

Studies on the mechanism of the structural evolution in Cu–Al–Ni elemental powder mixture during high energy ball milling

S. K. Vajpai · R. K. Dube · M. Sharma

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Abstract The present work is focused on the understanding of the phase and microstructural evolution during mechanical alloying of 82Cu–14Al–4Ni powder mixture. Morphology and phase evolution in the milled powder at different stages of milling were studied and a physical modeling of the mechanical alloying has been proposed. It has been demonstrated that milling process mainly consisted of four stages, i.e., flattening and cold welding of powder particles to form a porous aggregate followed by its fragmentation, plastic deformation of small aggregates to form layered particles, severe plastic deformation of layered particles to form elongated flaky particles, and fragmentation of elongated particles into smaller size flaky powder particles. It was also found that the initial period of milling resulted in rapid grain refining, whereas alloying was accomplished during the later period of milling. TEM study of the 48 h milled powder revealed that the microstructure was equiaxed nanocrystalline in nature. It was found that the grains were either randomly distributed or arranged as banded type. A possible explanation for such a behavior has been presented.

Introduction

In recent years, Cu-based shape memory alloys have emerged as a replacement of widely used Ni–Ti alloys, due to their comparable recovery force, lower material cost, and relative ease of processing. The potential application area of Cu-based shape memory alloys has been identified in various electrical equipments as actuators and sensors. Among the Cu-based shape memory alloys, Cu–Al–Ni alloys have been found to be a promising candidate for high temperature applications owing to their high thermal stability [1, 2]. However, Cu–Al–Ni alloys produced by conventional casting route are quite brittle, which limits its applicability. It has been pointed out that the high brittleness of Cu–Al–Ni alloys is primarily related to the large elastic anisotropy and large grain size, which enhance the susceptibility of alloys to intergranular fracture [2–4]. In pursuit of improved mechanical properties, several attempts have been made to refine grain size of Cu–Al–Ni alloys by adding various alloying elements, such as Ti, Zr, V, and Boron [5–8]. Other methods, such as rapid solidification [9] and controlled recrystallization [10], have also been applied to refine the grain size of Cu–Al–Ni shape memory alloys. Grain size refinement exhibited significant improvement in the mechanical properties as compared to coarse-grained Cu–Al–Ni alloys. However, the problem of composition control during casting, which is crucial for controlling the transformation temperature and the desired level of grain refinement, has hindered its further development.

It is well established that the grain size and composition can be controlled in materials produced by powder metallurgy route in a better way. In particular, mechanical alloying has emerged as a promising method to produce a variety of nanocrystalline and ultra-fine grained powders. Alloy powders produced by mechanical alloying have

S. K. Vajpai (✉) · R. K. Dube · M. Sharma
Department of Materials and Metallurgical Engineering, Indian
Institute of Technology, Kanpur 208016, Uttar Pradesh, India
e-mail: vajpaik@iitk.ac.in

R. K. Dube
e-mail: rkd@iitk.ac.in

M. Sharma
e-mail: mohitsh@iitk.ac.in

shown to possess better control over composition and chemical homogeneity as compared to their conventionally produced counterparts. In recent years, a few attempts have been made to develop Cu–Al–Ni alloys by a powder metallurgy route involving mechanical alloying followed by consolidation of milled powder via hot extrusion or hot isostatic pressing at elevated temperatures [11, 12]. Since the microstructural evolution in the consolidated material is derived from the microstructural characteristics of the mechanically alloyed powders, it is extremely important to acquire an in-depth understanding of the structural evolution in the Cu–Al–Ni powder during mechanical alloying. However, very little attention has been paid to this aspect in the literature. The present work describes the experimental results related to microstructural evolution, such as particle size, grain size, and phase evolution, during different stages of mechanical alloying of Cu–14 wt% Al–4 wt% Ni (hence forth designated as Cu–14Al–4Ni) powder mixture. A detailed analysis of the milled nanocrystalline powder was carried out by TEM for observing the nano-scale features present inside the mechanically alloyed powder particles.

Experimental procedure

Elemental Cu powder (median particle size = 38.0 μm , >99% pure), Al powder (median particle size = 15.0 μm , >99% pure), and Ni powder (median particle size = 9.0 μm , >99% pure) were used as starting material. Elemental Cu and Ni powders were annealed in H_2 atmosphere at 600 °C for 30 min for reducing the surface oxides present on the powder. The reduced powder mixture having composition 82Cu–14Al–4Ni (wt%) was mechanically alloyed in a high energy planetary ball mill (Fritsch Pulverisette 5) using high Ni–Cr steel balls as grinding media. The mechanical alloying was carried out at disc and vial rotation speed of 300 rpm, whereas ball-to-powder ratio (BPR) of 8:1 was maintained for each run. To avoid agglomeration, wet milling was carried out using excess toluene as suspension media. Powder samples were collected at various stages during milling for further investigations.

The phase evolution in the as-milled and annealed samples was studied by X-ray diffraction (XRD) technique using monochromatic Cr K_α (0.228970 nm) radiation. The average grain size of the samples was determined by XRD line broadening technique. The measured peak broadening consisted of contributions due to structural (grain refining and lattice strain) and instrumental effects. In the present work, single line profile analysis procedure based on Voigt-function representation was applied for correct grain size estimation [13]. This method is capable of separating peak broadening due to grain refining, strain, and instrumental

effects. The most intense peak of the desired phase was considered for grain size determination. The instrumental broadening was corrected using standard silicon powder as reference material. The morphology of the milled powder mixture at various stages during milling was studied by SEM and evolution of the internal microstructure in the mechanically alloyed powder was studied by TEM. Furthermore, the grain size and morphology of the internal structure of 48 h milled powder was studied by atomic force microscopy (AFM) also. The milled powder particles were dispersed in acetone and deposited on a silicon substrate. The AFM was operated in semi-contact mode to study the deposited powder particles.

Results and discussion

Figure 1a shows the XRD patterns of the as-mixed and milled powder at various stages of milling. The XRD pattern of the as-mixed powder shows that relative intensity of Al peaks was lower than that of Cu, and peaks of Ni were not visible in the XRD spectra. This observation can be related to the small amount of Al and Ni in the composition. Furthermore, the relative intensity of the Al peaks decreased with milling time, and Al peaks almost disappeared after 32 h of milling time. The gradual attenuation in the Al peak intensity indicated dissolution of Al in Cu matrix with increasing milling time. Therefore, the complete disappearance of Al peaks after 32 h of milling indicated that most of the Al dissolved in the Cu matrix to form a solid solution of Al in Cu. Similarly, it is highly probable that Ni is also dissolved in the Cu matrix to form a solid solution; but, such claim cannot be made on the basis of the present XRD data. However, other workers [12, 14] have shown that Ni also dissolved in the Cu matrix to form a solid solution. A slight shifting of Cu peaks toward lower angles, with increasing milling time, was a further confirmation of diffusion of Al and Ni in Cu matrix to form the solid solution. After 48 h of milling, only the peaks of a single phase with FCC structure appeared. The lattice parameter, as calculated using XRD data, of the resulting solid solution ($a = 0.36061$ nm) was found to be close to that of the starting Cu powder ($a = 0.35957$ nm). Therefore, it was concluded that a disordered single phase solid solution was formed after 48 h of milling of the elemental Cu, Al, and Ni powder mixture.

Figure 1a also shows a broadening of peaks with increasing milling time. Such an increase in broadening of peaks with milling time can be attributed to the increasing lattice strain and grain refining. Figure 1b shows the variation of lattice strain and grain size with increasing milling time. A rapid decrease in grain size and rapid increase in lattice strain within initial 10 h of milling can be clearly

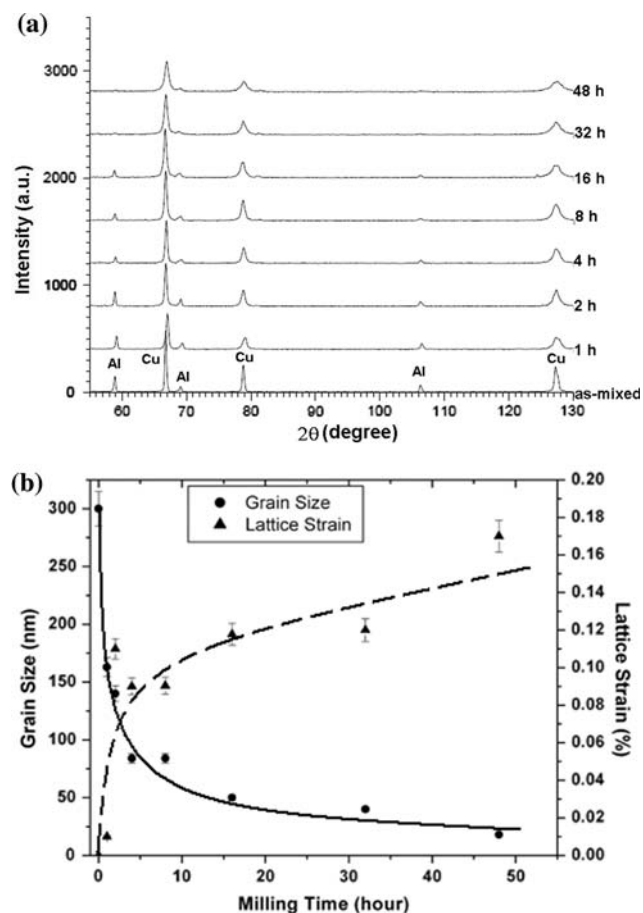


Fig. 1 **a** XRD profiles of as-mixed and milled 82Cu-14Al-4Ni powder mixture and **b** variation of grain size and lattice strain as a function of milling time

observed. Since the accumulation of dislocations and other lattice defects during milling are considered to be the key factor for grain refining and increased lattice strain, initial 10 h of milling can be identified as the stage of severe plastic deformation in the present case. These observations can be further strengthened by previously reported results where it was shown that hardness of the milled particles increases rapidly during initial period of milling followed by a slight decrease and saturation of hardness values [14].

Figure 2 shows the morphology of the as-mixed powder particles as well as powder milled for 2, 4, 8, 32, and 48 h. It was observed that initial 2 h of milling was mainly dominated by flattening and cold welding of the powder particles rather than any severe fracturing of individual particles, as shown in Fig. 2a, b. It was also observed that such a process of flattening and cold welding resulted in the formation of large clusters of cold welded flaky particles. The morphology of the clusters showed that cold welded particles still retained their identity and were loosely bound to each other, resulting in a fragile nature of clusters. Therefore, it is imperative that further milling would lead

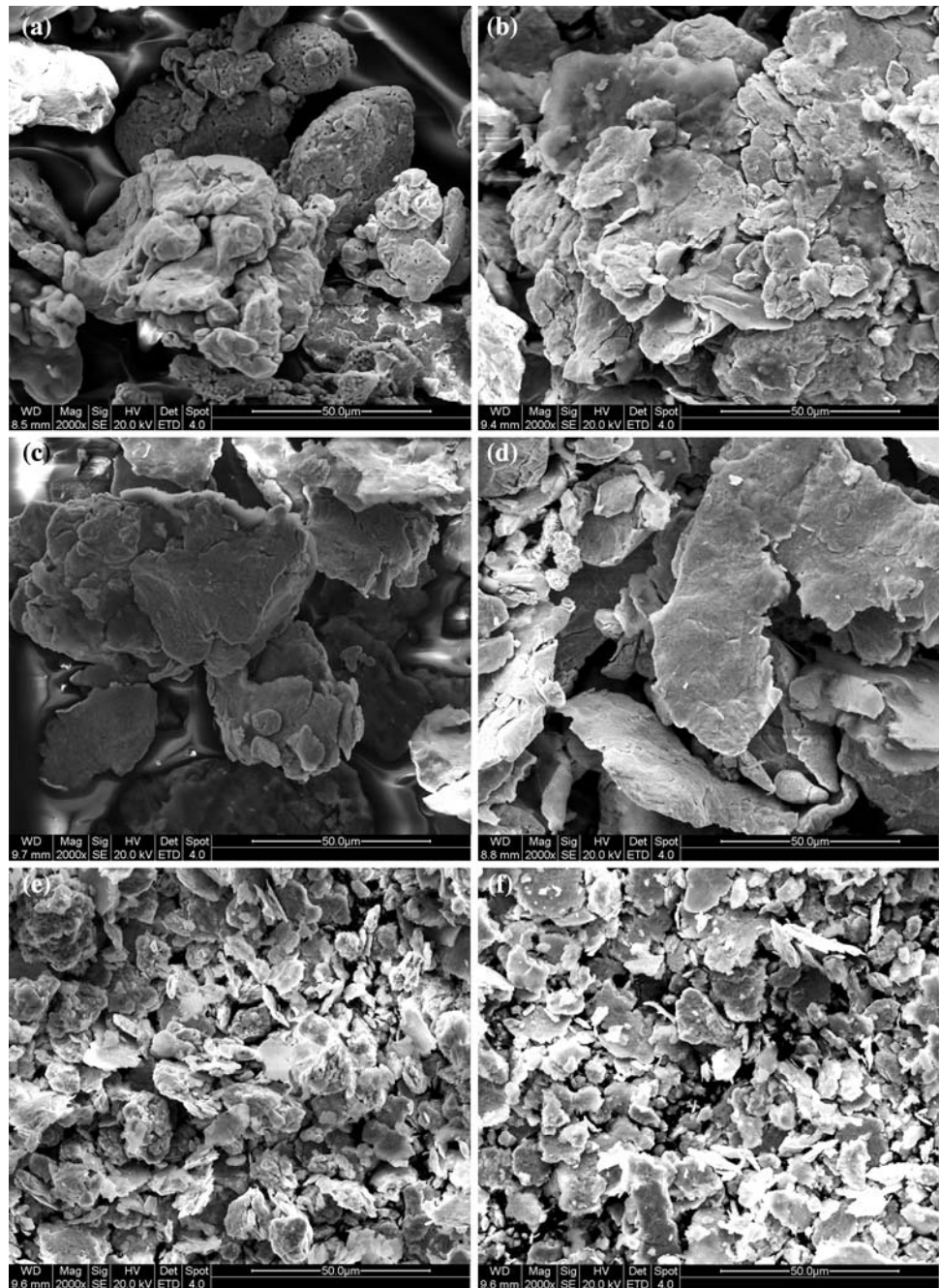
to the fragmentation of these clusters into several parts, as discussed in the following paragraph. However, it must be emphasized that this fragmentation of clusters is not same as the fracturing of individual powder particles.

Figure 2c shows the morphology of the powder milled for 4 h. It can be observed that further milling beyond 2 h has induced fragmentation of the large clusters of particles to form smaller particles/clusters. This stage can be identified as the transition stage where individual particles of the clusters are more coherently bound to each other, identity of the individual particles in the clusters started disappearing and clusters started appearing like a single powder particle. However, coarse layered structure of the particles can still be observed at this stage. Figure 2d shows the morphology of the powder particles milled for 8 h, wherein a presence of very thin flaky and fractured particles can be observed. The morphology of the powders transformed from irregular to very thin flaky shape. The particle size of the powder was larger than that milled for 4 h. Such morphology of particles indicated a severe plastic deformation leading to refining of layered structure together with fracturing of particles. Since the severe plastic deformation induces hardening to the particles, the dominance of significant cold welding can be easily ruled out at this stage of milling. Therefore, it seems that this stage of milling was the beginning of fracturing of severely plastically deformed particles.

From the above discussion, it can be inferred that most of the impact energy during initial 8 h of milling was expended toward plastic deformation of the particles leading to flattening, cold welding, and refining of layered particle substructure. The severe plastic deformation of particles leads to the accumulation of various lattice defects, which have been found to be instrumental in disintegrating the lattice to form nanocrystalline structure inside micron sized particles. These arguments can be further strengthened by the grain size estimations during various stages of mechanical alloying, as shown in Fig. 1b, where it can be clearly seen that initial 12 h of milling delivers maximum grain refining.

A comparison of Fig. 2d with Fig. 2e shows that there was a significant difference in the morphology and particle size of the mechanically alloyed powders milled for 8 and 32 h. It is clearly evident that large particles were disintegrated to form finer size particles. This observation indicates that period between 8 and 32 h of milling was dominated by severe plastic deformation induced thinning and fracturing of powder particles. Furthermore, a comparison of Fig. 2e with Fig. 2f shows that there was not much modification in the morphology and size of milled powder particles between 32 and 48 h of milling. These observations suggest that most of the particle size refining due to fragmentation of particles occurred during 8–32 h of

Fig. 2 SEM micrographs showing morphology of 82Cu–14Al–4Ni powder mixture milled for **a** 0 h, as-mixed, **b** 2 h, **c** 4 h, **d** 8 h, **e** 32 h, **f** 48 h



cumulative milling time period. However, it is interesting to note that grain size refining was not significant after 12 h of milling time. Therefore, it can be inferred that most of the mechanical energy, after 12 h of milling, is expended toward the particle fragmentation and particle size refining. Since much difference was not observed in the morphology and particle size of the mechanically alloyed powders milled for 32 and 48 h, no further modifications in the morphology can be expected on further milling after 48 h of cumulative milling time. However, it must be emphasized that extended milling times after 48 h may lead to the

amorphization of the milled powder. Furthermore, it would be important to mention that later stage of milling has been identified as the stage of rapid formation of solid solution.

Figure 3 shows a typical bright field TEM micrograph and its corresponding SADP of the 48 h milled powder. Figure 3a shows a typical microstructure of the highly plastically deformed metals consisting of a large amount of accumulated defects in the matrix, nano-sized banded regions, and regions having nano-sized randomly distributed equiaxed grains. A non-uniform contrast in the microstructure can be related to the distribution of defects in the

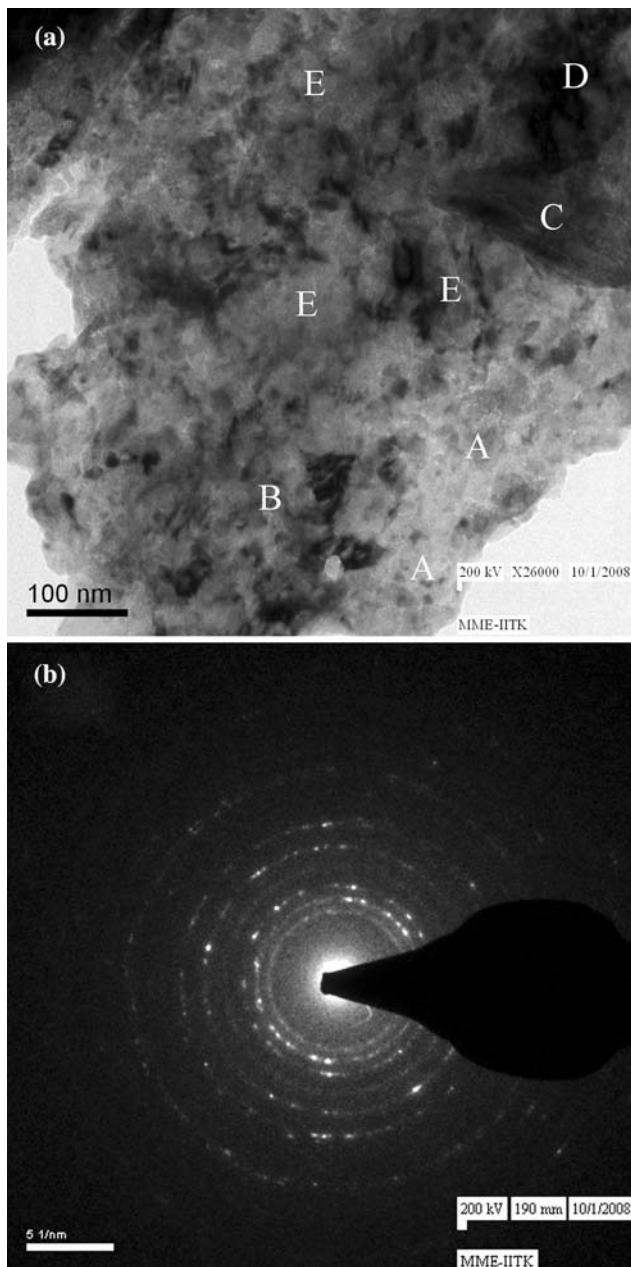


Fig. 3 **a** TEM micrographs and **b** corresponding SADP, of 48 h milled 82Cu–14Al–4Ni powder mixture showing highly deformed powder particle having nanocrystalline structure

matrix. It can be seen that areas near the edge of the particle (region ‘A’) consist of very fine equiaxed nanocrystalline grains having grain size in the range of 5 to 20 nm. The large elongated grains (region ‘B’) appear to be a shear band structure, which is frequently observed in highly deformed metallic alloys. Further, it can be observed that smaller equiaxed grains, having grain size in the range of 10 to 20 nm, also existed within these nanocrystalline layers. A band containing large dislocation densities (region ‘C’) can also be observed, which is believed to be

originated from the strain localization during ball milling [15]. It seems that these bands are transformed to layered nano-sized banded regions on subsequent deformation. The TEM micrograph also shows the areas containing relatively larger grains having grain size in the range of 50 to 100 nm (regions ‘D’ and ‘E’). It is interesting to note that deformed larger grains (indicated as region ‘E’) shows areas of very high dislocation densities, which contain very fine equiaxed nanocrystalline grains. It seems that these regions (region ‘E’) are transformed to the areas showing very fine equiaxed nanocrystalline grains (region ‘A’). In general, the microstructure primarily consisted of equiaxed nanocrystalline grains having grain size 5–100 nm. The existence of such a wide grain size range was also confirmed by SADP of the area, which showed ring pattern containing spots on it. A similar microstructural evolution has been observed by Liu et al. [15, 16] during ball milling induced nano-crystallization of Fe and Fe–C alloys. It is interesting to note that they have also reported a wide range of grain size distribution.

Figure 4 shows a TEM micrograph of milled powder together with its SADP of an area showing deformed large size grains. It can be seen that severely deformed regions, having large dislocation densities, contain very fine equiaxed nanocrystalline substructure (regions ‘A1’ and ‘A2’ in Fig. 4a). It seems that this substructure converts to randomly oriented nanocrystalline grains on further milling or annealing at low temperatures. Figure 5 shows a TEM micrograph of the milled powder and its corresponding SADP showing the presence of a featureless region. This featureless region indicates the existence of amorphous phases in the milled powder, which was confirmed by the diffused SADP of the region. A few spots in the SADP show that the amorphous region contains a very small amount of crystalline phases. An indexing of the SADPs (Figs. 3b, 4b) confirmed the presence of an FCC Cu–Al–Ni solid solution.

Figure 6 shows the 2-D and 3-D AFM images of the milled powder. The AFM images show the existence of equiaxed grains having grain size in the range of 50 to 100 nm. It is interesting to note that the grain size estimation by XRD line broadening analysis resulted in values approximately 18 nm, which is much smaller as compared to the grain size observed by TEM and AFM. This is not surprising as grain size estimations by XRD provide information based on the average crystallite size (coherently diffracting domains), which is usually much smaller as compared to that observed by any direct method. The reason for such a difference has been attributed to the hierarchy of the microstructure of the severely plastically deformed metals, where the grains confined by high angle boundaries are usually subdivided into subgrains [17]. Since the misorientation angle between subgrains is low, the contrast difference between them is not visible in TEM

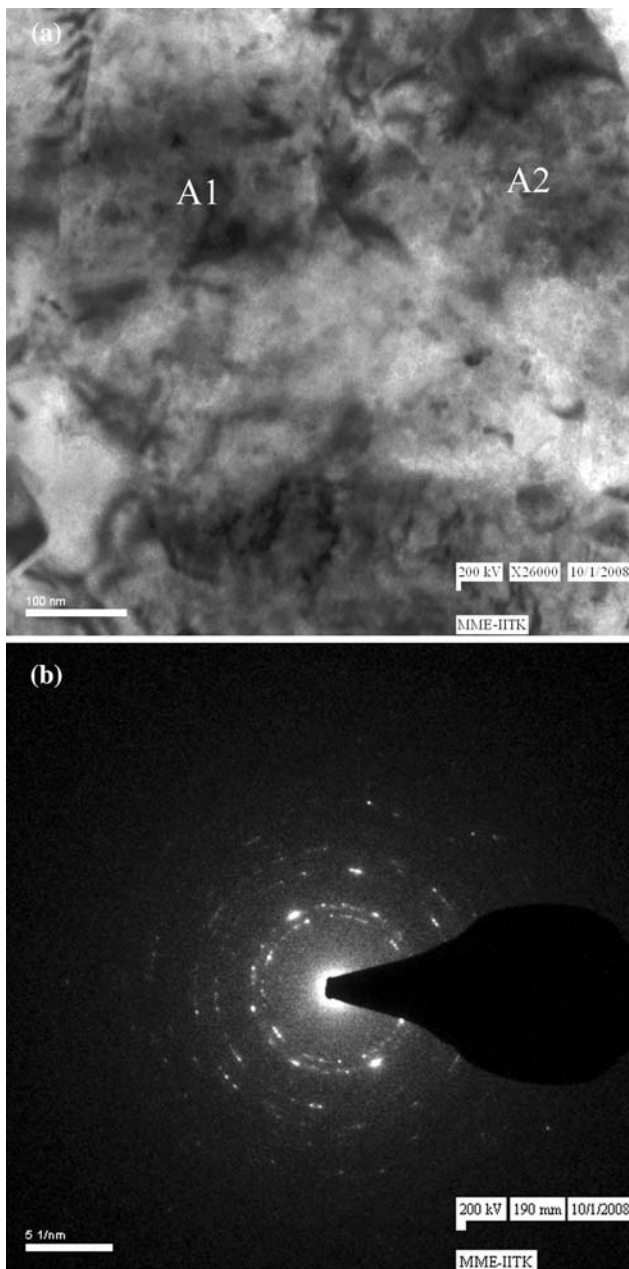


Fig. 4 **a** TEM micrographs and **b** corresponding SADP, of 48 h milled 82Cu–14Al–4Ni powder mixture showing deformed large size grains

micrographs and AFM images. On the contrary, lack of coherency between the X-rays scattered from the subgrains contributes toward the broadening of the XRD peaks and measures the size of the subgrains. Furthermore, most of the grain size estimation procedures by XRD method rely on peak broadening, which contains contributions due to instrumental broadening effect, lattice strain, dislocations, stacking faults, and other lattice defects. There are several methods available for correcting these contributions from the observed XRD profiles. However, all of these methods

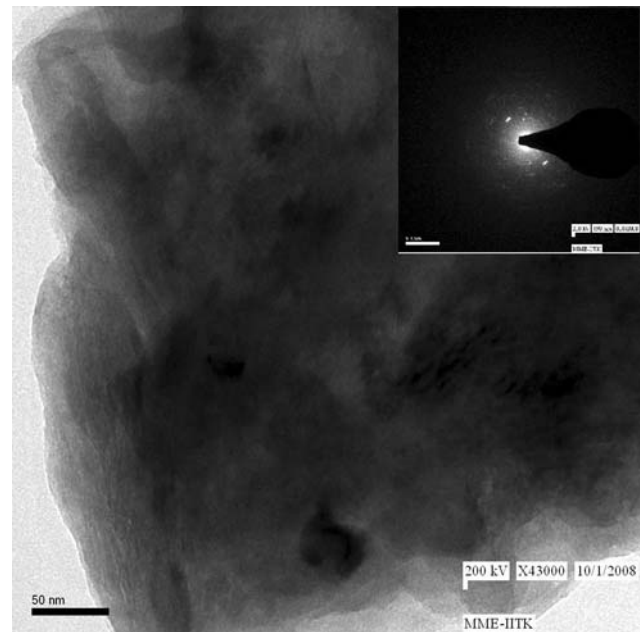


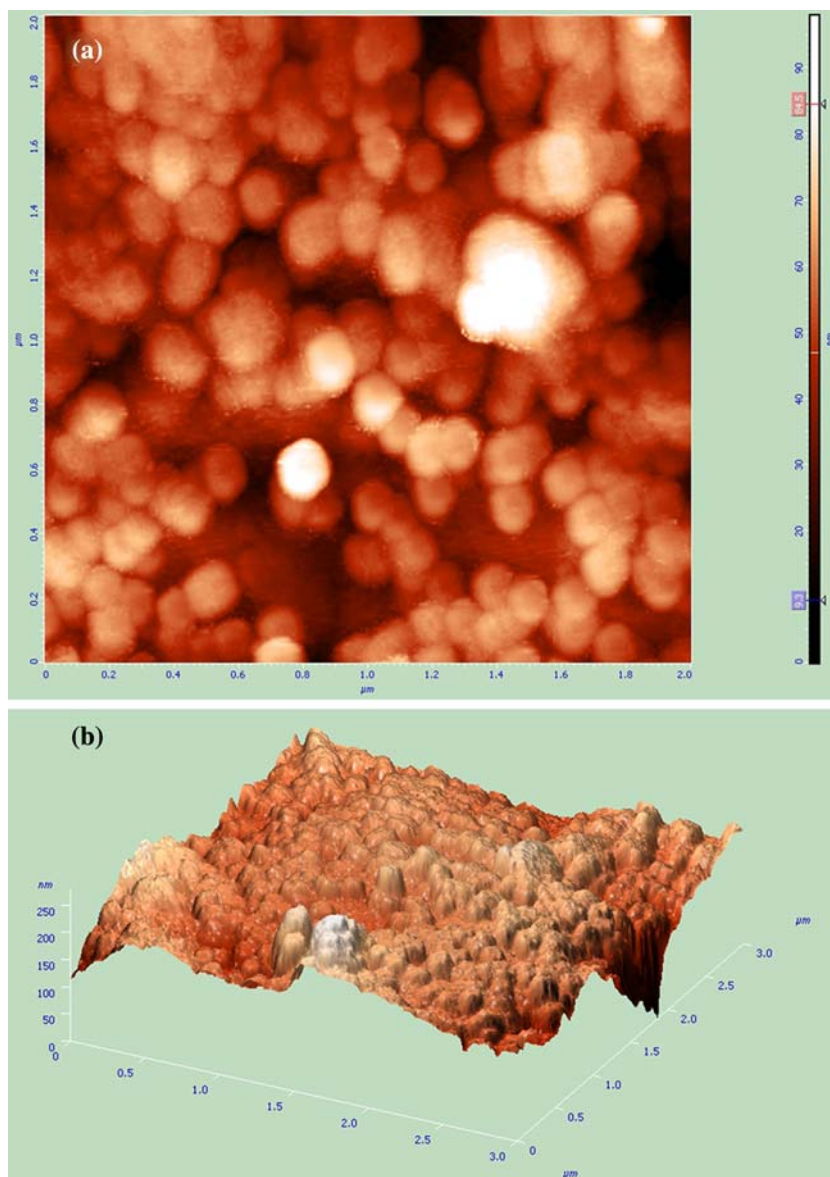
Fig. 5 TEM micrograph and corresponding SADP of 48 h milled 82Cu–14Al–4Ni powder mixture showing presence of amorphous phases in the milled powder

involve certain assumptions and none of the methods can take care of all these contributions due to complex nature of microstructure of milled powder and their effect on the XRD profiles.

It is well known that the mechanical alloying is a promising method of producing alloys having excellent chemical homogeneity. Recently, Xiao et al. [14] have shown homogeneous distribution of Cu, Al, and Ni elements in the powder particles produced by mechanical alloying under the milling conditions similar to the present work (BPR = 15:1, speed = 300 rpm, time = 50 h). Although no elemental mapping has been carried out, it is reasonable to believe that the mechanically alloyed powder in the present study is homogeneous in nature.

An important aspect related with the powder metallurgy route is the consolidation of mechanically alloyed powders to produce bulk material. In recent years, attempts have been made to consolidate mechanically alloyed powders by several methods, such as vacuum hot pressing, explosive compaction, hot isostatic pressing, spark plasma sintering, hot extrusion, and several combinations of these methods. In particular, Xiao et al. [12] consolidated mechanically alloyed Cu–Al–Ni powder by vacuum hot pressing followed by hot extrusion to produce crack-free material. The solutionized and quenched material showed evidence of formation of martensite and 100% shape recovery was observed when deformed to 4% strain level. Recently, Vajpai and Dube [18] consolidated mechanically alloyed Ni–Fe powder by sintering followed by hot-rolling of unsheathed compacts under protective atmosphere, and

Fig. 6 AFM images of 48 h milled 82Cu–14Al–4Ni powder mixture **a** 2-D image and **b** 3-D image



near-full density strip was obtained. A similar approach will be used to consolidate mechanically alloyed Cu–Al–Ni powder to obtain full density material with desired grain size.

Conclusions

Following conclusions can be drawn on the basis of the present study.

1. The grain size decreases very rapidly in the initial 10 h of milling followed by sluggish grain refinement on further milling.
2. The formation of solid solution due to milling induced mechanical alloying takes place during the latter stages of milling. The mechanically alloyed 82Cu–14Al–4Ni (wt%) powder milled for 48 h consists of a wide range of grain size within 5–100 nm range.
3. On the basis of the evolution of particle morphology, four different stages can be identified during milling: (i) flattening and cold welding of elemental powder particles to form a porous aggregate of particles, followed by its fragmentation to smaller size aggregates; (ii) plastic deformation of these small aggregates leading to the formation of particles having layered structure; (iii) severe plastic deformation leading to the formation of elongated flaky particles; and (iv) fragmentation in to smaller size flaky powder particles.
4. The formation of equiaxed nanocrystalline grains, as either randomly oriented region or banded region, depends on the nature of its parent deformation zone.

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