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DSC study of recrystallization in wiredrawn industrial copper

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Abstract. The goal of this work is to investigate the recrystallization reaction in cold wiredrawn industrial copper. We have used a differential scanning calorimetry and X-ray Diffraction techniques. The stored and apparent activation energies have been determined by differential scanning calorimetry under isochronal conditions. The differential scanning calorimetry results have been analyzed using models developed by Kissinger, Ozawa, Boswell, and Starink. In addition, the transformed fraction, as a function of temperature, and some kinetic parameters have been determined. We have found that cold wiredrawn affects some microstructure proprieties of the material, such the increase of stored and apparent activation energies, and dislocation density after deformation.

Introduction

In any study of recrystallization kinetic, it is very important to evaluate the volume fraction of recrystallized material as accurately as possible. Several techniques are currently in use to quantify the recrystallization behaviour of deformed metals. Vandermeer [1] pointed that optical microscopy is the most widely used direct method in determining the recrystallized fraction. It is so difficult to distinguish the deformed microstructure and the recrystallized microstructure, in heavily deformed materials. Consequently, other indirect methods have also been used to determine the recrystallized fraction. Electrical resistivity, hardness indentation tests, X-ray diffraction techniques have also been used. Chen et al.[2] employed the orientation imaging microscopy (OIM) method to determine the recrystallized fraction and they compared the OIM method with Optical microscopy in their work, and electron back scattered diffraction (EBSD) technique has been employed for this purpose by Tarasiuk et al.[3].
In addition to the methods which are mentioned above, it is well known that differential scanning calorimetry (DSC) is an important technique to study the recrystallization process. The advantage of this method is the possibility to obtain quantitative analysis such as the continuous monitoring of the transformed fraction, an accurate estimation of the heat of transformation and the dislocation density. In addition, the apparent activation energy of the reaction can be calculated from the shift of the recovery and recrystallization peaks with varying scan rates.
The scope of this work is to evaluate stored, activation energies and some other kinetic parameters of an industrial copper cold worked by wiredrawing. We used XRD and DSC techniques.

Experimental methods

Industrial copper wire (Ø=8.00mm) was cold wiredrawn to a diameter of 4.40mm, which corresponds to a deformation of 69.75%.
The deformation percentage is given by:

$$\varepsilon = (D_i^2 - D_f^2) \times 100 / D_i^2. \quad (1)$$

Where D_i and D_f are the initial and the final diameter of the copper wire, respectively.

Table 1, shows the chemical composition of the given material.

Table 1 Ratio impurities [ppm] in used industrial copper (99.97 wt. %).

Ag	S	As	Fe	Ni	Pb	Sn
6.50	3.50	1.00	3.40	0.20	1.70	1.00

The calorimetric analysis of the cold wiredrawn metal samples was made using a SETARAM differential scanning calorimeter (DSC131). Each specimen, with a mass about 150 mg, was placed in a platinum crucible and introduced into the DSC furnace. Continuous heating experiments under an Argon controlled atmosphere were carried out at four different heating rates (10, 15, 20, and 25 °C/min), from ambient temperature to 650 °C. The XRD experiment was carried out in continues scan, and a Bragg-Brentano configuration, with a step of 0.017° , by using a Philips X'pert PRO powder diffractometer with a Cu(Kα) radiation (λ = 0.15405 nm) from a copper anode (at 40 kV; 30 mA). The X-ray diffraction line profile analysis, microstructure, and lattice parameters calculus, were carried out using Materials Analysis Using Diffraction (MAUD 2.3) software [4], and which was developed a few years ago by Lutterotti [5].

Results and Discussion

Fig.1 presents the XRD pattern obtained from an wiredrawn industrial copper with the presence of five first characteristic diffraction peaks (111),(200),(220),(311) and (222) of an fcc structured Cu. The X-ray diffraction pattern of the specimen was subjected to detailed microstructural studies using MAUD software. The lattice parameter value of the deformed sample (a =0.361632nm) is less than value as received wire copper (a_i =0.363659nm), the coherent domains of diffraction (crystallites) size decrease from the value of 387.92nm to 107.64nm, this effect must been explained by increasing of microstrains during deformation.

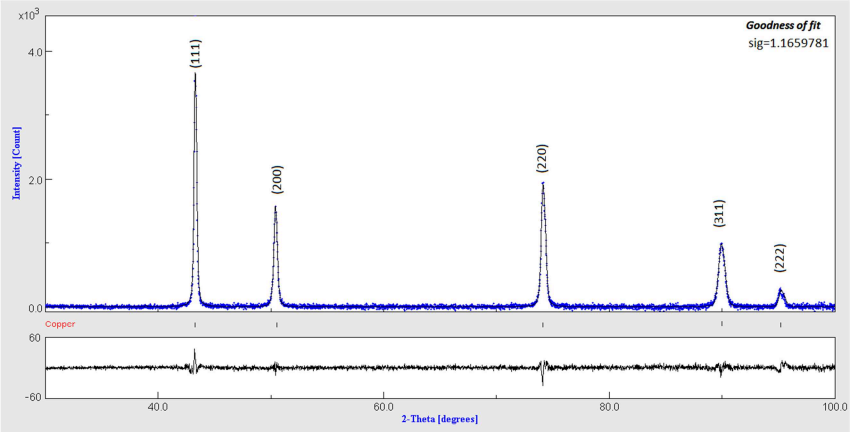

Fig. 1 X-ray diffraction patterns obtained from cold wiredrawn copper sample deformed at 69.75%.

Fig. 2(a) shows the DSC thermograms obtained by continuous heating of cold wiredrawn industrial copper at different heating rates. Each thermogram shows two exothermic peaks, the first peak is allowed to recovery reaction and the second one corresponds to the recrystallization reaction. The area of the second peak measures the stored energy released by the recrystallization process.

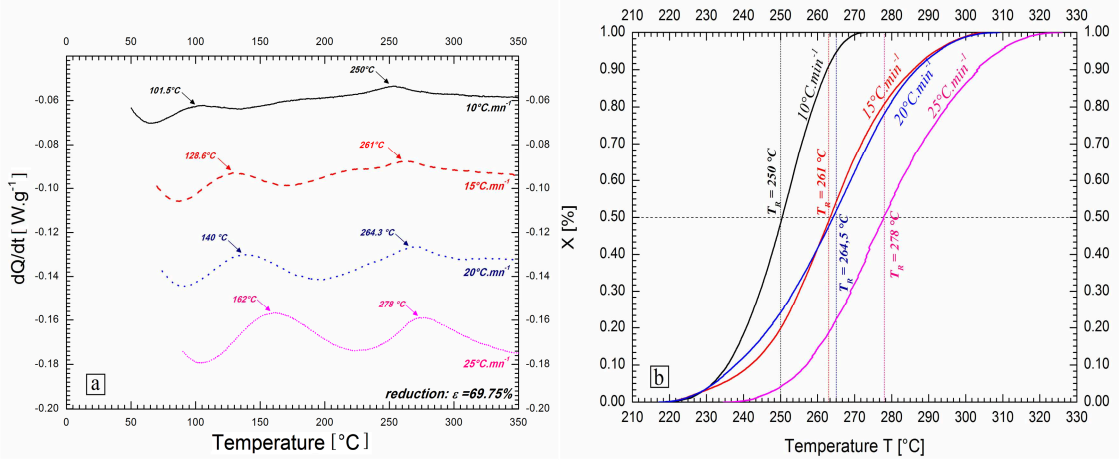

Fig. 2 a) DSC curves of 69.75% cold wiredrawn copper at different heating rates, b) Recrystallized fraction *X* vs. temperature at different heating rates.

Fig. 2(b) corresponds to the recrystallized fraction, for the different heating rates. Its shows a comparison of the recrystallized fraction of the deformed material obtained from the DSC analysis with a four different heating rates.

The recrystallization temperatures are usually defined as the temperatures at which the material is 50% recovered or recrystallized such was reported by Humphreys and Hatherly [6].
The values of recrystallization temperatures corresponding to the four different heating rates are given in Table 2. It appears that an obvious shift of the recrystallization temperature to higher temperature occurs with the increase in the heating rate. In a similar investigation of the recrystallization temperature in cold wiredrawn copper (Cu with different content of impurities), using DSC measurements, Jakani [7] found values between 257.5°C and 298.3°C after 38% section reduction.

Table 2 Values of Recrystallization temperatures, stored energies, and dislocation densities for different heating rates.

Heating rate [°C/min]	Recrystallization temperature [°C]	Stored Energy [J/mole]	Dislocation density $\rho[m^{-2}]$
10	250.0	29.09	$5.55\times10^{+15}$
15	261.0	43.28	$8.98\times10^{+15}$
20	264.3	75.76	$12.13\times10^{+15}$
25	278.0	109.08	$18.83\times10^{+15}$

The dislocation density was estimated, according to the following expression [6]:

$$E_{stored} = c\rho Gb^2. \quad (2)$$

Where ρ $[m^{-2}]$, G=48GPa, b=0.256nm, and c=0.5, are the dislocation density, the shear modulus of copper, magnitude of Burgers vector and a constant without dimension respectively. Table 2, shows the values of dislocation densities in the deformed industrial copper, the increasing of the density is due probably to the lengthening of the dislocations and multiplying of their number during plastic deformation process.

In order to evaluate the apparent activation energies Ea of the recrystallization process, we used different methods, called methods of Kissinger, Boswell, Ozawa and Starink; these methods were basically developed in order to study the variation of the maximum peak temperature with heating

rate according to the following expressions applying different numerical approaches, described by the following Eqs. (3-6), respectively:
Eq. 3 proposed by Kissinger [8]:

$$\ln(\alpha/T_p^2) = -E_a/RT_p + \text{constant} \quad (3)$$

Boswell [9] had established a modified expression of the Kissinger equation (see Eq. 4):

$$\ln(\alpha/T_p) = -E_a/RT_p + \text{constant} \quad (4)$$

Another isoconversion relation was utilized by Ozawa [10]:

$$\ln(\alpha) = -1.051.E_a/RT_p + \text{constant} \quad (5)$$

Based on a new approach, Starink [11] had discussed the new approximations for good and acceptable numerical solution of the temperature integral, and then he proposed Eq. (6):

$$-\ln(\alpha/T_p^{1.92}) = 1.0008.E_a/RT_p + \text{constant} \quad (6)$$

Where α is the heating rate, R=8.314J.mol.$^{-1}$K^{-1}, is the gas constant and T_p is the maximum peak temperature. Mittemeijer [12] reported that in most cases, this temperature is used because it approximately corresponds with the same degree of transformation.

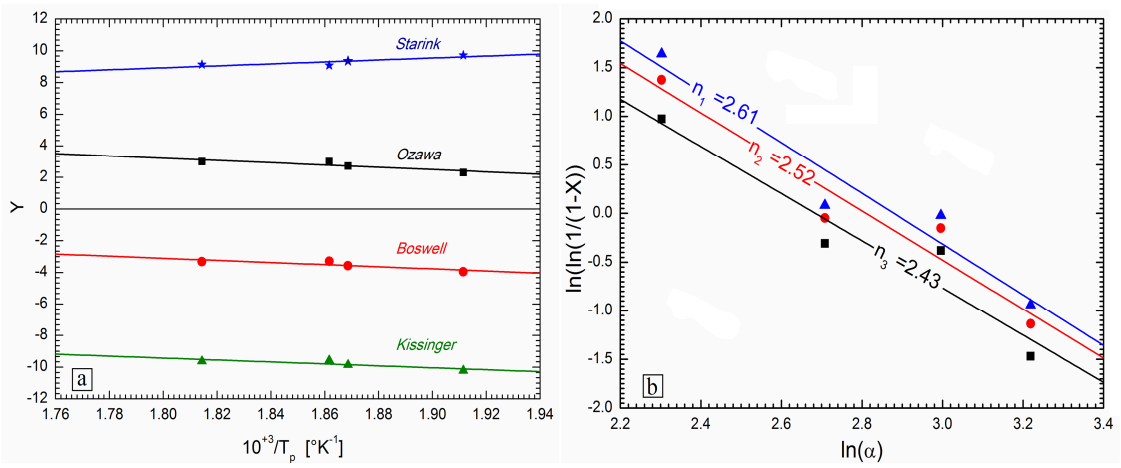

Fig. 3 a) Plots of Y against $10^3/T$: $Y= ln(\alpha)$ for Ozawa method, $Y= ln(\alpha/T_p)$ for Boswell method, $Y=ln(\alpha/T_p^2)$ for Kissinger method, and $Y=-ln(\alpha/T_p^{1.92})$ for Starink method,
b) Recrystallized fraction, X, versus $ln(\alpha)$ at different heating rates.

The plots of ln(α) , ln(α/Tp) , ln(α/Tp2) , and -ln(α/Tp1.92) versus 103/T yield straight lines (see Fig. 3(a). The apparent activation energy can be determined from the slope of line. We found the following values: 57.00, 55.48, 51.02, and 51.33kJ/mole by the methods of Ozawa, Boswell, Kissinger, and Starink respectively. An estimate of the Avrami exponent, n, provides information on the nucleation process and growth dimensionality.
The Avrami exponent and hence, the dimensionality of the growth have been evaluated using Matusita model [13].
In the Matusita equation, a plot of ln[ln(1-X)] vs. ln(α) at constant temperature, T, gives the value of n. The curves for three different constant temperatures are shown in Fig. 3(b).
We found an average value of n = 2.52. Hua and al. [14] found that Avrami exponents were mostly in the range from 2.48 to 2.68, which indicates a constant nucleation rate and a three-dimensional growth.

Conclusions

The recrystallization reaction in cold wiredrawn industrial copper has been investigated using both DSC and XRD techniques. The stored and activation energies of the recrystallization process were determined by the Kissinger, Ozawa, Boswell and Starink models using the DSC analysis. From DSC, the average values of the activation energies were found to be 54kJ/mole. These low values of activation energies indicate that for a strongly deformed material processes are triggered easily. The results obtained in this paper show good agreement with other works. Differential scanning calorimetry results reveal that a recrystallization peak in temperature ranges ~250–278 °C during this thermal analysis of cold wiredrawn industrial copper. The Avrami exponent n of the investigated industrial copper is found to be equal to an average value of n = 2.52, which indicates a constant nucleation rate and a three-dimensional growth.

References

[1] R. Vandermeer, The recrystallization characteristics of moderately deformed aluminum, Metallurgical Transactions, 1 (1970) 819-826.
[2] S. Chen, D. Hanlon, S. Van Der Zwaag, Y. Pei, J.T.M. Dehosson, Quantification of the recrystallization behaviour in Al-alloy AA1050, J. Mater. Sci., 37 (2002) 989-995.
[3] Tarasiuk, P. Gerber, B. Bacroix, Estimation of recrystallized volume fraction from EBSD data, Acta Materialia, 50 (2002) 1467-1477.
[4] MAUD, Material Analysis Using Diffraction on http://www.ing.unitn.it
[5] L. Lutterotti, MAUD, in: CPD NEWSLETTER, (IUCr), 2000.
[6] F.J. Humphreys, M. Hatherly, Recrystallization and Related Annealing Phenomena, Seconded., Elsevier Pergamon Press, Oxford, 2004.
[7] S. Jakani, Effet des impuretés sur les mécanismes de recristallisation du cuivre tréfilé, Ph.D thesis, Université de Paris XI, Orsay, France, 2004.
[8] H.E. Kissinger, Reaction Kinetics in Differential Thermal Analysis, Analytical Chemistry, 29(1957) 1702-1706.
[9] P.G. Boswell, On the calculation of activation energies using a modified Kissinger method, Journal of Thermal Analysis, 18 (1980) 353- 358.
[10] T. Ozawa, Estimation of activation energy by isoconversion methods, Thermochimica Acta, 203 (1992) 159-165.
[11] M. Starink, Analysis of aluminum based alloys by calorimetry: quantitative analysis of reactions and reaction kinetics, International Materials Reviews, 49 (2004) 191-226.
[12] E.J. Mittemeijer, Analysis of the kinetics of phase transformations, J. Mater. Sci., 27 (1992) 3977-3987.
[13] K. Matusita, T. Komatsu, R. Yokota, Kinetics of non-isothermal crystallization process and activation energy for crystal growth in amorphous materials, J. Mater. Sci., 19 (1984) 291-296.
[14] N. Hua, W. Chen, X. Liu, F. Yue, Isochronal and isothermal crystallization kinetics of Zr–Al–Fe glassy alloys: Effect of high–Zr content, Journal of Non-Crystalline Solids, 388 (2014) 10-16.