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Thickness dependence of internal stress in electrodeposited nano-twinned copper

S. Zhan [1], Y.L. Yang [2,*], W.Y. Peng [1,*], J.G. Chen[3], Z.B. Li[3], X.J. Hou[2], L. Feng[2], G.Q. Suo[2], Z.G. Chen[4], J. Zou[4], Y.D. Wang[5,*]

[1] *School of Materials Science and Engineering, Nanchang University, Nanchang, 330031, China*
[2] *School of Materials Science and Engineering, Shaanxi University of Science & Technology, Xi'an 710021, Shaanxi, China*
[3] *Key Laboratory of Electromagnetic Processing of Materials, Ministry of Education, Northeastern University, Shenyang, 110004, China*
[4] *Materials Engineering, The University of Queensland, Brisbane, QLD 4072, Australia*
[5] *State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China*

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Electrodeposited pure copper with nano-scaled twins was proved to be a tradeoff for the contradiction of high mechanical strength and high electrical conductivity. In this work the internal stress of the nano-twinned copper was explored by means of X-ray diffraction analysis. The results show that the internal stress is associated with the deposition thickness. The macro-stress of the film is very small and constant. The type-II micro-stress (grain-orientation-dependent stress) is also small, while it becomes higher with the increase of deposition thickness.

Keywords: Electrodeposition; Nano-twin; Copper; Stress

INTRODUCTION

Electrodeposition has been proven to be a technologically and economically viable production route to synthesize various materials with different functions [1-4]. In the study of various metallic structures, electrodeposition has become well established as a cost-effective fabrication technique compared with physical or chemical vapor deposition techniques [5]. Although there are some drawbacks associated with the electrodeposition process, such as the relatively limited number of elements that can be deposited from aqueous electrolytes and the need for a conducting substrate, electrodeposition does offer the clear benefits of high growth rates and the use of very simple apparatus. These benefits are as applicable to the fabrication of structures that are patterned in the growth plane.

A thorough understanding of the relationship between the electrodeposition parameters, the microstructure and the performance of electrodeposited films is required in order to tailor their microstructure and thereby design their properties and performance. Grain size, grain shape, dislocation density and inclusion content in electrodeposited layers markedly affect the properties of the deposit. Moreover, electrodeposited films are often crystallographically textured because of preferred growth of particular grain orientations. As a result, anisotropy of the elastic properties of the deposited films is anticipated [6].

Conventional methods for materials strengthening usually cause an obvious decrease in electrical conductivity. A reasonable explanation is that all of the strengthening methods, such as solid solution, second phase strengthening, and strain hardening, always introduce various kinds of defects, which at the same time increase the scattering of conducting electrons at these defects, and thus decrease the electrical conductivity. It is a contradiction for strengthened conducting materials. An ideal microstructure, twin, has been proved as a tradeoff, which could effectively block dislocation motion and greatly minimize the scattering of conducting electrons [7]. Lu *et al.* [8] have synthesized high-purity copper with high density of nanoscale grown twins using a pulse electrodeposition technique, which demonstrates ultrahigh strength and ultrahigh electrical conductivity. However, the thickness of the deposited copper film always has a limit of several or tens of micrometers because of the deteriorating surface with the increase in deposition duration. Moreover, some details in the process of twin formation through pulse electrodeposition are not fully understood. It is of significance to study the development of microstructure in such an electrodeposition process both for the structure design on nanometer scale in electronic industry and studies of the performance and lifetime of components used in microelectronics, tribological,

* To whom all correspondence should be sent.
E-mail: yanling_yang@126.com
The first two authors contributed equally to this paper.

mechanical, and electrochemical applications [9]. In this paper we studied the internal stress of nano-twinned copper by means of X-ray diffraction analysis, in the hope of obtaining a deeper understanding of the deposition process of nano-twinned copper.

A postulation is that the generation of the twins could be due to the stress in the deposited films [10]. Regardless of the method of deposition, it is well known that internal stress will be developed in thin films [11]. The close relationship between stress behavior and morphology of thin films is expected to facilitate the detailed description of thin film growth from analysis of stress development. Among existing methods to investigate strain in coatings, X-ray diffraction (XRD) is a powerful tool due to its capability to measure the full strain or stress and provide complementary information on crystallographic phase non-destructively [12].

EXPERIMENTAL DETAILS

A series of samples deposited at different durations were used for the study of stress evolvement as a time-dependent process. The samples were prepared with a cathode of Ni-P amorphous film deposited on pure Fe and with the pulsed electrodeposition parameters as reported by Lu *et al.* [8]. The standard sample (copper powder) is commercially available and was annealed in vacuum at 190°C for 10 min to remove the residual stress. Generally, there should be only instrumental broadening in the diffraction pattern of the standard sample and physical broadening was discarded.

The X-ray diffraction measurements were carried out using a ω diffractometer and a ψ diffractometer. Generally, a specific *hkl* reflection was scanned at several specimen tilts and possible rotation angles. The measured peak positions were used to calculate the lattice spacing and the lattice strain at every tilt and rotation angle. The samples were tilted around Eulerian cradle axis from 0 to 80° with an interval to get $Sin^2\psi$ equally split, which facilitates the data processing. For every ψ, a certain plane was scanned for the corresponding 2θ with interval of 0.05°. The classical stress analysis was done with the $sin^2\psi$ method. The general formula for the bi-axial case is:

$$\varepsilon_\psi = \frac{d_\psi - d_0}{d_0} = \frac{1+\nu}{E}\sigma_\phi \sin^2\psi - \frac{\nu}{E}(\sigma_1 + \sigma_2) \quad (1)$$

where E is the Young's modulus of the deposited film, ν the Poisson's ratio of the film, σ_φ the in-plane residual stress, σ_1 and σ_2 the in-plane major stress respectively. Derivate ε_Ψ by $sin^2\Psi$, it gives:

$$\sigma_\phi = \frac{E}{1+\nu} \bullet \frac{\partial \varepsilon_\psi}{\partial \sin^2\psi} \quad (2)$$

In our case we plotted micro-strain *vs.* $\sin^2$psi, from the slope of which the macro-stress σ_φ could be estimated. What is more, this method is adapted for assessment of average lattice distortion (strain) with increase of $sin^2\psi$, while the detailed strain distribution needs to be studied according to physical broadening obtained by a Fourier convolution method.

Generally speaking, the stress-free d-spacing should be calculated from the standard sample, or can be calculated from a corresponding $sin^2\psi$ strain-free value by interpolation *via* the linear fitting in the d-spacing (ψ) *vs.* $\sin^2$psi plot. In this case, the stress-free d-spacing (d_0) is an average one of d-spacings obtained at different tilt ψ for the standard sample.

RESULTS AND DISCUSSION

Fig. 1 shows the high-resolution TEM image of nano-twinned copper deposited for 24 h. A homogeneous microstructure with nano-scaled twins was obtained with lamella thickness of about 5 nm. The micro-strain vs. $sin^2\psi$ plots are given in Fig. 2. Before studying the graphs, one more thing should be considered. The self-annealing characteristic [13] of electrodeposited copper allows recrystallization at room temperature because of a high defect density that lowers the activation energy. Thus internal stress (σ) also evolves in the film; the decrease of σ starts immediately after plating, and then stops after a much shorter time.

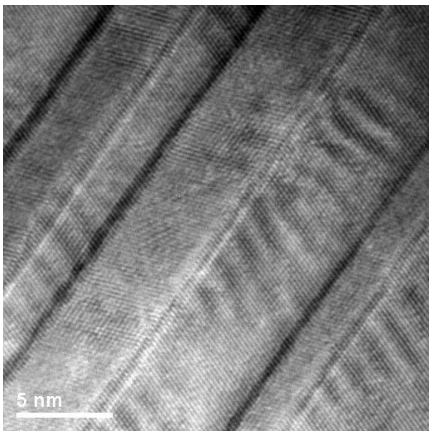
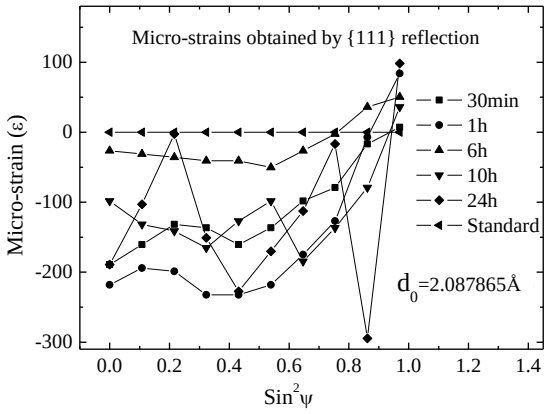
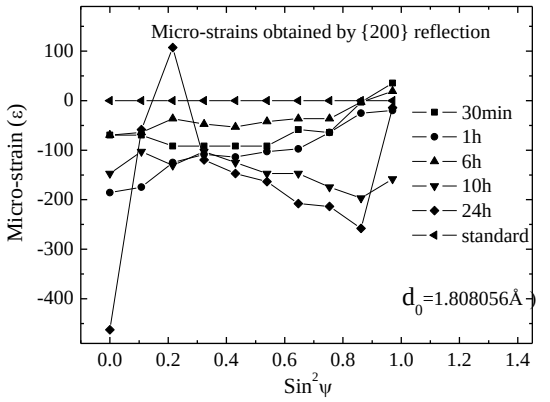


Fig. 1. High-resolution TEM image of nano-twinned copper deposited for 24 h

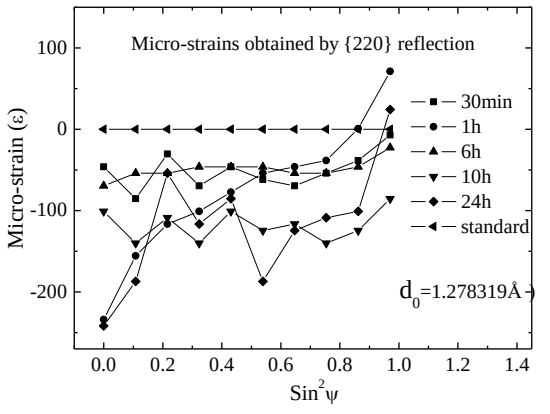
Although part of the stress is relaxed on open circuit at room temperature, there is still something that could be taken into consideration. The stress release tends to be stronger when the layer is thinner (with a shorter deposition duration), which is indicated by the average magnitude of the micro-strain of samples deposited for different durations or different deposited thickness. To account for these observations, it is believed that the diffusion would be much easier in the areas close to the surface, leading to an almost complete stress release for the thinnest layers while a larger stress would remain for thicker films.



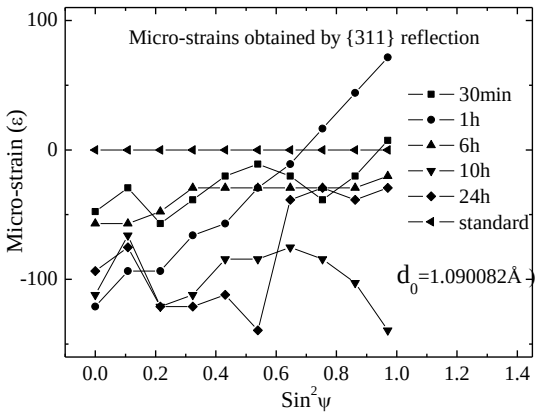
(a)



(b)



(c)



(d)

Fig. 2. Micro-strains obtained by {111}, {200}, {220} and {311} reflections

As shown in Fig. 2, the macro-stress is very small (less than 30 MPa), which is estimated from the slope of strain distribution for the (311) peak. People usually think that the linear relationship is very good for (311) and the macro-stress evaluation is accurate by using this one. The type II stress (grain-orientation-dependent stress) is also not big. However, the type-II stress becomes higher with the increase in deposition duration up to 24 h. The sawtooth-like figure may be described as at about the point a maximum in the tensile stress in the pole is reached which is then followed by the film stress turning compressive.

Anyway, it is not very big compared to the deposited Fe [9]. The measured accuracy in lattice strain using the lab X-ray was within 100 micro-strains. If the lattice strains with about over 700 micro-strains, it can only be believed that the type II stress is larger. Generally, the mechanism of stress-raising conditions may be classified as follows: crystallite-joining theory, hydrogen theory, excess energy theory and lattice-defect theory. Comparison made between pulse and direct plating indicated that with direct plating, higher stress values were obtained [14]. This is explained by the proposed crystallite-joining theory. As the current density increases, the residual stress increases when using conventional direct deposition. This is due to increased nucleation rate caused by an increase in overpotential, leading to a greater crystal boundary volume [15]. The intrinsic stress of the electrodeposited film is related to the number of grain boundaries that are formed when the individual crystallites grow together. It means that the tensile stress is proportional to the total twin boundary area, and therefore increases with the decrease in average thickness of twin lamella.

Unlike conventional electrodeposition in which the internal stress may come from the escaping hydrogen-induced shrinkage in the dendrites [9], there is little possibility that the internal stress in the nano-twinned copper film would come from the release of molecular hydrogen. Because in the pulse electrodeposition process, the actual growth process is controlled by the on-time/off-time ratio, there is little possibility that the deposits would grow into dendrites.

Another postulation is that the stress may come from the lattice mismatch. In the initial process of electrodeposition, the level of internal stress of the copper deposits may be attributed to the lattice misfit between deposit and substrate under conditions of assumed epitaxy (i.e. the deposit continues the structure of the substrate) or the two layers are deposited closely with different dimensions. The greater this mismatch or misfit between the lattice parameters of the deposit and substrate, or the dimension difference between the two layers deposited closely, the greater is the

associated strain energy. Tensile stress can be considered to be due to deposits being dimensionally less than substrate or the previously laid down layer while compressive stress is supposed to be the contrary. However, the model has to be modified to allow for the relaxation processes associated with pulse on-time and off-time. Even in conventional electroplating, it was found that the lattice strains weakly depend on depth [9], which means that if thick enough, the coating will minimize the influence of stress gradients. What's more, the cathode used is pure iron coated with Ni-P amorphous alloy, for which the epitaxial growth of the substrate could almost be discarded.

Vacancies can be also created during domain growth and this lattice defect may result in lattice distortion or increase of crystal volume which is indirectly represented by the tensile stress [16].

The diffraction intensity was measured as a function of the tilt angle, Ψ, with respect to the surface normal and the rotation angle Φ (in the plane perpendicular to the surface normal) at 2θ angles corresponding to the Bragg diffraction angle of the {111}, {200} and {220} reflections. The background intensities for the investigated {hkl} reflections were estimated from the intensity distribution experimentally and were determined as a function of Ψ and Φ.

CONCLUSION

The internal stress of nano-twinned copper was explored by means of X-ray diffraction analysis. It is found that the macro-stress is very small and constant. The type II micro-stress (grain-orientation-dependent stress) is also small, while it becomes higher with the increase of deposition thickness.

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ЗАВИСИМОСТ НА ВЪТРЕШНОТО НАПРЕЖЕНИЕ ОТ ДЕБЕЛИНАТА НА ЕЛЕКТРООТЛОЖЕНИ ДВОЙНИ МЕДНИ КРИСТАЛИ

С. Джан[1], И.Л. Ян[2]*, У. И. Пън[1], Дж.Г. Чън[3], З.Б. Ли[3], Кс.Дж. Хоу[2], Л. Фън[2], Г.К. Суо[2], З.Г. Чен[4], Дж. Зоу[4], И.Д. Уан[5]

[1] Училище по материалознание и инженерство, Университет в Нанчан, Нанчан 330031и, Китай
[2]Училище по материалознание и инженерство, Университет по наука и технология на Шаанкси, Ксиан 710021, Шаанкси, Китай
[3] Лаборатория по електромагнитна обработка на материали, Министерство на образованието, Североизточен университет, Шенянг 110004, Китай
[4] Материалознание, Университет на Куинсланд, Брисбейн, QLD 4072, Австралия
[5] Държавна лаборатория по нови метали и материали, Пекински университет по наука и технология, Пекин 100083, Китай

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(Резюме)

Установено е, че електроотложена чиста мед с наноразмерни двойни кристали е компромис между противоречащите си висока механична якост и висока електропроводимост. В настоящата статия е изследвано вътрешното напрежение на мед с наноразмерни двойни кристали с помощта на рентгенов дифракционен анализ и е установено, че вътрешното напрежение е свързано с дебелината на филма. Макро-напрежението е много малко, напрежението от тип II (зависещо от ориентацията на зърната) е също малко, но нараства с увеличаване на времето на отлагане.