Kinetic equation describing the annealing process of copper

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During the annealing process of cold-drawn copper with small amounts of impurities a multiple-sigmoidal behavior has been found, related to the overlapping of two or more process steps, corresponding to a simultaneous recrystallization of the copper matrix and the impurities placement processes. A kinetic equation is introduced to describe the overall process by means of an auto-catalytic kinetic model which could also be extended to describe any annealing process presenting a multi-sigmoidal character.
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1. Introduction

The kinetics of several solid state reactions can be described by a model based on a simple statistical expression known as JMAK equation, as it has been independently proposed by Johnson and Mehl [1], Avrami [2] and Kolmogorov [3]. The model is based on a nucleation and growth process and is particularly used to describe recrystallization processes. However, this model is only applicable under rather restricted conditions [4] and many cold-worked materials does not yield linear JMAK behavior [5, 6].

In the case of the recrystallization of copper, several authors agree upon the deviation of the kinetic data from the JMAK expression [7–9]. Other models have been proposed: Krüger *et al.* [4] introduce a model based on a distribution of activation energies that shows a high concordance with their experimental results for high purity copper; Bowen *et al.* [10] propose a fourth-order kinetic reaction based on the experimental results obtained by relating the residual resistance to the degree of recovery. The kinetics of nonisothermal recrystallization of copper has been previously studied by Kraft *et al.* [11] who propose a model to predict the annealing response for both isothermal and nonisothermal annealing cycles using a parameter called the "annealing index".

The annealing process of heavily worked copper wire has been previously studied by Mima *et al.*, by means of isothermal softening tests and calorimetric measurement of the release of stored energy [12]. These authors stated that isothermal softening of cold-drawn copper wires sometimes exhibits a multiple-sigmoidal char-

acter, from which it seems that the softening process should be regarded as an overlapping spectrum made up of a number of softening reactions.

Clarebrough *et al.* [13] have found that the behavior of nickel is similar to that of copper, which can be explained by the influence of impurities on the annealing of both metals after cold work. Measurements of stored energy and of changes in electrical resistivity, hardness, elongation and density accompanying annealing have been performed to evidence the different stages observed during annealing: in 99.6% pure nickel two stages are observed related to the disappearance of vacancies and to recrystallization respectively [14], whereas two stages of annealing appear prior to recrystallization of high purity nickel (99.85%), thus indicating that the first annealing stage is not observed in the presence of substantial concentrations of impurities.

Taking into account the results obtained by Clarebrough *et al.*, Sosin and Brinkman [15] have related the different stages observed in cold-drawn nickel to interstitial atom migration and vacancy migration, being the first completely masked by impurities.

This paper presents a kinetic equation that explains the different stages involved in the annealing of cold-drawn copper assuming that this is an auto-catalytic kinetic process. It has been found that other metals present similar results when annealing, so it is expected that their behavior will be analogous to copper.

2. Experimental

Different samples of copper were used in this study, one of them being electrolytic copper (sample 1) and

TABLE I Compositions (ppm) of studied samples

Sample	Oxygen	Pb	Ni	Sn	Ag	Sb	Fe	Zn
1	170	1.12	1.45	0.67	11.10	<1.25	17.11	1.44
2	165	546.30	44.90	35.90	31.20	22.00	19.20	21.90
3	203	369.80	55.90	46.50	55.00	41.00	18.00	19.10

the other obtained after smelting and fire-refining copper scrap, continuously casting and hot-rolling. After smelting and fire-refining, the studied samples were selected from different castings, whose compositions are shown in Table I.

Samples of different hot-rolled 7.85 mm diameter copper rods were cut in 10 mm long cylinders and compressed to 2 mm (80% reduction). Annealing treatments of samples for different times and temperatures were performed in salt bath (40% mass of $NaNO_2$ and 60% mass of KNO_3) in order to avoid surface oxidation. After each treatment, samples were quenched in cold water that had previously been slightly acidified with H_2SO_4 in order to remove copper oxide that could be formed. The softening degree has been determined from Rockwell-F hardness measurements in a Centaur durometer on annealed samples.

3. Results and discussion

Conversion at each time has been calculated from hardness measures by using the following expression:

$$X_t = \frac{HRF_{max} - HRF_t}{HRF_{max} - HRF_{min}} \qquad (1)$$

where HRF_{max} corresponds to the maximum Rockwell-F hardness value obtained among all the measures performed to copper samples with the same composition just after cold-working, HRF_t is the Rockwell-F hardness value measured at time t and HRF_{min} is the minimum Rockwell-F hardness value obtained among all the measures performed to copper samples with the same composition completely annealed, that is at the highest studied temperature and maximum annealing time. This expression has been previously used by Perryman [16] to determine the softening percentage when studying the annealing of pure aluminum. Values for HRF_{max} and HRF_{min} as well as annealing conditions to achieve this latter are shown in Table II.

The annealing kinetics of cold-worked copper exhibits a multiple-sigmoidal character indicating, as stated by other authors, that the softening process

TABLE II Maximum and minimum Rockwell-F hardness values and annealing conditions to achieve HRF_{min} for each sample

Sample	HRF_{max}	HRF_{min}	Annealing conditions	
			Temperature (°C)	Time(s)
1	93	33	220	7200
2	95	50	228	14400
3	95	57	260	14400

should be regarded as an overlapping spectrum made up of a number of reactions. It seems that the relative degree of progress of each reaction depends on the process temperature.

Cold-working produces an increase in dislocation and vacancy density, that gives rise to a substantial strain energy stored in the lattice, so that the cold-worked condition is thermodynamically unstable relative to the non-deformed one. Thermal energy allows the dislocations to move out, and dislocations of opposite signs come together and annihilate each other, whereas those of the same sign polygonize into well-defined cell walls. These *recovery* processes cause cold-worked metals to soften when heated. *Recrystallization* is a very drastic softening process in which large-angle grain boundaries sweep through the metal and replace the cold-worked grains by a new set of more perfect grains, giving complete softening. The process is closely related to grain growth but the driving force for moving the boundaries is provided by the line tensions of the dislocations. Essentially, recrystallization occurs by a nucleation and growth of the nuclei from the deformed matrix, and its rate is controlled by these two processes, nucleation and growth.

Nucleation does not occur immediately upon reaching the transformation temperature. The reason for that is the barrier presented by the energy requirements of the nuclei. So it needs the so-called incubation time that represents a period during which small nuclei are growing very slowly. This nucleation results in the formation of several regions in the lattice where the strain energy is lower than in the surrounding matrix. This lower strain energy lattice accelerates growth rate of these small nuclei so that they act as nuclei of recrystallized grains. This growth rate is faster than the nucleation rate.

The most important factor governing the grain growth process is the migration of the grain boundaries. A grain boundary has a surface tension because its atoms have a higher free energy than those within the grains. Consequently, after having gone through the activation energy for the nuclei to be formed the metal undergoes self-diffusion growth tending to achieve a lower free energy state. Grain growth rate is highly affected by impurities, which obstruct grain boundaries. Soluble impurities segregate strongly to boundaries, for example to reduce their elastic misfit energies, while insoluble impurities have a stronger effect, as boundaries become attached to inclusion particles and have then to be dragged away from them by the driving forces for grain growth. A misfitting solute atom can reduce its elastic energy by migrating to some other irregularity in the material, where it may find sites more suitable to its own size, that can be provided by incoherent boundaries and dislocations. A solute atom which expands the lattice will be attracted to the expanded region of dislocation, and one that contracts the lattice will be attracted similarly to the contracted side.

The annealing process of a deformed metal basically moves atoms, placing them in a lower energy state than the one they had after the deformation. Some atoms are still in a low energy state even after deformation. Those atoms catalyze the annealing process because they form

a fundamental cell that allows other atoms to be placed on it with low energy. So the annealing kinetic rate is proportional to the atoms that have been placed in the lattice and the ones that still have high strain energy for an instant.

3.1. Kinetic equation

Among the kinetic equations proposed to describe single sigmoid curves, the most used is the JMAK relation:

$$f = 1 - \exp(-kt^n) \tag{2}$$

where k and n are constants. This equation has been used to describe decomposition processes and can be used to describe semi-empirically the general auto-catalytic behavior. First, an interface must be created to catalyze the reaction; this interface will increase and therefore the reaction rate will also increase until a certain moment at which the interface will decrease as a consequence of the reaction, obtaining then a sigmoid curve. In the case of recrystallization of metals, this equation has also been used, but is only useful when the nucleation rate decreases exponentially, obtaining $n \approx 3$ for a fast and $n \approx 4$ for a slow decrease of nucleation rate. Provided that there is no change in the nucleation mechanism, n is independent of temperature but k depends on it. Nevertheless, this equation cannot explain the presence of more than one step during the annealing of copper. Thus, after studying processes in which a sigmoid curve is obtained for the conversion/time plot, and assuming that the process behaves as auto-catalytic, the following equation deduction has been performed.

Let N be the atoms that are in a high energy place for an instant after deformation and that have a tendency towards the low energy places in a cell during the annealing process. So N is the variable that changes with the annealing time. We may write,

$$\text{Annealing rate} = -\frac{\mathrm{d}N}{\mathrm{d}t} \tag{3}$$

considering that N_0 are all the atoms that initially are in a high energy place after deformation prior to annealing.

As the annealing kinetic is believed to follow an auto-catalytic model, its rate is proportional to the atoms that still are in a high energy place for a given moment and to those atoms that catalyze the process, these latter being the ones that are forming a fundamental cell that facilitate the placement of other atoms. This two processes take place with a parallel contribution. Therefore, we may write the following equation:

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = k_1 N + k_2(N_0 - N)N \tag{4}$$

where k_1 and k_2 are the kinetic constants and $(N_0 - N)$ are the atoms that have been already placed in low energy places from a cell.

The conversion of the atoms that are achieving their low energy places is:

$$X = \frac{(N_0 - N)}{N_0} = 1 - \frac{N}{N_0} \tag{5}$$

We can also write,

$$N = N_0(1 - X) \tag{6}$$

and

$$N_0 - N = N_0 X \tag{7}$$

Therefore, a combination of Equations 4, 6 and 7 results in:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_1(1 - X) + k_2 N_0 X(1 - X) \tag{8}$$

Taking into account that k_2 and N_0 are constant, we introduce the constant k' as:

$$k' = k_2 N_0 \tag{9}$$

Substituting:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = (1 - X)[k_1 + k'X] \tag{10}$$

Rearranging terms:

$$\frac{1}{k'}\frac{\mathrm{d}X}{\mathrm{d}t} = (1 - X)\left[\frac{k_1}{k'} + X\right] \tag{11}$$

$$\frac{\mathrm{d}X}{(1 - X)\left[\frac{k_1}{k'} + X\right]} = k'\mathrm{d}t \tag{12}$$

Integrating this latter equation, with $X = 0$ for $t = 0$, we obtain:

$$X = \frac{(k_1/k')(\exp[(1 + k_1/k')k't] - 1)}{1 + (k_1/k')\exp[(1 + k_1/k')k't]} \tag{13}$$

Considering

$$z = (1 + k_1/k')k' \tag{14}$$

we obtain

$$X = \frac{(k_1/k')[\exp(zt) - 1]}{1 + (k_1/k')\exp(zt)} \tag{15}$$

Dividing the numerator and the denominator by $\exp(-zt)$ the expression becomes

$$X = \frac{(k_1/k')[1 - \exp(-zt)]}{(k_1/k') + \exp(-zt)} \tag{16}$$

This latter equation is analogous to the general expression for an auto-catalytic kinetic model. Initially,

conversion increases as a consequence of the auto-acceleration, reaching an inflexion point and further levels off at a stationary state where X tends to 1 at infinite time. This curve has the aspect of a sigmoid.

When the metal contains small amounts of impurities, and the annealing temperature is low enough, the conversion/time curve becomes multiple-sigmoidal, that is more than one curve is observed. As all the segments of the curve are similar in form, it is expected that the different processes taking place during the overall process could be described by analogous equations, and the overall process described by the sum of all the segments. Therefore, if we consider that in the annealing of fire-refined copper two processes take place simultaneously, the first related to the copper matrix recrystallization (with Ea_1) and the second to impurities placement (with Ea_2), an overlapping of more than one sigmoid becomes a multiple-sigmoidal, so we may write:

$$X' = \sum_i f_i X_i \qquad (17)$$

where X_i ($i = 1, 2, \ldots$) are the equations for a single autocatalytic process and f_i the pre-factors of each
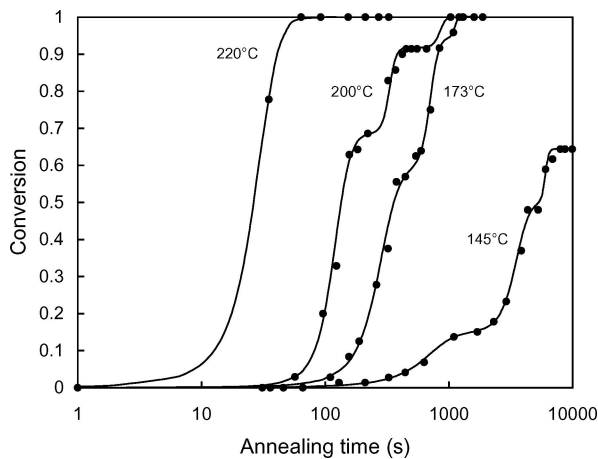

Figure 1 Conversion-time plot for sample 1 at different annealing temperatures.
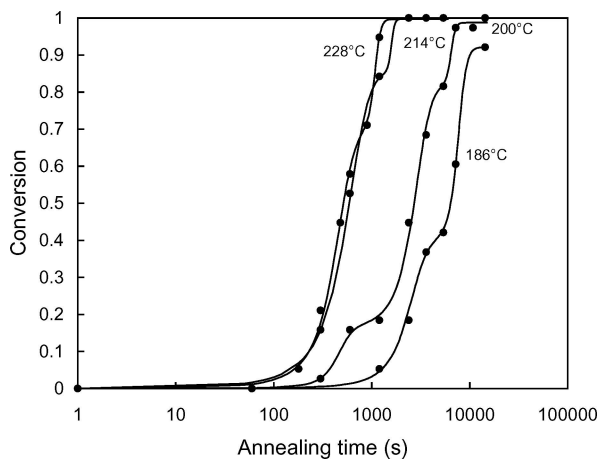

Figure 2 Conversion-time plot for sample 2 at different annealing temperatures.
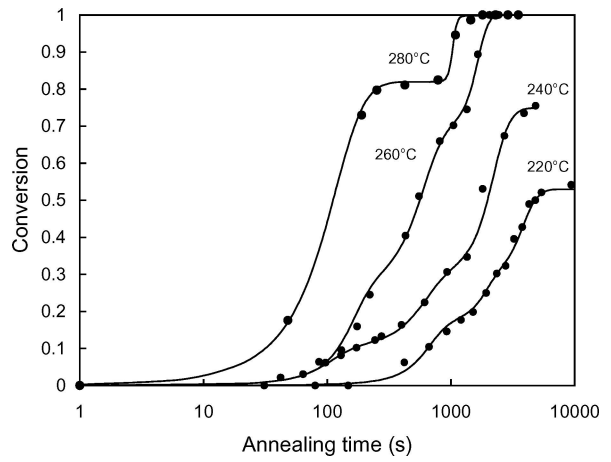

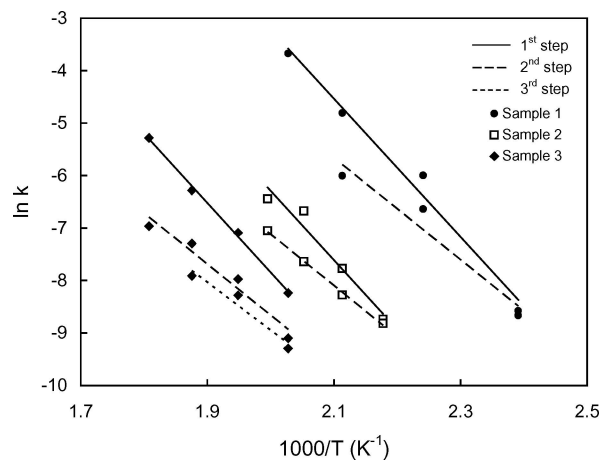Figure 3 Conversion-time plot for sample 3 at different annealing temperatures.

Figure 4 Arrhenius plot for the different studied samples.

equation that indicate the contribution of each process to the overall process.

Hence, to describe an annealing process at a given temperature with two steps on the experimental curve we have to write,

$$X' = f_1 X_1 + f_2 X_2 \qquad (18)$$

Agreement between theory and experimental data can be observed by plotting the annealing kinetic equation with the experimental points obtained for the softening of the studied copper samples at different temperatures (Figs 1–3).

Therefore, experimental conversion/time curves obtained for the softening of pure copper can be adjusted by this equation.

TABLE III Calculated activation energies for the different studied samples

Step	Sample 1 (kJ/mol)	Sample 2 (kJ/mol)	Sample 3 (kJ/mol)
1	109.4	109.5	109.8
2	80.5	81.0	80.9
3	–	–	75.8

TABLE IV Values for activation energies obtained by other authors

Copper purity	99.6%	99.999%	99.98% (OFHC)	99.99%	99.952%	99.98% (electrolytic)	99.91%	99.92%
E_a (kJ/mol)	101.4	93.7	125.1	82	120.5	109.4	109.5	109.8
Reference	[4]	[7]	[7]	[8]	[10]	This work	This work	This work

3.2. Experimental activation energies

Fire-refined copper presents a multiple-sigmoidal character, generally more than two steps. Therefore, two or more experimental activation energies (E_a) were found during the annealing process. The first one, that corresponds to the first step, is the same as that obtained when annealing pure copper and is the same, independently of the composition of the copper. The second one and the following, corresponding to the second and following steps, are lower. Hence, the process that take place is an overlapping of two or more parallel situations. That gives as a result the multiple-sigmoidal character of the microalloyed copper.

Fig. 4 shows the Arrhenius plot for each step of the different copper samples. The reaction rate constants for each step and sample have been calculated from the slope of the respective conversion/time plots. The calculated activation energies from this figure are shown in Table III.

It can be observed that the slope of the Arrhenius plot is of the same order for the first step (100 kJ/mol), related to the copper matrix recovery and recrystallization, independently of the copper composition. Values for the activation energies obtained by other authors are summarized in Table IV.

Note that the number of steps increases as the annealing temperature decreases for all the studied samples. When the copper sample is annealed at a temperature high enough (see sample 1 at 220°C, Fig. 1) only one step is observed. That is because the energy supplied to the sample is enough to recover and recrystallyze the copper matrix, and also to emplace impurities. When the temperature is low, there is not enough energy to complete all the processes, so each step can be observed separately.

For the second and following steps, the calculated activation energies are lower than the first and can be related to the impurities placement, being these energies of the same order for all the studied samples.

Therefore it can be stated that samples are going through the same processes as has been described above. First, and according to the first experimental E_a obtained, the copper atoms are placed (i.e., copper matrix recovers and recrystallizes). Second, the lower experimental E_a, corresponding to the second step, is believed to be the impurities placement process. Generally, impurities have different atomic volume than copper has, and because of this they cause strain on the deformed lattice, so strain is given to the neighbors around an impurity. The movement of dislocations and vacancies allows to place impurities more easily, so a lower energy is required. That is why the second step, during which impurity atoms are being placed in the lattice, has a lower E_a.

4. Conclusions

A multiple-sigmoidal behavior has been found for the annealing of cold-worked fire-refined copper, related to the simultaneous recrystallization of the copper matrix and the impurities placement processes. The kinetic model to describe the copper annealing, based on the auto-catalytic behavior of the process, and the equation proposed are in accordance with the experimental results. Different activation energies have been obtained for each step of the process, the first being of the same order as the value obtained for pure copper by other authors. The second and following activation energies are lower and related to the impurities emplacement. As other metals such as nickel and aluminum present similar behavior as copper during annealing, it is expected that the auto-catalytic kinetic model could describe these processes.

References

1. W. A. JOHNSON and R. F. MEHL, *Trans. Am. Inst. Engrs.* **135** (1939) 416.
2. M. AVRAMI, *J. Phys. Chem.* **7** (1939) 1103.
3. A. N. KOLMOGOROV, *Izv. Akad. Nauk. SSSR, Ser. Mat.* **3** (1937) 355.
4. P. KRÜGER and E. WOLDT, *Acta Metall. Mater.* **40** (1992) 2933.
5. R. DOHERTY, A.R. ROLLET and D. J. SROLOVITZ, in Annealing Processes-Recovery, Recrystallization and Grain Growth, *Proc. 7th. Risø Int. Symp.*, 1986, p. 53.
6. C. W. PRICE, *Acta Metall. Mater.* **38** (1990) 727.
7. B. F. DECKER and D. HARKER, *Trans. AIME* **188** (1950) 887.
8. J. HERNÁEZ and M. L. BLÁZQUEZ, *Rev. Metal. Madrid* **23** (1987) 117.
9. E. WOLDT and D. JUUL JENSEN, *Metall. Mat. Trans.* **26A** (1995) 1717.
10. D. BOWEN, R. R. EGGLESTON and R. H. KOPSCHOT, *J. Appl. Phys.* **23** (1952) 630.
11. F. F. KRAFT, R. N. WRIGHT and M. K. JENSEN, *J. Mat. Eng. Perform.* **5**(2) (1996) 213.
12. G. MIMA, Y. OGINO and J. SATO, *J. Instit. Met.* **96** (1968) 49.
13. L. M. CLAREBROUGH, M. E. HARGREAVES, M. H. LORETTO and G. W. WEST, *Acta Metall.* **8** (1960) 797.
14. L. M. CLAREBROUGH, M. E. HARGREAVES and G. W. WEST, *Philosoph. Mag.* **1** (1956) 528.
15. A. SOSIN and J. A. BRINKMAN, *Acta Metall.* **7** (1959) 478.
16. E. C. W. PERRYMAN, *Acta Metall. Mat.* **2** (1954) 26.