson-Hall equation (nm) | Particle size by Scherer’s equation (nm) |
|--------------------------|-----------------------------------------------|-----------------------------------------|
|                          | Cu-Zn                                         | Cu-Zn + 10% B₄C                        | Cu-Zn                                         | Cu-Zn + 10% B₄C                        |
|                          | 14.16                                         | 27.75                                  | 24                                            | 17.5                                   |
|                          | 13.87                                         | 38.54                                  | 29.12                                         | 19.58                                  |
|                          | 9.72                                          | 31.53                                  | 22.35                                         | 19.14                                  |

Figure 2 shows the XRD peaks of Cu-Zn alloys reinforced with 10% B₄C composites milled for various milling durations.

3.2. SEM analysis
From the SEM micrographs the dominant process of milling could be observed and inferred. Figure 3a, b & c shows the SEM micrographs of Cu-Zn alloy powders milled for 10, 20 and
30 hours respectively. From the images it could be seen that fracture has dominated resulting in reduction of particle size of the powders. Irregular grain boundaries depicts that ductile copper has undergone repeated deformation due to the impact of hardened steel balls on the surface of the powders. Since zinc is also partially brittle, it could also been an additional milling agent. Yet evidences to substantiate the above claim is not abundant in the current study.

Similarly figure 4 a, b & c shows the SEM micrographs of Cu-Zn composites reinforced with 10 % B4C. Images illustrates that in spite of undergoing repeated fracture, the particle sizes remain almost at larger sizes than unreinforced alloy. This could be possibly due to the fact that B4C is a material of high hardness which might have caused too much deformation in Cu-Zn system which reached saturation.

**Figure 3** – SEM micrographs of milled Cu-Zn alloys a) 10 h, b) 20 h, c) 30 h
After this the particle size could not be reduced further and the particles has established a tendency to agglomerate with each other resulting in increased particle size. This phenomenon is called cold welding in mechanical alloying [3]. As a result of cold welding of particles, their size was observed to be larger than the unreinforced alloy. Nevertheless, cold welding could not be claimed to be predominant as the particle size of the composite powders continuously reduce. Hence it could be concluded that the particle size had reached saturation within the process itself such that impossibility of further reduction increased the particle size when compared with the unreinforced alloy.

4. **CONCLUSION**
Copper zinc alloys were reinforced with boron carbide powders and the composites were synthesized using mechanical alloying. Conducted experiments and the characterization techniques rendered the following conclusions as results of the work.
- Unreinforced copper zinc powder particles reached the size of nano scale at 10 hours of milling and continuously reduced thereafter. Minimum particle size obtained was
9.72 nm by Williamson-Hall synthesis equation and 22.35 nm by Scherer’s equation after 30 hours of milling.

- From SEM image it could be concluded that reduction of particle size of unreinforced Cu-Zn alloy was due to continuous fracture of powder particles induced because of prolonged milling cycles.
- Particle size of Cu-Zn composite powders containing 10 % B₄C also reached nano scale and the minimum particle size was obtained as 31.53 nm by Williamson-Hall synthesis equation and 19.14 nm by Scherer’s equation after 30 hours of milling.
- SEM image of Cu-Zn with 10 % B₄C depicts that particle size reduction was due to fracture despite the fact that average particle size of B₄C reinforced composites was greater than unreinforced alloy.
- Increased particle size of B₄C reinforced composites could be due to the cold welding that might have occurred due to acute reduction of particle size of composite powders in presence of highly brittle and hard B₄C particles.

![Figure 4](image)

**Figure 4** – SEM micrographs of milled Cu-Zn + 10 % B₄C a) 10 h, b) 20 h, c) 30 h

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