Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 19(2009) 272−276
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

# Microstructure evolution and thermal stability of nanocrystalline Cu-Nb alloys during heat treatment

LEI Ruo-shan(雷若姗), WANG Ming-pu(汪明朴), GUO Ming-xing(郭明星),
LI Zhou(李　周), DONG Qi-yi(董琦祎)

School of Materials Science and Engineering, Central South University, Changsha 410083, China

Received 8 May 2008; accepted 26 August 2008

**Abstract:** The microstructure evolution and high thermal stability of the mechanically-alloyed supersaturated nanocrystalline Cu-10%Nb alloy during subsequent heat treatment were investigated by X-ray diffractometry and transmission electron microscopy (TEM). The results show that no significant change of the microstructure of the solid solution can be detected after annealing at 300−400 ℃. The pronounced phase separation can be detected at 700 ℃. After annealing for 30 min at 900 ℃, almost all the Nb atoms precipitate from the solid solution, and the average Cu grain size is about 37 nm. As the solute atoms hinder the migration of fcc phase, at Cu grain boundaries, no significant grain growth occurs before large amount of Nb atoms precipitates from Cu matrix, and the decrease of internal strain and density of dislocation is small. Furthermore, the nanosized Nb precipitates can also help to reduce the Cu grains growth through precipitating pinning effect. Therefore, the mechanically-alloyed nanocrystalline Cu-Nb alloys have a high thermal stability. And the contaminations brought into the Cu matrix by milling can influence the phase formation and the thermal stability of Cu-Nb alloys during heat treatment.
**Key words:** Cu-Nb alloy; mechanical alloying; nanostructured material; microstructure; thermal stability

## 1 Introduction

It is well known that nanocrystalline materials are characterized structurally by ultrafine grain size with extremely large number of grain boundaries to possess a variety of properties and performances compared with those of the conventional polycrystalline counterparts [1−2]. Because of the hindrance of grain boundaries to the dislocation motion, the mechanical strength of nanocrystalline metallic materials is enhanced, for example, pure copper[3−5]. Furthermore, the strength of copper can be improved by alloying with insoluble elements, such as Cr, Nb and Ta[6]. BOTCHAROVA et al[6−8] showed that an extremely fine nanocrystalline microstructure and a dissolution of up to 10% (molar fraction) for niobium in the copper lattice can be achieved by mechanical alloying(MA), though the Cu-Nb phase diagram shows a negligibly low mutual solubility in the solid state. The compacted samples of Cu-5% Nb (molar fraction) alloy show a high mechanical strength of about 1 GPa and a relatively good conductivity of about 50%(IACS) after annealing at 900 ℃ for 1 h[9]. Therefore, the mechanically alloyed nanocrystalline Cu-Nb alloys will be a promising conductor. Since the nanocrystalline structure and supersaturated solid solution are in nonequilibrium states, heat treating at elevated temperature will lead to the occurrence of structural relaxation, precipitation of the solute phase, coarsening of the precipitates and the grain growth. Consequently, it will affect the properties of the nanocrystalline materials. Therefore, the thermal stability of such materials is an important subject for both scientific and technological reasons[1].

In previous studies, we have reported the microstructure evolution of nanocrystalline Cu-10%Nb (mass fraction) alloy during MA[10]. The present investigation presents a detailed microstructure evolution and the thermal stability of mechanically alloyed Cu-Nb alloys during heat treatment. The tendency for decomposition of the supersaturated solid solutions at elevated temperatures is discussed. And knowledge of

**Foundation item:** Project(2006AA03Z517) supported by the National High-Tech Research and Development Program of China
**Corresponding author:** LEI Ruo-shan; Tel: +86-731-8830264; E-mail: leiruo@163.com
DOI: 10.1016/S1003-6326(08)60264-2

the relationship between this phase separation and the grain growth characteristics of nanocrystalline alloys is important. Furthermore, the influence of the contaminations of oxygen and iron presented during milling on phase formation and thermal stability of the Cu-Nb alloys in heat treatment is discussed according to thermodynamic conditions.

## 2 Experimental

The Cu-Nb alloy with Nb content of 10% (mass fraction) was prepared by MA and a subsequent heat treatment was applied. MA was performed in a QM−1F Mini-planetary ball mill with stainless steel containers and balls, using a rotational speed of 300 r/min at a constant rotation direction and a powder-to-ball mass ratio of 1:14 and was carried out for 100 h in argon atmosphere. After milling for 100 h, the alloying is regarded to be completed (detailed contents refer to Ref.[10]). Heat treatments were conducted at constant temperature from 300 ℃ up to 700 ℃ in argon atmosphere for 1 h and at 900 ℃ for 0.5 h. The samples were taken out for X-ray diffraction analysis and TEM observation. The microstructure of samples was investigated by X-ray diffraction analysis equipped with a DMAX2000 using Cu $K_\alpha$ radiation from $2\theta$=38° up to 98° at scanning rate of 2(°)/min. The lattice parameters were obtained using the DBWS Rietveld program[11]. The grain size and the internal strain were determined from the measured data using Williamson-Hall plots[12]. The powders prepared by ion-beam-thinning were examined by TEM in Tecnai $G^2$ 20 operating at 200 kV.

## 3 Results

### 3.1 X-ray analysis

After heat treatment at different temperatures, the samples were taken out for X-ray powder diffraction analysis in order to trace the phase formation. Up to 400 ℃, there was no significant change of the powder diffraction pattern (Fig.1). With further increase of temperature, the fcc Bragg peaks became sharp gradually and recovery took place above 600 ℃. The fcc peaks moved towards higher angles, resulting from the precipitation of Nb from Cu matrix. A very small Nb peak was detected after annealing at 700 ℃ for 1 h. The intensity of the Nb peaks was enhanced at 900 ℃. High annealing temperatures led to the formation of CuO, NbO as well as $Fe_7Nb_6$.

Due to the heat treatment, other properties changed, therefore the lattice parameter of the Cu matrix, the corresponding grain size, the internal strain and the dislocation density can be detected.

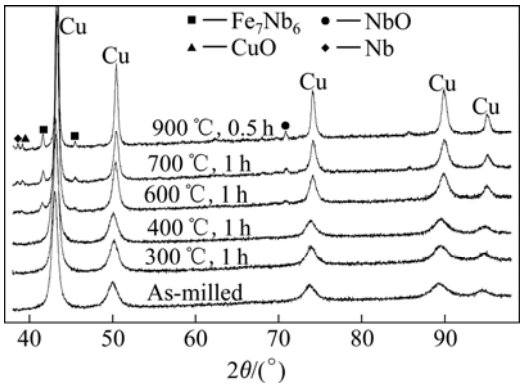


**Fig.1** X-ray powder diffraction patterns after heat treatment at different temperatures

The process of phase change for Cu-10% Nb alloy is illustrated in Fig.2, which shows the lattice parameter of the Cu matrix as a function of annealing temperature. The lattice parameters were determined from the measured diffraction data using the DBWS Rietveld program[11]. The lattice parameter of the Cu matrix after milling is very large, which is caused by the fact that Nb is dissolved into the Cu matrix. As the temperature goes up, the lattice parameter decreases until the value nearly converges to that of pure copper (0.361 5[6]), which indicates the precipitation of Nb from Cu due to the larger atomic size of Nb. And almost all the Nb atoms precipitate from the solid solution after annealing at 900 ℃ for 0.5 h.

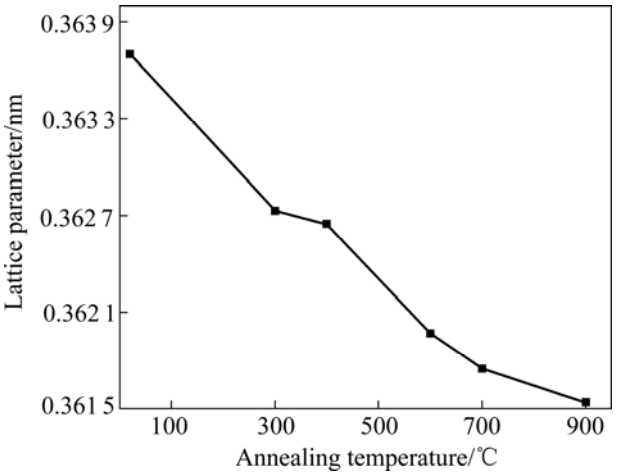


**Fig.2** Lattice parameter of Cu matrix as function of temperature

The X-ray diffraction data as a function of annealing temperature were used to gain further insight into recovery and recrystallization. A Wagner relationship, $\beta = \beta_g - \beta_i^2/\beta_g$, was assumed to extract the peak broadening contribution of the sample ($\beta$) from the total line broadening $\beta_g$, where $\beta_i$ is the instrumental line broadening[13]. The broadening of the diffraction peaks

as mentioned in Fig.1 is due to size broadening and/or microstrain broadening. In order to separate the two effects, a quantitative analysis was carried out by using a plot according to the Williamson-Hall method [12]: $\beta\cos\theta=K\lambda/d+2\varepsilon\sin\theta$, where $\lambda$ is the X-ray wavelength; $\theta$ is the Bragg angle; $d$ is the grain size; $\varepsilon$ is the internal strain; and $K$ ($K\approx1$) is the Scherrer constant. Therefore, a linear dependence of $\beta\cos\theta$ on $\sin\theta$ is expected, with the intercept corresponding to the particle size ($d$) as $d=K\lambda/\beta\cos\theta$. The internal strain $2\varepsilon$ can be determined by the slope of the straight line[12]. The Cu grain size and the internal strain of the Cu lattice of heat treated powder are shown in Fig.3(a). As shown in Fig.3(a), the Cu grain size of heat treated powder increases very slowly below 400 ℃. However, with further increasing of temperature, the grain size begins to increase fast, especially above 700 ℃. After annealing at 900 ℃ for 0.5 h, the average Cu grain size is about 37 nm. Meanwhile, the internal strain decreases with the increase of temperature. For milled samples, dislocations are the main defects besides grain boundary. The density of dislocations can be represented in terms of $D_{hkl}$ and $\langle\varepsilon^2_{hkl}\rangle^{1/2}$ by $\rho_{hkl}=(\rho_D\rho_S)^{1/2}=2\sqrt{3}\langle\varepsilon^2_{hkl}\rangle^{1/2}/(D_{hkl}\boldsymbol{b})$, where $\boldsymbol{b}$ is the Burgers vector and equal to 0.255 nm for Cu; $\langle\varepsilon^2_{hkl}\rangle^{1/2}$ is the lattice strain; $D_{hkl}$ is the grain size[14]. As shown in Fig.3(b), the dislocation density keeps decreasing with the increase of temperature, and the dislocation density reduces to about $1\times10^{11}$ cm$^{-2}$ after annealing at 900 ℃ for 0.5 h, which indicates the occurrence of recovery. The decrease rates for both microstrain and dislocation density speed up above 400 ℃.

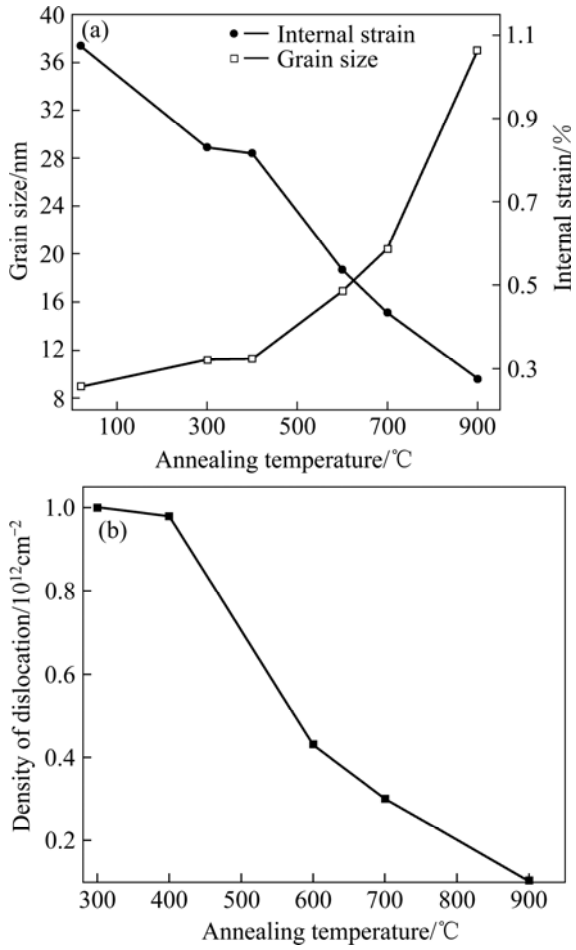


**Fig.3** Grain size, internal strain (a) and dislocation density (b) of Cu matrix as function of annealing temperature

### 3.2 Microstructural investigations

The microstructure of the mechanically alloyed powders after annealing at different temperatures was investigated by TEM (Fig.4). After annealing at 400 ℃ for 1 h, a fine-grained microstructure and a strong strain contrast due to milling are still remained (Fig.4(a)). The corresponding electron diffraction patterns exhibit both the characteristic Debye-Scherrer rings of fcc and bcc structures, confirming the precipitation of Nb. However, due to the small size and small amount of the Nb clusters, they cannot be detected by X-ray diffraction. The electron diffraction pattern with continuous rings obtained from the region with a diameter of 3.8 μm indicates that a number of different orientations existing within the selected area. After heat treatment at 700 ℃ for 1 h, the average grain sizes increases to about 30 nm and there are also some nano-sized twins (Fig.4(b)). The twin boundaries are flat, and the thickness of the lamellae is below 5 nm. The precipitation of only Nb particles with size of about 2 nm can be seen inside the Cu grain, but not along grain boundary. Fig.4(c) shows large particles embedded in Cu matrix using energy-dispersive X-ray analysis, rich in Nb after annealing at 900 ℃ for 0.5 h. However, the amount of large Nb particles is very small, and they are from the small Nb particles that do not dissolve into the Cu matrix during MA and then coarsen rapidly during heat treatment. By contrary, the growth of the Nb precipitates is relatively slow and their sizes are below 10 nm after heat treatment at 900 ℃. Furthermore, the grain size of the Cu matrix spans a wide range from several tens of nanometer up to about 100 nm. The average grain size is somewhat larger than that estimated using X-ray diffraction, but on the same order. Such discrepancy between the average grain sizes determined by the two techniques has been noted before[15].

## 4 Discussion

### 4.1 Thermal stability

The nanocrystalline Cu-10%Nb solid solution phase separates and coarsens upon heating to elevated temperatures. The decrease of the lattice parameter of the Cu matrix with temperature indicates an continued precipitation of Nb from the supersaturated solid solution between 300 ℃ and 900 ℃. After annealing at 400 ℃ for 1 h, the Cu lattice parameter reduces to about 0.3626 5

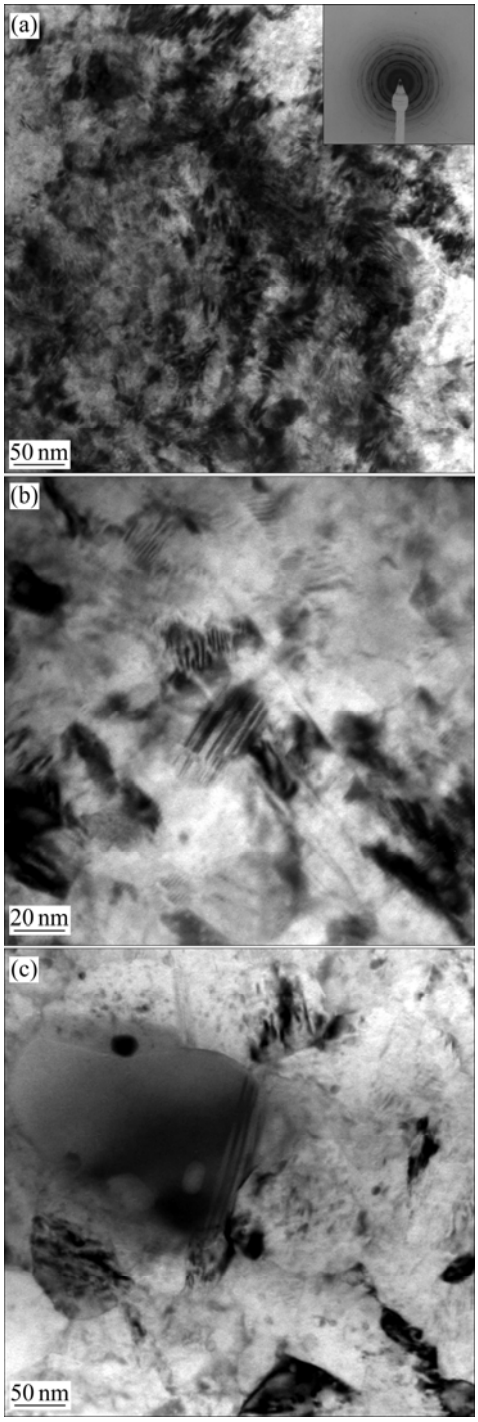


**Fig.4** TEM images showing microstructures of mechanically alloyed nanocrystalline Cu-10%Nb alloy annealed at 400 ℃ for 1 h (a), 700 ℃ for 1 h (b) and 900 ℃ for 0.5 h (c) (Inset in (a) shows electron diffraction of (a)

nm, and the increase of the grain size and the decrease of the internal strain are relatively small. However, with further increase of temperature, the decrease of the lattice parameter, the growth of Cu grains and the release of the internal strain speed up simultaneously. The results indicate that the stability of the metastable nanocrystalline Cu-Nb alloy is governed by the kinetics of phase separation and grain growth, which means that no significant grain growth occurs for these alloys before phase separation. This can be understood in terms of the cohesive energy of Nb and Cu. Since there are more broken bonds on grain boundaries, elements with lower cohesive energy tend to segregate to grain boundaries because of smaller grain-boundary energy. As the cohesive energy of Cu is smaller than that of Nb, migration of Nb atoms to grain boundaries is unlikely. And the phase separation can only occur when the mobility of Nb atoms is high enough to nucleate. It can be confirmed by Fig.4(b) that the Nb particles only form inside the grains. Therefore, pronounced precipitation of Nb from the supersaturated solid solution happens when the temperature reaches 700 ℃. As long as Nb atoms are dissolved in the copper lattice, these solute atoms might hinder the migration of fcc Cu grain boundaries due to solute drag. Therefore, no pronounced grain growth of fcc alloys can be observed before most of the Nb atoms are removed from the solid solution. The average Cu grain size is just about 20 nm (as measured by XRD) even after annealing at 700 ℃. Furthermore, even after almost all the Nb atoms precipitate from the solid solution at 900 ℃, the Cu grain size is still kept in nanoscale (Fig.3(a)), as the nanosized Nb precipitates can also hinder the migration of Cu grain boundaries and thereby reduce grain growth. Therefore, the temperature for grain growth in the Cu-Nb alloys is significantly higher than that in elemental nanocrystalline Cu, which indicates that the Nb addition enhances the stability of nanocrystalline fcc phase.

### 4.2 Influence of impurities on phase formation

Although milling was carried out under argon atmosphere, the contamination of oxygen cannot be avoided completely. And the oxygen content in the powder may increase constantly with milling time. It has been suggested that oxygen can be dissolved or occupy lattice sites according to the substitutional mechanism[6]. And the formation of NbO indicates that Nb atoms react with oxygen during heat treatment. It has been known that when the chemical bond energy between oxygen and another element is larger than half of the O—O dissociation energy, chemical absorption between O atoms and the other atoms will happen[16]. The Nb—O bond energy is 771.3 kJ/mol, while O—O bond energy is only 498 kJ/mol[17]. Thus, the absorption of O on Nb agrees with thermodynamics law. Furthermore, Nb will react with O, and form niobium oxide. Once the niobium oxide forms, the lattice parameter of the Cu matrix will decrease as Nb precipitates from the Cu matrix. The Nb precipitates, whose reflections are detected by X-ray analysis, originate from regions where the levels of Nb and O atoms become unbalanced and finally favor the

precipitation of Nb instead of the formation of niobium oxide from the entire Nb content.

The influence of Fe on the formation of phase during heat treatment must be taken into consideration, because the containers and milling balls are made of stainless steel. According to Miedema's model[18], the positive enthalpy of $\Delta H_{min}$ for Cu-50%Fe (molar fraction) is about 11.9 kJ/mol, while the enthalpy of $\Delta H_{min}$ for Fe-50%Nb (molar fraction) is about −61 kJ/mol, which indicates that the affinity between Fe and Nb is quite larger than Cu and Fe. Hence, the formation of Fe-Nb solid solution is much easier than the formation of Cu-Nb or Cu-Fe alloys. It is possible that the Fe-Nb alloys may form and precipitate from the Cu matrix in the later stage of milling. However, their sizes and amounts are too small to be detected[6]. During heat treatment, because the mobility of Fe and Nb increases with temperature, the formation of $Fe_7Nb_6$ and its grain growth are favored according to the thermodynamics law. The obvious $Fe_7Nb_6$ peaks can be detected after annealing at 600 ℃ for 1 h and its intensity keeps increasing with temperature. However, all these hypotheses need further experiments to be confirmed.

The total amount of impurities is low. And also the stability of the nanocrystalline Cu microstructure can be enhanced by the solute drag of the impurities, and precipitate pinning effects of NbO, CuO or $Fe_7Nb_6$ particles. However, the impurities may be influence the dissolving of Nb into Cu during milling and the formation of phases during heat treatment. Furthermore, the mechanical and electrical properties of the subsequent compacted samples will be largely affected. Therefore, other milling medium should be chosen to avoid impurity and improve the properties of Cu-Nb alloys.

## 5 Conclusions

1) Following the mechanical alloying, heat treatment leads to structural relaxation, precipitation of Nb phase and grain growth of the metastable nanocrystalline Cu-Nb alloy. Pronounced phase separation occurred at 700 ℃, and almost all of the Nb atoms precipitate from the solid solution after annealing at 900 ℃. Meanwhile, with the increase of annealing temperature, the growth of Cu grains is slow, and the internal strain and the density of dislocation decrease gradually. The structure of the Cu matrix remains nanocrystalline with average grain size of about 37 nm even after annealing at 900 ℃. Therefore, the mechanically-alloyed nanocrystalline Cu-Nb alloys have a high thermal stability.

2) The enhanced thermal stability of nanocrystalline Cu-Nb alloys is attributed to the solid solution of Nb in the Cu matrix and the nanosized Nb precipitates, as both of them can hinder the migration of fcc Cu grain boundaries due to solute drag or precipitate pinning effects.

3) The contaminations of O and Fe will influence the precipitation of Nb from Cu and lead to the formation of niobium oxide, copper oxide and $Fe_7Nb_6$ during heat treatment. Furthermore, the mechanical and electrical properties of the subsequent compacted samples will be largely affected. Therefore, effective methods should be taken to reduce the contaminations during MA.

## References

[1] LU L, TAO N R, WANG L B, DING B Z, LU K. Grain growth and strain release in nanocrystalline copper [J]. Journal of Applied Physics, 2001, 89(11): 6408−6414.

[2] SURYANARAYANA C. Mechanical alloying and milling [J]. Progress in Materials Science, 2001, 46(1/2): 1−184.

[3] BENSON D J, FU H H, MEYERS M A. On the effect of grain size on yield stress: Extension into nanocrystalline domain [J]. Mater Sci Eng A, 2001, 319/321A: 854−861.

[4] WANG Yin-ming, CHEN Ming-wei, ZHOU Feng-hua. High tensile ductility in a nanostructured metal [J]. Nature, 2001, 419(6910): 912−914.

[5] VALIEV R Z, ALEXANDROV I V, ZHU Y T. Paradox of strength and ductility in metals processed by severe plastic deformation [J]. Journal of Materials Research, 2002, 17(1): 5−8.

[6] BOTCHAROVA E, HEILMAIER M, FREUDENBERGER J, DREW G, KUDASHOW D, MARTIN U, SCHULTZ L. Supersaturated solid solution of niobium in copper by mechanical alloying [J]. Journal of Alloys and Compounds, 2003, 351(1/2): 119−125.

[7] BOTCHAROVA E, FREUDENBERGER J, SCHULTZ L. Cu-Nb alloys prepared by mechanical alloying and subsequent heat treatment [J]. Journal of Alloys and Compounds, 2004, 365(1/2): 157−163.

[8] FREUDENBERGER J, BOTCHAROVA E, SCHULTZ L. Formation of the microstructure in Cu-Nb alloys [J]. Journal of Materials Science, 2004, 39(16/17): 5343−5345.

[9] BOTCHAROVA E, FREUDENBERGER J, SCHULTZ L. Mechanical and electrical properties of mechanically alloyed nanocrystalline Cu-Nb alloys [J]. Acta Materialia, 2006, 54(12): 3333−3341.

[10] LEI Ruo-shan, WANG Ming-pu, GUO Ming-xing, LI Zhou, DONG Qi-yi. Microstructure evolution in nanocrystalline Cu-Nb alloy during mechanical alloying [J]. Trans Nonferrous Met Soc China, 2007, 17(s1): s603−s607.

[11] KUSCHKE W M, KELLER R M, GRAHLE P, MASON R, ARZT E. Mechanisms of powder milling investigated by X-ray diffraction and quantitative metallography [J]. Z Metallkde, 1995, 86(12): 804–813.

[12] WILLIAMSON G K, HALL W H. X-ray line broadening from filed aluminium and wolfram [J]. Acta Metall, 1953, 1: 22–31.

[13] RIETVELD H M. A profile refinement method for nuclear and magnetic structures [J]. J Appl Crystallogr, 1969, 2(2): 65−71.

[14] ZHAO Y H, LU K. Microstructure evolution and thermal properties in nanocrystalline Cu during mechanical attrition [J]. Physical Review B, 2002, 66: 085404-1−0854041-8.

[15] HE L, MA E. Processing and microhardness of bulk Cu-Fe naocomposites [J]. Acta Metall, 1996, 7(3): 327−339.

[16] GASSER R P H. An introduction to chemisorption and catalysis by metals [M]. Oxford: Calerendon Press, 1985.

[17] DOBERT C W. Handbook of chemistry and physics [M]. Boca-Raton: CRC Press, 1988.

[18] MIEDEMA A R, de CHATEL P F, de BOER F R. Cohesion in alloys—fundamentals of a semi-empirical model [J]. Physica, 1980, 100B: 1−28.

**(Edited by YANG Hua)**