Modernization of copper chips synthesized by top down approach in addition to W-H plot, EDAX and extensive X-ray diffraction studies

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In this present study, synthesis and characterization of copper (Cu) nanoparticles have been reported. The low-cost, effective and eco-friendly top down technique is adopted for the synthesis of Cu nano particles from machined Cu chips. The copper chips are treated in a high energy planetary ball mill using tungsten (W) grinding ball media for 25 h and 50 h at 300 rpm under the pure argon gas as the process control agent (PCA) for avoiding oxidation. The ball to powder weight ratio is maintained at 10:1. The obtained samples are characterized using ultra violet spectra, visible spectroscopy (UV-vis), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDAX). From the XRD results phase evolution, d-spacing, dislocation density, peak indexing remarks and particle size are determined. The XRD study shows that the prepared samples are holo crystalline in nature. X-ray peak analysis is carried out to calculate the lattice strain from Williamson-Hall (W-H) plot. The optical properties of the milled Cu sample are studied using UV-Vis spectra. The SEM images confirm the nanostructure of prepared copper nanoparticles. The EDAX results reveal that the samples are in pure form.

Keywords: Ball milling, Peak indexing, W-H plot, Dislocation density, SEM

In the nano materials science, the emerging trend is production of nano materials substances1,2. Rehani et al.3 produced silver-graphite nano substance and examined its microstructure, mechanical and electrical properties. Sil et al.4 and Feng et al.5 developed a new numerical simulation framework for applying it in planetary ball milling process. Mechanical alloying (MA) is one of the effective techniques used to obtain nanostructure materials. Especially low cost synthesis process is an important aspect in nano field. Vu et al.6 considered the top-down approach as a promising route for producing nano materials in great quantities, without any difficulty. Surface modification of Cu by ball-milling is a simple and convenient process. Yan et al.7 point out that Cu-based amorphous powder has been synthesized after milling for about 8 h to 12.5 h. If the time is more than 12.5 h, amorphous phase will transform into crystalline phase once again; otherwise, if it is less than 8 h, amorphous phase cannot be formed completely. In the present study, we focused on milling for more than 20 h. Kou et al.8 have observed that the milling time plays an important role in mechanical alloying process. It is observes that there exists a good agreement between milling time and crystalline size. Celal and Musa9 explained that nanostructured Fe–20Al–2Cr (wt%) powders have been prepared using high energy planetary ball-mill.

Estimated changes in structures and morphological properties of the powders during MA and during subsequent annealing were examined through XRD and SEM studies. Zerniz et al.10 described about the high energy ball milling speed was kept at a constant speed of 300 rpm and inert argon gas was used as PCA. The present study focuses on the preparation of Cu nano powders by a promising top down approach and using high-energy ball milling process with the addition of inert argon as PCA. The obtained samples were characterized using UV-Vis, XRD, SEM and EDX.

Experimental Procedure

Cu chip collection and ultrasonic cleaning

Copper chips of 30 mg were collected from the machining area. The collected chips were cleaned by ultrasonic process shown in Fig. 1. The copper chips were the source materials in the Cu nanoparticles synthesizing process.

Acetone (Merck & Co) was added to the Cu scraps and ultrasonic process was carried out with a regular time interval of 5 to 10 min. Sasikumar et al.11 cleaning was performed to remove the impurities present in the machined copper chips.
High energy Ball milling process

The cleaned copper chips were placed in a high energy ball milling equipment (Fritsch–planetary mono mill classic line pulverisette-6, rotational speed range: 100-600 rpm). The grinding chamber dimensions were 500 mm × 370 mm × 530 mm and the rotation was kept as constant speed of 300 rpm. The constant ball powder ratio (BPR) kept as 10:1, (ball diameter: 28 mm; ball and vial material: tungsten carbide balls; speed: 300 rpm). After placing the copper chips into the grinding chamber, inert argon gas was filled as shown in Fig 2.

Prosviryakov et al.12 reported that the inert argon gas was used to control the oxidation during milling. The planetary ball mill was run for 25 h and 50 h with a milling speed of 300 rpm.

Results and Discussion

UV-visible spectroscopic analysis

The optical study of milled copper was performed using UV-visible spectrophotometer (Shimadzu UV-2450, Japan) in wavelength the range of 400 to 1000 nm. Figure 3 shows the UV-vis spectrum of the milled copper. The 25 and 50 h milled copper show maximum absorption around 805 and 620 nm, respectively. The blue shift in UV-vis indicates that the size gets reduced and the red shift indicates that the size gets increased. From the UV-vis spectrum (Fig. 3), it is learnt that when milling time increases from 25 to 50 h, the blue shift is observed. Also, the increase in milling hour reduces the size of particles. The morphology of the Cu nanostructure significantly affects the band gap. The energy band gap of milled Cu has been estimated using the following Eq. (1).  

\[ E(g \text{eV}) = \frac{1240}{\lambda_{max}} \]  

where \( \lambda_{max} \) is the wavelength of the maximum absorber of UV-vis spectrum. Khoshkhoo et al.13 explained that the copper nano particle, optical band gap energy decreased from 2 eV to 1.5 eV with increase in milling hours. Ghorbabi14 and Mercy et al.15 attributed the blue shift of the optical absorption spectrum towards lower wavelength also confirms the decreasing size of the nanoparticles. In the UV-visible absorbance spectrum the red shift and the blue shift indicate the correspond to the formation of large size and small size particles, respectively.

EDAX Study

The elemental analysis was performed using EDAX analysis. Figure 4 shows the EDAX image of the milled copper sample. The main peak, and all its
associated peaks, are identified. Sheibani et al.\textsuperscript{16} revealed that the higher peaks gradually change to smaller peaks in sequence in recognisable form. The EDAX study shows that the samples are in pure form. Table 1 shows the weight and atomic percentages of elements of milled copper samples. The elemental composition of the milled copper samples was determined through EDAX study.

**X-ray diffraction studies**

X-ray diffraction techniques fall under the category of non-destructive tool to study the physical properties of materials. They can also be employed to determine structural characteristics such as grain size and defects in the structure of crystalline substances by Sharma et al.\textsuperscript{17} Samples of milled copper nanoparticles were characterized by XRD analysis using Rigaku advanced X-ray diffraction with CuKα radiation (λ = 1.54Å). In this XRD study the 2θ was maintained in the range of 20° to 90° with a gradual increment of 0.02° per minute. Figure 5 shows the XRD pattern of milled copper sample.

The XRD peak was observed at 2θ angle of 43.15°, 50.25°, and 73.95° correspond to (111), (200), and (220) planes, respectively. Pilloni et al.\textsuperscript{18} and Sheibani et al.\textsuperscript{19} compared their XRD analysis results with standard powder diffraction data from JCPDS, copper file no. (Cu 85-1326). A good correlation between observed data and the standard data. The XRD results of the milled copper samples indicate that the samples are crystalline in nature with face-centered cubic lattice.

**Scherrer formula for crystalline size calculation**

Cullity\textsuperscript{20} and Monshi et al.\textsuperscript{21} determined the crystalline size (D) using Debye Scherrer formula as given below Eq. (2).

\[ D = \frac{k\lambda}{\beta \cos\theta} \quad \ldots (2) \]

Where λ = 0.1541, \( k = 0.9 \), \( \beta \) is full width at half maximum (FWHM) of diffraction peak, \( \theta \) is Bragg’s diffraction angle and \( D \) is crystalline size. The calculated values of crystalline size of milled copper for 25 h and 50 h are 41.19 and 35.64 nm, respectively. It transpires that increase in milling time leads to reduction of crystalline size.

**Reflection plane (hkl) calculation**

Du et al.\textsuperscript{22} determined the unit cell dimensions from the peak positions. This is called indexing. It is one of the major steps in the diffraction pattern investigation. From the obtained XRD results, indexing was carried out in hypothesis method and data are presented in Tables 2 and 3 for milling time of 25 h and 50 h, respectively. A perfect correlation is seen between the Cu milled experimental plane values and standard plane values. Tables 2 and 3, show that peak position (2θ) has good agreement with XRD results.

| Table 1 — EDAX form milled Cu sample |
|-----------------|-----------------|------------------|
| Element | Weight % | Atomic % |
| Cu | 89.80 | 68.92 |
| O | 10.20 | 31.08 |
| Total | 100 | 100 |

| Table 2 — Peak indexing for milled Cu sample 25 hr |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Peak position (2θ) | Peak position (θ) | 1000 × Sin² θ | Experimental plane | Actual plane | Standard plane |
| 43.15 | 21.57 | 135.22 | 2.99 | 3 | 111 |
| 50.27 | 25.12 | 180.33 | 3.99 | 4 | 200 |
| 73.95 | 36.97 | 361.78 | 8.01 | 8 | 220 |

| Table 3 — Peak indexing form milled Cu sample 50 h |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Peak position (2θ) | Peak position (θ) | 1000 × Sin² θ | Experimental plane | Actual plane | Standard plane |
| 43.17 | 21.58 | 135.33 | 3 | 3 | 111 |
| 50.27 | 25.13 | 180.42 | 3.99 | 4 | 200 |
| 73.99 | 36.99 | 362.1 | 8.02 | 8 | 220 |
Prediction of \(d\)-spacing from XRD

Zhang et al.\(^{23}\) and Das et al.\(^{24}\) discovered the value of \(d\)-spacing (\(d=\)interplaner spacing correlation between the atoms) using Bragg’s law Eqs (3) and (4).

\[
2d \sin \theta = n \lambda 
\]  \hspace{1cm} \ldots (3)

\[
d = \frac{\lambda}{2 \sin \theta (n=1)} \]

\hspace{1cm} \ldots (4)

The values of \(d\)-spacing were determined using the above equations and are presented in Table 4.

Williamson-Hall plot

Mote et al.\(^{25}\) calculated the lattice strain of the prepared Cu samples, using Williamson Hall plot method. In the present research Williamson-Hall graph was drawn by plotting the values of \(4 \sin \theta\) on the x-axis and \(\beta \cos \theta\) on the y-axis (Fig. 6). The slope value was calculated using the standard equation \(y = mx + c\) from the linear fit, strain value was determined from the y-intercept. This method has been described by Kumari et al.\(^{26}\) Baruah et al.\(^{27}\) reported strain values (derived from Williamson-Hall plot) in the range of 0.005 to 0.009, and that decrease in microstrain values indicated strain free condition and the nano particles could be considered as nanoclusters.

Dislocation density

Zuhailawati et al.\(^{28}\) and Barai et al.\(^{29}\) stated that dislocation occurs in every crystalline structure. The dislocation density (\(\delta\)) in the copper sample was determined using the following formula.

\[
\delta = \frac{p}{D^2} 
\]  \hspace{1cm} \ldots (5)

where \(D\) is crystalline size and \(p=1\). Crystallite size (\(D\)), Yazdian et al.\(^{30}\) found that decreases in milling time increased dislocation density of copper alloys due to severe plastic deformation caused by ball milling.

Table 5 shows good agreement between crystalline size (\(D\)) and dislocation density. It is observed that there is a decrease in the values of dislocation density along with increase in ball milling time but the milling speed being constant. This shows that plastic deformation did not occur in this process.

SEM morphology

The surface morphology of the milled copper was studied using scanning electron microscope (SEM, JSM 6490, JEOL, Japan). Figures 7 and 8 depict the SEM images of milled copper for 25 h and 50 h, respectively. Marques et al.\(^{31}\) observed that the SEM image showed the clear morphology of milled copper particles and the particles were spherical in shape, clearly confirming the crystalline phases a continuous milling. The sizes of the particles estimated from

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<th>Table 4 — (d)-Spacing values of milled Cu sample</th>
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<th>Table 5 — Dislocation density</th>
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<td>Milling sample hours</td>
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Fig. 6 — Williamson-Hall plot of 25 h and 50 h copper milled sample

Fig. 7 — 25 h SEM morphology

Fig. 8 — 50 h SEM morphology
SEM images are 50 and 40 nm for copper milled for 25 h and 50 h, respectively.

The SEM images clearly show holocrystalline nature and nanostructure of the synthesized particles. As can be seen from Fig. 7 the particles are evenly distributed. The average size of the particles is 50 nm. Figure 8 shows the average size as 40 nm with slight aggregation, in layered structure. Increase in milling time leads to decrease in particle size. However, the particles tend to aggregate when the particle size is reduced.

Conclusions

The copper nanoparticles were successfully synthesized using high energy ball milling process. The copper nanoparticles were prepared from copper chips and characterized by UV-visible spectroscopic analysis, XRD, EDX and SEM. The XRD results show that the prepared particles are crystalline in nature with FCC structure. The SEM images reveal the well crystallized nature of the nanoparticles with nanostructure. The EDX analysis indicates that the prepared sample contains copper in its pure form and no impurity is present in the sample. The UV-visible absorption spectrum reveals that when milling time is increased the particle size is reduced, and the wave band tends to shift towards the blue wave length band (this is called blue shift). In the reduction of particle size and in the confinement of high quantum nanoparticles, a band gap is observed. W-H plot was prepared and used to determine the micro strain values. It is suggested that it could be extended to low cost production of nano powder by top down approach of the macro structured copper chips.

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