Kinetics of Nonisothermal Recrystallization

F.F. Kraft, R.N. Wright, and M.K. Jensen

The kinetics of recrystallization from nonisothermal cycles is modeled using an extension of the Arrhenius relationship. This model is used to predict the annealing response for both isothermal and nonisothermal annealing cycles. A nondimensional parameter called the "annealing index" is based on time and temperature and is related to the extent of anneal through physical properties. The effect of heating and cooling rate also can be quantified because the entire thermal cycle is evaluated. Nonisothermal anneals with heating rates of 10 and 100 °C/s were evaluated (along with isothermal anneals) for cold-drawn ETP copper wire. A numerical solution is set forth to evaluate nonisothermal cycles.

Keywords

annealing index, Arrhenius equation, kinetics, nonisothermal, recrystallization

1. Introduction

RECRYSTALLIZATION kinetics of cold-worked metals have been modeled extensively for isothermal annealing cycles. Equations that predict the amount of recrystallization as sigmoidal curves were established by Avrami (Ref 1-3), Johnson and Mehl (Ref 4), and Speich and Fisher (Ref 5). The fraction of recrystallized metal can be easily correlated to mechanical properties using these equations. Thus, the determination of mechanical properties is often used as a vehicle to estimate the extent of recrystallization. This is done by determining the percentage of the as-measured property with respect to the cold-worked and fully annealed properties (Ref 6-7). Another widely used equation to characterize isothermal reaction kinetics of recrystallization was introduced by Arrhenius (Ref 8). The Arrhenius relationship is a rate equation used to evaluate an activation energy for the nucleation and growth of new grains during recrystallization. Once again, this equation has been used exclusively to address isothermal annealing cycles.

In industrial practice, however, thermal cycles are rarely constant over an annealing cycle. Continuous and in-line annealing operations are generally not isothermal by their very nature. Thermal cycles in such processes can be of variable duration based on the method of heating. Continuous furnace annealers tend to have longer cycles whereas continuous electrical resistance type annealers can have thermal cycles of less than 1 s (Ref 9). Batch-type processing also exhibits some inherent thermal variability. Nevertheless, the recrystallization or annealing response to nonisothermal cycles has been largely overlooked.

Research addressing the kinetics of nonisothermal recrystallization has essentially applied isothermal kinetic models to predict the annealing response. The usefulness of such approaches may be limited because they do not consider the entire thermal cycle. Typically, an effective time and temperature must be determined. Magee et al. (Ref 7) applied the equations of Avrami (Ref 1-3) and Speich and Fisher (Ref 5) to model the annealing of cold-worked low-carbon steel under continuous heating operations. An important step in this approach, however, was the determination of a recrystallization start time. Wright (Ref 10) and Kraft et al. (Ref 11, 12) propose an "annealing index" that is based on the Arrhenius equation and isothermal annealing curves for predicting annealing response. The annealing index approach presented in these studies is also somewhat limited because it requires an effective time and temperature estimation for nonisothermal cycles. Therefore, the annealing index concept is fully developed here as a true nonisothermal (and isothermal) kinetic model, encompassing virtually any thermal cycle. This kinetic model is, in part, based on research by Kraft (Ref 9).

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2. Annealing Index

The annealing index is a nondimensional parameter that is derived from the Arrhenius equation. The Arrhenius relationship is generally presented as:

$$\frac{1}{t} = A\,e^{-Q/RT} \qquad \text{(Eq 1)}$$

where t is time, A is a constant associated with the number of atoms with the required energy at any instant and the frequency of vibration, Q is the activation energy for recrystallization, R is the universal gas constant, and T is absolute temperature. Assuming that the constant, A, is a function of the extent of recrystallization, then the extent of recrystallization is a function of the value $te^{-Q/RT}$. Thus, the terms of Eq 1 were rearranged to establish a parameter called the annealing index, I, in Eq 2.

$$I = \log_{10}\left(\frac{1}{A}\right) = \log_{10}(t) - \frac{Q}{2.303RT} \qquad \text{(Eq 2)}$$

Through experimental data, the annealing index can be related to the amount of material recrystallized or to physical properties. To achieve this, the activation energy for recrystallization associated with the specific amount of cold work in the metal must be determined. This can be done by plotting data as $1/T$ versus $\ln(1/t)$ for a specific partial (isothermal) anneal, usually half hard or 50% recrystallized. Q then is determined from the slope of a linear regression through these data. (Note that from Eq 1, $\ln(1/t) = (-Q/R)(1/T) + \ln A$). The times for these isothermal anneals generally span several orders of magnitude.

Data from several isothermal studies were evaluated to establish the validity of this model for different amounts of cold work and for a wide range of times and temperatures; they are presented in Fig. 1 to 4. The extent of annealing or recrystallization for these samples was determined by various methods, namely resistance measurements, an x-ray technique, and tensile testing. Annealing temperatures varied by at least 90 °C and for at least three orders of magnitude of time. The data show that the annealing response for these materials is reasonably predicted for some isothermal cycle using the annealing index and these annealing curves.

Although Eq 2 was shown to be a useful annealing model, its application to nonisothermal cycles is problematical. Estimation of an effective annealing time and temperature (as proposed in previous publications) may not be accurate. Therefore, an expression for the annealing index was derived to account for the entire thermal cycle. This was done by equating the recrystallization reaction rate to a differential change in condition with respect to time (dc/dt) and by expressing tem-

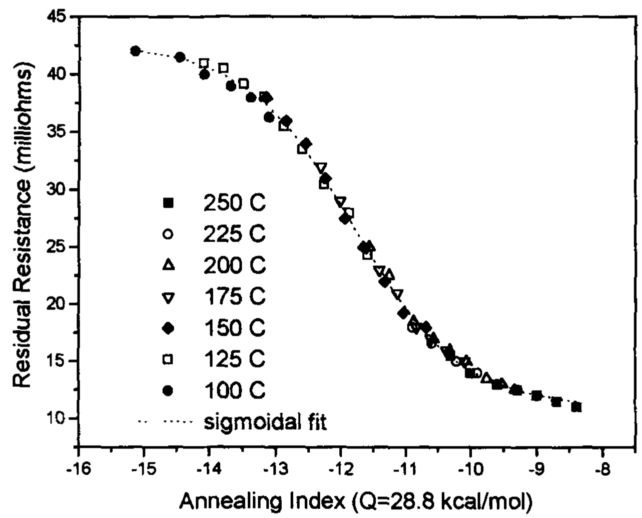

Fig. 1 Annealing curve for 97.0% cold-drawn, oxygen-free copper wire. The annealing index was evaluated with an activation energy, Q, equal to 28.8 kcal/mol. Annealing times were 1 min to 5 h. Based on residual resistance, data are from D. Bowen et al. (Ref 13).

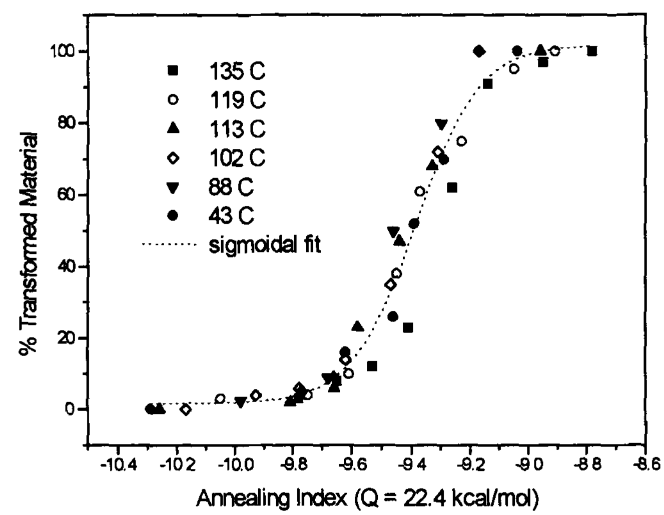

Fig. 2 Annealing curve for 98.0% cold-drawn, spectroscopic copper wire. The annealing index was evaluated with an activation energy, Q, equal to 22.4 kcal/mol. Annealing times were 3 to 5.3×10^4 min. Based on texture analysis (using x-ray diffraction), data are from B.F. Decker and D. Harker (Ref 14).

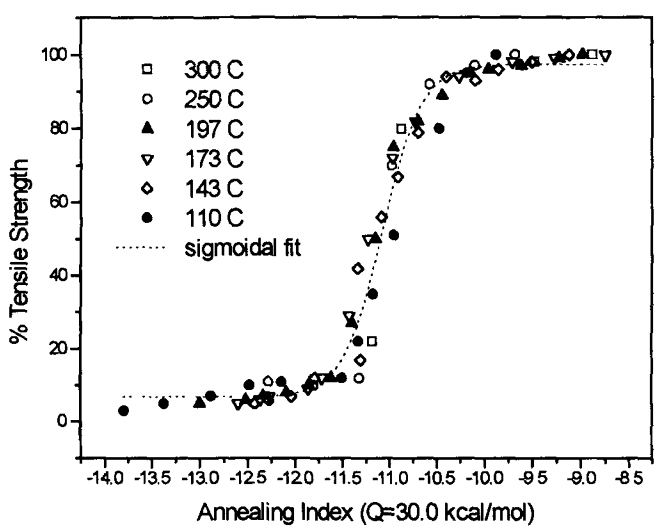

Fig. 3 Annealing curve for 66.6% cold-drawn, tough pitch copper wire. The annealing index was evaluated with an activation energy, Q, equal to 30.0 kcal/mol. Annealing times were 2 to 2×10^7 s. Based on tensile testing, data are from G. Mima et al. (Ref 15).

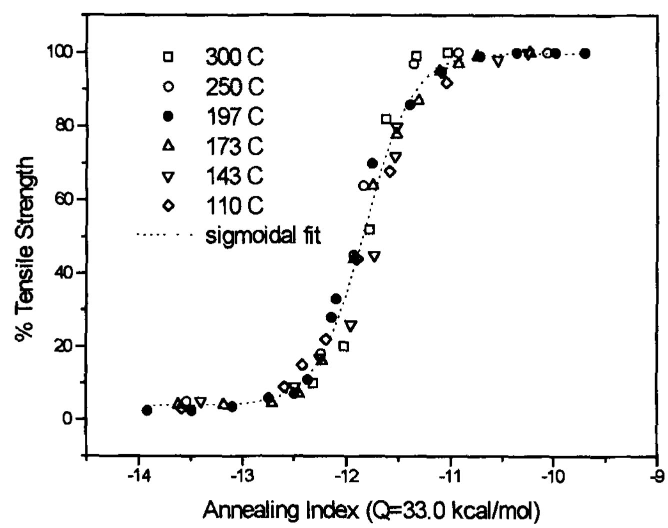

Fig. 4 Annealing curve for 40.0% cold-drawn, tough pitch copper wire. The annealing index was evaluated with an activation energy, Q, equal to 33.0 kcal/mol. Annealing times were 2 to 7×10^7 s. Based on tensile testing, data are from G. Mima et al. (Ref 15)

perature as a function of time ($T(t)$). In this respect, Eq 1 is rewritten as:

$$\frac{dc}{dt} = A\,e^{-Q/RT(t)} \qquad \text{(Eq 3)}$$

Integrating Eq 3 yields:

$$\frac{\Delta c}{A} = \int_0^{t_f} e^{-Q/RT(t)} dt \qquad \text{(Eq 4)}$$

where the integration limit t_f is the total duration of the thermal cycle (above room temperature) and Δc is the change in condition. Since $\log_{10}(\Delta c/A)$ is, in essence, the basis for the annealing index in Eq 2, then I is expressed as:

$$I = \frac{1}{2.303} \ln \int_0^{t_f} e^{-Q/RT(t)}\, dt \qquad \text{(Eq 5)}$$

Equation 5 allows for the evaluation of nonisothermal cycles; yet a constant temperature with respect to time simplifies the expression to Eq 2. Thus, nonisothermal and isothermal annealing cycles can be similarly evaluated with this model using Eq 5 and 2, respectively.

The solution to Eq 5 requires accurate knowledge of the thermal cycle and a suitable numerical integration method. The solution presented here is tailored to the requirements of this research. Time versus temperature data were computer recorded at a constant sampling rate and saved in the appropriate format.

Integration of Eq 5 is achieved by the Newton-Cotes trapezoid rule (Ref 16). A multiple application scheme, which divides the integration interval into discrete segments, is used to improve the accuracy of the solution. The general formula to evaluate the integral in Eq 5 is:

$$\int_0^{t_f} e^{-Q/RT(t)}\, dt \approx \left(t_f - t_0\right) \frac{f(t_0) + 2\sum_{i=1}^{n-1} f(t_i) + f(t_n)}{2n} \qquad \text{(Eq 6)}$$

where

$$f(t) = e^{-Q/RT(t)}$$

n is the number of equal time segments, t_0 is zero, and t_n is the total duration of the thermal cycle. A computer program was developed to solve Eq 5 for the annealing index and is based on an algorithm presented by Chapra and Canale (Ref 16). The complete program is presented in Ref 9. A specific activation energy and the time-temperature data of the anneal are the required input. Experimental verification of Eq 5 is the primary focus in the following sections.

Table 1 Chemical analysis of 12 AWG ETP Cu wire

Element	Composition, parts per million
Sb	0.4
As	<0.1
Bi	0.1
Fe	4.0
Pb	0.4
Ni	3.0
Ag	9.0
Se	0.3
Te	<0.1
Sn	0.2
S	<3
O	414

3. Material

The material used for this study was commercially drawn, electrolytically refined, tough pitch (ETP) copper (Cu) wire.

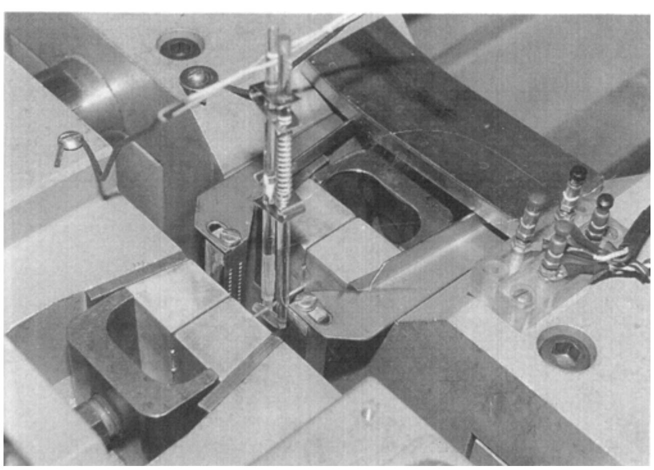

Fig. 5 Test configuration for controlled annealing on a Gleeble 1500. The jaw-to-jaw distance is 5 cm (2 in.).

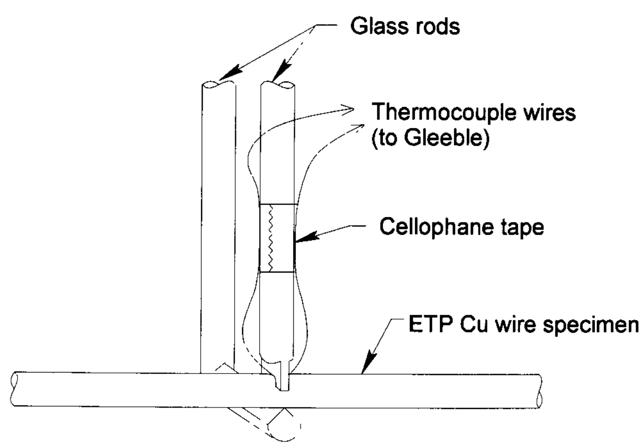

Fig. 6 Detailed sketch of wire specimen configuration for Gleeble thermal processing. The glass rods clamp on to the specimen using a spring mechanism (not shown).

The process history includes continuous casting, hot rolling to standard 5/16 in. diameter redraw rod, and drawing to the final diameter of 12 American wire gage (AWG) (0.0808 in., 2.052 mm). The corresponding amount of cold work is approximately 93%. A chemical analysis of this material is presented in Table 1.

4. Experimental

An array of anneals was performed using samples from the 12 AWG cold-drawn wire. All thermal cycles were generated with a Gleeble 1500 (Dynamic Systems Inc., Troy, NY) testing machine. This equipment was used to electrically heat the wire samples to predetermined thermal cycles. Wire samples 11.2 cm (4.4 in.) long provided a 5 cm (2 in.) jaw-to-jaw distance. A photo of the test configuration is shown in Fig. 5, and a detailed schematic diagram is presented in Fig. 6.

The wire samples were held by copper alloy jaws, through which electrical current passed to heat the samples. A 0.005 in. diameter, K-type thermocouple was held in place on the wire samples for feedback to the Gleeble control system and for the computer acquisition of thermal data. A quench head with compressed air was used to provide consistent rapid cooling of heated specimens. The Gleeble software interface was programmed to heat the wire samples at a specific rate, to hold temperature for a specific time (for isothermal anneals only), and to rapidly cool the specimens with the air quench system.

Annealing cycles consisted of 1 h, 6 min, 360 s and 3.6 s isothermal anneals and nonisothermal anneals with heating rates of 10 °C/s and 100 °C/s. Several process simulated nonisothermal anneals were also performed. Nonisothermal anneals were heated at specified rates to predetermined temperatures, at which point heating ceased and the pressurized air quench commenced. Data for these tests were taken at a sampling rate

Table 2 Nonisothermal Gleeble anneals on industry cold-drawn, 12 AWG ETP Cu wire

Peak temperature, °C	Heating rate, °C/s	I	Tensile strength, MPa	Tensile strength, ksi	Uniform elongation
251	100	-12.67	440	63.9	0.012
305	100	-11.50	318	46.2	0.076
270	100	-12.19	428	62.1	0.006
322	100	-11.12	285	41.3	0.166
344	100	-10.70	255	37.0	0.278
252	10	-11.83	386	56.0	0.009
272	10	-11.33	306	44.5	0.100
304	10	-10.65	253	36.7	0.310
326	10	-10.24	243	35.3	0.369
290	...	-12.13	422	61.3	0.027
410	...	-10.16	248	36.0	0.416
293	...	-11.43	318	46.2	0.134

Note: The area reduction is approximately 93%. The annealing index, I, is based on an activation energy of 28.8 kcal/mol. The last three thermal cycles in this table had nonisothermal heating cycles that simulated continuous in-line resistance annealing (Ref 9). I is from Eq 5.

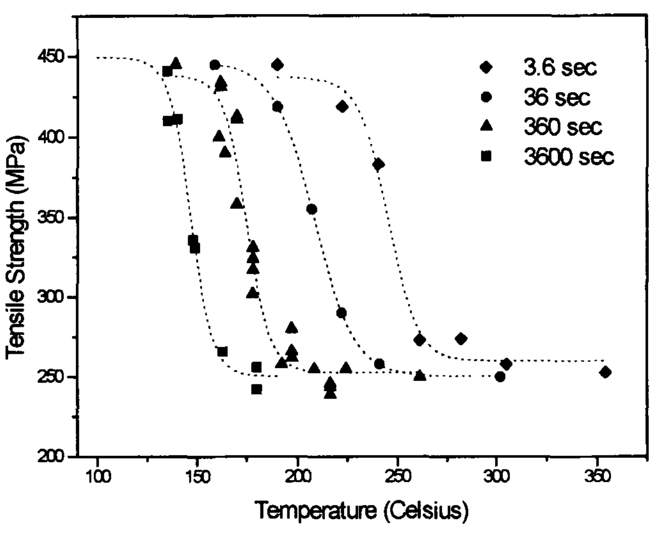

Fig. 7 Annealing curves based on isothermal cycles that ranged from 3.6 s to 1 h. The 12 AWG ETP copper wire had a cold-worked area reduction of approximately 93%. Sigmoidal curves were fit to these data.

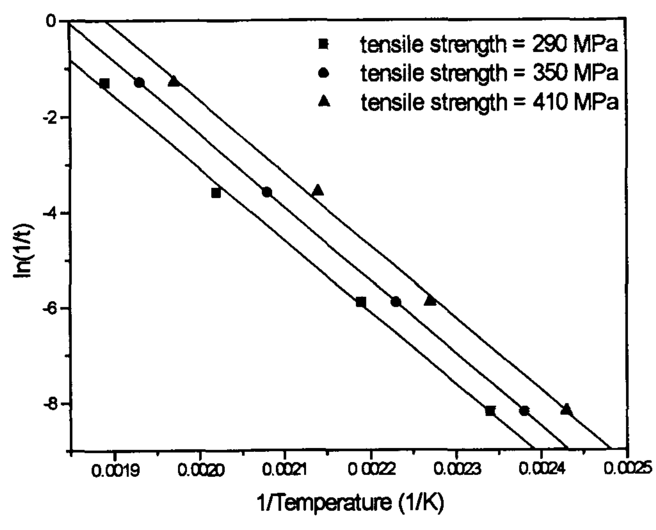

Fig. 8 A plot of $1/T$ versus $\ln(1/t)$ for different degrees of anneal; namely 20, 50, and 80% tensile strength. Data were interpolated from Fig. 7. The average of these slopes resulted in an activation energy of 30.3 kcal/mol.

of 59.6 Hz and were saved for analysis with a data reduction program. A more rigorous description of this procedure is presented in Ref 9.

The extent of recrystallization was evaluated by tensile testing of the annealed wire samples. An Instron (Instron Corporation, Canton, MA) screw-driven tensile tester with a 500 lb (2224 N) load cell was used for these tests. A cross-head speed of 0.02 in./min (0.051 cm/min) resulted in an estimated initial strain rate of approximately 1×10^{-3}/s. The tensile strength from these samples was determined by dividing the maximum force by the initial cross-sectional area. Elongation data from these tests were approximated by determining the true strain outside the necking region (elongation = ln(initial area ÷ final area)). Both tensile strength and elongation were used as indications of recrystallization.

5. Results

An array of isothermal annealing data were first generated to provide a reasonable estimate of the activation energy. An initial value of Q was determined by plotting data as $1/T$ versus $\ln(1/t)$ for several different partial isothermal anneals, ranging in time from 3.6 s to 1 h. The results from this initial study are shown in Fig. 7 and 8. The initial value of Q, which was determined from the average of the slopes in Fig. 8, was 30.3 kcal/mol. With this information, experimental nonisothermal annealing cycles were generated and evaluated with the data reduction program and the corresponding annealing index curve (such as those presented in Fig. 1 to 4). Some amount of trial-and-error was needed to gen-

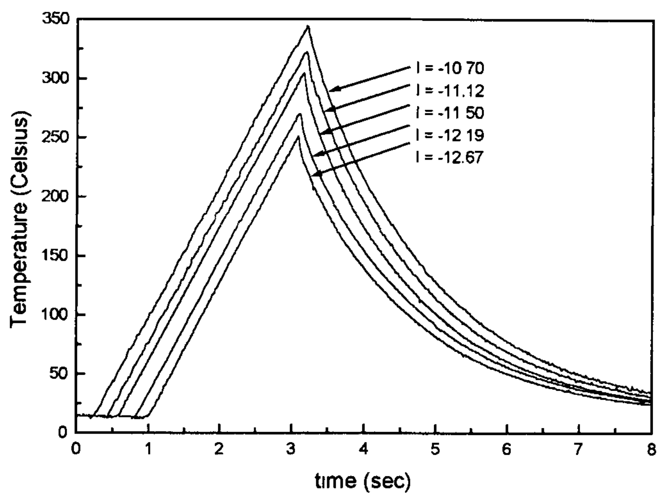

Fig. 9 Nonisothermal annealing cycles with a heating rate of 100 °C/s. The annealing index, I, for each thermal cycle was evaluated at an activation energy of 28.8 kcal/mol. Thermal cycles are offset on the time axis to allow the data to be effectively presented on one figure.

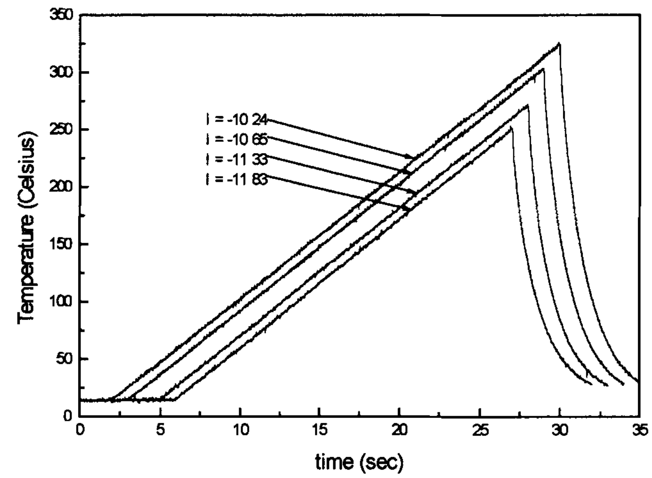

Fig. 10 Nonisothermal annealing cycles with a heating rate of 10 °C/s. The annealing index, I, for each thermal cycle was evaluated at an activation energy of 28.8 kcal/mol. Thermal cycles are offset on the time axis to allow the data to be effectively presented on one figure.

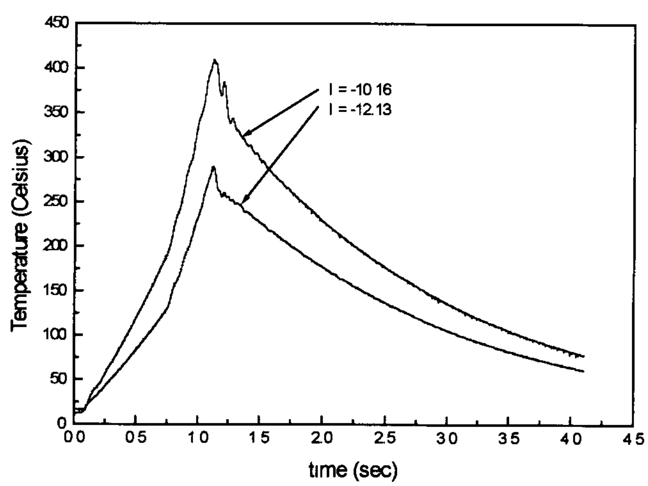

Fig. 11 Nonisothermal annealing cycles with heating rates that are simulations of the continuous electrical resistance annealing process. Annealing index was evaluated at an activation energy of 28.8 kcal/mol.

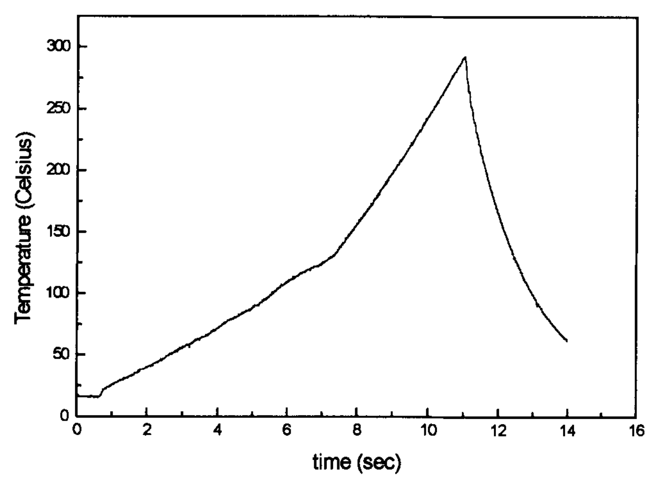

Fig. 12 Nonisothermal annealing cycle with a heating rate that is a simulation of the continuous electrical resistance annealing process. Annealing index was calculated as −11.43 for an activation energy of 28.8 kcal/mol.

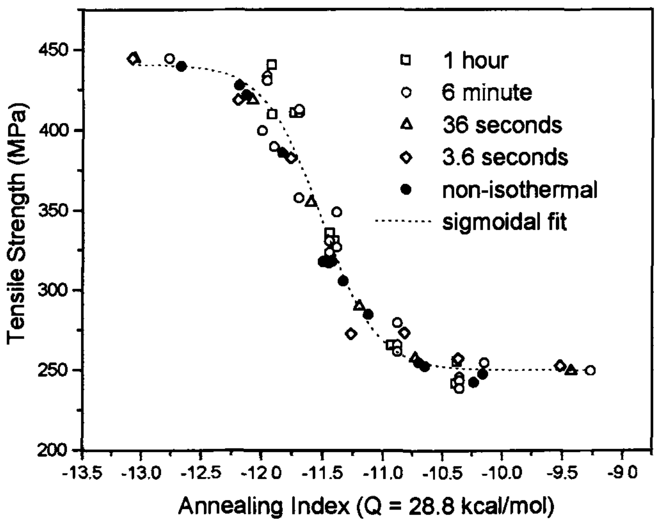

Fig. 13 Sigmoidal annealing data for 1 h, 6 min, 36 s and 3.6 s isothermal anneals and varying time nonisothermal anneals. Data are based on tensile strength. I was evaluated at an activation energy of 28.8 kcal/mol.

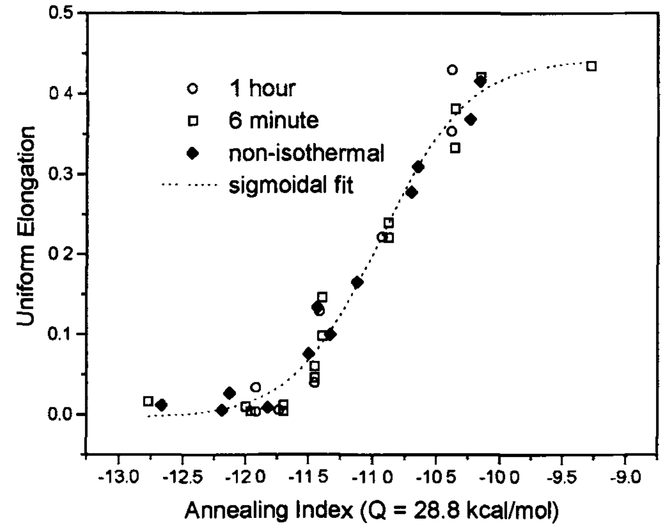

Fig. 14 Sigmoidal annealing data for 1 h and 6 min isothermal anneals and varying time nonisothermal anneals. Data are based on uniform elongation. I was evaluated at an activation energy of 28.8 kcal/mol.

erate nonisothermal cycles that would span the entire annealing spectrum of wire properties. Also, the initial value of Q needed to be adjusted to allow for the best fit of the nonisothermal data to the isothermal annealing data. This indicates that the sensitivity of the model to the activation energy increases as the annealing time decreases. The value for Q that provided the best fit was 28.8 kcal/mol.

Table 2 summarizes the various nonisothermal annealing cycles attempted and reflects the I values evaluated at 28.8 kcal/mol. The thermal cycles (from Table 2) with heating rates of 100 °C/s and 10 °C/s are graphically shown in Fig. 9 and 10, respectively. The last three thermal cycles, which represent process simulations, are shown in Fig. 11 and 12.

Figure 13 presents annealing index versus tensile strength data for the isothermal and the nonisothermal anneals. The curve that has been fit to these data is based on the sigmoidal Boltzmann equation and is expressed as:

$$\sigma = \frac{\sigma_{max} - \sigma_{min}}{1 + e^{(I - I_0)/dI}} + \sigma_{min} \qquad \text{(Eq 7)}$$

where σ is the tensile strength, the subscripts, max and min, denote the cold worked and fully annealed tensile strengths, respectively, I_0 is the annealing index at 50% tensile strength, and dI is a characteristic value that is related to the change about I_0.

For the data plotted in Fig. 13, σ_{min} is 250 MPa, σ_{max} is 441 MPa, I_0 is −11.5, and dI is 0.230. Thus, by substituting Eq 5 into Eq 7, the tensile strength, or degree of recrystallization for virtually any thermal cycle, can be calculated. Figure 14, which presents elongation data for the nonisothermal anneals and several isothermal anneals, is consistent with the tensile strength data.

6. Discussion

As demonstrated in Fig. 13 and 14, the annealing response of cold-worked metal can be predicted for virtually any thermal cycle with the use of the annealing index and the appropriate annealing curve or equation. The model was shown to be valid for both isothermal annealing times as long as 1 h and nonisothermal anneals that have no appreciable time at peak temperature (<1 s). Because this method is a true nonisothermal model that takes into account the entire thermal cycle, it can be used to quantify the effect of heating and cooling rates on recrystallization. For example, by plotting data from Table 2 as peak temperature versus tensile strength (in Fig. 15), the effect of heating rate on annealing response is readily seen. Figure 15 shows that anneals with a heating rate of 100 °C/s required about a 40 °C higher peak temperature to achieve the same degree of anneal (with the same mechanical properties) as those anneals with heating rates of 10 °C/s. This direct comparison of heating rates is made because the cooling rates for these anneals were consistent and nearly identical due to the pressurized air quench.

In most of the isothermal annealing studies where the Arrhenius equation was applied, the activation energy, Q, was assumed to be constant over the entire process of recrystallization (or anneal). Mima et al. (Ref 15), on the other hand, show that the apparent activation energy may actually be a function of fractional softening or the amount that the metal is recrystallized. Increases in apparent activation energy over the entire annealing spectrum were determined to range from 20 to 38% (Ref 15). However, such large variations were not seen in this study, as evident by Fig. 8. In the present model, an overall or effective activation energy is assumed to govern the entire process of recrystallization. Figures 3 and 4 use some of the data presented by Mima et al. (Ref 15) but were evaluated here with an average activation energy using the annealing index model. Using a constant Q, these data show reasonably ac-

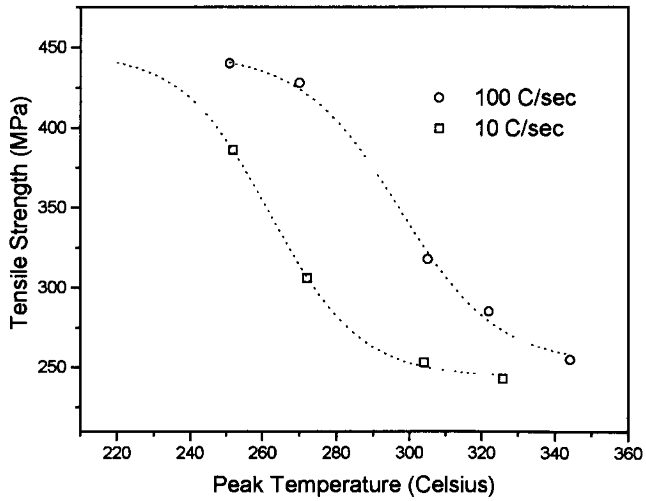

Fig. 15 Effect of heating rate on the annealing response of ETP copper wire for nonisothermal cycles. For similar anneals (same physical properties), a 40 °C difference in peak temperature exists for annealing cycles with heating rates of 10 and 100 °C/s. Sigmoidal curves were fit to the data.

curate results with this method. The results of this research (Fig. 13 and 14) also show that an average Q is reasonable for the entire recrystallization process.

Nevertheless, accurate determination of the activation energy, Q, is essential when applying this model. As annealing cycles become shorter, the sensitivity of the annealing-index data on Q increases. For this reason, Q should be determined using annealing cycles for which time is in the range of interest. For highly nonisothermal cycles, this may require testing similar to that presented here. Bounding the thermal cycles of interest will ensure reliable results.

7. Summary

The kinetics of recrystallization associated with nonisothermal cycles was modeled by extending the well-known Arrhenius rate relationship. With a known annealing cycle, the model is used to predict the annealing response for both isothermal and nonisothermal annealing cycles. Because the entire thermal cycle is evaluated, the effect of heating and cooling rates can be quantified. A significant difference in annealing response was observed for nonisothermal anneals with heating rates of 10 and 100 °C/s. Accurate determination of the activation energy and supporting annealing data is required with this method. A numerical solution was set forth to evaluate nonisothermal cycles. This annealing model can be combined with a simulation model of a thermal cycle to predict properties analytically rather than just relying on experimentation. Such an approach was proposed in Ref 9 for continuous electrical resistance annealing of copper wire.

Acknowledgments

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