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Isoconversional analysis of copper recrystallization

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Abstract

Recrystallization of Cu deformed under compression has been monitored by differential scanning calorimetry (DSC) with experiments carried out at constant heating rate. From these experiments, an isothermal crystallization process has been predicted by the classical Kolmogorov-Johnson-Mehl-Avrami (KJMA) kinetics and by model-free isoconversional analysis. Whereas prediction by KJMA does not match the experimental curve, the isoconversional prediction is successful. The paper also highlights the need to correct the raw DSC curves to obtain the actual sample temperature and to avoid curve distortion due to thermal inertia.

Introduction

Recrystallization of cold-worked metals is a very important metallurgical process because, by recovering the metal ductility, it allows further deformation steps to be done until the final shape is obtained. During recrystallization, new grains free of defects grow in the deformed material. This structural evolution can be described in terms of nucleation and growth steps. In the particular case where the nucleation and growth rates (\dot{N} and G , respectively) are time-independent, the recrystallized or transformed fraction, α , evolves with time according to the Kolmogorov-Johnson-Mehl-Avrami-(KJMA) equation [1]:

$$\alpha = 1 - \exp[-(kt)^n], \quad (1)$$

where n ($n < 4$) is the Avrami exponent and k is the kinetic constant that can be expressed as a function of \dot{N} and G . From eq.(1), one obtains the transformation rate:

$$\frac{d\alpha}{dt} = kf(\alpha), \quad (2)$$

where $f(\alpha) = n(1 - \alpha)[- \ln(1 - \alpha)]^{\frac{n-1}{n}}$ (3)

is the well-known conversion function of the KJMA kinetics [2]. The advantage of eqs.(2) and (3) over eq.(1) is that they can be generalized to non-isothermal conditions where \dot{N} and G depend on time through the temperature. It has been known [3] that the KJMA kinetics is still valid for Arrhenian temperature dependencies, i.e.

$$G = G_0 e^{-E_G/RT} \quad \dot{N} = \dot{N}_0 e^{-E_N/RT} \quad (4)$$

(E_i are activation energies; \dot{N}_0 and G_0 , pre-exponential constants; T , temperature; R , the gas constant) during experiments done at a constant heating rate:

$$\beta \equiv \frac{dT}{dt} \quad (5)$$

The only difference from the isothermal KJMA kinetics (eq.(3)) is a temperature-independent constant factor close to 1 that depends on n and E_N/E_G [3].

Recrystallization is an exothermic process. So, its transformation rate can be determined by means of Differential Scanning Calorimetry (DSC) assuming that the recrystallized fraction is proportional to the heat released:

$$\frac{d\alpha}{dt} = \frac{\dot{Q}}{\Delta H}, \quad (6)$$

where \dot{Q} is the heat evolved per unit time and ΔH is the enthalpy difference between the deformed and recrystallized states. Since ΔH is very low, the most accurate DSC experiments are those done at constant heating rate. These experiments deliver the value of n and the pre-exponential constant, k_0 , and activation energy of k , E :

$$k(T) = k_0 e^{-E/RT}. \quad (7)$$

So, in principle, DSC experiments can be used to predict $\alpha(t)$ during isothermal recrystallization processes through application of eq.(1). However, significant deviations from the KJMA kinetics are often encountered [4]. In particular, due to strain inhomogeneity [5, 6], n tends to diminish as recrystallization proceeds. Consequently, accurate predictions based on the KJMA kinetics are not possible because the real recrystallization kinetics is more complex.

To overcome this difficulty, model-free isoconversional methods have been proposed (see [7, 8, 9] and references therein). They are “model-free” because no assumption is made about $f(\alpha)$ of eq.(2), and the kinetics complexity is described by a formal dependence of the activation energy and pre-exponential constant on the transformed fraction (E_α , $k_{0\alpha}$)(isoconversional principle) [10]; i.e. the transformation rate is assumed to follow the generalization of eq.(2):

$$\frac{d\alpha}{dt} = k_{0\alpha}f(\alpha)\exp(-E_\alpha/RT) . \quad (8)$$

Similarly to the KJMA model, DSC experiments can be used to obtain the values of E_α and $k_{0\alpha}f(\alpha)$. Once they are known, numerical integration of eq.(8) allows to predict the evolution of α with time for isothermal [11] and non-isothermal [12,13] heat treatments.

Model-free isoconversional models have been successfully applied to structural transformations as diverse as CaCO_3 [14] and YTFA_3 [13] decomposition, or crystallization of amorphous silicon [14].

In the present paper, we will analyse the recrystallization of commercially pure copper with DSC experiments done at several constant heating rates. Emphasis will be put on the need to correct the raw DSC curves to obtain the actual sample temperature and to avoid curve distortion due to thermal inertia [15, 16] (Section 3). From the corrected curves, the KJMA kinetic parameters will be extracted and the crystallization at constant temperature predicted. An alternative prediction through a model-free isoconversional method will be done in Section 5. Both predictions will be compared with experiment. The paper will end with a brief discussion and summary.

2.- Experimental procedure

Rods of commercially pure Cu (height = 3 mm; diameter = 3.3 mm) were cut with a low-speed precision saw from a wire. They were uniaxially compressed at room temperature to a real deformation of 0.9. To minimize inhomogeneous strain due to friction with the press, a PTFE tape was put on the rod faces.

Once deformed, the samples were analysed with a differential scanning calorimeter of Mettler Toledo (DSC822). Their mass (200 mg) was large enough to allow detection of the heat evolved during recrystallization when the samples were heated at several heating rates ($\beta = 2 - 80 \text{ }^\circ\text{C min}^{-1}$). These experiments were done in an inert atmosphere of nitrogen to avoid oxidation. A complementary DSC experiment, intended to test the predictive methods, was done at constant temperature (169°C). The sample was put inside the apparatus furnace once the programmed temperature was reached.

3.- Experimental results

All the DSC curves contain a single exothermic peak that corresponds to recrystallization (Fig.1a). The recrystallization enthalpy, ΔH , varies in the 0.96-1.12 J g⁻¹ range for all the experiments except for that done at 2 °C min⁻¹ (0.81 J g⁻¹). This last value has a larger uncertainty because of the lower heat power associated with the slow heating rate. Although, the energy stored due to strain changes with the amount of strain, grain size, impurity content, etc., [17] our values have a similar magnitude than those reported in the literature for Cu [18, 4, 17]. However, at this point, the most important conclusion we can draw from the values of ΔH is the good reproducibility achieved with our sample preparation procedure.

The peak temperature, T_p , varies from 190 to 265°C when β increases from 2 to 80 °C min⁻¹. However, these temperatures as well as the peaks shape have to be corrected to obtain the actual dependence of the recrystallization rate [$\dot{Q}/\Delta H$, eq.(6)] on sample temperature.

Although we used a commercial DSC apparatus that, once calibrated, gives a “reference temperature” (T_{REF}) very close to the sample temperature (T_{SAMPLE}) by correcting for the apparatus thermal lag, this standard calibration procedure was not suitable for our experiments. This is so, because calibration is done with small reference metals inside a standard crucible, whereas our experiments involved large samples masses without crucible. So, we did an especial calibration experiment to quantify $T_{REF} - T_{SAMPLE}$. We melted an In reference on top of a Cu sample. The result is shown in Fig.2, where we see that the onset temperature is 2.9°C above the In melting point (156.6°C) when $\beta = 20 \text{ }^\circ\text{C min}^{-1}$. Since, under very general assumptions [19] the thermal lag can be described with a time constant, τ_{LAG} , according to the equation:

$$T_{SAMPLE} = T_{REF} - \tau_{LAG} \cdot \beta, \quad (9)$$

we obtain, from this calibration experiment, $\tau_{LAG} = 8.7$ s. Since copper is a very good thermal conductor, we can consider that the sample temperature is homogeneous and equal to that given by eq.(9).

Furthermore, thermal inertia due to the sample heat capacity and DSC sensor thermal resistance, distorts any DSC signal so that at time t it does not coincide with the heat produced at that time in the sample, \dot{Q} . Their values are related through equation [15, 20]:

$$\dot{Q} = DSC + \tau_{SIGNAL} \frac{dDSC}{dt}. \quad (10)$$

τ_{SIGNAL} is just the decay time constant of the melting peak of Fig.2 (17 s).

All the DSC curves have been corrected by eqs.(9) and (10) and the result is shown in Fig.1b. The peak temperatures are detailed in the inset in the form of a Kissinger plot. Notice that, as expected, the effect of the correction on the form of the peak and on its peak temperature is more relevant for high heating rates.

Finally, gradients inside the sample can be estimated. In general, they are due to [19]: a) the heating ramp itself, and b) to the reaction heat. The temperature difference between the top and bottom sample surfaces due to the first contribution can be easily calculated:

$$\Delta T_a = -\frac{1}{2} \frac{\beta}{D} h^2, \quad (a)$$

where D is thermal diffusivity (for copper at 250°C, $1.1 \cdot 10^{-4} \text{ m}^2 \text{ s}^{-1}$) and h is the deformed sample height (1.2 mm). If we consider that the reaction rate is the same at any point then, the second contribution can also be quantified:

$$\Delta T_b = \frac{1}{2} \frac{h}{A} \frac{\dot{Q}}{\kappa}, \quad (b)$$

where A is the deformed sample section (21 mm^2), κ , the copper thermal conductivity ($400 \text{ W m}^{-1} \text{ K}^{-1}$), and \dot{Q} the heat power. For the most unfavourable experiment ($\beta = 80^\circ\text{C min}^{-1}$) at its peak temperature ($\dot{Q} = 26 \text{ J s}^{-1}$, Fig.1b) we obtain $\Delta T_a = -8 \cdot 10^{-3} \text{ }^\circ\text{C}$, and $\Delta T_b = 1.8^\circ\text{C}$, that correspond to an average overheating above the temperature at the bottom of the sample of 1/3 of these values. We have neglected these minor deviations.

4.- KJMA analysis

The corrected peaks have been analysed assuming KJMA kinetics. First of all, the activation energy of the kinetic constant, k , can be obtained from the peak temperature thanks to the Kissinger plot (inset of Fig.1b) [21, 22]:

$$\ln \frac{\beta_i}{T_{pi}^2} = -\frac{E}{RT_{pi}} + \ln \frac{k_0 R}{E}, \quad (11)$$

where index i refers to the experiment given at the particular heating rate β_i . A linear fitting delivers $E = 131 \text{ kJ mol}^{-1}$ and the pre-exponential constant $k_0 = 1.31 \cdot 10^{12} \text{ s}^{-1}$.

On the other hand, the Avrami exponent, n , can be obtained from the shape of the recrystallization peak. For this particular kinetics, the plot of $\ln[-\ln(1-\alpha)]$ vs the reciprocal temperature, $1/T$, should be linear [23] and its slope, proportional to n :

$$\frac{d\ln[-\ln(1-\alpha)]}{d(1/T)} = -\frac{nE}{R}. \quad (12)$$

This kind of plot is shown for two particular heating rates in Fig.3. Notice that the slope is not constant, giving an Avrami exponent that diminishes as recrystallization proceeds. Its value, at $\alpha = 0.1$ falls between two characteristic values [4], $n = 3$ and $n = 4$. When the nucleation and growth rates only depend on temperature and are thermally activated, then $n = 4$. On the other hand, $n = 3$ means that nucleation is so fast that it has finished before any significant growth of the nuclei (site saturation).

Concerning the steady diminution of n , there is general agreement that it is due to spatial strain inhomogeneity [4]. Experiments have revealed that the most strained regions recrystallize first [6] and numerical simulations have shown that, when this occurs, n diminishes steadily [5].

Despite the deviation from the ideal KJMA kinetics, we have tried to predict the recrystallization DSC curve measured at 169°C through application of eq.(1). The results are plotted in Figs. 4a and 4b for two averaged values of n (2.3 and 2.8). Only a rough agreement is achieved on the time where recrystallization rate has a maximum value. However, the shape of the experimental curve is not reproduced at all. Of course, these discrepancies are not surprising in view that: a) n is not constant and b) eq.(6) is not exact for inhomogeneous strain because the regions with higher strain have more energy stored.

5.- Isoconversional analysis

Recrystallization of Cu at different heating rates β_i allows reaching a given transformed fraction, α , at different temperatures, $T_{\alpha i}$. If the isoconversional hypothesis is fulfilled, then any pair of $(\alpha, T_{\alpha i})$ values will be related by eq.(8) with the same kinetic parameters $k_{0\alpha}f(\alpha)$ and E_α . This is the basis of the Friedman method [24] that is used to extract them through equation:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha i} = -\frac{E_\alpha}{R} \frac{1}{T_{\alpha i}} + \ln[k_{0\alpha}f(\alpha)] \quad (13)$$

For a given transformed fraction, E_α is the slope and $\ln[k_{0\alpha}f(\alpha)]$, the intercept at $1/T = 0$ of the experimental points plotted as $\ln\left(\frac{d\alpha}{dt}\right)_{\alpha_i}$ vs $1/T_{\alpha_i}$.

This method has been applied to the corrected DSC curves of Fig.1b to obtain a collection of ‘‘Friedman plots’’ like those of Fig.5a. The fair alignment of the experimental points in the $0.1 < \alpha < 0.9$ range indicates that Cu recrystallization follows the isoconversional hypothesis quite well and, consequently, the kinetic parameters can be obtained by linear fitting. In Fig.5b, E_α and $k_{0\alpha}f(\alpha)$ have been plotted. Notice that, despite the Kissinger plot (inset of Fig.1b) delivered a series of well aligned points, suggesting single activation energy, E_α has a significant variation between 125 and 170 kJ/mol from the beginning to the end of recrystallization. The limitations of the Kissinger plot to elucidate kinetic complexities is discussed in refs.[22, 25].

Now, the kinetic values of Fig.5b can be used to integrate eq.(8) for predicting the isothermal recrystallization at 169°C. We have used our method described in ref.[14], that is a modification of the method by Roduit et al.[12]. Eq.(8) can be integrated by finite differences according to:

$$\alpha(t + \Delta t) = \alpha(t) + k_{0\alpha}f(\alpha)\exp\left(-\frac{E_\alpha}{RT}\right)\Delta t, \quad (14)$$

where E_α and $k_{0\alpha}f(\alpha)$ are the kinetic parameters of the previous integration step [$\alpha(t)$].

Apart from the initial transient, that is an artefact of the DSC curve related to sample thermalization, the predicted recrystallization rate fits very well the experimental DSC curve: it does not only predict the curve maximum but it also predicts its shape.

6.- Summary and conclusions

The recrystallization process of commercially pure Cu uniaxially compressed has been monitored by DSC by heating the samples at several heating rates (2-80 °C min⁻¹). The moderate applied deformation ($\epsilon = 0.9$) has led to a very small amount of energy stored in the material (0.96-1.12 J g⁻¹), in agreement with the literature. The small dispersion of measured heat indicates that the preparation method leads to good reproducibility. Due to the large samples mass (200 mg), the DSC peaks were severely distorted and displaced to higher temperature. Consequently, correction of the thermal lag and the peak shape was necessary before doing any kinetic analysis.

The corrected peaks showed significant deviations from the ideal shape expected for KJMA kinetics. Notably, although at the beginning of recrystallization the Avrami exponent took a reasonable value between 3 and 4, it diminished steadily to around 1.5, indicating

inhomogeneous strain. As a result, the KJMA kinetics was not able to predict the recrystallization course during isothermal conditions.

Alternatively, prediction through a model-free isoconversional method has been attempted. Friedman plots have been used to obtain the kinetic parameters as a function of the recrystallized fraction, and integration of the rate equation for isothermal conditions has led to good agreement with the isothermal DSC experiment.

It can be concluded that model-free isoconversional analysis can be satisfactorily used to predict the course of the recrystallization process of Cu, when kinetic complexity does not allow use of the KJMA kinetics. It would be very interesting to test the ability of isoconversional analysis to predict the annealing of other deformed metals such as Al, where recrystallization is preceded by recuperation but begins before recuperation is complete.

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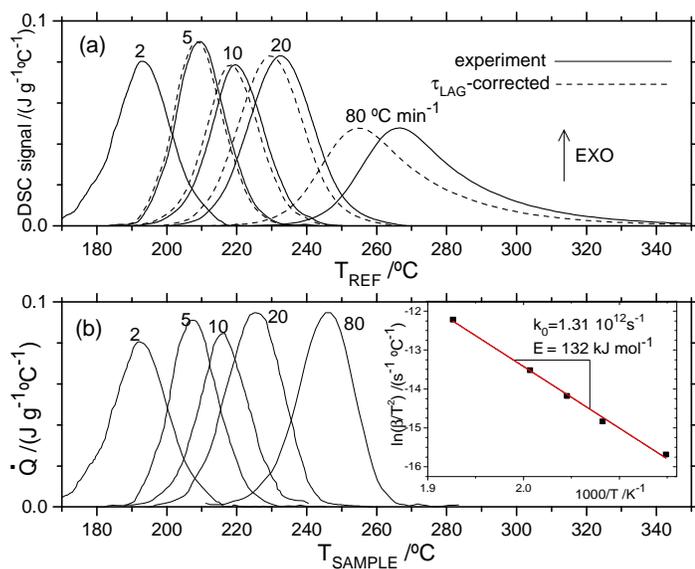


Figure 1.- DSC curves of Cu recrystallization. (a) As measured (solid lines) and corrected by τ_{LAG} (dashed lines). (b) Corrected by τ_{LAG} and τ_{SIGNAL} . Inset: Kissinger plot of the peak temperature.

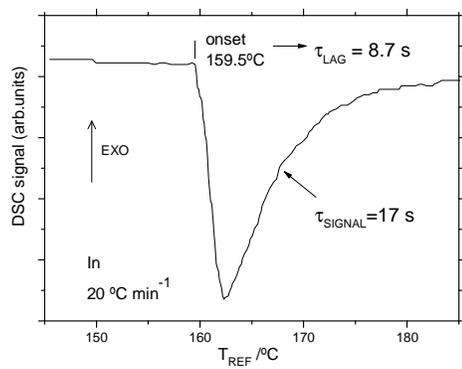


Figure 2.- From the DSC melting peak of In the time constants used to correct the experimental curves can be obtained.

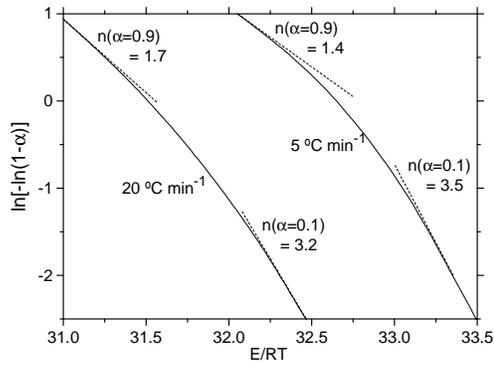


Figure 3.- $\ln(-\ln)$ plot obtained from the corrected DSC curves. The Avrami exponent is determined from the slope.

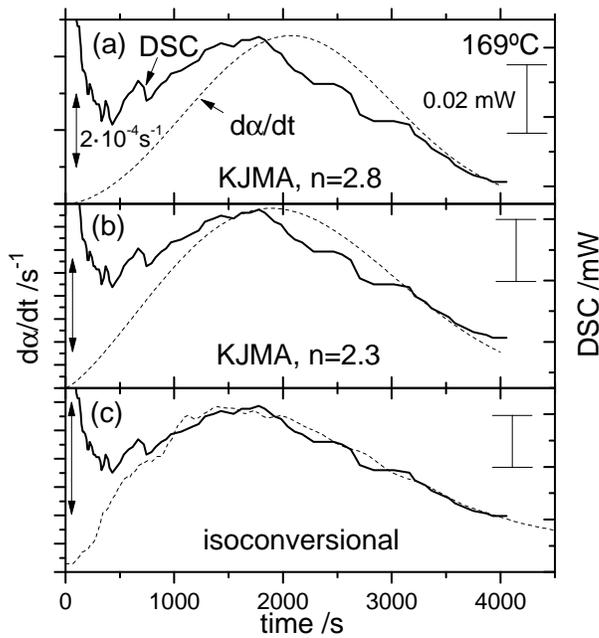


Figure 4.- Experimental DSC curve measured at 169°C compared with several predictions based on: a) and b) KJMA and c) isoconversional analyses. Bar scales have the same value for all the figures. The rapid initial decay of the DSC curve is an artefact.

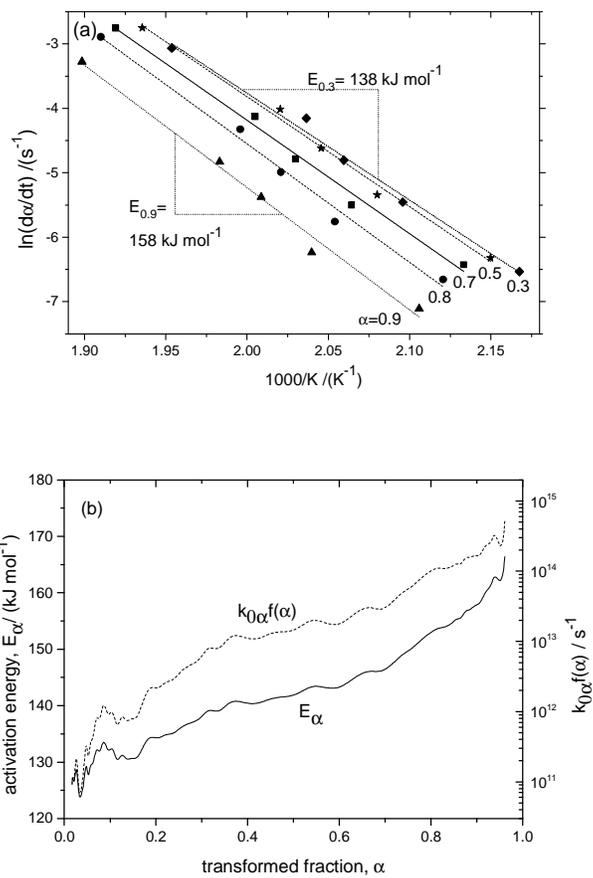


Figure 5.- (a) Representative Friedman plots at several values of α ; (b) kinetic parameters extracted from the Friedman plots.