



Recrystallization kinetics of ultrafine-grained Ni studied by dilatometry

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ABSTRACT

The release of excess volume upon recrystallization of ultrafine-grained Ni deformed by high-pressure torsion was measured with a high-precision difference-dilatometer employing constant heating rates in the range from 0.3 to 10 K min⁻¹. The kinetics of the recrystallization process was analyzed according to the Johnson–Mehl–Avrami–Kolmogorov theory adapted to the case of constant heating rates. An effective Avrami exponent of 2 and a value of 1.20 eV for the activation energy of recrystallization was determined. Analysis by the Kissinger method yielded the same result for the activation energy.

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1. Introduction

A high concentration of free volume is one of the characteristics of ultrafine-grained (UFG) and nanocrystalline materials and which influence their physical properties decisively. In most cases, free volume in these materials is characterized using indirect experimental methods such as differential scanning calorimetry (DSC) to determine the stored energy or by measuring the residual electrical resistivity. Only in a few, special cases the free volume associated with lattice defects has been studied directly and on an atomistic level, e.g., by transmission electron microscopy (TEM) [1]. The application of positron annihilation, which is also a specific and direct experimental technique to obtain information on free volume concentrations, is at the upper limit of its sensitivity range in the case of UFG materials due to saturation trapping of the positrons [2]. High-resolution difference dilatometry, however, is able to determine directly and specifically the absolute concentration of non-equilibrium excess volume even in high concentrations by measuring the irreversible macroscopic length change upon annealing [3,4]. Analyzing the time dependence of the equilibration process during defect annealing fundamental studies of the free volume kinetics are possible. In the following we report in detail on results of one characteristic process, the recrystallization and its kinetics in UFG-Ni.

The kinetics of recrystallization is often analyzed according to the Johnson–Mehl–Avrami–Kolmogorov theory (JMAK) [5–7], which was developed for the temperature dependence of isothermal transformation processes in solids. Later this theory was also adapted to the case of a non-isothermal annealing treatment, i.e., linear heating by Henderson [8]. In the present paper this adaptation was used to model the release of free volume in UFG-Ni during recrystallization upon linear heating with different heating rates. Additionally, the more frequently used and straightforward analysis according to Kissinger [9] was applied for the assessment of the activation energy of recrystallization.

2. Experimental

Billets of high purity nickel (99.99%) with a diameter of 30 mm and a height of 10 mm were severely plastically deformed in a high-pressure torsion (HPT) experiment by five revolutions applying a pressure of 2.2 GPa [10]. From these deformed disks prism-shaped specimens with dimensions of 3 mm × 3 mm × 7 mm were cut at a distance of about 12 mm from the center corresponding to a von Mises equivalent strain of $\epsilon \approx 30$.

For dilatometry a high-precision vertical differential dilatometer (Linseis L75VD500LT) was used equipped with two push rods allowing for two independent and simultaneous length change measurements. Each UFG-Ni specimen was measured together with a well annealed and recrystallized Ni-specimen. The difference curve between the two relative length change curves shows an irreversible shrinkage of the UFG sample due to its release of free volume. The respective difference curves for different heating rates are the master curves for further analysis.

The specimens were heated with constant heating rates in the temperature range from 273 to 673 K employing heating rates in the range 0.3–10 K min⁻¹. All measurements were performed under Ar gas flow. A variable temperature lag inherent to the experimental setup upon varying heating rates has been corrected after calibration using the heating rate-independent Curie temperature T_C of the ferro-

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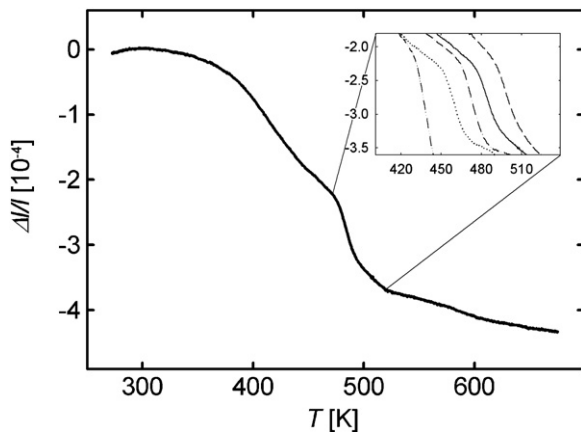


Fig. 1. Relative length changes $\Delta l/l$ as determined by dilatometry on HPT deformed Ni with a constant heating rate of 6 K min^{-1} (solid line). The insert shows recrystallization processes for all curves in detail measured applying heating rates of 0.3, 1.5, 3, 6 and 10 K min^{-1} (from left to right). The origin of the recrystallization process as a thermally activated process is manifested in the shift of the curves to higher temperatures for increasing heating rates.

to paramagnetic phase transition of a high-purity Ni specimen. For details see [3].

The microstructure and the grain size distribution at characteristic temperatures were determined at room temperature using scanning electron microscopy (SEM) in order to identify the recrystallization process.

3. Results

Fig. 1 shows the irreversible annealing of free volume in a difference curve of relative length changes for the whole temperature range investigated. The length change curve determined at a heating rate of 6 K min^{-1} shows two main processes. One broad, first process ranging from about 350 to 470 K and one sharp process around 500 K. The first low temperature process is due to annealing of vacancies and is described in detail elsewhere [4].

Here we want to concentrate on the second process which is entirely due to recrystallization as observed and confirmed by scanning electron microscopy on specimens taken at different stages during the annealing. For the sake of clarity the insert in **Fig. 1** shows only the recrystallization part of the other annealing curves with varying heating rates.

With increasing heating rate, the recrystallization process is shifted to higher temperatures as shown in the insert of **Fig. 1**. This shift is typical of a thermally activated process and along with the shape of the curve it can be used for the analysis of the recrystallization kinetics. The classical isothermal approach according to Johnson and Mehl [5], Avrami [6], Kolmogorov [7] can be written as:

$$f_A(t) = 1 - \exp[-(Kt)^n] \quad (1)$$

where $f_A(t)$ is the fraction of recrystallized material at the time t and the temperature T and with n and $K = K(T)$ the Avrami exponent and the temperature dependent rate constant, respectively. The time derivative of Eq. (1) is given by:

$$\frac{df_A}{dt} = n(1 - f_A)[-\ln(1 - f_A)]^{(n-1)/n} K(T) \quad (2)$$

For the temperature dependence of the rate constant $K(T)$ an Arrhenius-type behavior is assumed:

$$K(T) = K_0 \exp\left(-\frac{Q}{k_B T}\right) \quad (3)$$

with a pre-exponential factor K_0 , an activation energy Q and the Boltzmann constant k_B . In the general case the temperature T can be a function of time, e.g., linear heating with a heating rate

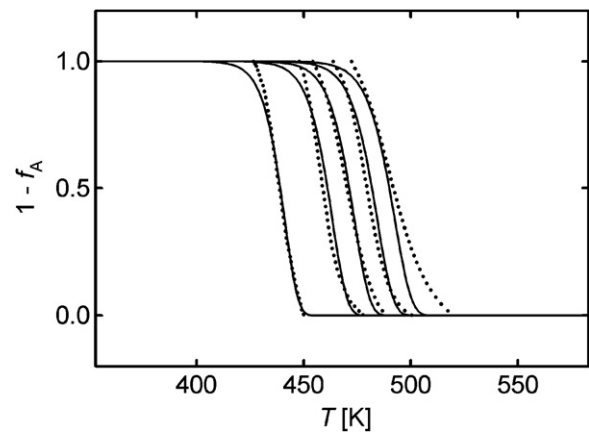


Fig. 2. Heating rate dependent shifts of the recrystallization stages (···) and non-isothermal JMAK kinetics based modeling by least-square fit (—). Heating rates from the left to the right are: 0.3, 1.5, 3, 6 and 10 K min^{-1} .

$\phi = dT/dt$, and Eq. (2) can directly be integrated [8] yielding the non-isothermal solution [11]:

$$f_A(t) = 1 - \exp\left[-\left(\frac{K_0 Q}{k_B \phi} \int_x^\infty \frac{\exp(-x)}{x^2} dx\right)^n\right] \quad (4)$$

$$\text{with } x = \frac{Q}{k_B T(t)} \quad (5)$$

This expression was used in the present study for modeling the recrystallization stage in HPT-Ni.

Five length change curves measured with different heating rates were fitted to the same parameter set applying the method of least squares with the activation energy Q , the frequency factor K_0 and the Avrami exponent n as fitting parameters. As a result values of $Q = 1.20 \text{ eV}$, $K_0 = 1.92 \times 10^{10} \text{ s}^{-1}$ and an overall Avrami exponent $n = 2.17$ were determined for the recrystallization process in UFG-Ni. The results are given in **Fig. 2** where the normalized experimental recrystallization data are shown as dotted lines together with the fitted curves as solid lines.

According to Kissinger [9] thermally activated reactions as function of linear heating can also be analyzed from the variation of the temperature of the maximum transformation rate T_{\max} and the heating rate ϕ applying the following equation:

$$\frac{\phi}{T_{\max}^2} = A \cdot \exp\left(-\frac{Q}{k_B T_{\max}}\right) \quad (6)$$

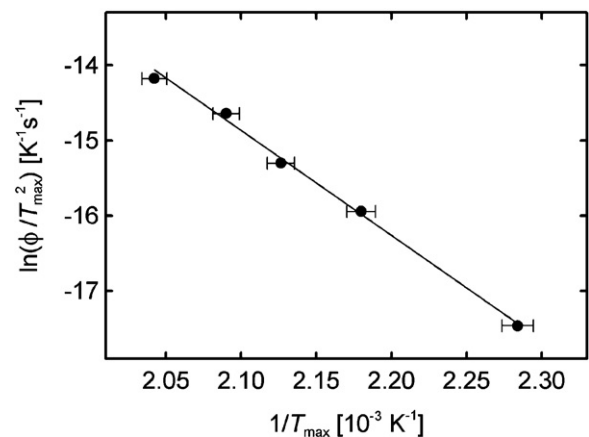


Fig. 3. Kissinger analysis of the temperatures T_{\max} of the maximum length change rate applying the heating rates ϕ .

Table 1

The activation energy, Q , and the Avrami exponent, n , for recrystallization of pure Ni processed by high-pressure torsion (HPT) or cold working analyzed with different experimental methods according to the Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory or according to Kissinger. JMAK analysis based on $f_A(t) = 1 - \exp[-(Kt)^n]$ is marked by 1 and results based on $f_A(t) = 1 - \exp(-Kt^n)$ is marked by 2.

Processing	Exp. method	Analysis	Q [eV]	n	Reference
HPT	Dilatometry	JMAK ¹	1.20	2.17	Present work
HPT	Dilatometry	Kissinger	1.20		Present work
HPT	DSC	Kissinger	0.95		Setman et al. [12]
Cold worked	TEM	JMAK ²	1.22–1.30	1.38	Detert and Dressler [13]
Cold rolled	Hardness, SEM	JMAK ²		1.3–2.1	Liao et al. [14]

For the present case, T_{\max} is the temperature where the length change rate $d(\Delta l/l_0)/dt$, i.e., the derivative of the length change curve, shows an extremum. Then Q gives the activation energy of the process and A is a pre-exponential factor, which is correlated to the pre-exponential factor K_0 of Eq. (3) by the expression $A = (k_B \cdot K_0)/Q$. Fig. 3 represents the data for the recrystallization process in UFG-Ni investigated in the so-called Kissinger-plot. The data are well described by the Kissinger analysis and a value of $Q = 1.20 \pm 0.04$ eV for the activation energy is determined. From the pre-exponential factor A a value of $K_0 = (2.4 \pm 0.7) \times 10^{10}$ was derived. Both values are in excellent agreement with the values derived from the non-isothermal JMAK analysis.

4. Discussion

The present results of the recrystallization kinetics of UFG-Ni are now compared to data of the literature of cold worked or HPT deformed Ni. The data are summarized in Table 1. It should be noted that for the JMAK analysis the rate constant K is either defined according to $f_A(t) = 1 - \exp(-Kt^n)$ or according to $f_A(t) = 1 - \exp[-(Kt)^n]$. The results presented in Table 1 have been marked accordingly. The different definitions have to be taken into account when comparing the activation energy derived from the temperature dependence of $K(T)$.

Fitting the recrystallization in HPT nickel with the non-isothermal JMAK-theory based formula revealed a value for the activation energy of 1.20 eV which is in good accordance with the value determined by the Kissinger analysis of the present work. Comparing this result to literature data, the value for the activation energy is somewhat higher than that obtained from DSC for HPT-Ni of 0.95 eV [12] and that derived for the cold worked Ni [13] taking into account the definition of $K(T)$. The present data may also be compared to available data on UFG-Cu prepared by severe plastic deformation. Scaling the value of the activation energy for Ni with the melting temperature the value corresponds to 0.92 eV in the case of Cu. This value is in fair agreement with recent recrystallization studies on UFG-Cu studied by TEM [15], X-ray diffraction and TEM [16] and DSC [12].

The Avrami exponent, n , of around 2 is lower than the JMAK model predicts for nucleation and homogeneous growth ($n = 4$) or homogeneous growth of pre-existing nuclei without a nucleation

process ($n = 3$). However, lower values of n seem to be typical of metals after cold working or severe plastic deformation [14,15,17].

5. Conclusion

Recrystallization of ultrafine-grained Ni deformed by high-pressure torsion has been analyzed with a high-precision difference dilatometer by measuring the irreversible release of excess volume. The kinetics of the recrystallization process was modeled according to the Johnson–Mehl–Avrami–Kolmogorov theory adapted to the case of constant heating rates. An effective Avrami exponent of around 2 and a value of 1.20 eV for the activation energy of recrystallization was determined.

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