Advances in Engineering Research, volume 113

International Forum on Mechanical, Control and Automation (IFMCA 2016)

Structure and phase evolution in Cu-Nb alloy under different types of mechanical alloying methods

Ruoshan Lei [1, a, *], Guangrun Chen [1,b] and Mingpu Wang[2,c]

[1] College of Materials Science and Engineering, China Jiliang University, Hangzhou, P. R. China

[2] School of Materials Science and Engineering, Central South University, Changsha, P. R. China

[a] leiruo@163.com, [b] cgrzdd@163.com, [c] wangmp@cus.edu.cn

Keywords: Cu-Nb, Mechanical alloying, Powder metallurgy, Wet milling, Structure

Abstract. Cu-10wt%Nb alloy powders were prepared via three different types of mechanical alloying (MA) methods: wet milling, dry milling as well as MA of pre-milled Nb and as-received Cu powders. X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical microscopy (OP) techniques were used to investigate the phase and structure of the as-milled samples. The results show that the MA method affects the alloying process and the grain size refinement process significantly. The product prepared by wet milling shows the largest crystalline size and the lowest solid solubility extension of Nb in Cu. In contrast, the supersaturated Cu-10wt%Nb solid solution with the smallest crystallite size is obtained by MA of pre-milled Nb and as-received Cu powders. The MA process was discussed to explain the phenomena.

Introduction

Due to the high strength and relatively good electrical conductivity, Cu-Nb alloys prepared by mechanical alloying (MA) are becoming a hot research subject nowadays. For example, it is reported that MA-ed Cu-5at%Nb alloys showed a high mechanical strength of about 1 GPa and a conductivity of about 50%IACS [1]. It has been suggested that a good combination of mechanical and electrical properties can be achieved, when the fine Nb particles are precipitated homogenously within the Cu nanocrystalline matrix [1-3]. Hence, one of the primary objectives for Cu-Nb alloy is to obtain a high solid solution of Nb in the Cu matrix. Since the Cu-Nb system shows a negligible solubility with each other at equilibrium state [4], the MA processing of Cu-Nb to extend the solid solubility limit has been widely studied [6-10]. Generally, Cu-Nb powder mixtures were MA under a dry condition, which shows the maximum solid solubility limit of Nb in Cu could be achieved to be ~10 at% Nb (corresponding to ~14wt%) [7]. However, the powder yield is low and the powder aggregation is severe under dry milling. Wet milling has been reported to be able to avoid the aggregation effect and improve the powder yield. Yet, few papers investigate the MA process of Cu-Nb under a wet condition. More importantly, few efforts have been made to investigate the effect of pre-milling of Nb on the alloying behavior of the immiscible Cu-Nb system.

In the present study, we have prepared the Cu-10wt%Nb powders under three different kinds of methods: wet milling, dry milling and MA of pre-milled Nb powders and as-received Cu powders. The phase and structural evolutions of the Cu-Nb powders under different MA conditions were investigated systematically. The corresponding MA process was also discussed.

Experimental methods

Elemental powders of Cu and Nb with high purity (>99.9%) were blended to the composition of Cu-10wt%Nb. Three different routes were used to prepare the powders. In the first method, as-received Cu and Nb powders were MA-ed in a wet condition using 80wt% ethanol as the process control agent (the alloy will be referred to as A1 sample). In the second method, the as-received Cu and Nb powders were MA-ed with no process control agent adding (A2 sample). In the third method, Nb powders were pre-milled for 10h firstly. The milling speed is 200rpm, and the ball-to-powder weight ratio is 10:1. Then, the pre-milled Nb and as-received Cu powders were MA-ed in a dry condition (A3 sample). For the three methods, the corresponding MA process was conducted in a high-energy planetary ball milling (QM-1SP4) with stainless steel containers and balls at a milling speed of 300 rpm for 50 h under an argon atmosphere. The ball-to-powder weight ratio is kept to be 15:1.

The phase and structural evolution of the milled powders were investigated by X-ray diffraction (XRD) using a DMAX2000 X-ray Diffractometer with Cu Kα radiation. Williamson-Hall method was used to calculate the crystallite size and internal strain of the samples. The structures of the samples were investigated using optical microscopy (OP) and scanning electron microscopy (SEM). OP was performed on NEOPHOT221 instrument. SEM was carried out on a Sirion 200 instrument.

Results and discussion

XRD patterns offer a quick analysis for the phase and structural evolutions of the samples during milling. Fig. 1 shows the XRD patterns of A1, A2 and A3 samples as a function of milling time. For the three samples, peaks broadening, loss of intensity and peaks shifting occur with increasing milling time. Peak broadening and intensity reduction are due to the grain refinement and internal strain generation during milling [11-13]. The movement of Cu peaks to the smaller angles indicates the expansion of the Cu matrix during MA, which may be resulted from the incorporation of Nb into the Cu matrix owing to the larger size of Nb atoms. Meanwhile, the intensity of Nb diffraction peaks decreases with increasing milling time. For A2 and A3 samples, the $(110)_{Nb}$ peak disappears into the background signal after 50 h and 32 h milling, respectively. However, in the case of A1 sample, the $(110)_{Nb}$ peak still exists after 50 h milling, which suggests that the complete dissolution of Nb into Cu has not been achieved by wet milling.

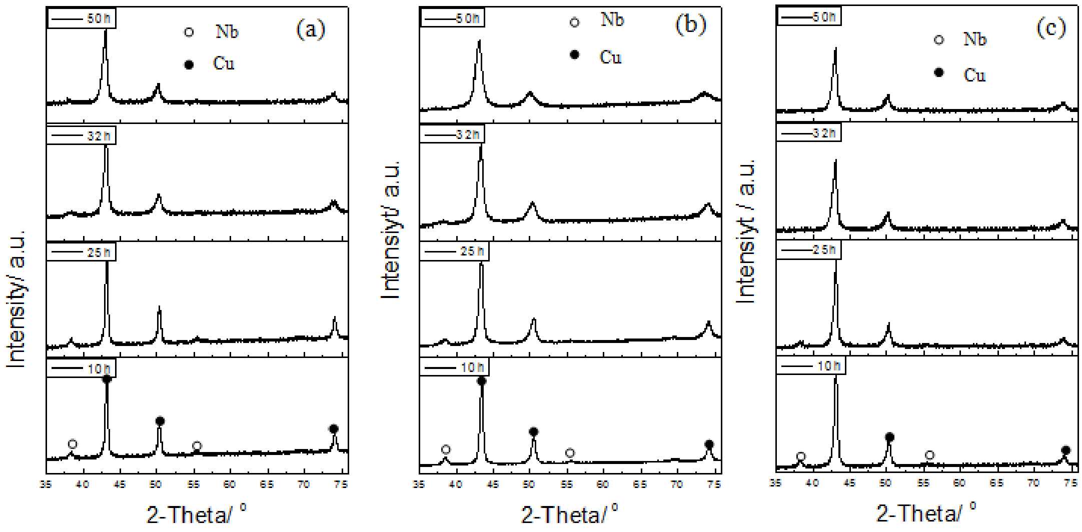

Figure 1. XRD patterns of A1 (a), A2 (b) and A3 (c) samples MA-ed for different times.

The crystallite size, lattice strain and lattice parameter of Cu phase after different milling times for A1, A2 and A3 samples are shown in Fig. 2. It can be seen that the Cu crystallite size decreases with the enhancement in milling time, while the internal strain and lattice parameter of the Cu matrix show the increasing trends. Especially, A3 sample shows the fastest change rate. After milling for 50 h, A3 sample reaches the finest Cu crystallite size of about 9 nm, the highest internal strain of about

1.67% and the largest Cu lattice parameter of about 0.3642nm. While A1 sample milled for 50 h exhibits the largest crystallite size of about 14 nm, the smallest internal strain of about 0.66% and the smallest lattice parameter of about 0.3629nm. Those values of A2 sample are moderate. Hence, the ethanol and also the process of pre-milling of Nb powders have remarkable influences on the alloying process and grain size refinement of the powders during MA.

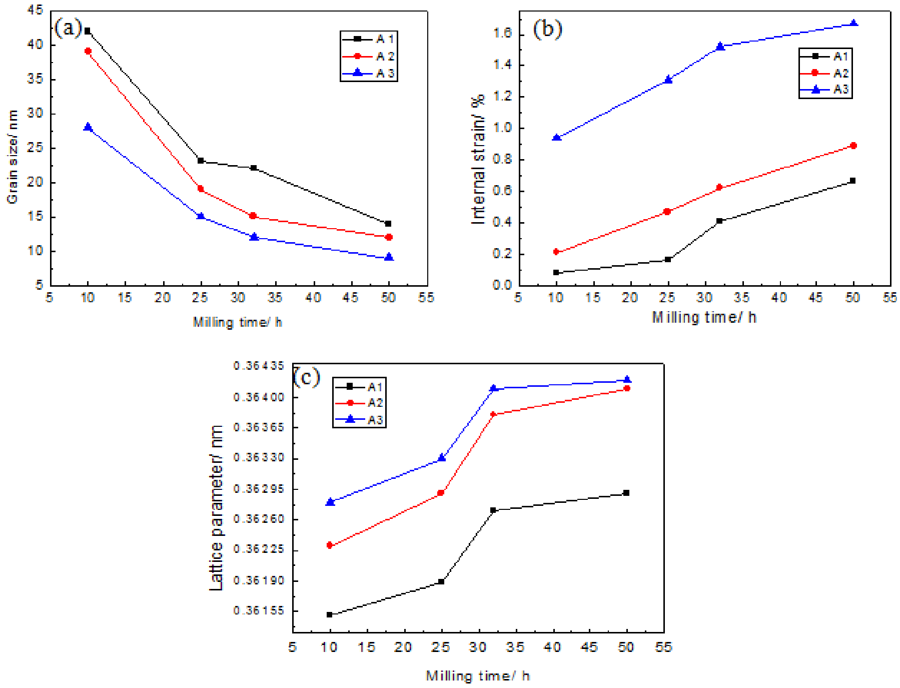

Figure 2. The variations of Cu crystallite size (a), internal strain (b) and lattice parameter (c) as a function of milling time for the Cu-Nb samples prepared by different methods.

Fig. 3 shows the OP images of A1, A2 and A3 samples MA-ed for 50 h, respectively. It can be seen that the smallest powder particle size is achieved in A1 sample; however, the lamellar structure is relatively coarse (Fig. 3(a)). This is because the ethanol tends to be adsorbed on the surface of the powders, which results in the suppression of the cold welding and agglomeration between the powders during milling. Therefore, the diffusion between Nb and Cu is inhibited and only small amount of Nb has been dissolved into the Cu matrix, since cold welding between the two elements plays a key role in the alloying process [14, 15]. On the other hand, A3 sample shows the finest and convoluted lamellar structure (Fig. 3(c)), indicating the achievement of the balance state. The accelerated alloying process of A3 sample may be contributed to the effect of the pre-milling process. After pre-milling for 10h, the hardness of the pre-milled Nb powder is much higher than the un-milled one owing to the work hardening. Thus, a higher impact force and stronger collision from the pre-milled Nb powders can be created on the Cu powders, benefiting the interdiffusion process between the Cu and Nb elements [16]. On the other hand, the hard Nb particles can be easily encapsulated and embedded into the soft Cu matrix during MA process. Then, the Nb particles gets further deformed and fractured, and the sizes of Nb particles become smaller with further milling. Meanwhile the interlamellar spacing decreases to the finest level due to the repeated cold-welding and fracturing processes. Thus, the intimate Cu-Nb contact can be established and the diffusion distances become smallest, leading to largely enhanced interdiffusion between the elements. Finally, compared with A1 and A2 samples, A3 sample can achieve the finest grain size and the extension of the solid solubility limit in the shortest time. The similar results have also been reported in ref. [16], which suggested that the pre-milling of Cr particles can promote the dissolution of Cr into Cu in the immiscible Cu-Cr system.

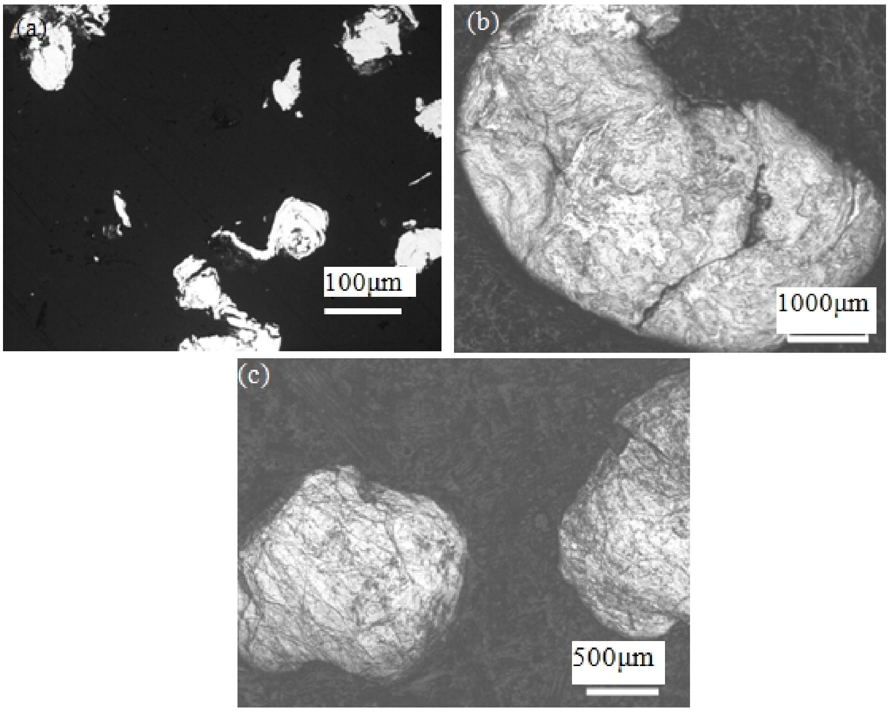

Figure 3. OP images of A1 (a), A2 (b) and A3 (c) milled for 50 h, respectively.

Fig. 4 shows the SEM images of A1 and A3 powders milled for 50h. From Fig. 4(a), it can be seen that there are still some Nb particles dispersed in the Cu matrix for A1 sample. In contrast, no Nb particles can be found in A3 sample (Fig. 4(b)), suggesting the totally dissolution of Nb into Cu. The results agree with the XRD analysis.

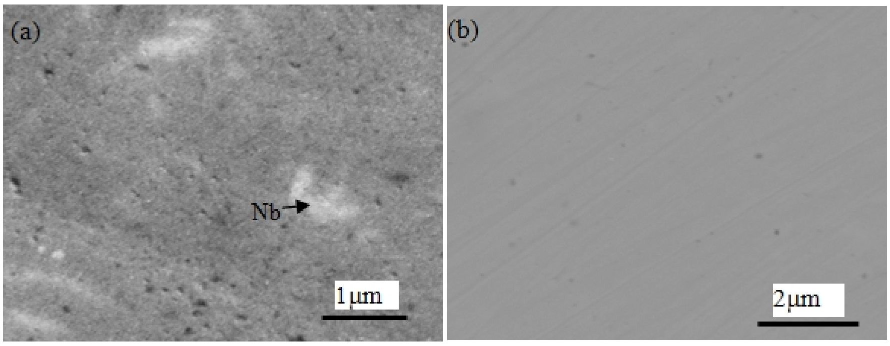

Figure 4. SEM image of the powders of A1 (a) and A3 (b) milled for 50 h, respectively.

Conclusions

Three different MA methods have been applied to prepare the Cu-Nb supersaturated nanocrystalline solid solution. The results reveal that the addition of process control agent weakens the collision between the balls and powders; therefore, the solid solution extension of Cu-Nb is smallest under a wet condition. Compared with singly wet milling and dry milling, MA of pre-milled Nb and as-received Cu powders can synthesize Cu-Nb powders with finest crystallite size. Moreover, as the pre-milling of Nb powders can lead to the formation of much finer and harder Nb particles, which decreases the diffusion spacing and increases the magnitude of impacts, the interdiffusion between Nb and Cu can be largely promoted and the supersaturated Cu-Nb solid solution forms in the shortest milling time.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (No. 51401197).

References

[1] E. Botcharova, J. Freudenberger, L. Schultz: Acta Mater. Vol. 54 (2006), p. 3333.
[2] R.S. Lei, S.Q. Xu, M.P. Wang, H.P. Wang: Mater. Sci. Eng. A Vol. 586(2013), p. 367.
[3] M.D. Abad, S. Parker, D. Kiene, M. M. Primorac, P. Hosemann: J. Alloys Compd. Vol. 630 (2015), p.117.
[4] M.A. Morris: Mater. Sci. Eng. Vol. AIII (1989), p.115.
[5] C. Suryanarayana: Prog. Mater. Sci. Vol. 46 (2001), p. 1.
[6]S. Mula, D. Setman, K. Youssef, R.O. Scattergood, C.C. Koch: J. Alloys Compd. Vol. 627 (2015), p.108.
[7] E. Botcharova, M. Heilmaier, J. Freudenberger, G. Drew, D. Kudashow, U. Martin, L. Schultz: J. Alloys Compd. Vol. 351 (2003), p. 119.
[8] Lei Ruoshan, Wang Mingpu, Wang Huanping, Xu Shiqing: Materials Characterization. Vol. 118(2016), p.324.
[9] E. Botcharova, J. Freudenberger, L. Schultz: J. Alloys Compd. Vol. 365 (2004) p.157.
[10]R.S. Lei, M.P. Wang, L. Zhou, H.G. Wei, W.C. Yang, Y.L. Jia, S. Gong: Mater. Sci. Eng. A Vol. 528 (2011), p.4475.
[11] C. Aguilar, F. Castro, V. Martínez, D. Guzmán, F. de las Cuevas, L. Lozada, N. Viema: Mater. Sci. Eng. A Vol. 548(2012), p.189.
[12] K.A. Darling, A.J. Roberts, Y. Mishin, S.N. Mathaudhu, L.J. Kecskes: J. Alloys Compd. Vol. 573 (2013), p. 142.