Negative temperature dependence of recrystallized grain size: analytical formulation and experimental confirmation

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Abstract. The catalyzing effect on nucleation of recrystallization from pre-existing grains is analyzed, analogy to the foreign nucleus size effect in heterogeneous nucleation. Analytical formulation of the effective nucleation site for recrystallization leads to a negative temperature dependence of recrystallized grain size. Non-isochronal annealing, where annealing time is set just enough for the completion of recrystallization at different temperature, is conducted on pure copper after severe plastic deformation. More homogeneous and smaller grains are obtained at higher annealing temperature. The good fitting between analytical and experimental results unveils the intrinsic feature of this negative temperature dependence of recrystallized grain size.

1. Introduction

The history of metalworking, including the procedures of deformation and heating, can be traced back to the early days of Neolithic Age, when the first metalsmiths began working with native copper [1]. The birth of “Recrystallization” was declared by a paper of 1887, where Sobey reported the emergence of new equiaxed grain when heating the deformed iron with elongated structure [2]. Establishing quantitative models based on the physics of recrystallization, and using them to improve, optimize and control microstructure, has long been the crucial mission of modern metal industry, and also the frontier researches of nanomaterials [3].

In summarizing the “laws of recrystallization”, it is stated by Burke and Turnbull that [4, 5] the final grain size depends chiefly on the degree of deformation and to a lesser degree on the annealing temperature, normally being smaller the greater the degree of deformation and the lower the annealing temperature. Experimental observations show that final grain size increases significantly with the increase of annealing temperature after pre-deformation in steel [6,7], Cu–Zn alloys [8,9], magnesium alloy [10], molybdenum alloy [11] and so on. However, on the other side, Eastwood et al. reported that recrystallized grain size is insensitive to annealing temperature and they disclosed that different annealing temperatures yield a similar grain size after recrystallization for brass [12].

In addition to these contradictory experimental results, a basic gap in our knowledge for many years has been the lack of a quantitative model to account for the grain size after recrystallization [13]. One principle reason for the existence of this basic gap is the complexity of recrystallization process, especially the complex nucleation behavior of the pre-deformed materials. In order to reach a quantitative formulation of the recrystallized grain size, and meantime to avoid the complex problem related to nucleation process, it will be helpful to estimate quantitatively the number of effective nucleation site, which serves as an essential base for calculating the nucleation rate for...
recrystallization, and is always proportional to the final number of recrystallized grains after the completion of recrystallization.

The existing high angle grain boundaries (HAGB) in the pre-deformed materials play an important role in promoting nucleation for recrystallization, through the mechanism, for example, strain-induced boundary migration (SIBM) [14, 15]. Severe plastic deformation introduces high density of non-equilibrium HAGBs, which serves as preferential nucleation site for recrystallization in the annealing subsequent to the deformation, and significantly promotes the nucleation rate which leads to much smaller recrystallized grain [16, 17]. Analogy to the catalyzed nucleation by “foreign particles” during phase transformation, the catalyzing effect on nucleation of recrystallization from HAGB can be analyzed following the foreign nucleus in Heterogeneous Nucleation [18,19].

2. Analytical formulation of catalyzed nucleation by HAGB in recrystallization

Consider the catalyzing effectiveness on nucleation of recrystallization from an existing grain with a diameter of \( d \) in the as-deformed microstructure with HAGBs, and the catalyzed embryo has a critical radius of \( r^* \), which can be calculated from the classical nucleation theory [18]:

\[
r^* = \frac{2\gamma}{\Delta G_V}
\]

where \( \gamma \) is the interfacial energy; \( \Delta G_V \), the difference of Gibbs free energies per unit volume of the parent and new phases; in the present case of recrystallization, this Gibbs free energy difference equals to stored energy from pre-deformation, and is basically constant upon change of annealing temperature.

Fletcher [18] showed that the free energy of formation of a critical embryo with a radius of \( r^* \) can be written as

\[
\Delta G^* = \frac{8\pi\gamma^3}{3(\Delta G_V)^2} f(m,x)
\]

in which \( f(m,x) \), known as the Fletcher shape factor for heterogeneous nucleation on a convex spherical catalyst particle, is given by

\[
f(m,x) = 1 + \left(\frac{1 - mx}{g}\right)^3 + x^3 \left[ 2 - 3\left(\frac{x - m}{g}\right) + \left(\frac{x - m}{g}\right)^3 \right] + 3mx^2 \left(\frac{x - m}{g} - 1\right)
\]

Where, \( g = (1 + x^2 - 2mx)^{1/2} \); \( x = d/(2r^*) \) is the dimensionless diameter of the spherical catalyst particle, normalized by the radius of critical embryo \( r^* \), and \( d \) is the actual diameter of the catalyst particle; \( m \), in the case of melt solidification, is the cosine of the contact angle of the new embryo on the catalyst surface, with \( 0 \leq m \leq 1 \); In the present case of recrystallization, \( m \) resembles the catalyzing efficiency of the pre-existing grain boundary on the forming of new embryo for recrystallization, and could be considered constant in the case of high angle grain boundary misorientation. Thus \( f(m,x) \) is a function depends solely on \( x \), the diameter of existing grains with HAGBs catalyzing the nucleation of recrystallization in subsequent annealing.

Generally, in dealing with the effect of foreign particle size on heterogeneous nucleation [20], and in dealing with the nucleation issue of a pre-deformed material during recrystallization, probability has been used to relate nucleation activities with structure parameters in the parent phases (such as grain boundary misorientation etc.) [13, 21]. Hence, the probability \( p \) for an existing grain in the pre-deformed matrix to act as an effective nucleation site for recrystallization is considered currently. It is reasonable to assume \( p \) to be proportional to a thermal activation factor with \( \Delta G^* \) as the energy barrier, and to \( f_{HAGB} \), the fraction of HAGBs which are evidenced to be preferential nucleation site. Thus

\[
p \approx C \cdot \exp\left(-\frac{\Delta G^*}{k_BT}\right) \cdot f_{HAGB}
\]

Where \( C \) is a coefficient, and \( k_B \) the Boltzmann constant.
In considering the catalyzed nucleation by “foreign particles” during phase transformation, it is clear that the larger the diameter of the “foreign particle”, the higher its efficiency in catalyzing the nucleation. Analogy to this tendency, suppose at \( x \geq x_c, p \approx 1 \), which means grains in the pre-deformed matrix with HAGB and normalized dimensionless diameter \( x \) larger than \( x_c \) will act as effective nucleation sites upon annealing at temperature \( T \) with 100% possibility; and considering equations (2) and (3),

\[
p \approx 1 \approx C \exp \left[ - \frac{8 \pi \gamma^3}{3 \Delta G_v k_B T} f(m, x_c) \right] f_{HAGB} \tag{5}
\]

This leads to a relation between the annealing temperature \( T \) and pre-existing grain size \( x_c \):

\[
\frac{8 \pi \gamma^3}{3 \Delta G_v k_B T} f(m, x_c) = T \cdot \ln(C \cdot f_{HAGB}) \tag{6}
\]

Using typical parameters of \( f_{HAGB}=0.67 \) [22], \( \Delta G_v = 57 \text{ J/mol} \approx 8 \times 10^6 \text{ J/m}^3 \) [23] after severe plastic deformation, and \( \gamma = 0.625 \text{ J/m}^2 \) [2] for copper, equation (6) gives a drastic dependence of \( x_c \) upon \( T \), through \( f(m, x_c) \). As shown in Figure 1, all the curves describing the dependence of \( x_c \) upon \( T \) at different catalyzing efficiency \( m \) indicate that, the higher the annealing temperature \( T \), the smaller the critical grain size \( x_c \), and thus more grains in the pre-deformed matrix will act as effective nucleation sites. This means that higher annealing temperatures lead to smaller recrystallized grain size, or an negative temperature dependence of recrystallized grain size, which is not only against the “laws of recrystallization” summarized by Burke and Turnbull that [4, 5], but also contradictory to the experimental results for copper [24-28], as well as other metals and alloys [6-11].

Figure 1. Dependence of critical grain size \( x_c \) upon annealing temperature \( T \) at different level of catalyzing efficiency \( m \), which is large enough to sufficiently catalyze nucleation of recrystallization.

In studying the recrystallization behavior of a two-phase brass, a negative temperature dependence of recrystallized grain size was observed by Naether et al. [9], where the reduction in the average grain size with increasing temperature was observed accompanied by a concurrent increase of the volume...
fraction of $\beta$ phase in the sample. This case did not indicate the intrinsic negative temperature dependence of recrystallized grain size itself, but the increasing effect of $\beta$ phase stabilization from the concurrent increase of the volume fraction of $\beta$ phase in the sample upon increase of annealing temperature [9].

The key to unlock this contradiction between the analytical formulation given in equations (2) to (6) and the experimental data in the literature might be the annealing time. Isochronal annealing at different temperatures is usually used for the annealing and recrystallization to obtain temperature dependence of grain size in the literature [24-28]. When the annealing time is set enough for completion of recrystallization at a lower temperature, this isochronal annealing time is far more than that for recrystallization to complete at higher temperatures, and the grain size obtained in this case for high temperature annealing inevitably includes the effect of grain growth subsequent to the completion of recrystallization, and this leads to the resulting “pseudo-morph” of positive temperature dependence of grain size after “recrystallization”.

To avoid the influence of this isochronal annealing issue and to obtain a true annealing temperature dependence of recrystallized grain size, kinetics of recrystallization process could be characterized first, and the time just enough for the completion of recrystallization at each annealing temperature could thus be determined, which could then be used for non-isochronal annealing at different temperatures to obtain grain size immediately after the completion of recrystallization process. This non-isochronal annealing may remove the effect of grain growth, and obtain the intrinsic annealing temperature dependence of recrystallized grain size.

3. Experimental confirmation
To confirm the negative temperature dependence of recrystallized grain size unveiled from the above analytical formulation, cold rolled (CR) high purity copper (99.97 wt%) after equal channel angular pressing (ECAP) was used.

![EBSD image](image.png)

**Figure 2.** An EBSD image of the cross section (a) and its grain size distribution (b) of high purity (99.97 wt%) copper pre-deformed by ECAP+CR.

Hot rolled high purity copper, with initial heat treatment at 873 K (600 °C) for 1 h to achieve a homogenous microstructure with an average grain size of ~100 μm, is used in this study. Billets with size of 32 × 32 × 160 mm are processed by ECAP at room temperature with a die angle of 90° for 8
passes using route B C. The sample is then cold rolled (CR) at room temperature to a thickness reduction of ~75%. After pre-deformation through ECAP+CR, annealing is conducted at temperatures ranging from 373 K (100 °C) to 573 K (300 °C), and for times ranging from 3 to 48000 s. Vickers microhardness is measured at room temperature with a load of 100 g for 10 s. More than 20 random indentations were made to obtain a representative bulk hardness value. Electron back-scattering diffraction (EBSD) technique is used to characterize microstructural evolution on the cross-sections of the ECAP+CR samples during annealing treatment. Figure. 2 shows the EBSD microstructure of the sample after cold rolling (Figure. 2(a)) and its grain size distribution (Figure. 2(b)). The HAGB fraction of the materials is ~68%.

The recrystallization kinetics of the ECAP+CR samples upon annealing is characterized by the microhardness variations versus annealing time for different isothermal annealing temperatures, as shown in Figure. 3, which indicates when the annealing temperature increases from 473 K (200 °C) to 573 K (300 °C), the time for the completion of the recrystallization is reduced from 25 mins to 35 s.

![Figure 3. Variation of the microhardness vs. time at different annealing temperatures for ECAP+CR samples.](image)

Figure 4(a, b) show the microstructure of the fully (~95% volume fraction) recrystallized specimens annealed at 473 K (200 °C) and 573 K (300 °C) respectively. The recrystallized grain size after 473 K/25 mins annealing ranges from 1 to 14 µm with an average grain size of 3.0 ± 0.6 µm; while that after the 573 K/35 s annealing ranges from 1 to 7.5 µm with an average value of about 1.9 ± 0.5 µm.

The microstructures clearly show that with increasing annealing temperature, the microstructure becomes more homogeneous with smaller average grain size, which means that the recrystallized grain size has a negative dependence on the annealing temperature. Grain size data from specimen annealed at other temperatures also confirms this negative dependence, as shown in Figure. 4(c). It is clear from this figure, that the recrystallized grain size at ~95% completion of recrystallization decreases, even the distribution span of grain size at each annealing temperature also decreases, upon the increase of annealing temperature.
To compare these experimental results with the prediction of equation (6), grain size distribution in the as-deformed matrix is needed. It has been demonstrated that the grain size $d$ distribution after severe plastic deformation follows the log normal distribution [29, 30]

$$f(d; \mu, \sigma) = \frac{1}{d \sigma \sqrt{2\pi}} \exp \left[ -\frac{(\ln d - \mu)^2}{2\sigma^2} \right]$$

(7)

where the two distribution parameters $\mu$ and $\sigma$ are the mean and standard deviation of $\ln d$ respectively. The number fraction of grains with a diameter $\geq d_c$ ($d_c = 2r^*x_c$) is:

$$F_N = 1 - \int_0^{d_c} f(x; \mu, \sigma) dx = \frac{1}{2} - \frac{1}{2} \text{erf} \left( \frac{\ln d_c - \mu}{\sigma \sqrt{2}} \right)$$

(8)

On the other hand, from the experimental data, the number of grains in the recrystallized microstructure annealed at temperature $T$ is inversely proportional to its average grain size $D_T$, and the number of grains in the pre-deformed matrix is inversely proportional to its average grain size $d_{av}$. Thus the number fraction of grains in the pre-deformed matrix which transformed into recrystallized grains after annealing at temperature $T$ is:

$$F_{NT} = \left( \frac{d_{av}}{D_T} \right)^3$$

(9)

**Figure 4.** EBSD images after ~95% recrystallization of the specimens upon annealing at (a) 473 K (200 °C), 25 mins (b) 573 K (300 °C), 35 s, and (c) the dependence of the recrystallized grain size at 95% recrystallization (RX) on annealing temperature.
Combination of equations, (8) and (9) gives:

$$
\text{erf}\left(\frac{\ln d_c - \mu}{\sigma \sqrt{2}}\right) = 1 - 2 \left(\frac{d_m}{D_T}\right)^3
$$

$d_m$ can be calculated from Figure 2(b), together with $\mu = -0.538$ and $\sigma = 0.424$ for the lognormal distribution of grain size, and $D_T$ is given in Figure 4c. Thus $F_{NT}$ and $d_c$ for recrystallized microstructure annealed at temperature $T$ can be calculated according to equations (9) and (10). An experimental relation of $x_c$ ($x_c = d_c/(2r^*)$) and $T$ can thus be obtained and is shown in Figure 5 by the hollow circles. A partial of the $m=0.980$ curve from Fig. 1, which is analytical prediction from equation (6), is also shown in Figure 5. It can be seen that the data points from experiments fit fairly well the analytical prediction for $m=0.980$. The high value of $m$ ($= 0.980$), which yields good fitting between analytical prediction and experimental data, reflects the high catalyzing efficiency of the pre-existing HAGB on the forming of new embryo for recrystallization.

4. Conclusion

In summary, the catalyzing effect on nucleation of recrystallization from pre-existing grains with HAGB is analyzed, analogy to the foreign nucleus size effect in heterogeneous nucleation. Analytical formulation of effective nucleation site leads to a negative temperature dependence of recrystallized grain size, where a critical grain size $d_c$ pre-existing in the as-deformed matrix, is formulated to be negatively dependent on the annealing temperature $T$; Grains with diameter larger than this critical $d_c$ in the as-deformed matrix will act as effective nucleation site for recrystallization in the subsequent annealing at $T$. The higher the $T$, the smaller the $d_c$, and the higher the fraction of grains in the as-deformed matrix can act as effective nucleation sites, and thus smaller recrystallized grain size is formulated. Non-isochronal annealing, where annealing time is set just enough for the completion of recrystallization at different temperatures, is conducted on a high purity (99.97 wt. %) copper after
room temperature severe plastic deformation. Negative temperature dependence of recrystallized grain size is confirmed, where more homogeneous and smaller grains are obtained experimentally at higher annealing temperature. The good fitting between analytical prediction and experimental results unveils the intrinsic feature of the negative temperature dependence of recrystallized grain size.

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