Influence of grain boundary energy on the grain size evolution in nanocrystalline materials

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Abstract. A study for the effect of grain boundary (GB) energy on the evolution of grain size in nanocrystalline (NC) materials was given. Incorporating an empirical relation for GB energy with a generalized parabolic law, numerically, an evolution of grain size was investigated. Subsequently, a combination of grain-size dependent GB energy with the generalized parabolic growth law allows an analytic description for the average grain size as a function of annealing time. Satisfactory agreement of the model predictions with the experimental results obtained from grain growth occurring in NC Ni-P and Ni-W alloys and oxygen-doped nickel was achieved.

1. Introduction
The thermal stability of nanocrystalline (NC) materials is an important property for industrial applications. So far, two strategies have been devised to improve the thermal stability of NC materials, i.e., a kinetic one, in which the grain boundary (GB) migration is controlled by a retarding force from solute or precipitates [1-3], or a thermodynamic one [4-6], in which the GB energy $\sigma_b$ as the driving force for the GB migration, is suppressed.

As for GB migration driven by the GB energy, the so-called parabolic growth law has been proposed and applied extensively [1-3]. Recently, Michels et al. [2] introduced a grain-size-dependent drag term to stabilize the grain size of the NC materials. Noticeably, an important assumption (i.e., constant $\sigma_b$) prevails in the above kinetic models. According to Gibbs adsorption theorem, $\sigma_b$ reduces with addition of solute atoms [7]. Kirchheim and co-workers [5, 6] derived additional analytical models recently. Above all, GB energy cannot be considered as constant covering throughout the grain growth for nano-sized alloy. Liu et al. [8] attempted to introduce variable activation energy $Q$ and $\sigma_b$ into the parabolic growth law. Unfortunately, from the thermodynamic aspect, a physically sounded description for the effect of GB energy on the evolution of grain size with time is not available yet.

In this work, we will incorporate the GB energy, as a function of solute segregation and grain size, into the generalized parabolic growth law, in order to analyze the effect of GB energy on the grain size evolution with time in NC materials.

2. Incorporation of the grain-size dependent GB energy into the parabolic growth law
A simple power law from Burke and Turnbull [1] of the type applicable to grain growth in highly pure and coarse-grained polycrystalline materials gives,

$$\frac{dD}{dt} = M\sigma_b/D \Rightarrow D^2 - D_0^2 = 2M\sigma_b t$$

(1)
with $M$ as the GB mobility and $D_0$ the initial mean grain size at annealing time $t=0$.

For nanosized alloy with a large fraction of interfacial volume, the decrease of GB energy caused by solute segregation can not be neglected. According to a thermodynamic treatment of Weissmüller [4] and Kirchheim [5], $\sigma_0$ reduces with solute segregation,

$$\sigma_b = \sigma_0 - \Gamma_0 \left( RT \ln \left( x_0 - 3\Gamma_0 V_m / D \right) + \Delta H_{seg} \right)$$

where $\sigma_0$ is the GB energy for pure solvent, $x_0$ the average concentration, $\Gamma_0$ the saturated solute excess, $V_m$ the molar volume of the alloy and $\Delta H_{seg}$ the segregation enthalpy. $\Gamma_b$ in Eq.(2) is the solute excess at GBs, which can be expressed as [9, 10]

$$\Gamma_b = \delta \left( \rho_b x_B^{GB} - \rho_\alpha x_\alpha^{GB} \right) \approx \delta \rho x_B^{GB}$$

with $\rho_b$ and $\rho_\alpha$ as the density, and $x_B^{GB}$ and $x_\alpha^{GB}$ as the concentration, of the GB and the matrix, and $\delta$ ($\approx 0.8 \text{ nm}$) as the GB thickness. Generally, a relation between the solute concentration in the matrix and in the bulk is given for a binary system as [9, 10]

$$f x_B^{GB} + (1-f) x_\alpha^{GB} = x_0^{GB}$$

Suppose that the volume fraction of GBs follows,

$$f = \left( (D + \delta)^3 - D^3 \right) / D^3 \approx 3\delta / D$$

The equilibrium GB segregation of solute can be described using Mclean’s equation [11]

$$\frac{x_B^{GB} - x_0^{GB}}{x_0^{GB} - x_\alpha^{GB}} = \frac{\exp \left( \Delta H_{seg} / RT \right)}{1 - \exp \left( \Delta H_{seg} / RT \right)}$$

with $x_B^{GB}$ as the saturation level for $x_B^{GB}$ i.e., the fraction of GB monolayer available for segregated atoms at saturation. Combining Eqs. (3-6), the grain size dependent solute excess $\Gamma_b$ can be rewritten as,

$$\Gamma_b = x_0 - \left( (D + \delta)^3 - D^3 \right) / D^3 \times \Gamma_\alpha / \delta \rho \exp \left( \Delta H_{seg} / RT \right)$$

with $\Gamma_{00} = \delta \rho x_B^{GB0}$ as the saturated solute excess. $\Gamma_b$ infinitely approaches $\Gamma_{00}$ with grain growth.

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**Figure 1.** (a) grain size and GB energy vs. annealing time; (b) GB energy and excess vs. grain size using Eqs.(1,2,7) and typical values of $\sigma_0=0.8 \text{ J/m}^2$, $\Delta H_{seg}=50 \text{ kJ/m}^2$, $\Gamma_{00}=2.0 \times 10^{-5} \text{ mol/m}^2$, $M=10^{-19} \text{ m}^4/\text{Js}$. 

Up to now, combining Eqs. (1), (2) and (7) gives an evolution of the average grain size with the annealing time (Fig.1) [10]. As shown in Fig. 1a, the grain size is increased rapidly (i.e., within a relative short time duration) and is then stabilized. This phenomenon has been observed in a lot of experiments [12].

As is well known, grain growth in a polycrystal with solute segregation is accompanied with a competitive process between the energy lost due to a decrease of GB area and the energy gain due to a transfer of solute atoms into the lattice caused by the decreased segregation sites. That is to say, $\Gamma_b$ increases up to its saturated value $\Gamma_{00}$ with grain growth (Fig.1b, the solid line), whereas, the GB energy reduces from the value of pure solvent $\sigma_0$ (the dashed lines in Fig.1a). As solute segregation is
strengthened upon grain growth, a metastable equilibrium will be established, corresponding to a thermodynamic zero $\sigma_b$.  

3. Analytic model for GB energy and grain size evolution

From Eqs. (1-7), the evolution of the average grain size can be given only by an iterated interpolation method. Furthermore, four adjusted parameters (i.e., $\sigma_0$, $\Delta H_{\text{seg}}$, $\Gamma_{b0}$ and $M$) will alleviate the validity of the procedure. If possible, a simple analytic relationship is preferred.

A reduction of GB energy can be illustrated by a simple model proposed by Krill [13]. Thus a useful expression for $\sigma_b$ is derived as [13],

$$\sigma_b = \sigma_0 - \Delta H_{\text{seg}} \Gamma_b$$  \hspace{1cm} (8)

Inserting typical values of $\Gamma_b=2.0\times10^{-5}\text{ mol/m}^2$ and $\Delta H_{\text{seg}}=50\text{ kJ/m}^2$ into Eq.(8), we obtain $\sigma_b\approx0$ when $\sigma_0=1\text{ J/m}^2$. $\sigma_b$ reduces at a linear rate with a slope equal to the enthalpy change $\Delta H_{\text{seg}}$ (Fig.2). Using the typical values in Section 2, $\sigma_0$ could also be calculated by Eqs. (2) and (7), as shown in Fig.2. It is shown that the solid line is almost overlapped with the dashed one within a $\Gamma_b$ range marked as 2, although there are relatively large differences within regions marked by 1 and 3. This could be attributed to the ignored entropic contributions in the system [13]. As for a physically realistic system, approximately, $\sigma_b$ following Eq. (8) could be considered as a substitution of Eq. (2).

Assuming the GB concentration as $x_{GB} = \xi x_a$ with $\xi$ as the distribution coefficient, for NC systems with strong segregation tendency, i.e., $\xi \gg 1$ [2], combining Eqs. (3-5) gives

$$x_{GB} - x_a = x_{GB} \xi - 1/\xi = x_a (\xi - 1)[1 + (\xi - 1)f/(1 + f)]$$  \hspace{1cm} (9)

![GB energy vs. solute excess. The solid and dashed lines are calculated by Eqs. (2,7) and Eq.(8), respectively. It is noted that the two lines are almost overlapped within 2.](image)

Further combining Eq. (3) reduces to

$$\Gamma_b = \delta \rho (x_{GB} - x_a) = x_0 \rho D/3(1 + 3\delta/D)$$  \hspace{1cm} (10)

Integrating Eqs. (8) and (10) gives,

$$\sigma_b = \sigma_0 - [\Delta H_{\text{seg}} x_a \rho (D + 3\delta)]/3$$  \hspace{1cm} (11)

Until now, a simplified model for the grain size dependent GB energy is obtained. Substituting Eq. (11) into (1) leads to,

$$\frac{\sigma_1}{\sigma_2} \frac{\ln \left( \frac{\sigma_1 - \sigma_0 D}{\sigma_1 - \sigma_2 D_0} \right)}{\sigma_1 - \sigma_2 D_0} + \frac{D - D_0}{\sigma_2} = -Mt$$  \hspace{1cm} (12)
where \( \sigma_1 = \sigma_0 - \Delta H_{\text{seg}} x_0 \delta \rho \) and \( \sigma_2 = \Delta H_{\text{seg}} x_0 \rho / 3 \). Eq. (12) shows that the grain growth kinetics is correlated with thermodynamics. It can be inferred from Eq. (12) that the grain growth is an integrative one coupling the effects due to thermodynamics and kinetics.

4. Comparison with experimental results

4.1. Grain growth in electrodeposited NC Ni-P and Ni-W alloys

The stability of Ni-P alloys with P-content from 3 to 13 at.\% [9] at an annealing temperature of 573 K has been shown in Fig.3 [9]. As grain growth proceeds, GB segregation leads to a metastable thermodynamic equilibrium corresponding to \( \sigma_b = 0 \) [5, 6]. From Eq. (11),

\[
D^* = 3\sigma_0 / \left( \Delta H_{\text{seg}} \rho x_0 \right) - 3\delta
\]

Simultaneous fits of Eq. (13) to the average grain sizes are shown in Fig.3 (the solid line). Note that \( \sigma_0 \) is estimated as 0.87 J/m\(^2\) [14]. The segregation enthalpy \( \Delta H_{\text{seg}} \) is fitted to be 36 kJ/mol, which is close to an estimated value using \( \Delta H_{\text{seg}} = R T \ln (x_{\text{opt}} / 10 \pm 6) \) kJ/mol with \( x_{\text{opt}} \) as the terminal solute solubility (\( x_{\text{opt}} = 0.32 \) at.\%P in Ni at 1143 K) [5]. As shown in Fig.3, a decrease of grain size is predicted by Eq. (13) as the increase of P content, which is analogous to the calculation of Liu [6] using Eq. (2). However, less fitting parameters (only \( \Delta H_{\text{seg}} \)) are employed, the validity of this fitting are enhanced.

![Figure 3. Relationship between grain size and solute content of Ni-P [5] and Ni-W [14] alloys.](image)

Different from Ni-P system, the electrodeposited Ni-W system exhibits significant solute solubility in the crystalline lattice [14]. On this basis, a weak tendency for GB segregation is expected in Ni-W. Suppose a threshold value of \( C \) below which grain growth is effectively suppressed, the stop of grain growth in Ni-W thus corresponds not to \( \sigma_b = 0 \), but \( \sigma_b = C \times \sigma_0 \). Then Eq. (11) is rewritten as

\[
D^* = 3(1 - C)\sigma_0 / \left( \Delta H_{\text{seg}} \rho x_0 \right) - 3\delta
\]

The fits of Eq. (14) to the average grain sizes are shown in Fig.3 (the dashed line). The parameters \( C = 0.4 \) and \( \Delta H_{\text{seg}} = 5.6 \text{kJ/mol} \) are close to the values from computer simulations [14]. Note that a reduction of about 60% from 0.87 J/m\(^2\) (for pure Ni) [14] is shown. This reduction in GB energy is significant and should substantially stabilize the NC structure. However, the thermodynamical ideal stability (i.e., \( \sigma_b = 0 \)) has apparently not been achieved because of the low \( \Delta H_{\text{seg}} (5.6 \text{kJ/mol}) \).

This further evidences that the so-called thermodynamical conclusion that the suppressing growth corresponds to zero GB energy can only occur in alloys with strong segregation tendency.
4.2. The evolution of grain size in NC nickel doped nickel oxide

According to Ref. [12], at a temperature of 673 K, the effect of GB nickel oxide on thermal stability of NC-Nickel was studied using samples with oxygen contents between 956 and 6039 wt. ppm. The current work could give good fits to the experimental data (Fig. 4). However, the generalized parabolic growth model cannot be brought into agreement. The parameters are listed in Table 1. As shown in Fig. 4 and Table 1, a decrease of $\Delta H_{\text{seg}}$ from 66 and 76 to 37 kJ/mol has to be performed to describe well the data point with oxygen content from 956 and 1805 to 6039 ppm. Since $\Delta H_{\text{seg}}$ can be defined as a difference in energy between a solute atom in the grain interior and in the GBs [11], the high value (66 and 76 kJ/mol) is expected in the dilute limit which is very close to the calculated value of Ni-P with the similar systems chemically and the low value (37 kJ/mol) corresponds to the substantially increased solute content (6039 ppm) [14].

The above analysis does show that grain growth is quite influenced by solute segregation to GBs.

5. Discussion

Either Eqs. (1, 2 and 7) or Eq. (12) could predict a stabilized grain size after a fast increase within a relatively short time duration. As is evidence by a detailed comparison between Ni-P and Ni-W data, thermodynamically, the solute segregation to GBs stabilizes the NC structure. This phenomenon strongly suggests the GB energy reduction due to GB segregation is a reasonable mechanism.

In order to analysis the effect of GB energy on the grain growth, differentiation of Eq. (11) over $t$, then combining Eqs. (1) and (11) gives,

$$-\sigma_1 \ln \sigma_0 / \sigma_0 + \sigma_0 - \sigma_0 = \sigma_0^2 Mt$$

(15)

| Parameter /wt.% | 956ppm | 1805ppm | 6039ppm |
|-----------------|---------|---------|---------|
| Mobility (m$^4$/J s) | $M$ | $2.2 \times 10^{-16}$ | $3 \times 10^{-17}$ | $1.4 \times 10^{-18}$ |
| GB energy (J/m$^2$) | $\sigma_0$ | 0.87 | 0.87 | 0.87 |
| Enthalpy change (KJ/mol) | $\Delta H_{\text{seg}}$ | 66 | 76 | 37 |
| Error | % | 2.3 | 2.19 | 3.7 |
Using the parameters listed in Table 1, the calculation of Eq. (15) is shown in Fig.5. The GB energy decreases with the grain growth, but with annealing time, it can only approaches infinitely zero (Fig.5). Thermodynamically, ‘zero’ value should be considered as an ideally limitation for $\sigma_b$.

Figure 5. The GB energy vs. annealing time with the O-contents of 956, 1805 and 6039 wt. It is shown that GB energy infinitely approaches zero with annealing time.

In connection with Fig.5 and Table 1, the stagnated time of grain growth increases with the increase of solute concentration, meanwhile, the GB mobility $M$ reduces. It is assumed that $M$ has an Arrhenius relation with temperature [8, 10]

$$M = M_0 \exp(-Q/(RT))$$

with $R$ as the gas constant and $M_0$ a constant. From Fig.5, it can be implied that increasing solute concentration reduces $M$ i.e., enhances $Q$. Since the consumed annealing time in the whole kinetic process of grain growth should be determined by GB mobility, which is described through $Q$ of atom diffusion [10], longer annealing is needed for the stagnation of grain growth (Fig.5).

6. Conclusions

The effect of GB energy on the evolution of grain size in NC materials was studied detailedly. Incorporating an empirical relation for GB energy with a generalized parabolic law, numerically, an evolution of grain size was investigated. A combination of grain-size dependent GB energy with the generalized parabolic law allows an analytic model for the evolution of the average grain size as a function of annealing time. Satisfactory agreement of the model prediction with the experimental results obtained from grain growth occurring in NC Ni-P and Ni-W alloys and oxygen-doped nickel was achieved. The inhibition of grain growth can be attributed to the elimination of driving force for solute segregation, whereas, the consumed annealing time before the stop of grain growth should be determined by GB mobility.

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References

[1] Burke J E, Turnbull D 1952 Recrystallization and grain growth. Prog. Met. Phys. 3 220.

[2] Michels A, Krill C E, Ehrhardt H, Birringer R, Wu D T 1999 Modelling the influence of grain-size-dependent solute drag on the kinetics of grain growth in nanocrystalline materials. Acta Mater. 47 2143.

[3] Rabkin E 2000 On the grain size dependent solute and particle drag. Scripta Mater. 42 1199.

[4] Weissmüller J 1993 Alloy effects in nanostructures. Nanostructured Mater. 3 261.

[5] Kirchheim R 2002 Grain coarsening inhibited by solute segregation. Acta Mater. 50 413.

[6] Liu F, Kirchheim R 2004 Nano-scale grain growth inhibited by reducing grain boundary energy through solute segregation. J. Cryst. Growth. 264 385.

[7] Gibbs J W Trans Conn Acad III 108 (1876); J. W. Gibbs: Trans Conn Acad III 343 (1878); JW Gibbs: The Collected Works of J. W. Gibbs vol. 1, Longmans, Green and Co, New York (1928) pp. 55–354.

[8] Liu F, Kirchheim R 2004 Comparison between kinetic and thermodynamic effects on grain growth. Thin Solid Films. 466 108.

[9] Färber B, Cadel E, Menand A, Schmitz G, Kirchheim R 2000 Phosphorus segregation in nanocrystalline Ni–3.6 at.% P alloy investigated with the tomographic atom probe (TAP). Acta Mater. 48 789.

[10] Chen Z, Liu F, Yang W, Wang H F, Yang G C, Zhou Y H Influence of grain boundary energy on the grain size evolution in nanocrystalline materials. J all. Compd.: 10. 1016 / j. jallcom. 2008. 08. 040.

[11] D. Mclean 1957 Grain Boundaries in Metals, Oxford University Press, Oxford.

[12] Natter H, Löffler M S, Krill C E, Hempelmann R 2001 Crystallite growth of nanocrystalline transition metals studied in situ by high temperature synchrotron X-ray diffraction. Scr. Mater. 44 2321.

[13] Krill C E, Ehrhardt H, Birringer R 2005 Thermodynamic stabilization of nanocrystallinity. Z. Metallkd. 96 1134.

[14] Detor A J, Schuh C A 2007 Grain boundary segregation, chemical ordering and stability of nanocrystalline alloys: Atomistic computer simulations in the Ni–W system. Acta Mater. 55 4221.