N.V. Tokiy, V.V. Tokiy

THE ACTIVATION ENERGY OF TWINNING FOR COPPER IN VOIGT APPROXIMATION

Donetsk Institute for Physics and Engineering named after A.A. Galkin

The formation of twins can significantly affect the plasticity and strength of materials. The possibility of applying the two-component model of single-phase hybrid materials to explain anomalous temperature dependence of elasticity moduli of copper with a submicrocrystalline structure has been discussed. An analysis has been performed that is based on previously existing experimental data. A twinning mechanism of changing the crystallite orientation has been proposed. Master Twinning Curve (MTC) is proposed to obtain the twinning activation energy. The apparent activation energies for the MTC are determined by minimising mean residual squares (MRS) method. The activation energy for twinning in copper characterized by an ultrafine-grained (nano- and submicroscopic) structure is found in Voigt approximation to be 0.123 eV.

1. Introduction

The temperature-induced change in the elastic properties of copper continuously attracts attention of researchers. First, the interest is of purely fundamental quantum-mechanics character, being focused on high-quality single crystals below room temperature down to the liquid-helium temperature [1]. Then, along with the fundamental interest, certain applied profit appears, and this fact results in the necessity of measurements on single crystals at the temperatures higher of the room temperature [2].

The observed decrease in the elastic modulus with increasing temperature agrees with the physical concepts of weakening of the interatomic interaction. However, the transition to studies of copper of an ultrafine-grained (nano- and submicroscopic) structure revealed the regions of anomalous temperature dependence of the elastic properties provided by unusual mechanical and physical characteristics. Namely, an increase in the elasticity modulus with the temperature rise is registered [3]. Three possible mechanisms (internal stresses, lattice deformations and boundary elastic modulus) are considered in [3] and the analysis of the estimations performed based on these mechanisms allows conclusion that further experimental and theoretical studies of this effect are necessary. As noted in [4], a specific mechanism of this phenomenon has not been completely understood yet, although there is a significant number of reports devoted to these

studies.

In the approach of hybrid materials [5], we proposed in [6]:

1) a single-phase two-component hybrid model for the examination of the temperature dependence of the elastic properties of materials and HCC, particularly copper;

2) a twinning mechanism responsible for the anomalous temperature dependence of the shear modulus of ultra fine copper.

However, the activation energy of the process responsible for the anomalous temperature dependence of the shear modulus in [6] has not been evaluated. Therefore, the aim of this study is estimation of the activation energy of this process, with using the experimental data [4] for the effect of the heating rate to changes in shear modulus.

2. Theory

In terms of the proposed model, we distinguish the components with different crystallographic orientations along the axis of the sample. The first component goes out on the cross section of the sample by plane 111, and the second component goes out by plane 100. The values of Yong's modulus E and shear modulus G denoted here as M are within the known Voigt and Reuss limits [6,7].

The composed modulus can be estimated more correctly (e.g., [7]), but, for simplicity, we restrict here by the foregoing consideration in the Voigt approximation.

When obtaining the upper limits of the moduli, it is postulated that both hybrid components have the same stress under load, and the deformation is calculated by averaging local deformations over the volume; then, the composed modulus is determined by relationship

$$M_U\left(T\right) = M_{100}\left(T\right) f^V\left(T\right) + M_{111}\left(T\right)\left(1 - f^V\left(T\right)\right) \tag{1}$$

where $f^V\left(T\right)$ is the volume fraction of the component with orientation 100; $1 - f^V\left(T\right)$ is the volume fraction of the component with orientation 111; $M_{100}(T)$ and $M_{111}(T)$ are the temperature dependences of the elastic modules of a single crystal in directions 100 and 111, respectively.

Therefore, the volume fraction f of the hybrid component with orientation 100 can be found in the Voigt approximation from Eq. (1):

$$f^V\left(T\right) = \frac{M\left(T\right) - M_{111}\left(T\right)}{M_{100}\left(T\right) - M_{111}\left(T\right)} \tag{2}$$

where $M(T)$ is the experimental temperature dependence of the related elastic modulus of the hybrid.

The volume fraction of the hybrid component with orientation 111 can be found in the Voigt approximation as $1 - f^V\left(T\right)$.

The described temperature changes in the volume fractions of the components of a

single-phase hybrid material can be physically explained by the formation of annealing twins [8] with the transformation matrix [9]:

$$Q = \begin{pmatrix} -1 & 1 & 2 \\ 1 & -1 & 2 \\ 1 & 1 & 0 \end{pmatrix}.$$

The matrix transforms the indices of the family of planes (*hkl*) of the «old» crystallite to the indices of the family (*h'k'l'*) of the «new» crystallite, which are represented in matrix form

$$\begin{pmatrix} h' \\ k' \\ l' \end{pmatrix} = Q \begin{pmatrix} h \\ k \\ l \end{pmatrix}.$$

3. Experimental procedure [4]

The temperature effect on shear modulus and internal friction in ultrafine-grained copper processed by equal channel angular pressing was investigated in the temperature range from 150 to 520 K. Acoustic measurements were performed on the inverted torsion pendulum at the frequencies of 18 and 45 Hz. An irreversible shear modulus increase and a concurrent decrease in sound attenuation were observed in the temperature region from 350 to 450 K in the course of the first heating of specimens.

The temperature dependencies of the shear modulus of the samples at two heating rates are shown in Fig. 1 [4] (the temperature rate is 0.5 K/min) and Fig. 3. [4] (the temperature rate is 1.05 K/min).

4. Results and analysis

The changes in the volume fractions of the components calculated by Eq. (2) are shown in Fig. 1. In these calculations, we use the experimental data for the shear modulus of copper $G(T)$ [4]. The temperature dependence of the shear modulus of the copper single crystal in direction 100 $G_{100}(T)$ is identical to the temperature dependence of the elasticity constant $c_{44}(T)$, as reported in [2]. The temperature dependence of the shear modulus of the copper single crystal in direction 111 $G_{111}(T)$ is calculated by formula

$$G_{111}(T) = \frac{3G_{100}(T)\left[c_{11}(T) - c_{12}(T)\right]}{\left[c_{11}(T) - c_{12}(T) + 4G_{100}(T)\right]}$$

where $c_{11}(T)$ and $c_{12}(T)$ are the elasticity constants [2].

The curves are of a familiar sigmoidal shape and generally shifted to higher temperatures with increasing heating rate.
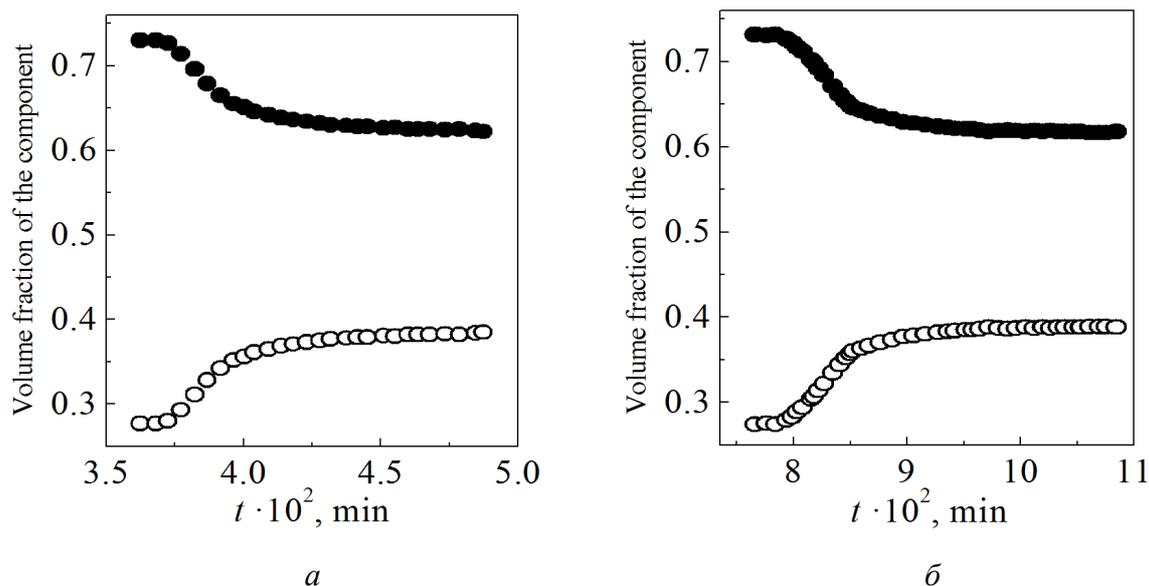
Fig. 1. Changes in the volume fractions of the low modulus f_{111}^V (●) and high modulus f_{100}^V (○) components of pure copper during the first heating with the varying temperature rate (a – 1.05 K/min, $б$ – 0.5 K/min) [4] calculated in the Voigt approximations by Eq. (2)

We assume that the relationship between f^V and $\log\left[\Theta\left(t, T(t)\right)\right]$, i.e. an S-shape curve, is the Master Twinning Curve (MTC) analogous to that reported in [10–14].

For the Master Twinning Curve approach, the measured volume fraction of the component is plotted as a function of the right-hand side, denoted by Θ,

$$\Theta\left(t, T(t)\right) = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \qquad (3)$$

where Q is the apparent activation energy for twinning, R is the gas constant, T is the absolute temperature, t is the time.

For the construction of MTC, the integral of Eq. (3) and the experimental volume fraction of the component should be known.

The apparent activation energies for the MTC are determined by minimising mean residual method. The mean residual used is defined as follows [12]:

$$\text{MRS} = \sqrt{\frac{1}{N\left(f_f - f_i\right)} \int_{f_i}^{f_f} \sum_{m=1}^{N} \left[\frac{\Theta_m}{\Theta_{\text{avg}}} - 1\right]^2 df}$$

where m is the dummy variable for summation, N is the number of experimental data, Θ_{avg} is the average value of work of twinning at volume fraction of the component for m_{th} experiment, Θ_m is the work of twinning for m_{th} experiment, f_i and f_f are the initial and final volume fractions of the component, respectively.

The standard statistical approach to evaluation of the dispersion of experimental data is the minimization of MRS.

It can be seen that the curves for different heating rates are not converging. Now a new value of activation energy is chosen and the calculation is repeated. The best convergence is found in the vicinity of 0.123 eV. Fig. 2 gives the mean residual squares for the various values of activation energy and the minimum appears to be equal to 0.123 eV.
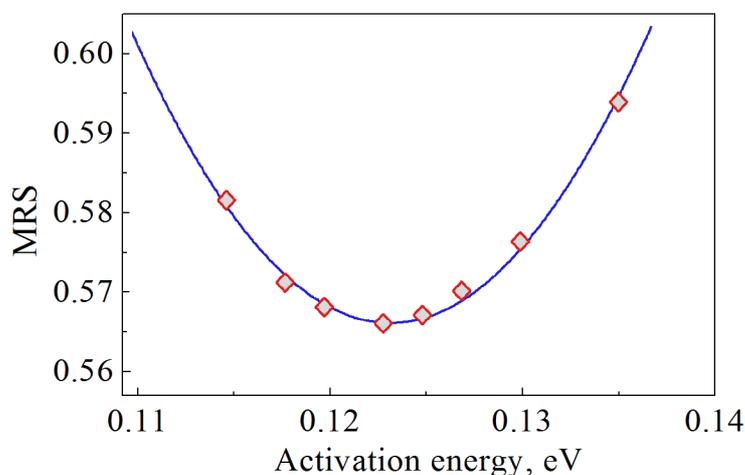
Fig. 2. Mean of residual squares (MRS) versus activation energy calculated by MTC method. Minimum occurs at ~ 0.123 eV

5. Conclusions

We proposed a possible mechanism of changing the elastic properties that explains anomalous temperature dependence of the elastic shear moduli of copper by the formation of annealing twins.

The densification behaviour and kinetics of twinning is evaluated with using internal friction in ultrafine-grained copper processed by equal channel angular pressing with constant heating rate experiments. To evaluate the activation energy of twinning, a master twinning curve approach has been used. The activation energy for twinning for the above material is found to be 0.123 eV.

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Н.В. Токий, В.В. Токий

ЭНЕРГИЯ АКТИВАЦИИ ДВОЙНИКОВАНИЯ ДЛЯ МЕДИ В ПРИБЛИЖЕНИИ ФОГТА

Обсуждается возможность применения двухкомпонентной модели однофазных гибридных материалов для объяснения аномальной температурной зависимости модулей упругости меди с субмикрокристаллической структурой. Анализ был проведен на основе известных экспериментальных данных. Для изменения ориентации кристаллитов предлагается использовать механизм двойникования. Для получения энергии активации процесса двойникования был предложен метод Master Twinning Curve (MTC). Эффективная энергия активации по методу MTC определяется путем минимизации методом наименьших квадратов (MRS). Установлено, что энергия активации двойникования для меди с ультрамелкозернистой (нано- и субмикроскопической) структурой составляет 0.123 eV в приближении Фогта.

Ключевые слова: двойникование, энергия активации, Master Twinning Curve, ультрамелкозернистая медь, гибридные материалы, аномальная температурная зависимость упругости

Рис. 1. Изменения объемных долей низкомодульной f_{111}^{V} (●) и высокомодульной f_{100}^{V} (○) компонентов чистой меди во время первого нагрева при различных скоростях (a – 1.05 K/min, $б$ – 0.5 K/min) [4], рассчитанные в приближении Фогта по формуле (2)

Рис. 2. Зависимость среднеквадратичного отклонения (MRS) от энергии активации, рассчитанной методом MTC. Минимум наблюдается при ~ 0.123 eV