J Mater Sci (2011) 46:6316–6322
DOI 10.1007/s10853-011-5312-3

ABBASCHIAN FESTSCHRIFT

Mechanical behavior of bulk nanocrystalline copper alloys produced by high energy ball milling

H. Bahmanpour · K. M. Youssef · R. O. Scattergood · C. C. Koch

Received: 15 November 2010 / Accepted: 19 January 2011 / Published online: 29 January 2011

Abstract Copper alloys with different amounts of zinc were synthesized via high energy ball milling at liquid nitrogen and room temperature. Bulk samples were produced in situ by controlling the milling temperature. It is shown that temperature plays an important role in formation of artifact-free consolidated samples via its effect on defect formation and annihilation during the milling process. The mechanical behavior of Cu–Zn nanocrystalline alloys was examined using Vickers microhardness and tensile tests. The nanostructure of the alloys was investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The hardness results of processed alloys vary as a function of the alloying elements. Considering typical low ductility of nanocrystalline materials, the improved ductility with the high strength observed in these alloys suggests that they are artifact-free and may have several deformation mechanisms, which may include dislocation activity and nano-twinning.

Introduction

Production of bulk nanostructured materials has been a challenging issue since introduction of superior properties of these materials such as ultra high strength and good ductility compared to microcrystalline materials. Several processing methods such as equal channel angular pressing (ECAE), high pressure torsion (HPT), and ball milling were examined and proposed to break down the grain size of samples to nano scale. Nanostructured materials produced by ball milling have the advantage of smaller crystallite sizes and also more homogeneous microstructure compared to other techniques. Ball milling has been of great interest due to its ability to produce a homogeneous mixture of powders with unique microstructural and mechanical properties. Its limitation has been consolidation of powders to produce bulk samples for testing.

Combination of milling at liquid nitrogen temperature and room temperature milling resulted in formation of sound and defect-free bulk samples that can compete very well with their counterparts produced by other methods such as ECAE or HPT. Youssef et al. reported successful production of bulk nanocrystalline copper samples with a narrow grain size distribution of $\sim$23 nm using high energy ball milling at liquid nitrogen and room temperature. Ultra high strength of 791 MPa and uniform elongation of 14% were obtained by in situ consolidation of ball-milled samples [1, 2]. The in situ consolidation of powder samples during the ball milling process has been reported in the literature [3] but there is no systematic research on this issue to find the optimum milling conditions to produce artifact-free samples.

Milling of ductile metals or alloys at room temperature in a dry and inert atmosphere causes welding to predominate and sample size will steadily increase with milling time. Milling at room temperature can result in formation of hollow spheres with inhomogeneous microstructure that contain cracks and pores. It is of great interest to understand and control the milling conditions and produce defect-free samples with superior mechanical and microstructural properties [4]. It has been shown that the temperature of the milling process plays an important role on the quality of the in situ consolidated samples [3, 5].

H. Bahmanpour (✉) · K. M. Youssef · R. O. Scattergood · C. C. Koch
Department of Materials Science and Engineering, North Carolina State University, Engineering Building I, 911 Partner's Way, Raleigh, NC 27695-7907, USA
e-mail: hbahman@ncsu.edu

Although the mechanism of growth of small spheres is not very clear, it is believed that material transfer from one sphere to another via the milling produces coalescence of particles [3].

In this article, the in situ consolidation behavior of Cu–Zn alloys is investigated. Successful experiments of in situ consolidation on pure copper are extended to copper alloys. As expected, alloying changes the microstructural and mechanical behavior of samples and therefore the in situ consolidation behavior also changes. Materials produced in this research are examined in order to study governing parameters for in situ consolidation of Cu alloys. Furthermore, mechanical properties of the bulk nanostructured copper alloys are investigated by microhardness and tensile tests. Considering the low stacking fault energy of the alloys studied, possible deformation mechanisms determining the high strength and good ductility are discussed.

Experimental procedure

Nanostructured Cu and Cu–Zn alloys were synthesized via mechanical alloying of elemental powders using a Spex 8000 mixer/mill. Hardened steel vials were loaded under argon atmosphere with oxygen content of less than 1 ppm. Different milling regimes were studied to assess the effect of temperature on the properties of the ball-milled samples. Powders were first milled at liquid nitrogen temperature and subsequent processing was followed by milling at room temperature to get sound and defect-free spheres.

X-ray diffraction was used to estimate the crystallite size, dislocation density, and dislocation character of samples. PM2K [6] software was utilized to fit the X-ray profiles, model the experimental pattern, and to extract microstrcutural data. Hardness of the milled samples was measured using Vickers microhardness at 50 g load. Tensile tests were performed on the artifact-free bulk nc samples using a miniaturized tensile test machine. TEM samples were prepared by electro polishing and the microstructure of the produced samples was studied using a JEOL transmission electron microscope at 200 kV.

Results and discussion

Figure 1 shows different pieces of in situ consolidated samples of a Cu–10wt%Zn alloy. Various products are seen after mechanical milling of ductile metals. As shown in Fig. 1, spheres as large as $\sim$6 mm in diameter can be formed after ball milling process. These samples can be pressed and sliced to make tensile test specimens. It is believed that formation of sound and defect-free samples is very sensitive to milling temperature such that a range of hollow spheres with different size and sound samples can be produced.

Figure 2 demonstrates the microstructure of a Cu–30wt%Zn sample milled for 6 h at 77 K followed by 2 h of room temperature milling. Bright field and dark field images show that nanostructure produced by this processing route is fairly homogeneous and consists of twinned grains, typical microstructure for Cu–Zn samples prepared in this research. Corresponding selected area diffraction pattern (SADP), lower left inset in Fig. 2a, represents a microstructure with randomly oriented grains. Image analysis showed that the average crystallite size for this sample is 21 nm.

Figure 3 shows hardness results as a function of milling time for pure Cu, Cu–10wt%Zn, Cu–20wt%Zn, and Cu–30wt%Zn alloys processed at liquid nitrogen temperature. For each sample almost constant hardness is obtained after few hours of the milling process. Powder evolution during the milling process involves five stages including particle flattening due to plastic deformation, particle welding, equiaxed particle formation, random welding of powder particles, and steady-state deformation, during which a balance between fracture and cold welding is established as microstructural refinement progresses [7]. From Fig. 3 it is seen that compared to copper alloys, longer time is needed

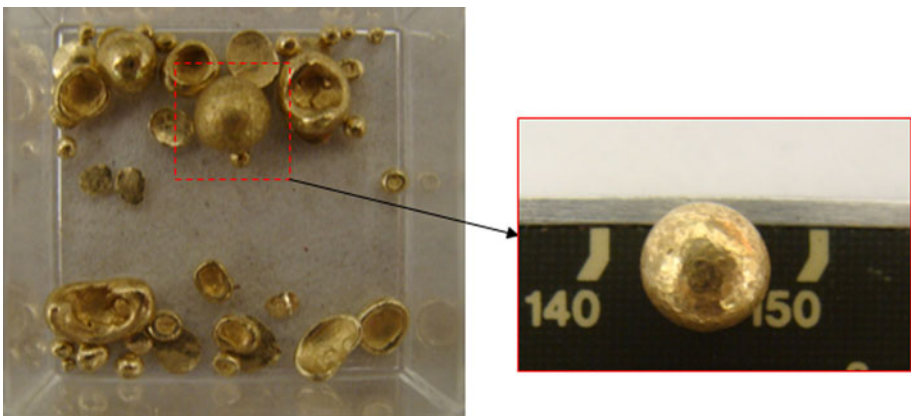

Fig. 1 In situ consolidated samples of Cu–10wt%Zn alloy. *Left* different pieces of hollow and defect-free spheres. *Right* A sound 6 mm sphere

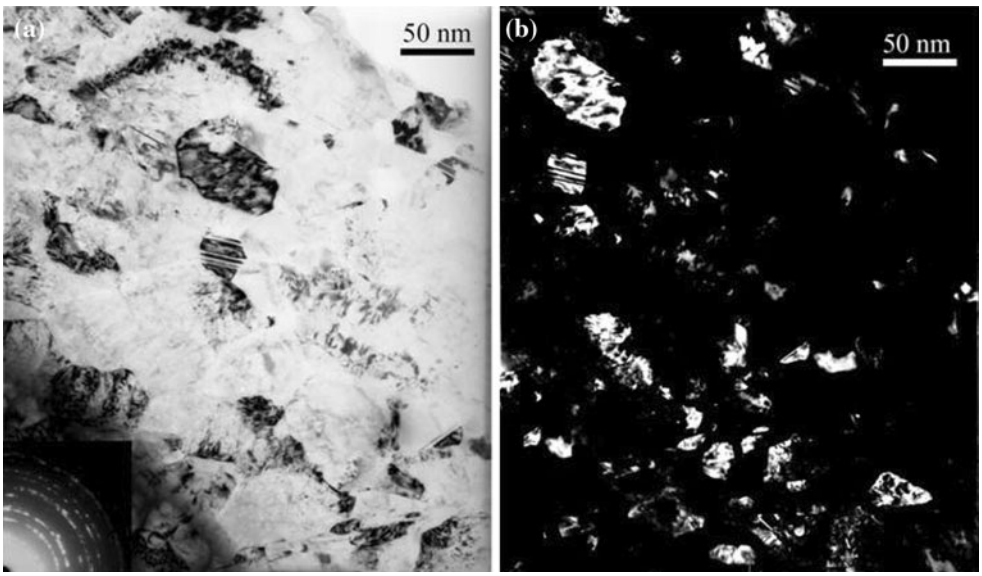

Fig. 2 **a** Bright field and **b** dark field TEM image of in situ consolidated Cu–30wt%Zn sample after 6 h cryomilling and 2 h milling at room temperature. *Lower left inset* in the bright field image shows the electron diffraction pattern

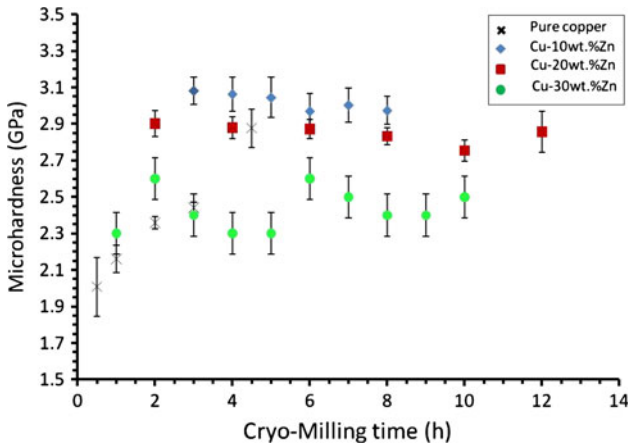

Fig. 3 Microhardness vs. cryomilling time for pure Cu, Cu–10wt%Zn, Cu–20wt%Zn, and Cu–30wt%Zn alloys

for pure copper to achieve steady-state deformation due to a higher rate of dynamic recovery in pure copper. This is reflected as a gradual increase of hardness in pure copper.

Assuming that the hardness and yield strength correlate with Tabor relation, $H_v \approx 3\sigma_y$, the strength obtained in these Cu–Zn alloys are higher than the results published in the literature on the same alloys with different processing such as high pressure torsion. For example Zhao et al. [8] reported 1.7 and 2.1 GPa for Cu–10wt%Zn and Cu–30wt %Zn, respectively. Mean grain size obtained by HPT in [8] was 110 and 10 nm for Cu–10wt%Zn and Cu–30wt%Zn, respectively. High frequency multi axial loads could result in smaller crystallite size, higher density of lattice defects, and hence higher strength for samples produced by high energy ball milling compared to plastic deformation induced by high pressure torsion, a typical severe plastic deformation process to make bulk ultrafine materials.

Small crystallite size obtained by ball milling at 77 K is demonstrated in Fig. 4 that shows the change in crystallite size, calculated from X-ray profile, as milling time increases. It can be seen that the crystallite size also stays almost constant over the milling period. Electrical resistivity measurements showed saturation of lattice defects after a certain time period in low temperature fatigue tests of copper crystals [9]. It could be also true for ball-milled materials when saturation of hardness and crystallite size is observed after 4–6 h of cryomilling for Cu–Zn alloys. Possible dynamic recovery of defects generated due to severe plastic deformation results in a stable microstructure after a certain milling time. At very low processing temperature of these alloys, i.e., 77 K, the rate of recovery should be less than the rate of defect formation for the first few hours of the process and hence a microstructure with lower crystallite size and higher defect density is expected to be generated during the cryomilling process.

It is noteworthy to address the distinct grain refinement behavior of Cu–30wt%Zn alloy observed in this research (Fig. 4). Smaller crystallite size obtained in this composition is also observed by Zhao et al. [8] for HPT-processed samples. As mentioned earlier, severe plastic deformation by HPT results in a crystallite size of 110 and 10 nm for Cu–10 wt%Zn and Cu–30wt%Zn alloys, respectively [8]. Wang et al. [10] suggested that the grain size of 10 nm in HPT-processed Cu–30wt%Zn is related to the very low stacking fault energy of the alloy, 7 mJ/m^2, making the sample capable of producing a high density of stacking faults and deformation twins. It was found that incoherent

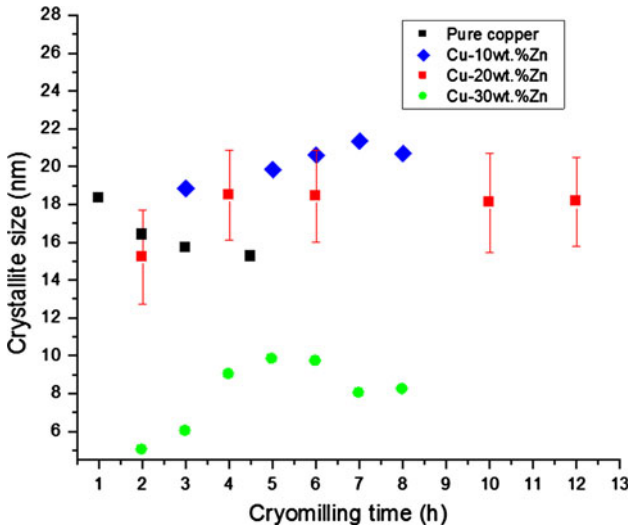

Fig. 4 Crystallite size vs. cryomilling time for pure Cu, Cu–10wt%Zn, Cu–20wt%Zn, and Cu–30wt%Zn alloys

high angle grain boundaries can be formed by the accumulation of a high density of dislocations at stacking faults and twin boundaries. These boundaries emit secondary stacking faults and twins that give rise to further refinement of the grains [10]. The differences in crystallite size of copper and copper alloys processed by ball milling could also be related to the stacking fault energy and capability of different alloys to break down the initial microstructure to nano sized grains.

Although the crystallite size of samples with higher zinc content is equal or smaller than alloys with lower concentration of zinc, Fig. 4, there is a decreasing trend of hardness as zinc content increases to more than 10 wt% (Fig. 3). It is also worthy to note that the hardness of pure copper sample after 4.5 h cryomilling is less than the hardness of Cu–10wt%Zn and almost equal to the hardness of Cu–20wt%Zn. This is rather an unusual trend seen in these alloys. Samples with the same compositions but processed with other severe plastic deformation techniques, e.g., high pressure torsion, show the expected results of hardening by increasing solute content of the material [8]. Shen and Koch [11] reported apparent solid solution softening observed in Ni–Cu, Fe–Cu, and Cr–Cu systems prepared by mechanical attrition is due to increase of crystallite size. Governing strengthening mechanisms in nanostructured materials such as solid solution and grain boundary hardening should be considered. For Ni in [11], it is believed that decreased grain boundary hardening is the reason for total reduction of hardness. The small contribution of grain boundary hardening to total strength of the material due to grain size increase results in the observed decrease of hardness [11]. But this is not the case for copper and copper–zinc system in this research and further studies are needed to investigate the hardening up to 10 wt% zinc and then softening behavior of Cu–Zn alloys at nanoscale grain sizes.

To have a deeper understanding of microstructure and mechanical properties, we need to consider dislocation density and their arrangement in the microstructure. Arrangement of dislocations in these samples and effect of temperature on their activity are studied by Whole Powder Pattern Modeling approach. WPPM has been applied to different metallic systems such as nanocrystalline FeMo [12] and Cu [13] to derive information about line defects. In this research, the Wilkens approach [14] was used by PM2K software [6] to calculate dislocation density and model the contribution of edge and screw dislocations to the X-ray profile of the processed alloys. Figure 5 demonstrates the effect of milling time on dislocation density and character for Cu–20wt%Zn sample. Dislocation density decreases at the beginning of cryomilling and then stays almost constant. First 2 h of cryomilling results in high dislocation density and further milling at 77 K up to 6 h brings about formation of dislocation cell structure. Figure 6 shows the TEM bright field image of the Cu–20wt%Zn alloy milled for 3 h at room temperature followed by 3 h cryomilling. The heavily deformed microstructure shown in Fig. 6 demonstrates dislocation cell-wall structures formed during the ball milling process. Movement of dislocations is constrained to local regions during low temperature processing of these low stacking fault energy alloys. With restricted cross-slip, continued deformation leads to reorganization of dislocations into cell-wall configurations to reduce the strain energy. Subsequent stabilization of the microstructure takes place by formation of sub-grains. This eventually leads to formation of new crystallite boundaries and, consequently a reduction of the X-ray coherent domain. This is consistent with the fact that the average dislocation density, obtained from X-ray diffraction, decreases as the milling time increases, i.e., the initial dislocation density of 0.55×10^{18} m^{-2} at 2 h is decreased to 0.39×10^{18} m^{-2} at 6 h cryomilling. The slight increase in dislocation density with increase in deformation from 6 to 10 h can be explained by the nucleation of a new generation of dislocations as the dislocation cell-wall configuration saturates. Further milling at room temperature leads to decrease of dislocation density that could be an evidence for annihilation of edge dislocations at primary grain boundaries or dislocation walls formed during cryomilling period by providing enough thermal energy to the system.

As shown in Fig. 5, the dislocation character of the cryomilled sample is a mixture of edge and screw dislocations but when the processing temperature is increased by milling at room temperature, the share of screw dislocations is increased. In light of temperature increase during

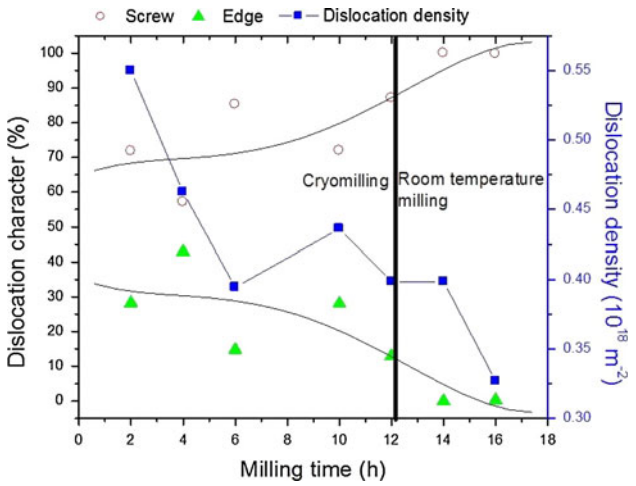

Fig. 5 Dislocation density vs. milling time for Cu–20wt%Zn milled for 12 h at 77 K followed by 4 h milling at room temperature

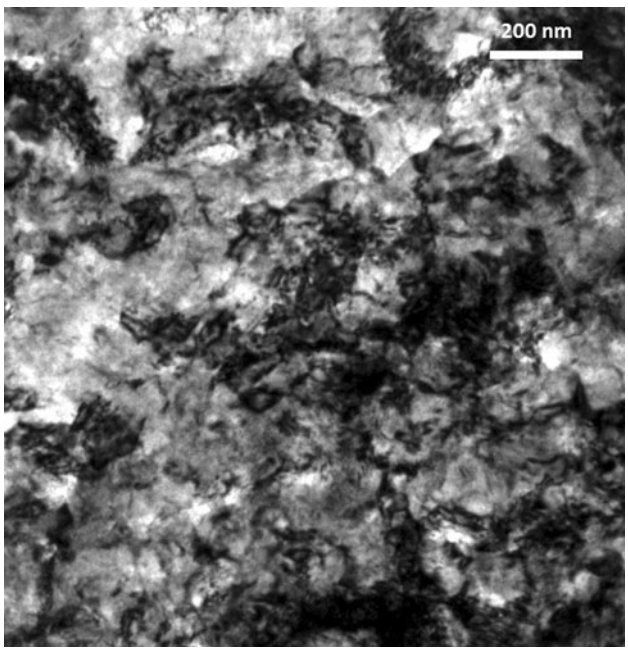

Fig. 6 Microstructure of Cu–20wt%Zn alloy milled for 3 h at room temperature followed by 3 h milling at 77 K

room temperature milling, the decrease of dislocation density, and change of dislocation character can be understood. Several researchers reported different values for temperature rise during mechanical milling. Using a computer model, Davis et al. [15] reported that the temperature increase in a Spex mixer/miller is less than 350 K. Xi et al. [16] concluded that under the maximum milling intensity the temperature rise is not more than 125 K. Joardar et al. [17] reported a maximum of $\sim$473 K temperature increase for $Al_{35}Ni_{35}Fe_{30}$ system in a planetary ball mill. Although there are some discrepancies between results obtained by different researchers, the temperature rise during room temperature ball milling seems to be enough to trigger thermally activated processes such as diffusion of vacancies and annihilation of dislocations.

It is well known that plastic deformation generates lattice defects such as dislocations and vacancies. Vacancy concentration in the order of 10^{-4} are found in pure copper processed by HPT and ECAP [18–21] that is considerably higher than the $\sim 3 \times 10^{-20}$ calculated for the thermal equilibrium vacancy concentration at room temperature, but close to the $\sim 1.5 \times 10^{-4}$ calculated at the melting temperature [22]. Ungar showed that for ECAP processed material, deformation-induced vacancy concentrations in the grain boundaries of compressed copper polycrystals are close to the equilibrium values at the melting temperature [23]. This result is interpreted by assuming that the vacancy accumulation in the grain boundary region is larger than in the grain interior or matrix regions. This would indicate that the state of the grain boundary region in strongly deformed metals is somewhat similar to the state at or close to the melting temperature [23]. Such high concentration of point defects should be considered as they can alter mechanical properties and work hardening behavior of the material in two ways [21].

(1) An indirect one allowing edge dislocations to annihilate via climb, e.g., in recovery or recrystallization and (2) A direct one which gets apparent when the vacancies collect to clusters and/or agglomerates markedly impeding the dislocation motion.

Considering the above explanation about the role of vacancies in mechanical properties and microstructure of these alloys, one can assume that vacancies annihilate at edge dislocations upon temperature rise during room temperature milling and cause the dislocation density and share of edge dislocations to decrease (Fig. 5). Studies on the kinetics of recovery of the complex dislocation structures have shown that recovery is controlled by dislocation climb and/or thermally activated glide of dislocations [24]. As far as low stacking fault energy materials are concerned, glide of dislocations is less important as the dislocation motion through glide is limited in low SFE samples. Hence, dislocation climb is the controlling mechanism for the recovery process. Dislocation climb is controlled by formation and movement of vacancies in the microstructure. It is well known that severe plastic deformation causes a high concentration of vacancies in the sample [25]. Therefore, it is also expected that a high concentration of vacancies is generated in cryomilled samples processed at 77 K. Higher thermal energy provided at room temperature milling results in higher mobility for the deformation-induced vacancies that are already formed at 77 K. These vacancies can be absorbed to the dislocation cores helping the climb process and recovery to occur. This significantly helps the annihilation process and the recovery and hence

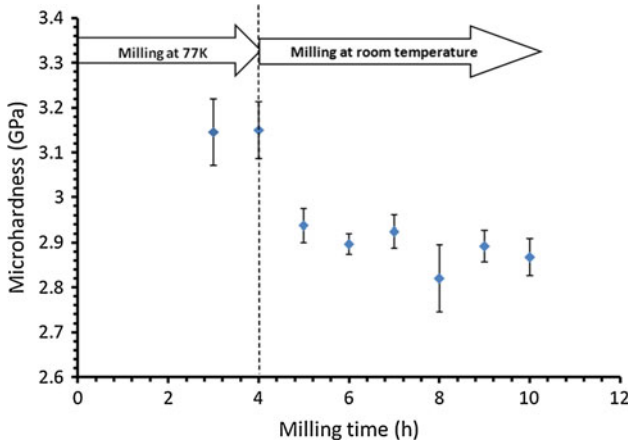

Fig. 7 Microhardness versus milling time for Cu–10 wt% Zn cryomilled for 4 h at 77 K followed by 6 h room temperature milling

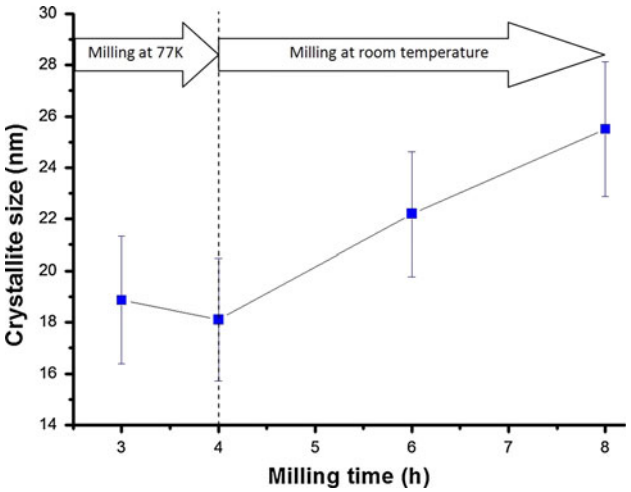

Fig. 8 Crystallite size versus milling time for the Cu–10 wt% Zn alloy processed 4 h at 77 K followed by 4 h milling at room temperature

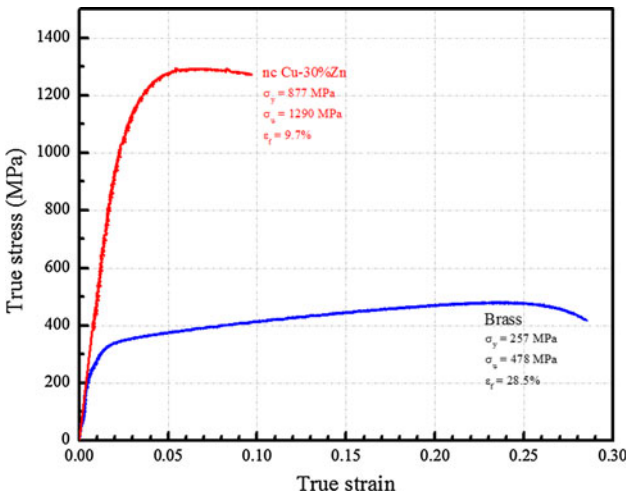

Fig. 9 Tensile curve for Cu–30wt%Zn sample milled for 6 h at 77 K and 2 h at room temperature

contributes to the reduction in dislocation density and lower microhardness values. It should be considered that cross-slip is the key process for annihilation of screw dislocations. Therefore, in copper alloys with low stacking fault energy and limited cross-slip, thermal activation leads to annihilation of edge dislocations and leaves screw dislocations in the microstructure. On the other hand, as the milling process proceeds new generation of dislocations, screw or edge, are being formed. Competitive processes of annihilation of edge dislocations at room temperature and formation of new generation of edge and screw dislocations lead to the observed behavior of the dislocation character and density at room temperature, Fig. 5.

Figure 7 demonstrates the effect of processing temperature on microhardness of the Cu–10wt%Zn alloy. Change of milling temperature after 4 h of cryomilling results in about 200 MPa decrease in microhardness of the sample. The softening and decrease of strength after milling at room temperature could be due to partial annihilation of dislocations and increase in grain size as shown in Figs. 7 and 8. Figure 8 demonstrates the change of crystallite size upon temperature increase by switching from cryomilling to room temperature milling. It is obvious that temperature rise is sufficient to decrease dislocation density, increase grain size, and alter mechanical properties of the highly deformed samples milled at 77 K.

Considering the changes in properties upon switching to room temperature processing, the cryomilled powder is then a good precursor for successful in situ consolidation via room temperature milling. Easier plastic flow of the particles prepared at 77 K leads to coalescence and welding of small particles and formation of defect-free samples with superior mechanical properties.

As an example, Fig. 9 shows the tensile behavior of Cu–30wt%Zn sample produced by cryomilling for 6 h and subsequently milled for 2 h to consolidate the particles at room temperature. Yield strength of 877 MPa for the in situ consolidated sample is well above the 690 MPa for the sample processed by HPT. 9.7% elongation to failure is almost twice of the 4.7% for the counterpart of this sample processed by HPT [8].

Conclusion

Nanocrystalline Cu–Zn alloys were synthesized using high energy ball milling at liquid nitrogen and room temperature. Combination of cryogenic and room temperature milling results in production of bulk nanostructured spheres with superior mechanical properties. The highly defected and fine nanostructured sample prepared at 77 K is a very

good precursor for in situ consolidation when it is followed by a few hours of room temperature milling. When the milling temperature is increased, thermal energy necessary for diffusion-assisted processes is provided. Therefore, the cryomilled powder is consolidated to get defect-free spheres with a homogeneous microstructure. Higher strength, better ductility, and finer crystallite size are obtainable via controlled milling of Cu–Zn alloys compared to processing with HPT.

Softening was observed in ball-milled samples upon increase of zinc content. Decreased hardness of these alloys at nano scale crystallite size has not been reported in the literature and further investigation is needed to understand the softening behavior of nanostructured Cu–Zn alloys.

Acknowledgement Financial support of National Science Foundation under contract DMR-0806323 is gratefully acknowledged.

References

1. Youssef KM, Scattergood RO, Murty KL, Horton JA, Koch CC (2005) Appl Phys Lett 87(9):0919041
2. Youssef KM, Scattergood RO, Murty KL, Koch CC (2004) Appl Phys Lett 85(6):929
3. Harris AM, Schaffer GB, Page NW (1993) J Mater Sci Lett 12(14):1103
4. Harris AM, Schaffer GB, Page NW (1996) Scr Mater 34(1):67
5. Calka A, Wexler D (2001) In: Schumacher P, Warren P, Cantor B (eds) Metastable, mechanically alloyed and nanocrystalline materials, ISMANAM-2000, vol 360–363. Materials Science Forum, Trans Tech Publications Ltd, Zurich-Uetikon, p 301
6. Leoni M, Confente T, Scardi P (2006) Z Kristallogr 23:249
7. Lavernia EJ, Han BQ, Schoenung JM (2008) Mater Sci Eng A 493(1–2):207
8. Zhao YH, Liao XZ, Horita Z, Langdon TG, Zhu YT (2008) Mater Sci Eng A 493(1–2):123
9. Basinski ZS, Basinski SJ (1989) Acta Metall 37(12):3275
10. Wang YB, Liao XZ, Zhao YH, Lavernia EJ, Ringer SP, Horita Z, Langdon TG, Zhu YT (2010) Mater Sci Eng A 527(18–19):4959
11. Shen TD, Koch CC (1996) Acta Mater 44(2):753
12. Scardi P, D'Incau M, Leoni M, Fais A (2010) Metall Mater Trans A 41(5):1196
13. Fais A, Scardi P (2008) Z Kristallogr 27:37
14. Wilkens M (1969) J Res Nat Bur Stand A 73(5):552
15. Davis RM, McDermott B, Koch CC (1988) Metall Mater Trans A 19(12):2867
16. Xi SQ, Zhou JG, Wang XT (2007) Powder Metall 50(4):367
17. Joardar J, Pabi SK, Murty BS (2004) Scr Mater 50(9):1199
18. Schafler E, Steiner G, Korznikova E, Kerber M, Zehetbauer MJ (2005) Mater Sci Eng A 410–411:169
19. Ungar T, Schafler E, Hanak P, Bernstorff S, Zehetbauer M (2007) Mater Sci Eng A 462(1–2):398
20. Zehetbauer MJ, Kohout J, Schafler E, Sachslehner F, Dubravina A (2004) J Alloys Compd 378(1–2):329
21. Zehetbauer MJ, Steiner G, Schafler E, Korznikov A, Korznikova E (2006) In: Horita Z (ed) Nanomaterials by severe plastic deformation, vol 503–504. Materials Science Forum, Trans Tech Publications Ltd, Zurich-Uetikon, p 57
22. Cao WQ, Gu CF, Pereloma EV, Davies CHJ (2008) Mater Sci Eng A 492:74
23. Ungar T (2006) In: Horita Z (ed) Nanomaterials by severe plastic deformation, vol 503–504. Materials Science Forum, Trans Tech Publications Ltd, Zurich-Uetikon, p 133
24. Humphreys FJ, Hatherly M (2004) Recrystallization and related annealing phenomena, 2nd edn. Boston, Elsevier, Amsterdam
25. Zehetbauer M, Schafler E, Ungar T (2005) Zeitschrift Fur Metallkunde 96(9):1044