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Grain size reduction of copper subjected to repetitive uniaxial compression combined with accumulative fold*

Zou Yong-Tao(邹永涛), Lei Li(雷 力), Wang Zhao(王 赵),
Wang Jiang-Hua(王江华), Zhang Wei(张 伟), and He Duan-Wei(贺端威)†

Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, *China*
College of Physical Science and Technology, Sichuan University, Chengdu 610064, *China*

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This paper reports a novel method of repetitive uniaxial compression combined with accumulative fold for preparing bulk submicron- to nanocrystalline copper starting with a coarse grained counterpart. Grain size reduction and microstrain variations of the high purity copper samples after different passes of compression and fold are investigated by scanning electron microscope and x-ray diffraction (XRD), respectively. Our results show that the average grain size of samples decreases from about 830 nm to 127 nm as the number of compression passes increases to 30. Microstrain in the compressed sample is found to increase for the first 20 passes, but to decrease at the last 10 passes. The variations of compressive yield strength and the shift of XRD peaks to larger diffraction angles are observed in the squeezed sample. Our experimental results demonstrate that the repetitive uniaxial compression combined with accumulative fold is an effective method to prepare bulk nanocrystalline metallic materials, in particular for soft metals such as Cu, Al and Pb.

Keywords: uniaxial compression, accumulative fold, grain size reduction，bulk nanocrystalline materials

PACC: 8116, 8100, 7865E

1. Introduction

Submicron- to nano-crystalline bulk material shows many advantages in comparison with the coarse grained counterpart, such as improved mechanical /physical properties, enhanced electrical resistivity and the combination of high strength and high ductility, super-plasticity at low temperature.[1−4] As for nanocrystalline metal Cu, some peculiar behaviours have been also observed, such as cold rolling at a very high rate[5] and near-perfect elasto-plasticity of nanostructured copper.[6] These properties are of particular interest because they enable the fabrication of light engineering structures and the shaping of nano- and/or micro- objects more easily. In recent years, various techniques have been applied to prepare bulk submicron- to nano-crystalline metallic materials,[7−12] but it is still a challenge in preparing soft bulk metallic materials such as Pb, Al and Cu. The current methods for producing bulk submicron- to nano-crystalline metallic materials can be classified into two categories.[13] One category involves the preparation of atom clusters or nano-scaled particles as precursors to obtain bulk nanocrystalline materials followed by a further consolidation or sintering process.[14−17] The nanometre-sized precursors are usually fabricated using chemical vapour deposition, physical vapour deposition, sol-gel process and/or ball milling.[18] The second type of methods is conventional severe plastic deformation (SPD) techniques, such as high pressure and torsion,[19,20] repetitive corrugation and straightening,[21,22] equal channel angular pressing[23,24] and accumulative roll bonding.[25−27] The first group of methods can produce finer nanocrystalline metallic materials in comparison with the second one. However, applications of the first type of method meet difficulties in preparing large bulk nanocrystalline materials and inevitably lead to imperfections, such as porosity and impurities during the course of preparing nanocrystalline precursors and the late consolidation or sintering process. The porosity and impurities significantly affect the mechanical properties of the bulk materials, and often make them brittle.[28,29] As a consequence of these dif-

*Project supported by the National Natural Science Foundation of China (Grant No 50572067).
†Corresponding author. E-mail: duanweihe@yahoo.com

ficulties, much attention has been paid to alternative procedures of introducing ultrafine grains in materials by SPD. SPD[19−27] is certainly an effective method for grain refinement to prepare bulk nanocrystalline materials avoiding pollution and porosity, but the expense of the SPD is usually high as the mould used in the SPD process is easy to be damaged.

Sung *et al*[30] find that each kind of metallic material owns its critical thickness h_c and the different initial-thickness of the samples is eventually consistent with a same value h_c under the same loading force if plastic deformation happens freely during the compression. This means that the compression alone without other processes such as accumulative fold, corrugation and/or straightening is unlikely to prepare nanometre-sized metallic material due to its limited critical-thickness. In this work, a novel method of repetitive uniaxial compression combined with accumulative fold has been applied to prepare bulk submicron- to nano-crystalline copper at room temperature. Analysis of scanning electron microscope (SEM) images and x-ray diffraction (XRD) patterns of being squeezed samples shows some different features in comparison with that of the starting sample, such as crystalline size reduction, variations of compressive yield strength and a shifted centroid position of XRD peaks to larger diffraction angles. Our experimental results demonstrate that the repetitive uniaxial compression combined with accumulative fold is an effective method to prepare bulk nanocrystalline metallic materials, especially for soft metals such as Cu, Al and Pb.

2. Experimental details

The starting materials, namely coarse-grained copper, with a purity of $\sim$ 99.99% (Chengdu Yatai Copper Trading Ltd. Co., China), were machined into a disc shape with $\sim$20 mm in diameter and $\sim$0.92 mm in thickness as starting samples. Our experiments were performed at a 300 KN Multifunctional Pressing and Testing Machine controlled by its corresponding test-work software. Carrying out an experiment, we first folded the starting sample once and then placed it between two WC plates. In the subsequence, the uniaxial force to the sample was loaded at a rate of 200 N/S. The loading force increased from 0 to the maximum value of 2×10^5 N each time at room temperature. Keeping the loading force of 2×10^5 N for 60 s, we decompress the squeezed sample at the same rate of 200 N/S. After that, the compressed sample was taken out for the next pass of fold and compression. The as-squeezed samples subjected to 10, 20 and 30 passes of fold and uniaxial compression, as well as the starting samples were examined by SEM and XRD, respectively.

For microstructural characterization, the starting sample as well as the compressed ones was observed under JEOL SEM (JSM6490LV). Grain sizes of the compressed samples were calculated from the image analysis software.

XRD measurements of the Cu samples were performed on a Philips X'pert pro-type diffractometer. The rotating Cu target was operated at a voltage of 40 KV and a current of 40 mA. The x-ray of wavelengths $\lambda_{K\alpha1}$ (1.54056Å) (1 Å = 0.1 nm) and $\lambda_{K\alpha2}$ (1.54439 Å) were reflected by a graphite crystal. Using flat plate geometry, we collected the diffraction patterns over 40° to 110° in 2-theta with step scanning size equal to 0.02° and step scanning time of 1 s. The intervals of angle and time were chosen to be identical to the same (hkl) Bragg peaks of all the experimental samples. With the same conditions, it was possible to compare the integrated intensities of Bragg reflections for these samples.

In order to determine the instrumental broadening, a coarse-grained copper disc was annealed at 923 K for 3 hours and then cooled down slowly to get rid of the possible residual stress and to obtain the good crystallinity. It was found that this annealed sample had an almost perfect crystalline structure and its Bragg reflections could be regarded as a reference for the instrumental broadening.

3. Results and discussion

3.1. Analysis of crystallite size and microscopic strain (microstrain)

Figure 1 is the multi-plotting of XRD patterns for the squeezed samples subjected to 10, 20 and 30 passes of fold and uniaxial compression, as well as for the starting samples. The magnified images (Figs.2 and 3) show that the centroid positions of Bragg peaks (111), (200), (220), (311) shift to larger diffraction angles after passes of compression and fold. It indicates that residual compressive stresses exist in the Cu samples after passes of uniaxial compression and accumulative fold. It is also found that the integral widths of the

Bragg peaks (111), (200), (220), (311) for the compressed samples become larger with the compression passes increasing to 30, it suggests a physical broadening. Microscopic stress exists in a polycrystalline copper sample caused by grain-to-grain contact. The magnitude and orientation of this stress generally distribute randomly and lead to broadening of diffraction peaks.[31−34] XRD peak broadening (β) can be caused by the presence of microstrain as well as the small crystallite size / grain size. Although the broadening effects of crystallite size and microstrain are superimposed, the contributions of crystallite size and microstrain to peak broadening are able to be separated with the Scherrer and Wilson equation:[34]

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{L} + \frac{\varepsilon\sin\theta}{\lambda}. \tag{1}$$

Where β represents the physical peak broadening, L is the average crystalline size, θ is the Bragg angle, λ is the x-ray wavelength, and ε is the mean magnitude of microstrain distribution.

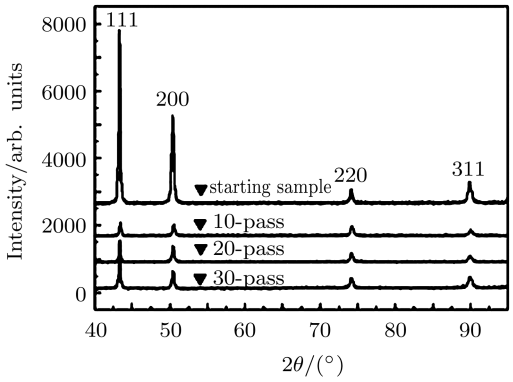


Fig.1. XRD patterns for the starting sample and the other three samples subjected to different passes of compression and fold.

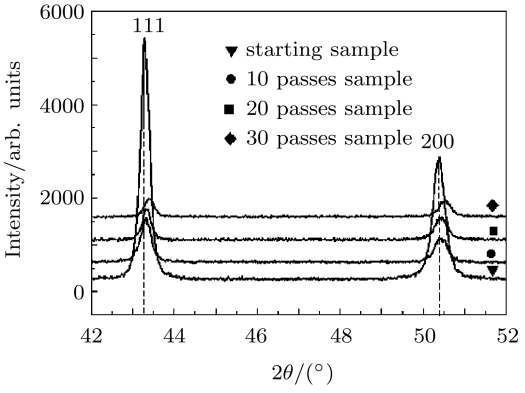


Fig.2. The magnified XRD patterns which show that a physical broadening and/or the centroid positions of Bragg reflections of (111) and (200) orientations shifted to larger diffraction angles.

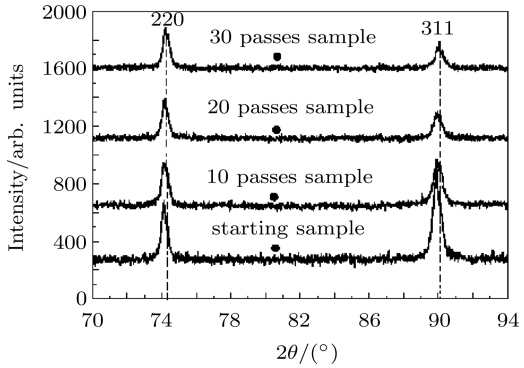


Fig.3. The magnified XRD patterns which show that a physical broadening and/or the centroid positions of Bragg reflections of (220) and (311) orientations shifted to larger diffraction angles.

Taking account of the instrumental broadening β_{inst}, we can modify Eq.(1) as

$$\beta^2 = \beta_{\text{o}}^2 - \beta_{\text{inst}}^2. \tag{2}$$

Where β_{o} represents the observed peak broadening.

The diffraction pattern of an annealed sample with an almost perfect crystalline texture could be regarded as a reference for the instrumental broadening. In accordance with Eq.(2), different diffraction peaks should give a linear plot of $\beta\cos\theta/\lambda$ versus $\sin\theta/\lambda$ with slope ε and ordinate intercept $1/L$.

Figure 4 shows the separation of crystalline size and microstrain contributions in the plot of $\beta\cos\theta/\lambda$ against $\sin\theta/\lambda$ of the sample subjected to 10 passes of compression and fold. The slope of the straight line reflects the microstrain ε of ∼0.2030% from the sample due to grain-to-grain and/or grain inside compression, and the intercept reflects the crystallite size/grain size L of ∼417 nm. SEM micrograph of the starting sample as well as compressed samples is presented in Fig.5.

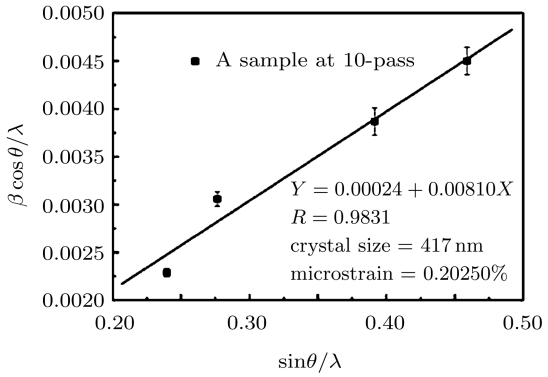
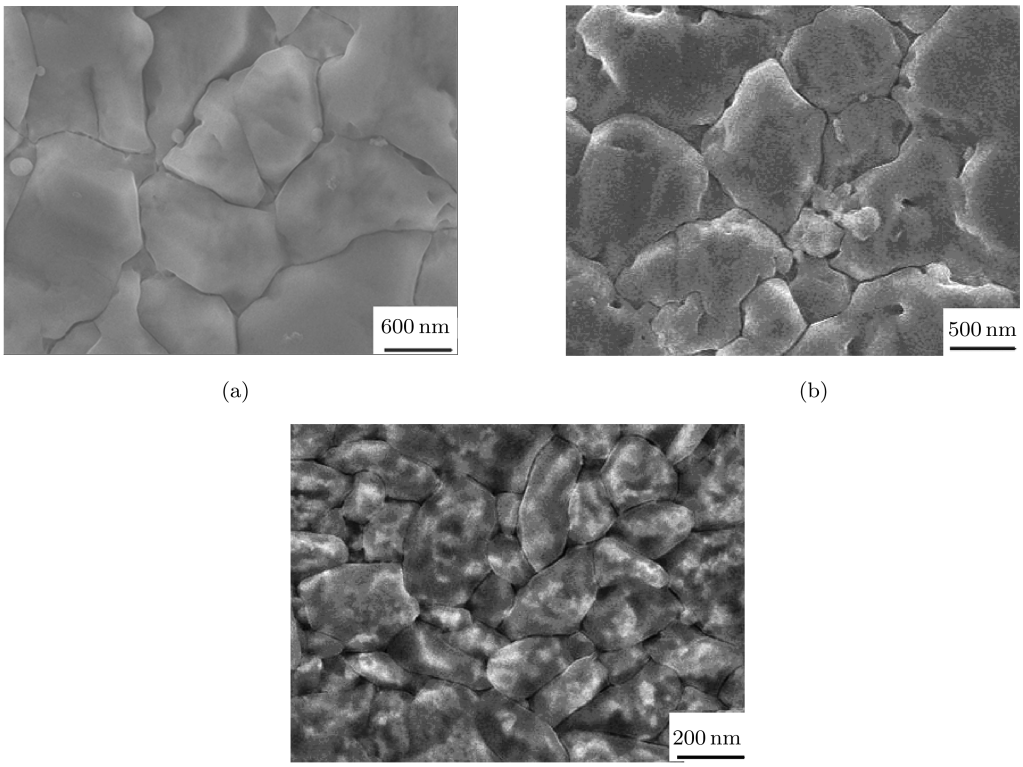


Fig.4. Separation of crystalline size and microstrain contributions in the plot of $\beta\cos\theta/\lambda$ against $\sin\theta/\lambda$ of the sample subjected to 10 passes of compression and fold. The slope of the straight line reflects the microstrain ε from the sample due to grain-to-grain and/or grain inside compression, and the intercept reflects the crystalline size L.



(a) (b)

(c)

Fig.5. SEM micrographs of metallic copper samples: (a) the starting material; (b) subjected to 10-pass compression and fold; (c) subjected to 30-pass compression and fold.

If we consider the crystallite size as the grain size, the diagrammatic relations between crystallite size and the passes of compression is shown in Fig.6. It can be seen that the average grain size of copper samples decreases from about 830 nm to 127 nm as the passes of compression and fold increase to 30. The average grain size/crystalline size observed under SEM is in good agreement with the value from XRD pattern. The phenomenon of compression-induced reduction of grain size is remarkable at the first 20-pass, however the average grain size reduces slowly with the compression passes increasing from 20 to 30. The reasonable explanations for the above results may be the limited critical- thickness h_c.[30]

Microstrain of samples as a function of the passes of compression and fold is also shown in Fig.6. Microstrain in the squeezed sample is found to increase at the first 20-pass, but to decrease at the last 10-pass. Our results are in agreement with the results of Weir *et al*[35] and Meade *et al.*[36] Such phenomenon is called 'strain-softening' by Bridgman.[37] As the actual microscopic stress of samples at the latter passes is sufficient, local fragmentation or broken pieces will appear under a further compression, which offered a convenient channel to release the microstrain.

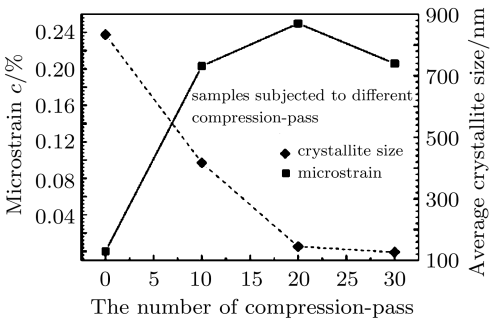


Fig.6. Experimental values on the crystallite size/ microstrain versus the number of compression passes. It can be seen that the average grain size of copper samples decreases from about 830 nm to 127 nm as passes of compression and fold increase to 30. The microstrain at the first 20-pass increases in a sound sequence, however it begins to decrease slowly at the last 10-pass.

3.2. Analysis of compressive yield strength

Microstrain exists in a polycrystalline sample of copper caused by grain-to-grain and/or grain-inside

contact. Once the microstrain distribution ε is known, the microscopic stresses ν can be determined by multiplying the aggregate Young's modulus E. If sufficient stress is generated to deform the sample plastically, then this stress represents the yield strength of the sample.[38,39] Thus we have

$$\upsilon = \varepsilon \cdot E = Y. \tag{3}$$

In present work, we take Young's modulus E of ∼112.52 GPa from Ref.[40] for our experimental samples. Similar to the microstrain, the calculated compressive yield strength shown in Table 1 presents a modest increase at the first 20-pass, but it decreases at the last 10-pass. The compressive yield strength of ∼228.4 MPa from samples at the 10-pass is larger than that of ∼200 MPa for Cu with the same grain size ∼417 nm in Ref.[41]. At the 20 passes of compression, the yield strength of ∼281.1 MPa from Cu sample is consistent with that of ∼280 MPa from Cu reported by Youngdahl *et al.*[41] In our experiments, the actual Young's modulus of the sample should increase with the increasing compression passes (work hardening). So the compression strength is likely underestimated by using the above way. As the number of compression passes increases to 30, the yield strength of ∼ 231.7 MPa for the compressed sample is found to decrease. The calculated compressive strength decreases at the last 10 passes, which may be due to the broken texture of the samples. The compressed Cu material became brittle and broke into small pieces at the last 10 passes of compression. That leads to a release of the residual stress, and the microscopic stress in the compressed sample is less than the compressive strength.

Table 1. The calculated microstrain and compressive yield strength at different passes of uniaxial compression combined with accumulative fold.

	10-pass	20-pass	30-pass
Microstrain/ε	0.2030 %	0.2498 %	0.2059 %
Yield strength/MPa	228.4	281.1	231.7

4. Conclusions

It is found that the integral widths of the Bragg peaks (111), (200), (220), (311) for the compressed samples become larger with the number of compression passes increasing to 30. Our experimental results indicate that residual compressive stresses exist in the Cu samples after passes of fold and compression. The average grain size of Cu sample decreases from about 830 nm to 127 nm as the number of compression passes increases to 30. Microstrain in the compressed sample is found to increase for the first 20 passes, but to decrease for the last 10 passes. The compressive yield strength of Cu sample is consistent with the previous values. Our experiments demonstrate that the repetitive uniaxial compression combined with accumulative fold is an effective method to prepare bulk nanocrystalline metallic materials, in particular for soft metals such as Cu, Al and Pb. Above all, application of such method embodies the advantages of low expenditure and pollution.

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