I. INTRODUCTION

It is vital to understand the grain growth process in conventional polycrystalline materials for the development of synthesis and processing strategies that optimize grain-size-dependent properties. This is even more important for nanocrystalline (nc) materials that are characterized structurally by ultrafine grain size and an extremely large number of grain boundaries that enables nc materials to possess a variety of improved properties and performances compared with those of the conventional polycrystalline counterparts. Meanwhile, the high stored energy in numerous grain boundaries in nc materials may offer a significant driving force for the grain growth (even at room temperature) as indicated by the Gibbs–Thomson equation that relates the driving force for the grain growth with the grain size.\(^1\)

However, contrary to the expectations,\(^4\) experimental results indicate that most nc materials whether metals or compounds, synthesized by using various methods, exhibit a remarkable resistance to growth,\(^5\) manifested by a relatively high grain growth onset temperature (sometimes as high as 0.6\(T_m\), where \(T_m\) is the melting point).

Extensive investigations in recent years have indicated that the thermal stability and the underlying grain growth mechanism in nc materials are not only associated with grain growth kinetics, but also related to the microstructural and compositional parameters of the ultrafine grains and their boundaries, such as the porosity,\(^6\) impurity,\(^7\) grain size distribution, level of dopants, texture,\(^10\) and microstrain, which may be induced in the processing procedures of nc samples. Most of thermal stability studies in nc metals have been done on consolidated nc samples from ultrafine powders, in which there are normally large microstrain, contamination, flaws and/or porosity due to the imperfect particulate bonding. The impurity effect on the thermal stability in a nc Ag sample has been demonstrated.\(^9\) They found that an addition of 7 at. % oxygen in a pure nc Ag sample increased the grain growth onset temperature by about 80 °C relative to the impurity-free nc Ag sample, and the value of activation energy for grain growth in nc Ag–7 at. %O was twice as much as that of pure nc Ag.\(^11\) Porosity (voids or pores as well as the triple junctions) in the nc samples might be effective in suppressing the grain boundaries movement, and then enhancing the thermal stability.

In the literature, investigation on the thermal stability of porosity-free nc materials were reported, that were synthesized by means of electrodeposition and crystallization of amorphous solids.\(^12\) However, up to now, little is known about the effect of microstrain on the thermal stability of nc materials. Apparently, in order to reveal the intrinsic thermal stability of nc materials, “ideal” nc specimens are necessary, i.e., single phase with a high purity and free of contamination, porosity, and microstrain.

In this work, we prepared a nc Cu sample with a very high purity by means of electrodeposition in which microstrain is negligible. In order to study the microstrain effect on the grain growth process, we introduced different levels of microstrain in the nc Cu by means of cold deformation (rolling) while the average grain size remains unchanged.\(^14\) The thermal stability of the as-deposited and the as-rolled nc Cu samples were investigated by means of different analysis techniques, including differential scanning calorimetry (DSC), electrical resistance measurement (ERM), as well as structural characteristic techniques such as x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) observations. Our experimental results revealed that the grain growth kinetics of the nc metal is corrected with the level of microstrain in the nc material.

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II. EXPERIMENTAL PROCEDURES

The nc copper samples were synthesized by means of electrolysis technique with an electrolyte of CuSO₄. The nc Cu sheet (with a sheet thickness of about 2 mm) was deposited on a substrate of Ti. The purity of the Cu cathode was about 99.99 wt %. The current density in the present electrodeposition process was about 13 mA/cm² with a double pulsed power. The acidity of the electrolyte was about 0.9 mol/l. The bath temperature was kept at 20 °C. It needs an agitation per 20 min. The NaCl and gelatin were selected as the bath additions with a moderate ratio.

The chemical analysis of the as-deposited nc Cu indicated that purity (exclusive of oxygen) was better than 99.993 at. %. The total oxygen content in the as-deposited nc Cu sample was determined by using a LECO TC-436 oxygen/nitrogen determinator analysis, being about 0.009 53 at. % (by taking the oxygen into account, the purity of the as-deposited nc Cu sample is about 99.983 at.%). The sample density was measured by means of Archimedes principle, being about 8.91 ± 0.03 g/cm³, which was equivalent to 99.4 ± 0.3% of the theoretical density for pure Cu (8.96 g/cm³). The full density of the as-deposited nc Cu sample was verified by the positron annihilation spectroscopy measurements, showing that the sample contains no vacancy-cluster-like volumes or no missing crystallites.

The microstructure and the grain size of the samples were characterized by means of XRD analysis and HRTEM observations. Quantitative XRD measurements of the nc Cu samples were carried out in a Rigaku D/MAX 2400 x-ray diffractometer with Cu Ka radiation. X-ray wavelengths λ Ka = 1.54056 Å and λ Kα₂ = 1.54439 Å were selected by using a graphite monochromator. The experiment temperature was 20 ± 1 °C. The average grain size (d) and the mean microstrain (ε) of the samples were determined in terms of the diffraction line broadening by using the Scherrer and Wilson. The integral width of seven single Bragg reflection peaks (111), (200), (220), (311), (222), (400), and (331) were used in calculations. The (111)/(222) and (200)/(400) peak pairs were used to estimate the microstrain in (111) and (100) planes (ε₁₁₁ and ε₁₀₀), respectively. The grain sizes determined from (111)/(222) and (200)/(400) peak pairs are very close to the average grain size calculated from the seven peaks. The calibration of the instrumental line broadening was performed by using the standard SiO₂ sample. HRTEM experiments were performed on a JEM 2010 high-resolution transmission electron microscope at an operating voltage of 200 kV. The thin film samples for HRTEM observations were prepared by using electrochemical polishing at a low temperature (liquid N₂).

DSC (Perkin-Elmer, Pyris 1) and ERM were used to study the thermal stability of the nc Cu samples. The temperature and energy measurements of the DSC were calibrated by using pure In and Zn standard specimens. The calibration of the DSC was performed by using the standard SiO₂ sample. HRTEM observations indicated that the as-deposited sample contained fairly large grains or domains (a few micrometers).

The isothermal experiment was carried out in DSC in the following procedure heating at a heating rate of 5 °C/min to the annealing temperature, holding for a certain period of time, and then cooling down to room temperature. The measurements were performed in a flowing pure Ar atmosphere in order to avoid oxidation of the Cu samples.

In the ERM, the sample of about 60 mm long and 1 × 0.2 mm² across was fixed onto four Pt line probes in a vacuum chamber (5 × 10⁻³ Pa). The samples were heated from room temperature up to 250 °C at a heating rate of 1, 2, 5, and 10 °C/min, respectively. The temperature was calibrated by using a pure Ni foil and the accuracy of temperature is ±1 °C. The measurement error for the electric resistance value of the nc Cu is less than 10%. The resistance measurement results were automatically collected and treated by a personal computer.

The electrodeposited nc Cu specimen was cold deformed by rolling at room temperature. The degree of deformation (ε) of the cold rolled nc Cu sample was determined by: ε = (δ₀ − δ)/δ₀, where δ₀ is the initial thickness of the nc Cu sample and δ is the final thickness of the nc Cu sample after rolling. The strain rate during rolling was controlled to be around 1 × 10⁻³ – 1 × 10⁻²/s. The maximum degree of deformation can be as much as 5100%.

III. RESULTS AND DISCUSSION

A. Thermal stability of the as-deposited nc Cu

The x-ray diffraction patterns of the as-deposited nc Cu and as-annealed Cu samples (at 500 °C for 30 min in flowing argon atmosphere) are shown in Fig. 1. It is obvious that in the as-deposited nc Cu sample only a fcc Cu phase was identified. By comparing the relative peak intensities of the seven Bragg reflections in the as-deposited nc Cu and the as-annealed Cu, the as-deposited nc Cu sample exhibited an evident <110> texture while the annealed sample exhibited a different one. According to the XRD line broadening analysis by using the seven Bragg reflections, we obtained an average grain size of 30 nm and a mean microstrain of about 0.03%. When the (220)/(331) reflections are used for an approximate calculation of the grain size in (110) plane, a much larger value is derived, being about 100 nm. It means there is an evident grain size anisotropy in the as-deposited nc Cu sample.

Microstructure characterization by means of HRTEM observations indicated that the as-deposited sample contained fairly large grains or domains (a few micrometers),
within which ultrafine crystallites (or crystalline domains) with sizes ranging from a few nanometers to about 80 nm can be identified. Statistical results showed that the average crystallite size is about 20 nm, which is close to the XRD result. Most of the nanometer-sized crystallites are equiaxed and separated by small-angle grain boundaries that are consisting of dislocation arrays, in contrast to the conventional large-angle grain boundaries in the consolidated and ball-milling nc materials. This phenomenon is similar to what is observed in the electrodeposited Ni in which numerous small-angle grain boundaries have been also. Both growth twinning and stack faults were quite common occurrences in the microstructure. Figure 2 shows a typical HRTEM observation of a few nanocrystallites, between them are small-angle grain boundaries. The misorientation angle of (111) plane between crystallite A and B is about 1°, and about 9° between B and C, about 10° between A and D. From HRTEM observations in various areas of the as-deposited Cu sample, we found the grain boundaries separating the nanocrystallites are mostly of small-angle ones with misorientation angle ranging from 1° to 10°.

When the as-deposited nc Cu was heated by means of DSC at a heating rate of 5 °C/min from room temperature to 250 °C, a rather weak exothermal peak was observed in the DSC curve at about 150 °C ($T_p$). The integrated enthalpy is about 0.05 J/g. No more thermal (exothermic or endothermic) effect was observed when the sample was heated up to 500 °C. Two possibilities are responsible for the origin of the exothermic peak, including (1) grain growth and/or (2) strain release (relaxation) in the as-deposited nc Cu sample. We did not observe any oxidation in the nc Cu samples after DSC runs.

The variation of resistivity of the as-deposited nc Cu sample as a function of temperature was measured at a heating rate of 5 °C/min. At room temperature, the resistivity of the nc Cu sample is about 2.88 $\mu\Omega$ cm, which is much larger than that for the conventional polycrystalline Cu (1.58 $\mu\Omega$ cm). This might be contributed to the small grain size and a large amount of grain boundaries in the present nc Cu sample. The high resistivity of the nc Cu sample verifies its ultrafine microstructure. Upon heating the nc Cu sample, the resistivity increases at the initial stage below 55 °C and begins to decrease when the temperature exceeds 55 °C. When the sample is heated to 150 °C, the resistivity drops to a minimum value of about 2.52 $\mu\Omega$ cm. A further heating resulted in a linearly increase in the resistivity from 200 to 250 °C. The slope of the resistivity increase within a temperature range of 200–250 °C is about $4.62 \times 10^{-3}$ K$^{-1}$, which is slightly higher than the temperature coefficient of resistivity (TCR) for the conventional polycrystalline Cu ($4.3 \times 10^{-3}$ K$^{-1}$). After cooling the sample down to the room temperature, the sample was heated up again at the same heating rate. A simple linear increment of the resistivity with temperature was observed, of which the slope is $4.47 \times 10^{-3}$ K$^{-1}$, which is close to the TCR value of the polycrystalline Cu. Analogy to the DSC measurement results, the decrease of resistivity upon heating the nc Cu sample may imply either a grain growth process (a reduction of the total number of grain boundaries) or a relaxation process (strain release) leading to an increase in the conductivity, or both of them.

In order to explore the origin of the exothermal peak in the DSC runs and the resistivity variation, various samples annealed at different temperatures (heated at a rate of 5 °C/min to the annealing temperature and cooled down immediately to the room temperature by using DSC) were analyzed by means of the quantitative XRD for determining the microstructure parameters including the grain size and microstrain. Figure 3 shows the XRD results of the variation of average grain size and microstrain with the annealing temperature. From Fig. 3(a), one can see that no obvious grain growth occurs below 75 °C. In the temperature range from 75 to 200 °C, an increase in the average grain size is observed from about 30 to 80 nm. With a further increase of the annealing temperature, the average grain size tends to a saturation value, approximating 80 nm. When the annealing temperature reaches 300 °C, the grain size is still around 80 nm, indicating no significant grain growth process occurs between 200 and 300 °C.

Figure 3(b) shows the mean microstrain ($\epsilon$) and the microstrain in (111) and (100) planes, $\epsilon_{111}$ and $\epsilon_{100}$, in the nc Cu specimens as a function of the annealing temperature. In the as-deposited sample, the $\epsilon_{100}$ is much higher (0.13%) than $\epsilon_{111}$ (about 0.08%) and the mean value ($\epsilon$) from different crystallographic planes ($\sim0.03\%$). Almost no change was found in the microstrain when the sample was annealed up to 75 °C. Above 75 °C, an evident drop was observed in $\epsilon_{111}$, while slight changes were seen in $\epsilon_{100}$ and $\epsilon$. The $\epsilon_{100}$ and $\epsilon$ drop to essentially zero within a narrow temperature range (150–170 °C).

Table I lists the characteristic temperature ranges for the events observed in DSC and ERM, which are compared with XRD results. From the comparison one may clearly see that the exothermic peak in DSC curve corresponds to the microstrain release process in (100) and the mean microstrain, as indicated in XRD measurements [as shown in Fig. 3(b)].
While the resistivity drop in ERM corresponds well to the grain growth and microstrain release processes in (111) that onset simultaneously at about 75 °C.

It is known that the exothermic energy during grain growth can be expressed by
\[
\Delta H = c \gamma (1/d - 1/d_0),
\]
where \( \gamma \) is the grain boundary energy, \( d_0 \) is the initial average grain size, \( d \) is the grain size after annealing, and \( c \) is a constant dependent on the weight and density of the sample.

For example, in our experiment the sample mass is about 30 mg, one may calculate the heat effect of a grain growth process. When the grain growth from 37 nm (125 °C) to 70 nm (175 °C), the enthalpy release per unit time is about 0.0143 mW in the present nc Cu sample with small-angle grain boundaries (taken sample density of 8.91 g/cm\(^2\) and \( \gamma = 0.1 \) J/m\(^2\)). The critical accuracy of the energy measurement is about 0.01 mW for the current calorimeter (Perkin-Elmer DSC, Pryis 1). Therefore, the thermal effect of grain growth in the present nc Cu sample is too weak to be detected by the DSC. It means the thermal signals in DSC measurements of the present nc Cu sample originate from the strain release process only.

In ERM tests, the characteristic temperatures for the decrease of the resistivity agree well with the grain growth process. It means that the effect of grain growth on resistivity is more significant than that of the strain release. During the strain release process, no specific change in the resistivity was detected.

It is interesting to note that in the as-deposited nc Cu sample, the grain growth process occurs evidently prior to the major strain release process. And the temperature range of grain growth is much wider compared with that of the strain release process. This interesting phenomenon may relate to the special microstructure of the nc Cu sample, which will be discussed in the following sections.

### B. Grain growth kinetics in the as-deposited nc Cu

One of the key kinetic parameters for the grain growth process is its activation energy, which can be determined by means of Kissinger analysis\(^23,24\), using the characteristic temperatures at different heating rates
\[
\ln(B/T^2) = -E/RT + \text{constant},
\]
where \( B \) is the heating rate, \( E \) is the activation energy, \( R \) is the gas constant, and \( T \) is a characteristic temperature for the grain growth, such as the onset temperature (\( T_{on} \)) or the peak temperature (\( T_p \)). Heating the as-deposited nc Cu samples at different heating rates, ranging from 1 to 10 °C/min in ERM, we obtained different characteristic temperatures for the grain growth process, as listed in Table II. The activation energy for the grain growth process in the as-deposited nc Cu sample was calculated by using the onset temperature, being about 90±16 kJ/mol. This value is close to the activation energy for the grain boundary self-diffusion in polycrystalline Cu (102–120 kJ/mol).\(^25\) The same consistency was obtained for the grain growth process in an as-deposited nc Ni sample, which is controlled by grain boundary diffusion, too.\(^26\)

### TABLE I. A comparison of the characteristic temperature ranges detected by different measurement methods.

<table>
<thead>
<tr>
<th>Event</th>
<th>Measurement</th>
<th>Characteristic temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain release</td>
<td>DSC, exothermic peak</td>
<td>140–160 °C</td>
</tr>
<tr>
<td></td>
<td>XRD, decrease of ( e _100 ) and ( e _150 )</td>
<td>150–170 °C</td>
</tr>
<tr>
<td></td>
<td>XRD, decrease of ( e _111 )</td>
<td>75–125 °C</td>
</tr>
<tr>
<td>Grain growth</td>
<td>ERM, ( \rho ) decrease</td>
<td>55–200 °C</td>
</tr>
<tr>
<td></td>
<td>XRD, grain size increase</td>
<td>75–200 °C</td>
</tr>
</tbody>
</table>

### TABLE II. The onset temperatures of the grain growth process detected in ERM at different heating rates. Activation energy was calculated by using the Kissinger analysis.

<table>
<thead>
<tr>
<th>Heating rate ( B ) (°C/min)</th>
<th>( T_{on} ) (°C)</th>
<th>( E ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41±1</td>
<td>90±16</td>
</tr>
<tr>
<td>2</td>
<td>49±2</td>
<td>90±16</td>
</tr>
<tr>
<td>5</td>
<td>55±2</td>
<td>90±16</td>
</tr>
<tr>
<td>10</td>
<td>62±3</td>
<td>90±16</td>
</tr>
<tr>
<td>25</td>
<td>64±11</td>
<td>90±16</td>
</tr>
</tbody>
</table>
The activation energy can be alternatively derived by using the isothermal measurements of the grain growth process. The kinetics of isothermal grain growth in the polycrystalline materials is usually represented by

\[ d^N - d_0^N = K_T t, \]  
(3)

where \( d_0 \) is the initial grain size, \( d \) is the grain size after annealing for a time period of \( t \), \( N \) is the grain growth exponent, and \( K_T \) is a kinetic constant. Following the classical grain growth mechanism, we know that when \( N=2 \), the grain growth process usually is the curvature-driven migration of grain boundaries in pure materials, if \( N=4 \), is the stochastic jumping of atoms across the grain boundaries, and \( N=3 \), is controlled by volume diffusion.\(^{10,27–29}\)

The kinetic constant \( K_T \) is related to the temperature by

\[ K_T = K_{70}\exp\left(-E/RT\right), \]  
(4)

where \( K_{70} \) is a constant, \( E \) is the activation energy for grain growth, and \( T \) is the annealing temperature. Experimental studies on the grain growth are usually designed to evaluate the values of \( N \) and \( E \), and to determine the mechanism of grain growth process by comparing the experimental values with theoretical predictions.\(^{30}\)

Experimental results of the isothermal grain growth kinetic for the as-deposited nc Cu specimens (of which the initial average grain size is about 24 nm determined by the XRD analysis) are summarized in Fig. 4. It shows the variation of the average grain size with annealing time at three different annealing temperatures (100, 125, 150 °C). Based on the variation of grain size in Fig. 4, the activation energy \( E \) for the grain growth process may be calculated by using Eqs. (3) and (4). The resultant activation energy for the isothermal grain growth is 83 ± 13 kJ/mol. It is found \( N \) increases from 3.4 to 4.0 with a decreasing annealing temperature (150–100 °C). Table III summarized activation energies for the grain growth in Cu with different initial grain sizes prepared by means of different synthesis methods. It can be seen that most of the results of the nc Cu are close to the activation energy of grain boundary diffusion, suggesting that the grain growth mechanism in nc materials is dominated by grain boundary diffusion, similar as that in the conventional polycrystalline Cu. The calculated grain growth exponent \( N \), which is close to 4, also reflected that the grain growth process of the nc Cu sample in present study was controlled by the stochastic jumping of atoms across grain boundaries. The earlier results verify that the grain growth process in pure nc Cu specimen without porosity and contamination is controlled by the grain boundary self-diffusion.

### C. Thermal stability of the as-rolled nc Cu samples

In order to explore the underlying mechanism of the grain growth process and its correlation with the strain release process in the nc Cu, the as-deposited nc specimens were rolled at room temperature for introducing different levels of microstrain in the nc samples. XRD measurements indicated that the average grain size of the rolled specimens remained the same as that in the as-deposited sample, being about 30 nm, but the microstrain increases with an increase in the degree of deformation. The thermal stability of the as-rolled nc Cu samples (in a shape of the thin ribbon) was measured by means of DSC. Figure 5 shows DSC curves for the as-rolled nc Cu samples with different degrees of deformation. For the nc Cu sample with \( \varepsilon =100\% \), an exothermal peak was observed at about 155 °C \( (T_{\text{eq}}) \). With an increment in \( \varepsilon \), the exothermal peak shifts to a lower temperature. When \( \varepsilon =2300\% \), the onset temperature drops to 120 °C.

### Table III. Literature data of activation energy for grain growth in Cu prepared by means of different methods (IGC=inert gas condensation; PTS=plastic torsion straining; ED=electron deposition; CG=coarse grained polycrystalline Cu; and NM=not mentioned).

<table>
<thead>
<tr>
<th>Grain size (nm)</th>
<th>Preparation</th>
<th>Density (g/cm(^3))</th>
<th>Purity (%)</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>Sliding wear</td>
<td>&gt;99</td>
<td>0.8Fe</td>
<td>30 × 9</td>
</tr>
<tr>
<td>20</td>
<td>IGC</td>
<td>&gt;95</td>
<td>NM</td>
<td>86</td>
</tr>
<tr>
<td>25</td>
<td>IGC</td>
<td>NM</td>
<td>NM</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>IGC</td>
<td>NM</td>
<td>NM</td>
<td>39 (&lt; 80 °C)</td>
</tr>
<tr>
<td>160</td>
<td>PTS</td>
<td>NM</td>
<td>99.98</td>
<td>107 (200 °C)</td>
</tr>
<tr>
<td>30</td>
<td>ED</td>
<td>&gt;99</td>
<td>99.993</td>
<td>(41–62 °C)</td>
</tr>
<tr>
<td>CG</td>
<td></td>
<td>100</td>
<td>99.999</td>
<td>(85)</td>
</tr>
</tbody>
</table>

\[ E = 3 \times 10^4 (1 - 0.1 \varepsilon) \]
Table IV lists the mean microstrain, the onset temperatures and the enthalpy change ($\Delta H$) of the exothermal DSC peaks for the as-rolled nc Cu samples with different degrees of deformation.

Figure 6 shows XRD measurement results of the variation of the average grain size and microstrain with the annealing temperature for the as-rolled nc Cu samples with $\varepsilon = 2300\%$. One can see that after rolling, the average grain size of the nc Cu specimen remains the same as that of the as-deposited nc Cu sample. The mean $e$ and $e_{100}$ in the as-rolled nc Cu sample with $\varepsilon = 2300\%$ increased remarkably up to 0.14\% and 0.19\%, respectively, but $e_{111}$ is diminished. The reason may be that dislocation sliding in the $\{111\}$ plane is easier than that in other planes during the cold-rolling process. From Fig. 6 we can see that the $e$ and $e_{111}$ of the rolled nc Cu sample drop down to zero within a temperature range of 115–160 °C, which coincides well with the temperature range for the exothermal peak (120–160 °C) in DSC experiments (as shown in Fig. 5). That implies that the DSC exothermal peak originates from a strain release process, similar to that in the as-deposited sample. The grain growth process takes place in a temperature range from 150 to 250 °C, according to the XRD measurements. It is evident that, in the as-rolled nc Cu sample with $\varepsilon = 2300\%$, the strain release process occurs prior to the grain growth process, that differs evidently from the observation in the as-deposited nc Cu sample with the same initial grain size but much lower microstrain.

The onset temperatures for the grain growth (by means of XRD) and strain release processes (by DSC and XRD) in different cold rolled nc Cu samples have been measured. As shown in Fig. 7, the onset temperatures of grain growth and strain release varied with the mean microstrain in the nc Cu samples. It is evident that with an increase in the microstrain from 0.03\% to 0.15\%, the onset temperature for the grain growth process increases from 75 to 150 °C, while the onset temperature for the strain release process decreases from 150

<table>
<thead>
<tr>
<th>$\varepsilon$ (%)</th>
<th>$e$ (%)</th>
<th>$T_{on}$ (°C)</th>
<th>$\Delta H$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.031±0.005</td>
<td>140±5</td>
<td>−0.05±0.01</td>
</tr>
<tr>
<td>100</td>
<td>0.082±0.016</td>
<td>155±4</td>
<td>−0.54±0.04</td>
</tr>
<tr>
<td>200</td>
<td>0.097±0.019</td>
<td>143±3</td>
<td>−0.75±0.03</td>
</tr>
<tr>
<td>400</td>
<td>0.120±0.014</td>
<td>133±3</td>
<td>−0.80±0.03</td>
</tr>
<tr>
<td>1000</td>
<td>0.132±0.013</td>
<td>126±4</td>
<td>−0.93±0.02</td>
</tr>
<tr>
<td>2000</td>
<td>0.148±0.013</td>
<td>120±3</td>
<td>−0.96±0.04</td>
</tr>
</tbody>
</table>
to 115 °C (from the XRD measurement results). It means that both the grain growth and the strain release processes are related to the level of microstrain in the nc material.

The obvious increment in the grain growth onset temperature with a higher microstrain in the as-rolled nc Cu could be understood in terms of the density of dislocations in the nc sample. A large microstrain results from a higher density of dislocations and/or other lattice defects. Actually, HRTEM observations confirmed that there is a no obvious difference in the grain size of the as-deposited and that of the as-rolled nc samples. But the dislocation density (mainly located in grain boundaries) in the as-rolled specimens is increased significantly, which leading to an evident increase in the grain boundary misorientation angles among the nanocrystallites. The observed enhancement in the grain size stability with a higher microstrain implies that the large density of dislocations may interact on grain boundaries and interfere with the grain boundary movements. Although at the present, the intrinsic mechanism for the dislocation or grain boundary interaction is not clear, the enhanced grain size stability due to a high dislocation density needs more detailed investigations, which are in progress.

The strain release process shifts to a lower temperature when the microstrain is higher. The origin of the strain release process is the annihilation of various defects in the nc samples. A high density of dislocations in the crystallites may provide a larger driving force for the strain release, and consequently depress the temperature at which the annihilation of the dislocations onsets.

In the literature, most of experiment results showed that the strain release process in nc samples occurs prior to or simultaneously with the grain growth process, as seen in nc Cu and Ag samples. This phenomenon may be attributed to the high level of microstrain (as high as 1%–3%) in the nc samples which were prepared by means of consolidation of ultrafine powder or ball milling methods. As seen in Fig. 7, this situation is possible only when the microstrain is large enough ($\varepsilon > 0.12\%$ in this case). Therefore, our observations in the as-rolled nc Cu with different amounts of microstrain demonstrate clearly the microstrain dependence on the grain size stability and the relationship between the grain growth and the strain release processes.

IV. CONCLUSIONS

1. In the as-deposited fully dense nc Cu sample with a high purity and small grain boundaries, the grain growth process and the microstrain release in (111) onset at about 75 °C, which is evidently lower than the strain release in (100) and the mean microstrain.

2. The activation energy for the grain growth in the as-deposited nc Cu sample is determined by means of Kissinger and isothermal kinetics analysis, being about 90±16 and 83±13 kJ/mol, respectively. These values are close to the activation energy for the grain boundary self-diffusion in polycrystalline Cu, implying the grain growth process in the nc Cu is dominated by the grain boundary diffusion.

3. Rolling the as-deposited nc Cu increases the level of microstrain in the nc samples without a change of grain size. With an increase in microstrain, the onset temperature of the grain growth process increases and that of the strain release process drops evidently. When the mean microstrain is large enough ($\varepsilon > 0.12\%$), the strain release process occurs prior to the grain growth process in the as-rolled nc Cu specimens.

ACKNOWLEDGMENTS

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