High thermal stability of submicron grained Cu processed by asymmetrical rolling

Wei Li ^{a,b}, Yao Shen ^{a,b,*}, Chaoying Xie ^{a,b}

^a State Key Lab of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China.

^b Shanghai Key Laboratory of Advanced High-temperature Materials and Precision Forming, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China.

* Corresponding author. Tel. /fax: +86 21 342033763. *E-mail address:* yaoshen@sjtu.edu.cn (Y. Shen)

Abstract

In this paper, we report the microstructure evolutions of symmetrically and asymmetrically rolled Cu at different temperatures, and reveal an important role of asymmetry induced microstructure homogeneity and removal of local severely distorted structures on the enhancement of thermal stability. With the same total reduction of 90%, two kinds of submicron grained (SMG) Cu were processed by symmetrical and asymmetrical rolling respectively. The temperature dependent boundary spacing curves show the asymmetrically rolled Cu has significantly higher

thermal stability, with the onset temperature of obvious grain coarsening being 40°C higher than that for symmetrical rolled Cu. The enhanced thermal stability of asymmetrically rolled Cu can be attributed to the retardation of nucleation mainly realized by the improvement in microstructure homogeneity and the removal of local severely distorted structures. Our results demonstrate the feasibility of using asymmetrical rolling to improve the thermal stability of bulk SMG metals.

Keywords: Thermal stability; Submicron grained Cu; Asymmetrical rolling

1. Introduction

For decades, material scientists have been actively searching for connector materials that boast concurrent high-conductivity, high-strength and high-thermal stability in the electronic industries [1-6]. Cu and its alloys were the most widely used materials in this field [4-8]. Compared to highly alloyed and ultra-pure Cu, the commercially pure Cu deformed to a large strain usually has a good compromise on the high-conductivity and high-strength, since the limited impurities and large deformation can significantly increase the strength with a little sacrifice of conductivity [9]. However, the heavily deformed commercially pure Cu possesses poor thermal stability due to the high deformation energy stored in the submicron grained (SMG) structures. For instance, the SMG pure Cu processed by dynamic plastic deformation (DPD) could even recrystallize at room temperatures [10].

Tremendous research efforts have been made in past decades to improve the thermal

stability of SMG materials. For alloys, the most common approach is to employ the pinning effects of solute atoms or second phase particles to impede grain boundary migrations and retard the recrystallization nucleation [11, 12]. However, this method is not applicable to pure metals and for these materials the only way towards enhanced thermal stability is by changing their own microstructures. For instance, Saldana and Zhang et al have significantly enhanced the thermal stability of SMG Cu by introducing dense nano-twins through fast plastic deformation or electro-deposition [13-15]. The high thermal stability could be explained by the following: firstly, the driving force for twin boundary migration is limited by its low boundary energy, which is usually an order of magnitude lower than that of high angle boundaries (HABs, whose misorientations are above 15°); secondly, the mobility of coherent twin boundary is low due to its high activation energy (almost equal to self-diffusion activation energy). Recently, Liu et al also found that the thermal stability of pure Ni can be also enhanced by the low angle boundaries (LABs, whose misorientations are below 15°) dominating 2D nano-structured lamellar grains for basically the same reasons [16].

It can be inferred from the above analysis that the thermal stability of bulk SMG materials, regardless of being alloys or pure metals, can be substantially enhanced by reducing the mobility of grain boundaries and the driving force for recrystallization nucleation and growth. For deformed metals typical nucleation sites usually concentrated on such distorted regions as pre-existing HABs, misoriented 'transition' bands inside grains, and highly misoriented deformation zones around large particles etc. [11]. In general, only a very small minority of regions ($\sim 1/10^6$) meet these

conditions [11] and recrystallization could be retarded if these defects are dramatically reduced and weakened. Based on this rationale we report a new way, asymmetrical rolling (ASR), to substantially improve the thermal stability of SMG commercially pure Cu in this study. Microstructural analysis reveal that the enhanced thermal stability can be ascribed to the retarded recrystallization, mainly caused by the microstructure homogeneity and removal of local severely distorted structures.

2. Experimental processes

The starting material was commercially pure (97.53%) Cu ingot with an average grain size of $\sim 80\text{ }\mu\text{m}$. The chemical composition of commercially pure Cu is shown in Table 1. The Cu ingot with a size of 50 (length) x 20 (width) x 15 (thickness) mm^3 was asymmetrically rolled to 1.5 mm through 28 passes. The thickness reduction for each pass is about 8% and the total thickness reduction is 90% (thickness from 15 to 1.5 mm). For introducing asymmetry during rolling, a rolling speed ratio of 1.5 was adopted and the normal and rolling direction of the sheet were kept the same for each pass. The diameter of upper and lower rollers is 25 mm and the rotation speed ratio is 1.5. During the whole asymmetrical rolling procedures, neither lubrication nor grinding were applied to the rollers. To be noted, due to the limited thickness reduction ($\sim 8\%$) per pass, the sliding between sheet and the faster rollers was observed. For comparison, another group of the starting sheet with the same sizes was rolled to the same final thickness (1.5 mm) by conventional symmetrical rolling (SR) in similar rolling conditions.

Small block samples with the of $2 \times 2 \times 1.5 \text{ mm}^3$ were cut from the central parts of the same rolling sheet and then annealed at 100, 150, 175, 200, 250, 300, 325 and 350°C for 30 minutes respectively. The strength of the sheets before and after annealing was characterized by microhardness. The Vickers microhardness was measured at a loading of 200 g for 10 seconds on a Buehler Micromet Hardness Tester. To minimize the error, at least 15 indentations were made at the center of longitudinal section of the sheets.

The microstructures in the longitudinal section of rolled sheets, which contains the normal direction (ND) and the rolling direction (RD) of the sheets, were characterized by Quanta 250 SEM (equipped with electron backscatter diffraction (EBSD) system) and JEOL 2100 TEM. The grain orientations were obtained from the big EBSD maps of $200 \times 200 \mu\text{m}^2$ using a step size of $0.5 \mu\text{m}$ and the fractions of texture component were determined by applying a 15° deviation from the exact corresponding $\{hkl\}\langle uvw \rangle$ orientations. Microstructural morphologies were obtained by TEM under a multi-beam or double-beam condition, which is capable of distinguishing contours of sub-boundaries of orientation mismatch as small as 0.1° . Lamellar boundary spacings of 300 grains from dozens of TEM images were measured by the intercept line method and the boundary misorientations were measured by a manual analysis of Kikuchi diffraction patterns. After annealing, we tracked the changes of microstructural morphologies, texture components and grain sizes of the sheets. The average boundary spacings (larger than 500 nm) in recrystallized states were measured using random intercept line method by EBSD.

3. Results

3.1. Thermal stabilities of rolled materials

Compared with SR Cu, ASR Cu shows significantly higher thermal stability. The temperature dependent curves of microhardness in Figure 1 a show that the microhardness of SR and ASR Cu are identical (1330 ± 10 MPa vs 1320 ± 20 MPa) in the rolled state, but the softening rate of ASR Cu is lower than that of SR Cu. At annealing temperatures below 175°C , the microhardness changes for ASR and SR Cu are negligible; when the annealing temperature is in the range of 200 - 350°C , the softening of ASR Cu is smaller than that of SR Cu.

As shown in Figure 1 b, the evolutions of boundary spacing with temperature also suggest that ASR Cu has higher thermal stability, which can be corroborated in the following aspects: firstly, as can be seen from the inset of Figure 5 b, the coarsening rate of ASR Cu is smaller than that of SR Cu in recovery stage (identified by no occurrence of bulky recrystallized grains); secondly, the onset temperature for obvious grain coarsening of ASR Cu (325°C) is about 40°C higher than that of SR Cu (285°C); finally, the starting temperature of recrystallization for ASR Cu (325 - 350°C) is at least 25°C higher than that of SR Cu (250 - 300°C) since the recrystallized grains (identified as bulky and dislocation free grains) were not observed for ASR Cu below 350°C , in contrast to 300°C for SR Cu.

3.2. Microstructures of rolled materials

3.2.1. Textures

Pole figures shown in Figure 2 reveal some differences in texture between SR and ASR Cu. As summarized in Table 2, the dominating texture components (volume fraction >10%) in either SR or ASR Cu are the same, namely rolling textures like S, Cu and Bs. But the volume fraction in ASR Cu (30%, 15%, 12% respectively) are lower than that in SR Cu (39%, 18%, 17% respectively). However, other texture components (volume fraction < 10%) show different trends in the variation. For instance, the fraction of Cube component in ASR Cu is lower than that in SR Cu (3% vs 9.9%), and in contrast the fraction of Goss component is significantly higher (7% vs 0.9%). The asymmetry induced texture changes (Figure 1 and Table 2) basically coincide with the results reported by Polkowski et al [17], who ascribed these changes to the additional shear strain induced by asymmetry.

3.2.2. TEM microstructures

Large numbers of TEM observations, covering more than 200 μm along ND, show that SR Cu developed a heterogeneous microstructure. As shown in Figure 3 a, the vast majority regions in SR Cu are submicron lamellar structures, whose spacings are 100-600 nm and the elongation (shown by white arrows) is almost parallel to the RD; a minority of regions are severely distorted structures consisting of nano-structured lamellar grains (lamellar boundary spacings: 25-100 nm) with their elongation

unparalleled to the RD (indicated by the white dash arrows). The enlarged image of the nano-structured regions (indicated by the white dotted block) is shown in Figure 3 b and the corresponding schematic illustration is shown in Figure 3 c. It can be seen that the lamellar boundaries of nano-structured grains are even and all belong to LABs. This finding is consistent with that of the 2D nano-structured lamellar grains in SMG Ni [16] and is believed to originate from local high strain gradient during plastic deformation. Moreover, HABs generally aggregate on either side of severely distorted regions and separate the nano-grains from the surrounding submicron grain, as shown in Figure 3 c. Interestingly, nano-structured deformation twins (the layer thickness ≈ 15 nm) were also observed in SR Cu. TEM statistics show that the nanosized twin regions were small (area fraction $\approx 0.5\%$) and were generally located in the severely distorted regions where driving force is sufficient for the nucleation of deformation twins [18].

Compared with symmetrical rolling, the asymmetrical rolling removed the severely distorted structures and developed a more homogeneous microstructure. As shown in Figures 3 d-f, ASR Cu shows lamellar structures whose spacings are in the range of 150-400 nm and elongation is parallel to the RD (indicated by the white arrows shown in Figure 3 d). Moreover, the lamellar boundaries of ASR Cu are more even than those of SR Cu, leading to an orderly arrangement of the lamellar grains.

The distributions of lamellar boundary spacings and boundary misorientations measured over ~ 75 μm along ND by TEM statistics are shown in Figure 4 a and b

respectively. It is seen that, due to the removal of severely distorted regions induced by asymmetrical rolling, ASR Cu shows a much narrower distribution of lamellar boundary spacings than SR Cu (100~450 nm vs 25~750 nm). Despite all this, the distributions of boundary misorientations in SR and ASR are very similar. The average lamellar boundary spacings and distributions of boundary misorientations of SR and ASR Cu are summarized in Table 3. It can be concluded that the asymmetry rolling did not lead to more significant grain refinement and pronounced increase of HABs compared with the symmetrical rolling.

3.3. Microstructures of annealed materials

After the isothermal annealing SR and ASR Cu exhibited different microstructural changes. Figure 5 displays the typical microstructural morphologies of SR and ASR Cu after annealing at 300°C for 30 minutes. After the annealing SR Cu developed partially recrystallized microstructures featured by the mixtures of new bulky recrystallized grains and pre-existing lamellar subgrains. Large numbers of TEM statistics show that the recrystallized grains were mainly generated in the severely distorted regions where nano-structured lamellar grains and/or deformation twins existed, and tended to grow toward those nano-structured grains as shown in Figure 5 a. It is worth mentioning that the nano-structured lamellar grains and deformation twins in SR Cu remained almost unchanged after annealing at 300°C (Figure 5 a), in good agreement with the high thermal stability of nano-structured grains reported by Liu [16] and Saldana et al [14, 15]. Compared with SR Cu, the annealing induced

microstructural changes in ASR Cu were much uniform. As shown in Figure 5 b, instead of generating any localized recrystallized grains, the overall lamellar spacings of ASR Cu increased uniformly and the lamellar structures remained after the annealing.

The temperature dependent textural evolutions of the rolled Cu are shown in Figure 6. The S and Cu texture components in either SR or ASR Cu decreased significantly and whereas the shear texture components increased notably in the *recrystallization stages* (e.g. higher than 250°C for SR Cu and 325°C for ASR Cu). However, the evolutions of other texture components show some differences between SR and ASR Cu. For instance, the Bs texture component decreased in SR Cu but remained almost unchanged in ASR Cu.

4. Discussion

4.1. Effects of impurities on the microstructures of rolled and annealed materials

As compared to the rolled Cu with higher purity (e.g. 99.995%) [21], the commercially pure Cu (97.53%) sheets show smaller lamellar structures and weaker rolling textures after the cold rolling. These differences could be mainly attributed to the higher impurities (e.g. C, P, As, Si, Fe, Mn etc.) in commercially pure Cu, since these impurities could not only decrease the average grain/subgrain size by retarding the dynamic recovery, but also weaken the sharp textures found in pure metals [19, 20].

After annealing to recrystallization (e.g. 350°C), although the fraction of rolling texture components decreased significantly, the formation of new texture components like

typical Cube is absent for both recrystallized SR and ASR Cu (e.g. 350°C), which is different from the previous studies [11]. This discrepancy might be also attributed to the relatively high impurities (~2.5%) of the material used in this study, since a tiny amount of impurities (such as C, P, As, Si, Fe, Mn etc.) can significantly reduce the volume fraction of Cube texture [11, 19, 21, 22]. The suppression of Cube texture was mainly attributed to the paucity of available cube-nuclei and to the reduction in growth rate of recrystallized grains, because the growth of cube grain might be so greatly reduced by these impurities with strong solute-drag effect and more and more alternative nuclei were brought into operation [19]. In addition, the relatively lower annealing temperature (350°C) and shorter annealing time (0.5 hour), compared with those (500°C and 1~2 hours) of previous studies [11], might be another reason for negligible increase in the Cube texture.

4.2. Effects of asymmetry on the microstructural homogeneity

The uniformly distributed microstructures and removal of local severely distorted structures in ASR Cu were considered to be closely related to the additional shear strain caused by asymmetry. The asymmetrical rolling with a relatively high rolling speed ratio (e.g. > 1.5) was usually utilized from the viewpoint of deformation texture and grain refinement [23-25]. In this study the effective rolling speed ratio was expected to be small, because the sliding between sheet and the faster rollers occurred during the asymmetrical rolling. Previous studies have shown that a small rolling speed ratio/asymmetry can cause a remarkable reduction of the rolling pressure and torque,

thereby bringing a better control of size and shape of rolled sheets and an improved surface quality [26-28]. These reports implied that a small additional shear strain and a reduced rolling pressure induced by asymmetry had a big influence on the microstructures of rolled materials. The stress states of asymmetrical rolling used in this study were in the similar situation, which might be closely related to the microstructure homogeneity. Moreover, the small additional shear strain in the rolling process can significantly decrease the spatial variation of Taylor factors [29], which may help to decrease the spatial variation of amount of plastic deformation and lead to a more uniformly deformed microstructure and therefore the removal of local severely distorted structures in ASR Cu.

In particular, no deformation twins were observed in ASR Cu. The common reasons for the absence of deformation twins are high temperature and refinement of grain sizes (to submicron) induced by SPD [30, 31]. However, the temperature rise from a low rolling reduction per pass (8%) was too trivial and the grain sizes of ASR Cu were on the same length scale as that of SR Cu, largely ruling out these two factors as major contributors. Therefore, the most probable cause for the absence of deformation twins in ASR Cu is microstructure homogeneity, since it reduced the stress concentration significantly and the corresponding driving force for the nucleation of deformation twins turns weak.

4.3. Factors influencing the thermal stability of rolled materials

The primary cause of the highly improved thermal stability of ASR Cu can be traced to

the microstructure homogeneity and the removal of local severely distorted structures. As shown in Figure 3, SR Cu developed a heterogeneous microstructure containing a minority of local severely distorted regions. Although the nano-structured lamellar grains and deformation twins within the distorted regions have high thermal stability, their proportion is too low to enhance the thermal stability of SR Cu. On the contrary the stored high local energy makes it easy to form recrystallized grains at relatively low temperature and these nascent grains then grow rapidly and swallow surrounding high-thermal-stable nano-structured grains (Figure 5 a), leading to low thermal stability of SR Cu. Compared with SR Cu, the overall microstructures of ASR Cu were more homogeneous and lamellar boundaries were more even, suggesting uniformly and orderly distributed stored energy. More importantly, the removal of severely distorted structures in ASR Cu helps in retarding the nucleation for recrystallized grains in these severe defects.

The decreased rolling textures (S, Cu and Bs) in ASR Cu may also have contributed to the improved thermal stability, but could not be the controlling factor. In face centered cubic metals, the rolling textures usually have relatively higher Taylor factor and larger mean stored energy [11, 32]. So the decrease of rolling textures may lead to the total reduction of stored energy and the driving force of recrystallization in ASR Cu. However the nucleation of new recrystallized grains is a key factor when discussing the thermal stability of deformed metals, and the nucleation depends largely on the local fluctuations in stored energy rather than on the spatial average energy. The temperature dependent variation in the major texture components (Figure 6) is in

support of this reasoning. For instance S component began to decrease as early as 250°C in SR Cu, which is significantly lower than 300°C in ASR Cu. A small 20% difference of rolling textures (73% in SR Cu vs 58% in ASR Cu) induced variation in average stored energy can hardly explain such a huge difference.

4.4. New directions to improve thermal stability

Using a simple asymmetrical rolling we removed the local severely distorted structures and obtained uniformly distributed SMG lamellar grains with even boundaries, which possess not only similar morphology features but also identical high thermal stability of 2D nano-structured lamellae in SMG Ni [16]. For instance, the onset temperature for noticeable coarsening of ASR Cu is about 40°C higher than that of SR Cu, and such an enhancement of onset temperature is comparable to the value in 2D nano-structured Ni lamellae [16]. As a way of enhancing the thermal stability of materials, asymmetrical rolling is much more cost-effective compared with inducing dense nano-structured lamellar grains or deformation twins through high rate and high strain gradient plastic deformation, and has huge potential in processing bulk SMG materials with high thermal stability on an industrial scale.

5. Conclusions

(1) Compared with symmetrical rolling, the asymmetrical rolling led to not only the decrease of rolling texture components, but also the uniformity in microstructures with the removal of local severely distorted structures. These microstructural changes can

be traced to the additional shear strain induced by asymmetry.

(2) The ASR Cu exhibited high thermal stability, with the onset temperature of obvious grain coarsening being almost 40°C higher than that for SR Cu. The enhanced thermal stability of ASR Cu can be mainly attributed to the removal of local severely distorted structures, which helps in retarding the nucleation for recrystallized grains in these severe defects. The decreased rolling textures in ASR Cu may also have contributed to the improved thermal stability, but could not be the controlling factor.

(3) Our results demonstrate the feasibility of using microstructure homogeneity and removal of local severely distorted structures to improve the thermal stability of deformed metals, and these factors could offer new design flexibilities for a variety of heat treatment and machining processes.

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Figure captions

Figure 1. Changes of microhardness (a) and boundary spacing (b) of ASR and SR Cu after isothermal annealing for 30 minutes. 25°C stands for rolled state. The inset in (b) shows the enlarged image of boundary spacing evolutions in recovery states and the boundary spacing is characterized by the lamellar boundary spacing. The red arrows indicate the onset temperature for obvious coarsening, i.e. 285°C for SR Cu and 325°C for ASR Cu.

Figure 2. Pole figures of SR and ASR Cu. TD stands for the transverse direction of sheets.

Figure 3. Detailed TEM microstructures in the longitudinal section of SR (a-c) and ASR (d-f) Cu. a) Overview TEM microstructures of SR Cu. b) Enlarged image of white dotted block in (a). The inset is selected area diffraction pattern (SADP) of deformation twins within the white block. c) Schematic of microstructures in (b). d) Overview TEM microstructures of ASR Cu. e) Enlarged image of white dotted block in (d). f) Schematic of microstructures in (e). The white arrows indicate the extend direction of lamellar grains, which is parallel to RD of rolled sheets and the white dotted arrows indicate that unparallel. In the schematic, the black lines indicate extended lamellar boundaries and the gray lines are subgrain boundaries inside lamellar grains.

Figure 4. Distributions of lamellar boundary spacings and boundary misorientations in

SR and ASR Cu. 300 grains covering $\sim 75\mu\text{m}$ along ND were measured for the distributions of lamellar boundary spacings, among which more than 150 grain boundaries were measured for the distributions of misorientations.

Figure 5. TEM microstructures of SR and ASR Cu after annealing at 300°C for 30 minutes. a) Annealed SR Cu. b) Annealed ASR Cu. The white dotted lines and arrows in (a) indicate the recrystallized grain boundaries and their migration directions respectively.

Figure 6. Changes of texture components of SR (a) and ASR (b) Cu after isothermal annealing for 30 minutes. 25°C stands for the rolled state.

Tables

Table 1 Chemical composition of commercially pure Cu studied

Element	C	O	P	As	Si	S	Cr	Fe	Mn	Zn	Cu
Content(wt%)	0.49	0.37	0.2	0.17	0.14	0.07	0.74	0.14	0.13	0.02	Balance

Table 2. Texture components of SR and ASR Cu

Texture components	{hkl} <uvw>	Fraction (%)	
		SR-Cu	ASR-Cu
S	{123} <634>	39	30
Cu	{112} <111>	18	15
Bs	{110} <112>	17	12
Cube	{100} <100>	9.9	3
Goss	{110} <100>	0.9	7
shear1	{100} <110>	0.3	0.8
shear2	{111} <112>	0.9	1.4
shear3	{111} <110>	1	1.4
shear4	{112} <110>	1.2	1.9

Table 3. Microstructural parameters of rolled Cu

Sample	D _L (nm)	f _{0.1°-3°} (%)	f _{3°-15°} (%)	f _{>15°} (%)
SR-Cu	235	60.0	35.6	4.4
ASR-Cu	210	63.2	31.6	5.3

Notes: D_L, is the average lamellar boundary spacing; f_{0.1°-3°}, the fraction of boundaries with misorientations between 0.1 and 3°; f_{3-15°}, between 3 and 15°; f_{>15°}, larger than 15°.