Phase-field model with plastic flow for grain-growth in nanocrystalline material

Ingo Steinbach, Xiaoyan Song, Alexander Hartmaier

► To cite this version:

Ingo Steinbach, Xiaoyan Song, Alexander Hartmaier. Phase-field model with plastic flow for grain-growth in nanocrystalline material. Philosophical Magazine, 2010, 90 (01-04), pp.485-499. 10.1080/14786430903074763 . hal-00556064

HAL Id: hal-00556064

<https://hal.science/hal-00556064>

Submitted on 15 Jan 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Phase-field model with plastic flow for grain-growth in nanocrystalline material

Journal:	<i>Philosophical Magazine & Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-08-Nov-0424.R1
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	27-Apr-2009
Complete List of Authors:	Steinbach, Ingo; Ruhr-University Bochum, Interdisciplinary Centre for Advanced Materials Simulation (ICAMS) Song, Xiaoyan; Beijing University of Technology, School of Materials Science and Engineering Hartmaier, Alexander; Ruhr-University Bochum, Interdisciplinary Centre for Advanced Materials Simulation (ICAMS)
Keywords:	computational mechanics, grain boundary structure, grain growth, nanograined structures, plasticity, simulation
Keywords (user supplied):	phase-field

RESEARCH ARTICLE

Phase-field model with plastic flow for grain-growth in nanocrystalline material

Ingo Steinbach^{a*}, Xiaoyan Song^b, Alexander Hartmaier^a

^a*Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr-University Bochum, Germany;*

^b*School of Materials Science and Engineering, Beijing University of Technology, China*

(November 2008)

A phase-field model is presented which considers the accumulation of structural defects in grain boundaries by an isotropic eigenstrain associated with the grain boundaries. It is demonstrated that the elastic energy caused by dilatation of the grain boundary with respect to the bulk crystal contributes largely to the grain boundary energy. The sign of this contribution can be both positive and negative dependent on the local stress state in the grain boundary. Self diffusion of atoms is taken into account to relax the stress caused by the dilatation of the grain boundary. Application of the model to discontinuous grain growth in pure nanocrystalline Cobalt material is presented. Linear grain growth is found in the nanocrystalline state which is explained by the interpretation of grain boundary motion as a diffusive process defining an upper limit of the grain boundary velocity independent of the grain boundary curvature but dependent on temperature. The transition to regular grain growth at a critical temperature, as observed experimentally, is explained by the drop of mean grain boundary velocity during coarsening of the nanograin structure below the maximum velocity.

Keywords: Phase-field, grain growth, nanocrystalline material

1. Introduction

It is known that mechanical and functional properties of crystalline materials strongly depend on the grain structure being even more important in the nanocrystalline state. These properties may be greatly weakened when nanograin growth sets in and the grain structure evolves into a polycrystalline structure. On the one hand it is very important to understand the nanograin growth behavior in order to control the thermal stability of the nanograin structure over a useful interval of temperature and/or time to retain the attractive properties of the nanomaterials. On the other hand, the study of grain growth in nanocrystalline material, where the volume associated with the grain boundary is a large fraction of the total volume, will give new insight in nature and properties of grain boundaries in general. Studies on the grain growth behavior of nanocrystalline materials have been well progressed in recent years by a variety of approaches, including experimental techniques such as TEM [1, 2] and EBSD [3], DSC [4, 5], X-ray diffraction [6, 7], and Mössbauer spectroscopy [8], theoretical models [9–13], and computer simulations such as Monte-Carlo [14] and molecular dynamics simulations [15]. It has been found that grains grow very slowly at low homologous temperatures in

*Corresponding author. Email: ingo.steinbach@rub.de

the nanocrystalline sample while rapidly above a certain temperature [1–3, 16]. In the present work a phase-field model is presented which explicitly takes the dilatation of the grain boundary area by the accumulation of structural defects into account. This will lead to a long range interaction between the defects through the stress field in the material, similar to the long range interaction of precipitates in materials with crystalline mismatch, as described by the classic Khachaturyan theory of micro elasticity [17]. In this theory it is demonstrated how the morphology of the precipitates in solids is controlled by the elastic energy which tends to a minimum. In the same way a evolution of a grain structure with dilatation of the grain boundary will be controlled by elastic interactions. Now we may ask ourselves which volume to address to a grain boundary. Figure 1 illustrates two idealized views: On the left hand side the grain structure is simply divided into two volumes, bulk and grain boundary volume. In this picture, however, we make no attempt to figure out the atomic order in this area. On the right hand side TEM pictures of a tilt grain boundary are displayed (from [18]) that show clearly that the atomic positions in both crystals are almost undisturbed at the grain boundary which appears sharp. Nevertheless even this special grain boundary shows a finite area of distorted atomic structure which is associated with an excess volume. There are stresses and distortions of the crystalline lattice reaching out in the grain volume as well as dislocations. Most grain boundaries have a more complex structure than the displayed tilt grain boundary. It will also depend on the process of assembly. In the following we will adopt the pragmatic view that the grain boundary can be associated with a finite width and a given excess volume where defects are accumulated. This accumulation in nanomaterials can lead to an expansion of up to 20% with respect to a single crystal [19]. During grain growth we shall assume that the defects move with the grain boundary and consequently the mechanical equilibrium in the grain structure will change. In order to relax elastic distortion self diffusion of atoms will be taken into account which leads to a simplified form of plastic flow. **An alternative view on the role of void formation or annihilation is presented by Estrin et al. [20, 21]. They discuss the thermodynamic ballance of voids in crystalline materials and the necessity of releasing voids into the bulk material due to the reduction of grain boundary area during grain growth. This increases the free energy of the system and thereby hinders grain growth. The present model adds a mechanistic view to these considerations. Another aspect is triple junction drag that is discussed to explain anomalies in nano grain growth [22]. We do not contradict these explanations and there will be other effects of importance like impurity drag and grain rotation which are not considered here. The present model shall start from a situation as simple as possible.** The model is described in the next section where also implication of the model with respect to grain boundary energy and grain boundary width are discussed. In section 3, experimental observations of nano grain growth in nanocrystalline Co [12, 16] are described. Section 4 presents situations of the using the proposed phase-field model and conclusions are drawn with respect to the experimental observations.

2. Phase-field model

We start from the multi-phase-field (MPF) model with elastic strain [23–26], where each grain α is attributed by its individual phase-field $0 \leq \phi_\alpha(\vec{x}, t) \leq 1$. The governing field variables are the phase-fields, the elastic stain tensor $\bar{\epsilon}(\vec{x}, t)$ and density of the material $\rho(\vec{x}, t)$. In order to use the standard formalism of the phase-

field model the density is related to a concentration of mobile atoms $c(\vec{x}, t)$ with the average density ρ_0 and the matrix concentration c_0 of atoms to be considered immobile, $\rho(\vec{x}, t) = \rho_0(c_0 + c(\vec{x}, t))$. The void concentration c_{void} is then given $c_{void} = 1 - c_0 - c(\vec{x}, t)$. **For the simulations the actual value of c_0 is not of importance and the void concentration will adjust according to the expansion of the grain boundary. There must be, however, enough voids available to compensate for the excess volume.** As we will treat the model in the limit of small deformation, i.e. there will be considered no true dilatation of the numerical domain, the void concentration is, as the concentration of mobile atoms, a conserved quantity. This approximation is not well justified for the applied strain $> 10\%$, however, it is simply a technical restriction for the present state of development of the model and will be generalized in the future. There may be additional defects like dislocations, however in this simple model we only treat voids with a “volume” corresponding to one atom. The voids are assumed not to contribute to the chemical free energy of the pure substance, therefore the free energy F is simply given by the integral over the interfacial f^{intf} and elastic free energy density f^{elast}

$$F = \int_{\Omega} d^3x (f^{intf} + f^{elast}) \quad (1)$$

$$f^{intf} = \sum_{\alpha, \beta=1..N} \frac{4\sigma_{\alpha\beta}^0}{\eta^0} \left\{ -\frac{(\eta^0)^2}{\pi^2} \nabla \phi_{\alpha} \cdot \nabla \phi_{\beta} + \phi_{\alpha} \phi_{\beta} \right\} \quad (2)$$

$$f^{elast} = \frac{1}{2} \sum_{\alpha=1..N} \phi_{\alpha} \left\{ \left[\bar{\epsilon}_{\alpha} - \bar{\epsilon}_{\alpha}^*(\{\phi_{\beta}\}) - c\bar{\epsilon}_{\alpha}^1 \right] \bar{\bar{H}}_{\alpha} \left[\bar{\epsilon}_{\alpha} - \bar{\epsilon}_{\alpha}^*(\{\phi_{\beta}\}) - c\bar{\epsilon}_{\alpha}^1 \right] \right\} \quad (3)$$

$N = N(x)$ is the local number of grains (2 in a grain boundary, 3 in a triple line ...) and we have the sum constraint $\sum_{\alpha=1..N} \phi_{\alpha} = 1$. $\sigma_{\alpha\beta}^0$ is the stress free interface energy (see discussion below) that will be in general a function of the misorientation between the grains but is treated isotropic here. η^0 is the interface width related to the stress free interface energy. The elastic part of the free energy is defined from the total strain tensor $\bar{\epsilon}_{\alpha}$ in grain α , the eigenstrain of the grain boundary $\bar{\epsilon}_{\alpha}^*(\{\phi_{\beta}\})$ as a function of all phase-fields forming this grain boundary, the strain caused by density variations $\bar{\epsilon}_{\alpha}^1$ set linear in c and the elasticity or Hook's matrix $\bar{\bar{H}}_{\alpha}$. In the following we will treat the elastic constant equal for all grains and skip the respective indices. The elastic energy then becomes simply

$$f^{elast} = \frac{1}{2} \left\{ \left[\bar{\epsilon} - \bar{\epsilon}^*(\{\phi_{\beta}\}) - c\bar{\epsilon}^1 \right] \bar{\bar{H}} \left[\bar{\epsilon} - \bar{\epsilon}^*(\{\phi_{\beta}\}) - c\bar{\epsilon}^1 \right] \right\} \quad (4)$$

The most important part of the model is the grain boundary strain tensor $\bar{\epsilon}^*(\{\phi_{\beta}\})$. In general, it will depend on the misorientation between the grains, but for simplicity is taken as isotropic with the average expansion $\epsilon_0 = 1 - \frac{\rho_{gb}}{\rho_{bulk}}$, where ρ_{gb} is the mass density of the material in the grain boundary and ρ_{bulk} is the bulk density. $\bar{\bar{I}}$ is the identity tensor.

$$\bar{\epsilon}^*(\{\phi\}) = \frac{8\pi}{\eta^0} \sum_{\alpha,\beta=1..N, \alpha \neq \beta} \phi_\alpha \phi_\beta \epsilon_0 \bar{I} \quad (5)$$

The prefactor in (5) is chosen to normalize the average expansion of the grain boundary in the limit of small expansion, i.e. when the phase-field profile is close to the stress free solution. In triple and multiple junction the expansion increases slightly with respect to interfaces as we superpose the contributions from all interfaces. Application of eigenstrain associated with grain boundaries will cause elastic strains under the assumption that no relaxation of the free volume in the grain boundary is taking place.

The multi-phase-field equations, or grain boundary migration equations in this case, **are derived consistently with the principle of entropy maximization applying relaxational dynamics and decomposing the phase-change rates at multiple junctions into dual contributions only depending on pairs of phases or grains.** (see [24, 27])

$$\dot{\phi}_\alpha = -\frac{\pi^2}{8\eta^0} \sum_{\beta=1..N} \mu_{\alpha\beta} \left(\frac{\delta F}{\delta \phi_\alpha} - \frac{\delta F}{\delta \phi_\beta} \right) \quad (6)$$

$$\begin{aligned} \dot{\phi}_\alpha = \sum_{\beta=1..N} \mu_{\alpha\beta} \{ \sigma_{\alpha\beta}^0 [\phi_\beta \nabla^2 \phi_\alpha - \phi_\alpha \nabla^2 \phi_\beta + \frac{\pi^2}{2(\eta^0)^2} (\phi_\alpha - \phi_\beta)] \\ + \bar{S} \bar{\epsilon}_0 (\phi_\alpha - \phi_\beta) \} \end{aligned} \quad (7)$$

$\bar{S} = \bar{H} [\bar{\epsilon} - \bar{\epsilon}_\alpha^*(\{\phi_\beta\}) - c \bar{\epsilon}_\alpha^1]$ is the stress tensor. The elastic contribution on the grain boundary has the same structure as the potential part in the stress free interfacial energy, but it is dependent on the local stress distribution. For constant stress throughout the sample this will lead to a redefinition of the interfacial energy $\sigma(\bar{S})$ and interfacial width $\eta(\bar{S})$

$$\sigma(\bar{S}) = \sigma^0 \sqrt{1 - \frac{\bar{S} \bar{\epsilon}^* \eta^0}{\sigma^0}}, \quad \eta(\bar{S}) = \frac{\eta^0}{\sqrt{1 - \frac{\bar{S} \bar{\epsilon}^* \eta^0}{\sigma^0}}} \quad (8)$$

The interfacial energy and width, the latter treated as a physical entity on the nanometer scale, are dependent on the solution of the coupled phase-field and mechanical equilibrium problem. This is similar to the intrinsic dependence of the interfacial energy and width on the concentration field in the alloy model by Wheeler et al. [28]. Taking materials data of Cobalt one may check that for an elastic energy density of the order of $100 \frac{J}{cm^3}$, which corresponds to an unrelaxed expansion of the grain boundary by a few %, the elastic contribution to the total grain boundary energy becomes significant and positive (compression means a negative hydrostatic stress). In general, however, the stress distribution will not be constant but a solution of the mechanical equilibrium equation in quasi static approximation

$$\vec{0} = \nabla \bar{S} = \nabla \frac{\delta F}{\delta \bar{\epsilon}} = \nabla \bar{H}(\bar{\epsilon} - \bar{\epsilon}^* - c\bar{\epsilon}^1) \quad (9)$$

The diffusion equation consists for the pure substance only of the stress driven part, i.e. mobile atoms diffuse out of compressed zones along the gradient of the hydrostatic stress into zones under tension to relax these stresses. With the atomic mobility M it reads

$$\dot{c} = \nabla \left\{ M \nabla \frac{\delta F}{\delta c} \right\} = -\nabla M \nabla \bar{\epsilon}^1 \bar{S} \quad (10)$$

Sheering or glide cannot be described by this simple model; however these phenomena are unlikely to be of importance in grain growth of nanocrystalline material.

3. Experiments

Using nanocrystalline Co as an example, both the temperature-dependent and the isothermal grain growth behaviors in pure nanocrystalline metals were investigated experimentally. The starting material of nanocrystalline Co was prepared by high energy ball milling and subsequent consolidation. By chemical analysis, the high purity of the prepared nanocrystalline Co was confirmed, thus the effects of the impurities (e.g. the solute atoms or the contaminations) on the nanograin growth can be eliminated. For the studies on the temperature-dependent grain growth, the nanocrystalline Co was annealed for one hour at different temperatures in a wide range from room temperature up to 1173K. During heat-treatment, the samples were sealed in the high-strength quartz tubes filled with highly purified argon gas. After annealing, the samples were quenched into cold water to minimize the possibility of further grain growth during cooling. The changes of the grain size as a function of annealing temperature are shown in figure 2. It is found that there is a sharp increase in the grain size in a narrow temperature range between 773K and 873K. There is a large difference of changes of grain size compared to the low temperature region; moreover, the transition between the two stages is discontinuous. In the low temperature region the grain size does not change significantly up to 500 C, then a rapid grain growth occurs between 500 and 600 C, and sequentially grains grow with a relatively slow rate (but still much higher than that in the low temperature region) . The experimental results of isothermal nanograin growth in the pure nanocrystalline Co at $T=803K$ is shown in figure 3. It is observed from figure 3 a) that the finer grains have a higher growth rate than the coarser ones. For the isothermal normal grain growth, the kinetics can be written as

$$r(t) = (Kt + r_0^n)^{\frac{1}{n}} \quad (11)$$

where $r(t)$ and r_0 are the mean grain size at time t and initial grain size, respectively. K characterizes the migration rate of the grain boundary at the given temperature. n is the grain growth exponent and is a constant of $n=2$ for pure polycrystalline metals. To investigate the isothermal nano-grain growth kinetics, the growth rate is deduced as

$$\frac{dr}{dt} = \frac{K}{n} + (1 - n)r^{1-n} \tag{12}$$

$$\ln \frac{dr}{dt} = \ln \frac{K}{n} + (1 - n) \ln r \tag{13}$$

Based on the experimental data, the variations of $\ln \frac{dr}{dt}$ with $\ln r$ is shown in figure 3 b). Obviously, there is no constant relationship between these two parameters. As roughly calculated from the slope of the tangent of the curve (examples shown with $1-n = -0.1, -0.6$ and -3.4), n varies approximately in a range of $1.1 \sim 4.4$. This result shows convincingly that the nanograin growth kinetics is different from that of the polycrystalline materials, and the traditional models of grain growth cannot describe the nanograin growth behavior appropriately. In particular there is an almost linear grain growth observed in nanocrystalline materials which suggests a constant grain boundary velocity, independent of the grain radius.

4. Simulations

The driving force for grain growth is simply reduction of interfacial energy. This is naturally realized by the phase-field approach and the rearrangement of interfaces and junctions is provided by the solution of the multi-phase-field equations (7). Figure 4 shows a typical simulation in 3D. The geometry is discretized in $120 \times 120 \times 120$ cells with a dimension of $0.4nm$. The interface width is taken to be 5 cells, i.e. $2nm$. These dimensions will be kept fixed in all calculations. Interfacial energy σ^0 is set isotropically to $10^{-4} \frac{J}{cm^2}$. Since the interfacial mobility is largely unknown, it shall be kept open and the timescale will be set inversely proportional to the mobility, measured in units of $\frac{\eta^2}{\sigma^0 \mu}$. The calculations are performed in a rectangular box that can freely expand or contract, but keeps its rectangular shape. The boundary condition for the phase- and concentration field is periodic. **The calculations are performed on a single processor of a state of the art workstation with 16 GByte memory. The software currently does not provide the option of distributed simulations. Initial conditions for plastic flow could be either elastically expanded grain boundaries, elastically contracted bulk or a relaxed, stress free initial structure. Relaxation is done technically by subtracting the initial strain from the total strain. This initial strain is omitted in equation 3 for readability. It was checked carefully that the initial conditions for plastic flow do not affect the significance of the results. In the case of relaxed structures as initial conditions first a short period of rapid coarsening sets in until the elastic barrier is built up like in the case of an unrelaxed starting structure. Then both structures show a similar dynamics. Most simulations presented here start from an relaxed structure as this can be assumed closer to reality. The calculations start from a structure generated randomizing a hexagonal ordered structure. This procedure ensures that no isolated grain sits inside one bigger grain as it can happen by generating the grain structures from random centers. First the conditions of grain growth without void diffusion is examined by setting the parameter $\bar{\epsilon}^1$ to 0 and not solving the concentration equation.** Here the material is assumed stress free for the start and a moving grain boundary will expand the local volume when it passes one grain. In contrast, if material from the grain boundary is transformed back to bulk material it is contracted. Correspondingly the grain boundary generates high elastic stresses if passing the material. Already for a low

grain boundary expansion coefficient ϵ^* of 1% the stress in elastic approximation exceeds 1000MPa . The grain boundaries are under compression and the bulk under tension. Clearly a high elastic energy is now stored in the material. If the generation of elastic energy will exceed the reduction of interfacial energy during grain growth, grain growth will be stopped. Furthermore, the release of free grain boundary volume during the shrinking of small grains causes generation of vacancies in the bulk, which also reduces the driving force for grain growth. Figure 5 shows the average grain radius over time for simulations with different expansion coefficients. With an expansion coefficient of above 1%, no more grain growth can be found in the elastic limit. Driving forces for grain growth here are easily calculated as $\Delta G = \frac{\sigma^0}{r}$ of the order of 100MPa for grain radii of a few nanometer. Elastic energies will reach this level easily. It is noted that stresses on that order (or even higher stresses for higher values of ϵ^*) would not be sustained by the material, but immediately lead to plastic relaxations or even grain boundary fracture. Therefore it is essential to take plastic stress relaxation into account.

Switching on diffusion of atoms we include plastic relaxation. The grain boundary is, as described before, associated to a fixed number of voids that expand the volume of the grain boundary. In order to reduce elastic energy generated by the local volume expansion, atoms have to diffuse out of the grain boundary. Figure 6 shows the hydrostatic stress and concentration of mobile atoms in cut through a 3D grain structure with 10% grain boundary expansion. The concentration of mobile atoms reaches a minimum of $\sim 0\%$ in triple junctions. Hydrostatic stress is limited to $\pm 200\text{MPa}$. In shrinking particles the defects will move towards the center of the grains. Conversely, atoms from the center of the grain have to diffuse out of the grain. Hydrostatic stress is treated in quasi-static equilibrium. The atoms, however, diffuse slowly and follow the grain boundary with some delay. This is similar to the case of solute drag, however in the present case, the grain boundary cannot detach from the structural defects or voids as they are geometrically necessary. Diffusion and plastic relaxation is needed to relax the elastic barrier against grain boundary motion. Thereby the mobility of the atoms or voids limits the velocity of the grain boundary. Another way to look at these results is to consider the free volume in the grain boundary as point defects in the crystal lattice. During grain boundary migration defects must move together with the grain boundaries, which is a diffusive process. The result is a nearly linear grain growth behavior in the regime where the mobility of atoms limits grain growth. This is depicted in figure 7 for different expansions of the grain boundary. Obviously, the exact value of the expansion coefficient has no effect on the grain growth kinetics in this regime. If the grain structure has coarsened in such a way that the grain growth kinetics has fallen below the critical velocity, normal grain growth can be expected. The latter explains experimental findings of a transition of linear grain growth kinetics to normal grain growth of even retarded grain growth (see figure 3). As the calculations with stress driven diffusion are difficult to perform in a large area corresponding to the experimental set up we are unable to simulate this transition in its whole at present. However, we may conclude that the model gives clear evidence that linear grain growth kinetics in nanocrystalline material can be explained by finite atomic mobility. As a detail, we may evaluate the average stress in the bulk dependent on the grain size (figure 8). Within scatter a clear tendency is visible that small grains are under compression while large grains are under tension. This is consistent to the observation that atoms of shrinking small grains have to diffuse through the grain boundary out into the large grains which are growing. Thus, we get the picture of grain growth in nanocrystalline material being moderated by grain boundary expansion and plastic flow.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

5. Discussion

From the presented simulations it is evident, that under the assumptions of the model grain boundary motion has a maximum velocity which is related to the diffusivity of vacancies in an inhomogeneous stress field. The model thereby assumes a finite width of the grain boundary which determines the width the voids have to move. This assumption is justified only if motion of a grain boundary includes reordering of atoms and site change processes besides rearrangement of local atomic positions at sites that may belong to the different crystals forming the grain boundary.

From a more general point of view, however, one can rationalize that grain boundary motion is inevitably connected with the formation of mechanical strain. Let us consider one single spherical grain with radius r_0 in the center of a second spherical matrix grain with larger radius r_1 and both grains having a finite misorientation. Without loss of generality the initial state may be assumed stress free due to the assembly process of this bi-grain structure. The grain boundary, and in particular a large angle grain boundary, is from geometric reasons associated with a free volume corresponding to a strain ϵ^* . The inner grain will shrink releasing free volume that is proportional to the reduction of interfacial area (see also discussion in [20]). As this volume has to be distributed somewhere a dilatation of the bulk follows and stresses are generated. At the end of the process the whole grain boundary excess volume $4\pi r_0^2 \eta$ has to be distributed in the matrix if we assume the matrix grain large enough that the voids cannot diffuse to the surface.

The stresses caused by this process are far beyond the elastic limit of metallic materials for grain boundary expansions larger than 1%, as demonstrated. Plastic relaxation must be taken into account to explain finite growth rates. Furthermore a finite length scale need to be involved. In a real multi grain structure the grain boundary migration requires the propagation of triple lines, while the circumferential area of the small grain is decreasing (see figure 9 for illustration). Hence, if the diameter of a small grain shrinks by the amount ΔD , its circumference shrinks in proportion to that. Consequently, the free volume in the grain boundary in average has to migrate over this distance to be incorporated into the associated growing grain boundaries at the triple lines. During every time interval Δt of grain growth not only lattice site changes of the adjacent atoms are occurring, but rather atoms or free volume has to be transported over a length scale given by the grain growth rate $\Delta D/\Delta t$. Hence, the grain growth rate itself must be limited by this diffusive process, which must be considered to be thermally activated.

Indeed, during grain growth there is no true driving force acting on the grain boundary, as there is no volumetric energy gain for the growing crystal. In an atomistic picture one may rationalize that the motion of atoms out of the center of curvature is more likely than towards the centre. This statistical process is reflected in the classical picture of grain growth by the substitute of a driving force being proportional to the curvature of the boundary. In the phase-field model the diffusive nature of grain growth is inherent in the balance between the diffusion operator and the potential operator (see equation 7). However, volumetric effects and physical diffusion of atoms and voids is not included in the classical model. In the present model this is realized by the coupling to the elastic distortion in the crystals and grain boundary and the relaxation by void diffusion, or, which is the same, by diffusion of mobile atoms in the stress gradient through the grain boundary. The upper limit of grain boundary velocity is then caused by limited diffusion and will (for a given material) only depend on temperature.

The model explains experimental observation of nearly linear grain growth in

nanocrystalline material independent of the grain size below a certain temperature. The mobility of the voids can be assumed to have an Arrhenius type of temperature dependence. The onset of rapid grain growth at 800K, as seen in the experiments, can be associated with a cross-over from diffusion limited growth to normal grain growth at elevated temperatures. At the critical temperature this cross-over takes place in one experiment between linear grain growth regime (small grains) and a regular grain growth regime (large grains) as the grain boundary velocities during grain growth fall below the maximum velocity. Due to the large calculation domains needed to span the range from the nm scale to the μm scale this effect cannot yet be simulated. However, the presented model gives clear evidence of the mechanisms active in the different regimes. A further consequence of the model is the dependence of the interfacial energy on the hydrostatic stress state at the grain boundary. The latter should lead to a dependence of grain growth kinetics on isostatic pressure applied to a sample which should be easily detectable in experiments. Future work will concentrate on the quantitative comparison of experiment and simulation and on molecular dynamic studies to gain better insight into the molecular mechanisms of grain growth.

6. Conclusion

A phase-field model of grain growth associated with a volumetric expansion of the grain boundary is presented. The new feature of this model is, that the interfacial energy becomes significantly dependent on the local stress state. Void diffusion in the inhomogeneous stress field near moving boundaries is taken into account to relax the elastic distortion. It is demonstrated, that grain growth in the elastic limit is prohibited by the generation of elastic energy if the grain boundary excess volume exceeds 1%. As the grain boundary cannot detach from geometrically necessary voids, its velocity is limited to the maximum diffusive velocity of the voids. The maximum velocity of this diffusive process can be assumed to be strongly temperature dependent. Grain growth in nanocrystalline materials at low and medium temperatures is bound by this mechanism to a linear regime. At elevated temperatures the nano grains within the time of experimental observation grow to a size regime in which the growth rate has fallen below the maximum velocity. This explains the discontinuous transition from linear to normal grain growth observed in experiment. The model does not contradict to other effects being important in different materials like triple junction drag and void drag.

7. Acknowledgment

I. Steinbach and A. Hartmaier acknowledge the support from the sponsors of ICAMS, ThyssenKrupp Steel AG, Salzgitter Mannesmann Forschung GmbH, Robert Bosch GmbH, Bayer Materials Science AG and Bayer Technology Services GmbH, Benteler AG and the state of North Rhine-Westphalia. X. Song acknowledges the National Natural Science Foundation of China (50871001) for the financial support for the experimental work.

8. References

References

- [1] T.R. Malow C.C.Koch. *Acta. Mat.*, 45:2177, 1997.
- [2] F. Ebrahimi H. Li. *Scripta Mat.*, 55:263, 2006.
- [3] M. Ames J. Markmann R. Karos A. Michels A. Tschoepe R. Birringer. *Acta Mat.*, page 4255, 2008.
- [4] L.C. Chen F. Spaepen. *Nature*, page 336, 1988.
- [5] I. Yu R.K. Wunderlich R.Z. Valiev H.J. Fecht. *Scripta Mat.*, (49):947, 2003.
- [6] K. Lu. *Scripta Mat.*, 25:2047, 1991.
- [7] M. Winning A.D. Rollett. *Acta Mat.*, 53:2901, 2005.
- [8] P. Duhaj P. Sveca J. Sitek J. Janikovic. *Mater Sci Eng A*, 304:178, 2001.
- [9] H.J. Fecht. Intrinsic instability and entropy stabilization of grain boundaries. *Phys. Rev. Lett.*, 65:610, 1990.
- [10] H.J. Fecht. *Acta Mat.*, 38:1927, 1990.
- [11] M. Wagner. Structure and thermodynamic properties of nanocrystalline metals. *Phys. Rev. B*, 45:635, 1992.
- [12] X. Song J. Zhang L. Li K. Yang G. Liu. Correlation of thermodynamics and grain growth kinetics in nanocrystalline metals. *Acta Mat.*, page 5541, 2006.
- [13] A.H. Chokshi. *Scripta Mat.*, 59:726, 2008.
- [14] Z.J. Liu Y.G. Shen. *Acta Mat.*, 52:729, 2004.
- [15] P.C. Millett R.P. Selvam A. Saxena. *Acta Mat.*, 54:297, 2006.
- [16] X. Song J. Zhang J.J. Nanosci. *Mater. Res.*, pages 3054–3060, 2005.
- [17] A.G. Khachaturyan. Theory of structural transformations in solids. *Wiley, New York*, 1983.
- [18] Y. Ikumura N. Shibata T. Watanabe F. Oba T. Yamamoto T. Sakuma. *Ann. Chim. Sci. Mat.*, pages 21–30, 2002.
- [19] R. Birringer H. Gleiter. *Advance in Materials Scienc, Encyclopedia of Materials Science and Engineering (edited by R.W.Cahn), Pergamon Press, Oxford*, page 339, 1988.
- [20] Y. Estrin G. Gottstein E. Rabkin L.S. shvindlermann *Scripta Mat.* 34, page 141, 2000.
- [21] Y. Estrin *Recrystallization and Grain Growth*, G. Gottstein and D.A. Molodov, Eds. *Springer*, page 135, 2001 2000.
- [22] G. Gottstein L.S. shvindlermann *Acta Mat.* 50, page 703, 2002.
- [23] I. Steinbach F. Pezzolla B. Nestler M. Seeßelberg R. Prieler G.J. Schmitz J.L.L. Rezende. A phase field concept for multiphase systems. *Physica D*, 94:135–147, 1996.
- [24] I. Steinbach F. Pezzolla. A generalized field method for multiphase transformations using interface fields. *Physica D*, 134:385–393, 1999.
- [25] J. Eiken B. Böttger I. Steinbach. Multi phase field approach for alloy solidification. *Rev. E*, 73:066122–1–9, 2006.
- [26] I. Steinbach M. Apel. Multi phase field model for solid state transformation with elastic strain. *Physica D*, 217:153–160, 2006.
- [27] I. Steinbach. Phase-field models in materials science. *Mod.Sim.Mat.Sci.Engin*, page in press, 2009.
- [28] A.A. Wheeler W.J. Boettinger G.B. McFadden. Phase-field model for isothermal phase transitions in binary alloys. *Phys. Rev. A*, 45:7424–7439, 1992.

9. Figurecaptions

Figure 1. Dividing a grain structure into bulk and grain boundary volume (left). (right) TEM image of a $\langle 110 \rangle$ tilt grain boundary in ZrO_2 (from [18]).

Figure 2. Experimental results of temperature-varying nanograin growth in pure nanocrystalline Co: the mean grain size (the linear intercept) as a function of the annealing temperature.

Figure 3. Experimental results of isothermal nanograin growth in pure nanocrystalline Co at $T=803K$ with changes of (a) the mean grain size r with the holding time t and (b) $\ln \frac{dr}{dt}$ with $\ln r$.

Figure 4. Simulation of nano grain growth in 3D. The simulation starts from 100 grains in a domain of $48^3 nm^3$.

Figure 5. Grain radius over time for different levels of grain boundary expansion, 0%, 0.5%, 1%. Beyond 1% expansion no more grain growth can be observed in the elastic limit.

Figure 6. Cut through a 3D grain structure with grain boundary expansion of 10% and relaxation of stress by diffusion of mobile atoms. The colors indicate structure (left), concentration of mobile atoms (middle) and hydrostatic stress (right).

Figure 7. Grain radius over time for different levels of grain boundary expansion, 5%, 10%, 15%. The grain size increases nearly linearly with time due to the limitation of grain boundary velocity by diffusion of mobile atoms. On the other hand there is no more limitation of grain growth by an elastic barrier as this is fully relaxed by diffusion.

Figure 8. Hydrostatic stress in the bulk grains over grain size for different time steps. Small grains are under compression as these grains are shrinking and bulk volume is transformed to grain boundary volume. Large grains which are growing are under tension as here grain boundary volume is converted to bulk volume.

Figure 9. Schematic drawing of a shrinking grain. During the grain boundary migration towards the new position (dashed lines), the free volume in the grain boundary has to diffuse towards the newly created grain boundary (curved arrows). The size of the small grain decreases by the amount ΔD as indicated by the straight arrows.

Figure 1: Dividing a grain structure into bulk and grain boundary volume (left). (right) TEM image of a <110> tilt grain boundary in ZrO₂ (from [18])

Figure 2: Experimental results of temperature-varying nanograin growth in pure nanocrystalline Co: the mean grain size (the linear intercept) as a function of the annealing temperature.

Figure 3: Experimental results of isothermal nanograin growth in pure nanocrystalline Co at T=803K with changes of (a) the mean grain size r with the holding time t and (b) $\lg(dr/dt)$ with $\lg r$.

Figure 4: Simulation of nano grain growth in 3D. The simulation starts from 100 grains in a domain of 48^3 nm^3 .

Figure 5: Grain radius over time for different levels of grain boundary expansion, 0%, 0.5%, 1%. Beyond 1% expansion no more grain growth can be observed in the elastic limit.

Figure 6: Cut through a 3D grain structure with grain boundary expansion of 10% and relaxation of stress by diffusion of mobile atoms. The colors indicate structure (left), concentration of mobile atoms (middle) and hydrostatic stress (right).

Figure 7: Grain radius over time for different levels of grain boundary expansion, 5%, 10%, 15%. The grain size increases nearly linearly with time due to the limitation of grain boundary velocity by diffusion of mobile atoms. On the other hand there is no more limitation of grain growth by an elastic barrier as this is fully relaxed by diffusion.

Figure 8: Hydrostatic stress in the bulk grains over grain size for different time steps. Small grains are under compression as these grains are shrinking and bulk volume is transformed to grain boundary volume. Large grains which are growing are under tension as here grain boundary volume is converted to bulk volume.

Figure 9: Schematic drawing of a shrinking grain. During the grain boundary migration towards the new position (dashed lines), the free volume in the grain boundary has to diffuse towards the newly created grain boundary (curved arrows). The size of the small grain decreases by the amount ΔD as indicated by the straight arrows

Figure 1: Dividing a grain structure into bulk and grain boundary volume (left). (right) TEM image of a <110> tilt grain boundary in ZrO₂ (from [18])

Figure 2: Experimental results of temperature-varying nanograin growth in pure nanocrystalline Co: the mean grain size (the linear intercept) as a function of the annealing temperature.

Figure 3: Experimental results of isothermal nanograin growth in pure nanocrystalline Co at T=803K with changes of (a) the mean grain size r with the holding time t and (b) lg(dr/dt) with lgr.

Figure 4: Simulation of nano grain growth in 3D. The simulation starts from 100 grains in a domain of 48^3 nm^3 .

Figure 5: Grain radius over time for different levels of grain boundary expansion, 0%, 0.5%, 1%. Beyond 1% expansion no more grain growth can be observed in the elastic limit.

Figure 6: Cut through a 3D grain structure with grain boundary expansion of 10% and relaxation of stress by diffusion of mobile atoms. The colors indicate structure (left), concentration of mobile atoms (middle) and hydrostatic stress (right).

Figure 7: Grain radius over time for different levels of grain boundary expansion, 5%, 10%, 15%. The grain size increases nearly linearly with time due to the limitation of grain boundary velocity by diffusion of mobile atoms. On the other hand there is no more limitation of grain growth by an elastic barrier as this is fully relaxed by diffusion.

Figure 8: Hydrostatic stress in the bulk grains over grain size for different time steps. Small grains are under compression as these grains are shrinking and bulk volume is transformed to grain boundary volume. Large grains which are growing are under tension as here grain boundary volume is converted to bulk volume.

Figure 9: Schematic drawing of a shrinking grain. During the grain boundary migration towards the new position (dashed lines), the free volume in the grain boundary has to diffuse towards the newly created grain boundary (curved arrows). The size of the small grain decreases by the amount ΔD as indicated by the straight arrows