MICROSTRUCTURAL STUDY AND RECRYSTALLIZATION KINETICS OF DEFORMED COMMERCIAL COPPER WIRES

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Abstract
This work aims to investigate the microstructure after the cold-wiredrawing process of commercial copper and its recrystallization kinetics under isochronal annealing. In this paper, the samples of commercial copper wires were analysed after six different reductions by a wiredrawing at room temperature. Optical microscopy, Scanning Electron Microscopy (SEM), and DSC was used as characterization techniques. The samples were annealed under Argon atmosphere with four different heating rates by using DSC. The Kissinger, Ozawa, Boswell, and Starink methods were used to determine the recrystallization kinetics. The results showed that the cold-wiredrawing had caused the elongation of grains along the main axis of the wires also showed the existence of slip bands. It has been found, on the one side, that the recrystallization temperature increased and shifted to higher temperatures as the heating rate increased, which means that this reaction is thermally activated; on the other side recrystallization temperature clearly shifted to lower temperatures as the deformation increased, which indicated that recrystallization is profoundly enhanced by high deforming. We noted a decrease in the activation energy values when the reduction increases, the activation energy for the most reduced materials were lower than that in the less reduced wires.

Keywords: commercial copper; recrystallization; activation energy; isochronal annealing; optical microscopy; DSC

1 Introduction
Optical microscopy is an analysis technique that can be used to study the microstructure evolution of metals during deformation [1, 2]. The scanning electron microscopy (SEM) is a good way, which is used to observe the micro-strain within the materials [2, 3]. The investigation of the different solid-state transformations that occur during the main processing steps (recovery, recrystallization, growth), and their kinetics can be carried out by differential scanning calorimetry (DSC) technique [4-6].
Last years, many researchers were focused on the recovery and recrystallization kinetics of copper and its alloys during and after deformation by using different techniques.

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By using the optical microscopy, scanning electron microscopy, X-ray diffraction (XRD), and DSC techniques, Hutchinson and Ray [2] investigated the recrystallization in pure copper (5N purity) strained at ε = 1.63 by cold-rolling process; they found activation energy in range of [46(0.48)-151(1.57) kJ/mol (eV/atom.)]. Hansen et al. [7] investigated the recrystallization kinetics in copper (3N purity) cold-rolled at ε = 3.0 by in-situ texture measurements by mean of neutron diffraction (ND); they found activation energy in the range of [125(1.30)-170(1.76) kJ/mol (eV/atom.)]. Krüger and Woldt [8] found activation energy equal to 85 kJ/mol (0.88 eV/atom.) for recrystallization of pure copper (3N purity) cold-rolled at ε = 2.5 by isochronal DSC. Donthu et al. [9] measured the apparent activation energy for recrystallization during self-annealing of 1.5μm thick electroplated copper films by using DSC. They found a value 59.40 kJ/mol (0.62 eV/atom.). Kalu and Waryoba [1] investigated the restoration mechanisms in inhomogeneous microstructure of copper (5N purity) reduced at ε = 2.31 by cold-wiredrawing process by using different techniques such as optical microscopy, orientation imaging microscopy (OIM), and microhardness measurements; they found activation energy equal to 129 kJ/mol (1.34 eV/atom.). Amouyal et al. [10] used the tracer diffusion technique to study the recrystallization in ultrafine grain copper (3N purity) strained at ε = 4.6 by ECAP and annealed at a constant temperature. The calculated activation energy was about 160 kJ/mol (1.66 eV/atom.). By using the both techniques (DSC and Vickers microhardness), Benchabane et al. [11] investigated the recrystallization in copper (5N purity) cold-rolled at ε = 1.2; they found 58 kJ/mol (0.60 eV/atom.). Jägle and Mittemeijer [3] used the isochronal DSC and electron backscatter diffraction (EBSD) to study the kinetics of/and the microstructure induced by the recrystallization of copper (5N purity) strained by wiredrawing at ε = 3 at room temperature. The calculated activation energies were in the range of [109(1.13)-113(1.17) kJ/mol (eV/atom.)]. In the present paper, we focused on the evolution of the microstructure and recrystallization kinetics of commercial copper wires drawn at different reduction levels using the optical microscopy, SEM, and DSC techniques.

2 Experimental material and methods

In our study, we were interested in the commercial Cu. The main chemical elements in this commercial Cu alloy are given in **Table 1**.

Table 1 Results of chemical analysis of Cu (98.9687%) by the producer laboratory

Elements	Ag	S	Fe	Pb	P	Zn	As	Se, Te, Bi, Ni, Cd, Mn…
Results (ppm)	6.50	3.50	3.40	1.70	1.40	1.00	1.00	< 13

We chose a copper wire rod (Ø=8.00 mm) and six wires of different diameters, which correspond to six different true strains (1.20, 1.80, 2.10, 2.45, 3.35 and ε = 3.63, where $\varepsilon = 2\ln(d_0/d)$, d_0 and d are the initial and final diameters, respectively). Prior to microstructural examination, the longitudinal section of samples was mechanically ground by using SiC paper (2 400# in the final step) and finished with a lubrified diamond paste. The samples were etched by using a solution of (68%) nitric acid at room temperature. The microstructure was analyzed using a Hund-T100/Wetzlar (Wilowert’s company) optical microscope equipped with a Canon EOS 650D camera (Canon Inc., Japan). A scanning electron microscopy (Jeol JSM-LV6390 SEM) equipped with EDS detector from EDAX-TSL (AMETEK Inc.) was used to examine both

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morphology and elemental analysis of the samples. DSC tests were carried out using a SETARAM (DSC131) differential scanning calorimeter. The samples for the DSC measurements weighted between 250 and 300 mg. Each sample was processed under Argon atmosphere, from 20 to 650°C, with four different heating rates (10, 15, 20 and 25°C/ min).

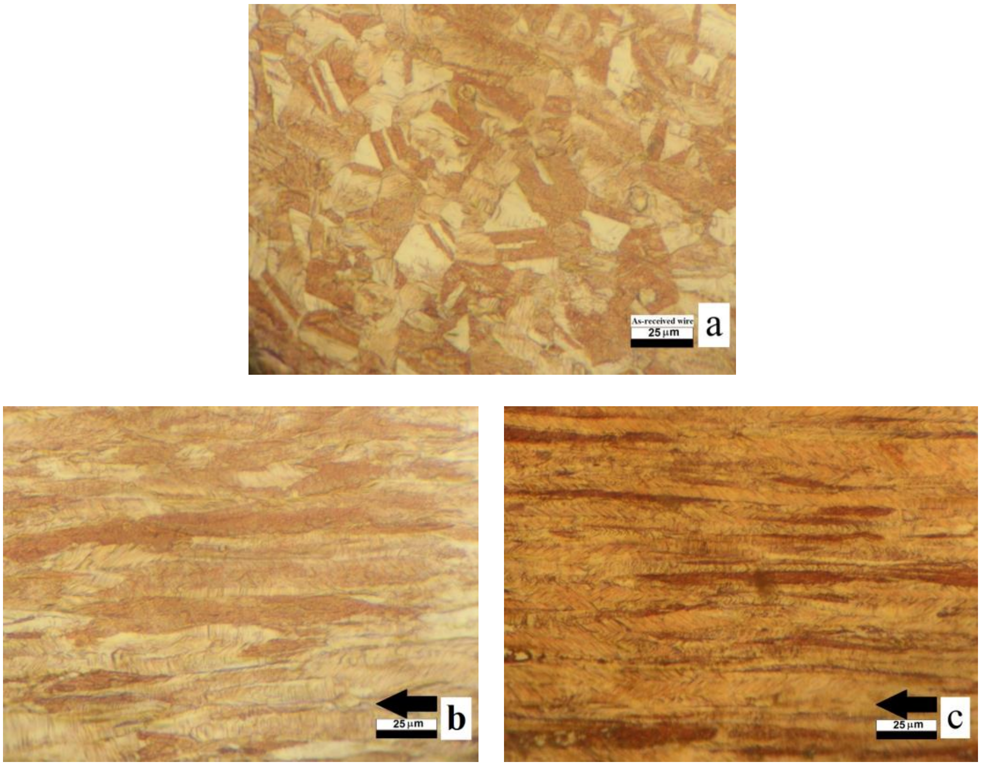
3 Results and discussion

3.1 Microstructure

Fig. 1 and **Fig. 2** show the microstructure of the commercial copper wire rod and commercial copper wires after six different reductions processed by wiredrawing at room temperature**.**

Fig. 1 shows the microstructure of the wires, obtained from their longitudinal section. As can be seen in **Fig. 1a**, the microstructure of the as-received copper wire rod presents equiaxed grains with many deforming twins**.** The average diameter of grains was about 49.59 µm.

Fig. 1b presents the microstructure of the copper wire deformed at ε =1.20, we observed elongated grains along the drawing direction (DD). After passing through several dies, the copper wire undergoes a series of more intense deformations as shown in **Fig. 1c-1g**. The grains become longer, thinner and the average length of the grains was close to 210.43 µm for the wire drawn at ε = 3.63. The elongated grains align parallel to the drawing direction. According to Fellah [12] and Baci et al. [13], when the degree of deformation increases, the drawn wire acquires a textured microstructure so-called "wire-drawing of texture" [14, 15]. Zidani et al. [16] have also observed this kind of texture in the cold-drawn aluminum alloy (6101).



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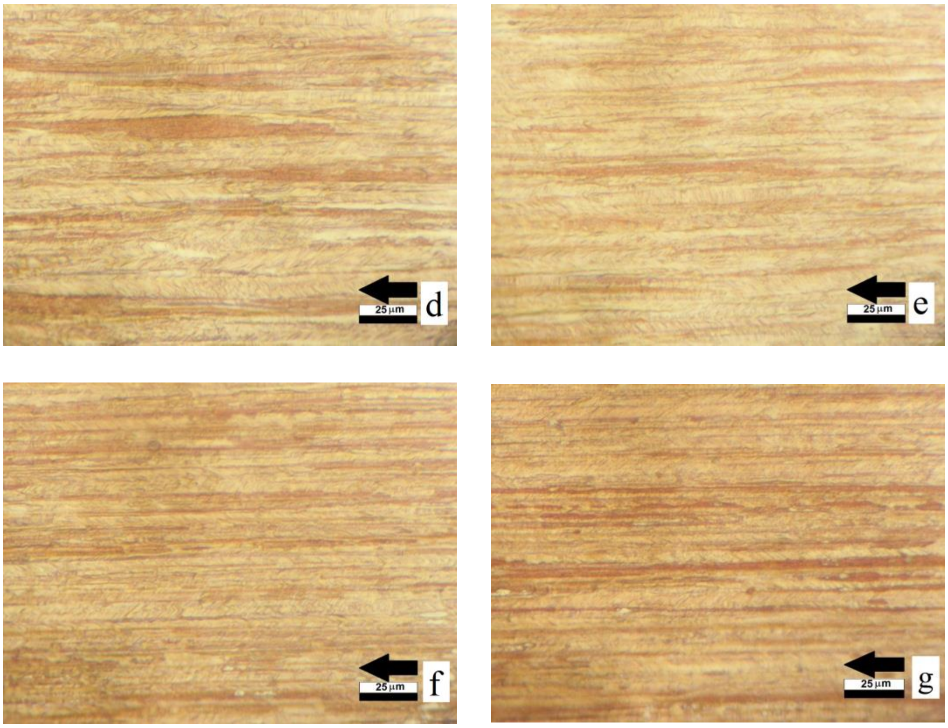

Fig. 1 Microstructure of commercial copper: a) wire rod, and wires drawn at b) 1.20, c) 1.80, d) 2.10, e) 2.45, f) 3.35, g) ε = 3.63. (Arrow indicates the wiredrawing direction)

Fig. 2 shows straight slip bands in industrial copper wire after cold-wiredrawing at ε = 2.45 reduction area and multiple slip bands could be seen. Each band is made up of a large number of slip steps on closely spaced parallel slip planes. The width of slip bands is in the range [0.10 – 0.85 μm].

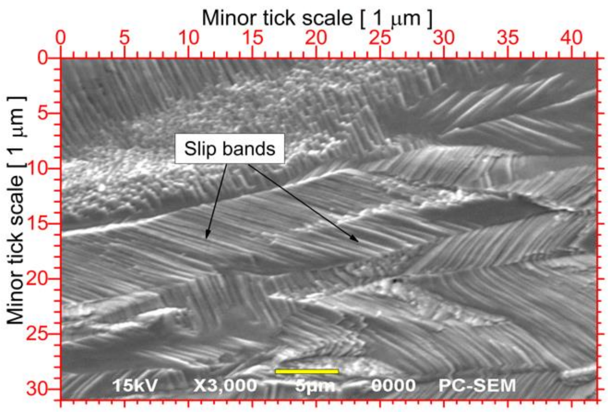

Fig. 2 SEM micrograph showing slip bands developed by wiredrawing in a studied copper sample of ε = 2.45 reduction

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3.2 DSC analysis

Fig. 3 presents the DSC thermograms of the as-received commercial copper wire rod (a) and the copper wire drawn at ε = 3.63 (b). DSC curve (b) shows three exothermic peaks which correspond to recovery reaction (peak 1), recrystallization reaction (peak 2), and the second recrystallization so-called grain growth (peak 3). The latter appears at a high heating rate and prolonged holding time.

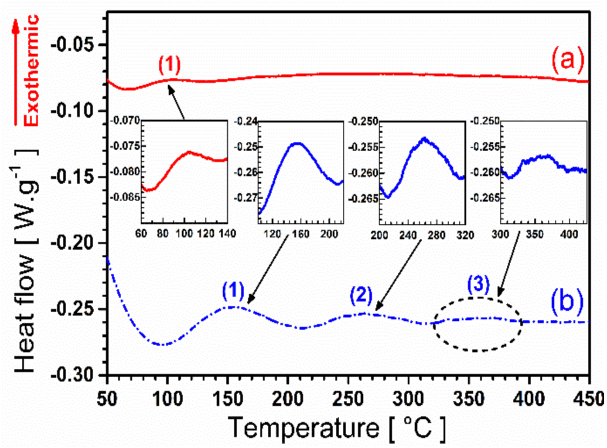

Fig. 3 DSC curves of the as-received copper wire rod and copper wire deformed at ε =3.63, recorded at heating rate β =25 °C/min

Fig. 4 shows the DSC thermograms of the studied deformed copper wires, obtained by continuous heating at different heating rates. DSC curves (**Fig. 4a**) correspond to isochronal annealing at β = 15 °C/min rate, and DSC curves (**Fig. 4b**)) correspond to isochronal annealing at β = 25 °C/min rate. We noted that each thermogram shows two exothermic peaks, which correspond to the stored energies released by the recovery and recrystallization reactions, respectively. The maximums of these peaks can be attributed to the recovery (first peak) temperatures and recrystallization (second peak) temperatures, respectively [17]. The maximum second peak temperatures of the detected exothermic peaks are indicated in **Fig. 5**.

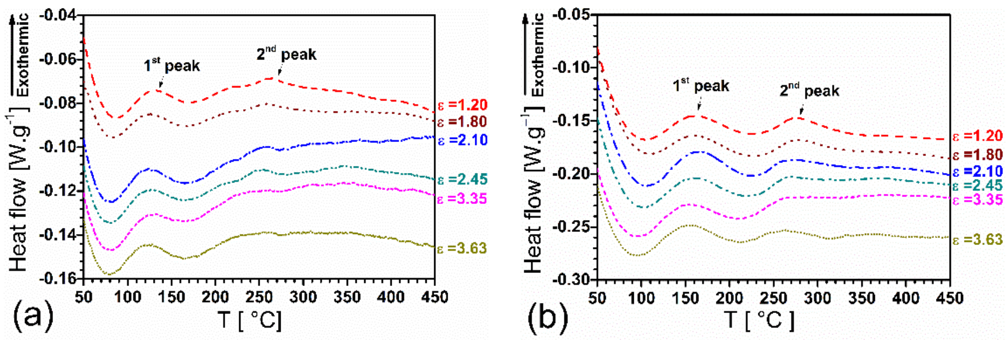

Fig. 4 DSC curves of the studied wires heated at rates: (a) β = 15 °C/min, (b) β = 25 °C/min.

Fig. 5 presents the evolution of the recrystallization temperature versus reduction level (by wiredrawing) and heating rate for the as-received copper wire rod and copper is drawn wires.

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It can be seen that the recrystallization temperature for the as-received commercial copper wire rod has the highest recrystallization temperature (376.1 °C) because this copper wire rod is dimly deformed compared with the drawn wires. For the deformed copper wires, **Fig. 5** shows, on the one hand, the recrystallization temperature increases and shifts to higher temperatures with the increase of heating rate, which means that this transformation is thermally activated; On the other hand, the recrystallization temperature clearly shifts to lower temperatures with increasing the number of wiredrawing passes, which indicates that recrystallization reaction is greatly enhanced by high straining as it was reported by other authors [18,19].

Fig. 6 shows a plot of the recrystallization temperature as a function of deformation strain for different types of cold-drawn copper. It can be seen that the recrystallization temperatures that we have detected using DSC appear to be close to those measured by Fernandez et al. [20], Waryoba [19], and Jakani [21]. By studying the effect of impurities on the temperature and kinetics of recrystallization in the copper wire (ε = 0.47), Jakani [21] detected high recrystallization temperatures in the range [276.7 -298.1 °C] using DSC with a heating rate of 10 °C/min. He concluded that the impurities shift the recrystallization temperature to higher values and lower the kinetics of the recrystallization process. Based on this finding, the differences between our measurements and those of other authors can be explained by the content of impurities in the different materials studied. The presence of the impurities impedes the movement of the dislocations and/or the sub-joints, which makes the recrystallization kinetics slower [22].

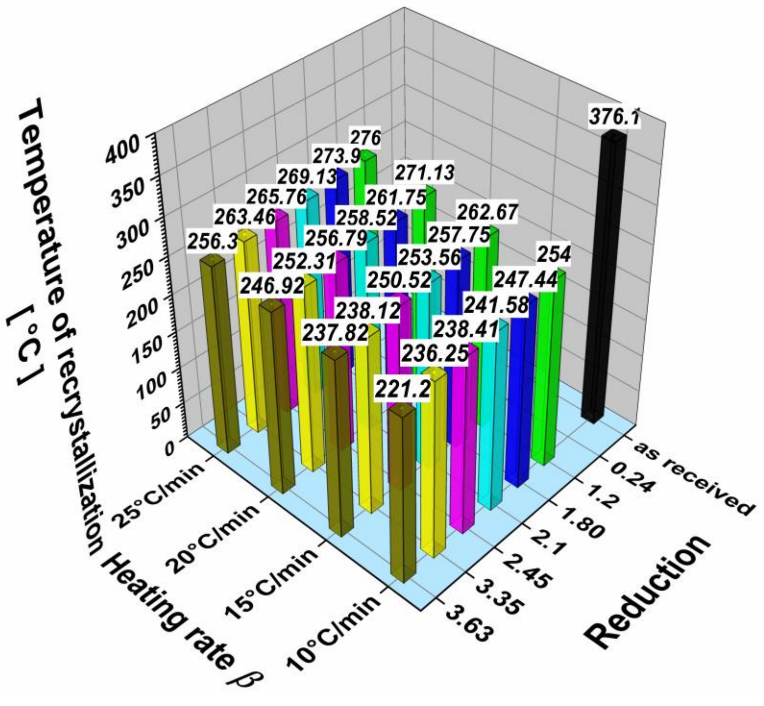

Fig. 5 3D graph summarizing the temperature of recrystallization detected by DSC

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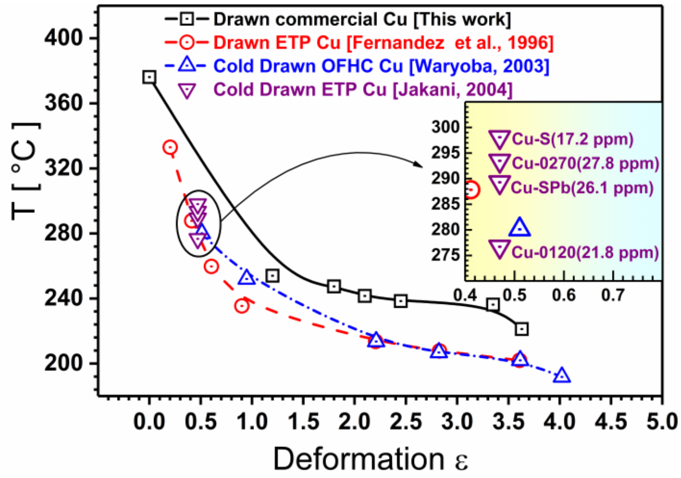

Fig. 6 Comparison of the recrystallization temperature versus reduction for types of cold-drawn copper [19-21]

3.3 Activation energy of recrystallization

The activation energy for recrystallization reaction, E_a, is determined by four methods: Kissinger [23], Boswell [24], Ozawa [25], and Starink [4] methods of second peaks which have been observed in **Fig. 4**. These methods are basically developed in order to study the variation of the maximum temperature peaks with heating rate according to the following expressions:

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + c_1 \qquad \text{(Kissinger equation)} \qquad (1.)$$

$$\ln\left(\frac{\beta}{T_p}\right) = -\frac{E_a}{RT_p} + c_2 \qquad \text{(Boswell equation)} \qquad (2.)$$

$$\ln(\beta) = -1.051\frac{E_a}{RT_p} + c_3 \qquad \text{(Ozawa equation)} \qquad (3.)$$

$$-\ln\left(\frac{\beta}{T_p^{1.92}}\right) = +1.0008\frac{E_a}{RT_p} + c_4 \qquad \text{(Starink equation)} \qquad (4.)$$

Where β is the heating rate, R = 8.314 J.mol.$^{-1}$K^{-1} is the universal gas constant, and T_p is the maximum peak temperature and (c_1, c_2, c_3, c_4) are constants.

Fig. 7 shows the plots of $\ln(\beta/Tp^2)$, $\ln(\beta/Tp)$, $\ln(\beta)$, and $-\ln(\beta/Tp^{1.92})$ versus $10^3/T_p$. These plots yield straight lines. The activation energy is calculated from each slope. The estimated values from the copper drawn wires using the above the four methods are presented in **Fig. 8**.

Fig. 8 presents the evolution of the activation energy of recrystallization as a function of the reduction level, for the studied copper wires. As shown in **Fig. 8**, the activation energy of the

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recrystallization process calculated by the four above methods as well as its mean value decreases with deformation strain. During deformation by cold-wiredrawing, the copper wires accumulate energy in linear and planar defects such as dislocations. The driving force of the recrystallization process is the free energy stored in the dislocations. The density of dislocations (i.e. stored energy) increases with the increase of the deformation [26].

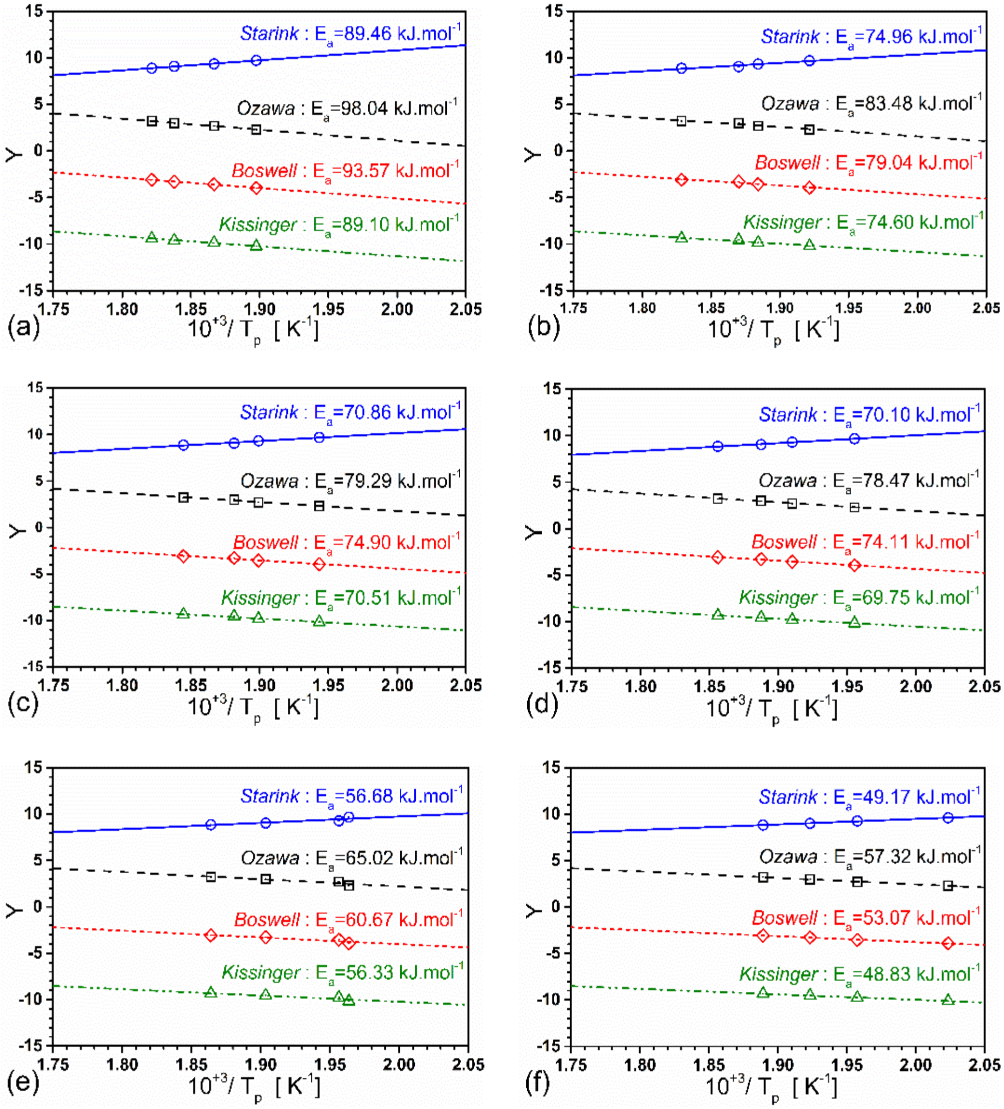

Fig. 7 Plots of Y against $10^3/T_p$: $Y=-\ln(\beta/T_p^{1.92})$, $Y=\ln(\beta)$, $Y=\ln(\beta/T_p)$, and $Y=\ln(\beta/T_p^2)$ corresponding to Starink, Ozawa, Boswell, and Kissinger methods respectively; (a) 1.20, (b) 1.80, (c) 2.10, (d) 2.45, (e) 3.35, and (f) $\varepsilon = 3.63$

A highly deformed material has lower activation energy and recrystallizes more easily than a less deformed material.

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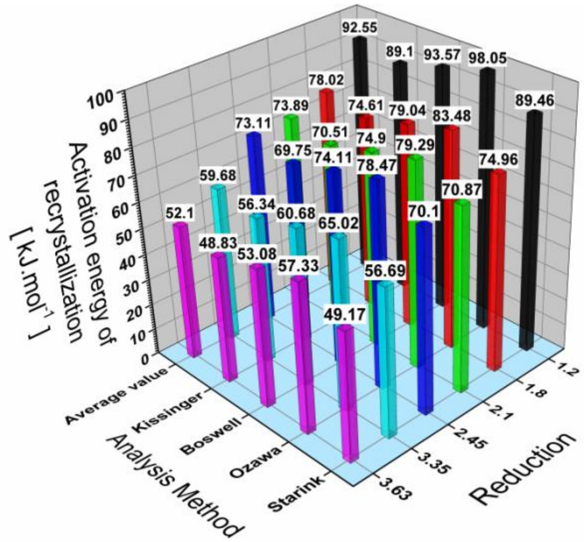

Fig. 8 3D graph is summarizing the calculated recrystallization activation energies by using different methods

Conclusions

In this paper, the commercial copper wires drawn at 1.20, 1.80, 2.10, 2.45, 3.35, and ε = 3.63, were investigated. The microstructure evolution and recrystallization kinetics were studied by using optical microscopy, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC) techniques. We can draw the following conclusions:

- At room temperature, the wiredrawing of copper caused elongation of grains along the main axis of the wires. The average diameter of grains was about 49.59 µm (wire rod), and for the wire drawn at 3.63, the average length of the grains was close to 210.43 µm.
- It has been remarked the existence of slip bands. The width of slip bands was between 0.10 and 0.85 µm.
- Under isochronal annealing, the recrystallization temperature increased and shifted to higher temperatures when the heating rate increased.
- The recrystallization temperature shifted to lower temperatures as the reduction increased.
- The measured recrystallization temperatures were between 221.2 and 254.0 °C (10°C/min heating rate) and between 256.3 and 276.0 °C (25°C/min heating rate).
- The activation energy of the recrystallization decreased with the increase of reduction. The higher and lower calculated average values were 92.55 and 52.10 kJ/mol respectively.

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