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GRAIN GROWTH IN THIN METALLIC FILMS

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Abstract—Grain growth in thin films deposited on a substrate was studied theoretically. The thrust of the model proposed is the effect of vacancy generation accompanying grain growth on the rate of the process. In addition, the magnitude of a tensile stress developing in the film was considered. It was shown that due to the contribution of vacancies to the free energy of the system, discernible grain growth is preceded by an "incubation" period, during which the grain structure can be considered as stable, as the rate of growth is relatively small over this incubation time. During this time, the vacancy concentration remains nearly constant, staying at a level much higher than the thermal equilibrium concentration. Based on numerical analysis, a simple expression for the incubation time in terms of the vacancy sink spacing, temperature and grain boundary characteristics was derived. With this formula, the stability of the grain structure of a thin film can be assessed for given conditions.

Keywords: Thin films; Grain growth; Vacancies

1. INTRODUCTION

In an early paper by Chaudhari [1], it was suggested that two distinctive features of grain growth in thin films deposited on a substrate should be observed. First, the cohesion between a film and a substrate should lead to internal stresses in the film. Second, under certain conditions, an equilibrium grain size can exist beyond which no grain growth occurs. This latter result followed from the consideration of an interplay between the elastic strain energy and the total grain boundary energy during grain growth. The model proposed by Chaudhari appears to be commonly accepted, see, e.g., a recent review [2]. In that approach, it was tacitly assumed that the excess free volume of grain boundaries released during grain growth disappears instantly, giving rise to a tensile stress. This strong assumption limits the applicability of the model, as the free volume release would normally occur via generation of lattice defects, notably the injection of vacancies into the bulk of the material [3]. Accordingly, volume changes will be determined by the vacancy diffusion kinetics. The present authors discussed the importance of vacancy effects in grain growth [4–6] which may be particularly significant in thin films. The aim of this paper is to examine the effect of vacancy generation accompanying grain growth on the kinetics of the process and to compare it with the build-up of internal stresses proposed by Chaudhari [1]. It will be shown that grain growth induced vacancy generation is much more important as a grain growth inhibiting effect. Some very specific predictions with regard to the grain growth induced vacancy concentration, impediment of grain growth, and the internal stress in a thin film will be made which, it is hoped, will motivate experiments in this area.

2. THE MODEL

2.1. *Internal stress in a thin film*

Consider a polycrystalline film deposited on a substrate and assume the film is initially in a stress-free state. If grain growth occurs, the reduction of the volume fraction of the grain boundary "phase", whose density is lower than that of the bulk material, would lead to a decrease in the film volume. Provided the film thickness is not changing, this would result in a decrease of the area of the film. However, cohesion with the substrate prevents this "shrinkage", thus giving rise to a tensile stress. In the spirit of [1], the

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stress in a given direction of the film (assumed to be isotropic) can be estimated by equating the amount of the relative "would be" shrinkage, $\Delta l^{(-)}/l_o$, where l_o is the initial film dimension in the direction of interest, to the elastic strain associated with the stress σ that arises in the film:

$$\frac{\Delta l^{(-)}}{l_o} = \frac{\sigma}{E}(1-\nu). \tag{1}$$

Here $E/(1-\nu)$ is the biaxial elastic modulus expressed in terms of Young's modulus E and Poisson's ratio ν. The left hand side of equation (1) can easily be rewritten in terms of the number of grains in the direction of interest,

$$n = \frac{l_o}{2r+\delta} \cong \frac{l_o}{2r}, \tag{2}$$

and the corresponding initial number of grains

$$n_o = \frac{l_o}{2r_o+\delta} \cong \frac{l_o}{2r_o}. \tag{3}$$

Here r and r_o are the average grain radius and the average initial grain radius, respectively, and δ is the grain boundary thickness. With

$$\Delta l^{(-)} = (n_o - n)\delta\beta \tag{4}$$

one obtains using equations (1)–(3):

$$\sigma = \frac{E}{2(1-\nu)}\delta\beta\left(\frac{1}{r_o}-\frac{1}{r}\right). \tag{5}$$

Here β is the relative density difference between the bulk and the grain boundary, the latter being less dense than the bulk. Stresses associated with the difference in the thermal expansion coefficient between the film and the substrate are not considered, implying that the film and the substrate are similar with respect to the thermal expansion coefficient.

Equation (5) going back to [1] does not take the elongation of the specimen due to the generation of vacancies into account. Indeed, the excess volume released when the grain boundary area decreases with grain growth has to be accommodated in the film. One possibility is converting it into individual vacancies. As long as the vacancies thus generated stay in the film, no net volume change occurs. (This implies that the excess free volume is considered to be equal to the total volume of vacancies generated, i.e. possible relaxation effects are neglected.) However, when vacancy removal by diffusion (e.g. to the film surface) occurs, film shrinkage due to loss of grain boundary area will outweigh its extension due to vacancies. If an individual vacancy leads to the specimen elongation αa, where a is the atomic spacing in the direction of interest and α is a numerical constant of the order of unity, the resulting stress can be expressed by

$$\sigma = \frac{E}{1-\nu}\left\{\frac{1}{2}\delta\beta\left(\frac{1}{r_o}-\frac{1}{r}\right)-\alpha(c-c^{eq})\right\}. \tag{6}$$

(It is assumed that in the initial state, at which $r = r_o$, the vacancy concentration c had its thermal equilibrium value c^{eq}.) As mentioned above, in the case when no vacancy removal occurs, the stress should vanish yielding the condition

$$\frac{1}{2}\beta\delta\left(\frac{1}{r_o}-\frac{1}{r}\right) = \alpha(c-c^{eq}) \tag{7}$$

On the other hand, one has under such "adiabatic" conditions (cf. equation (14) below)

$$c-c^{eq} = \delta\beta\left(\frac{1}{r_o}-\frac{1}{r}\right). \tag{8}$$

A comparison of equations (7) and (8) yields $\alpha = 1/2$. Equation (6) thus gives an expression for the tensile stress developing during grain growth and depending on the grain size and vacancy concentration. In the analysis to follow we shall use equation (6) to describe the stress in the film. It should be noted that this equation was derived by assuming that the change of the film volume is accommodated by elastic strain only. As in Chaudhari [1], possible effects of plastic strain were not considered. Furthermore, it was assumed that no film thickness reduction occurs during grain growth. This implies a situation when a protective (e.g. oxide) layer impermeable to vacancies "seals" the film surface and the film/substrate interface does not act as an efficient vacancy sink either.

In the following, we temporarily adopt this assumption that vacancies can only be annihilated at internal sinks in the bulk of the material, rather than at the film surface or the interface. However, it will be shown that the effect of the in-plane stress developing in the film under such restraining conditions is insignificant compared to the effect of vacancy energetics in inhibiting grain growth. Thus, the above assumption can be dropped safely, without loss of generality of the thermodynamic treatment to follow.

2.2. *Thermodynamic considerations*

The Gibbs free energy of the film (per unit volume) can be written as a sum of three contributions: the elastic strain energy,

$$G_s = \frac{\sigma^2}{2E}(1-\nu), \tag{9}$$

the grain boundary free energy (also taken per unit volume),

$$G_{GB} = \frac{\gamma}{r} \tag{10}$$

and, finally, the free energy associated with vacancies [4, 6]

$$G_{vac} = \frac{1}{2}\frac{NkT}{c^{eq}}(c-c^{eq})^2. \tag{11}$$

Here γ is the surface tension (grain boundary free energy per unit area), N is the number of atoms per unit volume, T is the absolute temperature and k the Boltzmann constant. In deriving equation (10) it was assumed that the grains are cylindrical, with the height equal to the film thickness, and are normal to the film plane. This does not impose any serious restrictions on the validity of the model. For example, for a three-dimensional arrangements of grains within the film, only the numerical coefficient in equation (10) will be changed (from 1 to 3/2).

Consider the derivative of the full Gibbs free energy, $G = G_s + G_{GB} + G_{vac}$, with respect to the average grain size r:

$$\frac{dG}{dr} = \left[\frac{NkT}{c^{eq}}(c-c^{eq})-\alpha\sigma\right]\cdot\frac{dc}{dr} + \left\{\frac{1}{2}\frac{E}{1-\nu}\delta\beta\left[\frac{1}{2}\delta\beta\left(\frac{1}{r_o}-\frac{1}{r}\right)-\alpha(c-c^{eq})\right]-\gamma\right\}\cdot\frac{1}{r^2} \tag{12}$$

The behaviour of the system can be diagnosed by an analysis of the sign of this derivative. The thermodynamic viability of the grain growth process requires that the derivative be negative.

In order to monitor the development of G with time (or grain size), one needs to analyse the evolution equations for r and c.

The evolution of the vacancy concentration with time t is given by

$$\frac{dc}{dt} = \frac{\delta\beta}{r^2}V-\frac{D_v}{d^2}(c-c^{eq}) \tag{13}$$

The first term on the right-hand side represents the rate of vacancy generation accompanying grain growth (V being the grain growth rate, or the velocity of grain boundary migration). The second term describes the vacancy removal by diffusion to sinks, D_v being the vacancy diffusivity and d the sink spacing.

2.2.1. "Adiabatic" case. When vacancy removal can be neglected (which can be referred to as the "adiabatic" case), the last term in equation (13) can be dropped leading to

$$\frac{dc}{dr} = \frac{\delta\beta}{r^2}. \tag{14}$$

This yields the solution given by equation (11). As already mentioned, in this case $\sigma = 0$. Equation (12) then assumes the form

$$\frac{dG}{dr} = \frac{1}{r^2}\left\{-\gamma + (\delta\beta)^2\frac{NkT}{c^{eq}}\left(\frac{1}{r_o}-\frac{1}{r}\right)\right\} \tag{15}$$

It is seen that in the early stages of grain growth, when r is close to r_o, the derivative dG/dr is negative, meaning that the process is favourable thermodynamically. However, at a certain critical value of r given by

$$r_c = \frac{r_o}{1-\frac{\gamma c^{eq} r_o}{(\delta\beta)^2 NkT}} \tag{16}$$

the derivative dG/dr vanishes. This critical value of r can be seen as an "equilibrium" grain size beyond which no growth will occur. Obviously, such a critical grain size is only possible if the denominator of equation (16) is positive, i.e. if

$$r_o < \frac{(\delta\beta)^2 NkT}{\gamma c^{eq}}. \tag{17}$$

A simple estimate using representative values of the parameters,

$\delta = 10^{-7}$ cm, $\beta = 2\times10^{-2}$, $\gamma = 1$ Jm^{-2}, $T = 500$ K, and $c^{eq} = 10^{-8}$,

shows that this condition is fulfilled for $r_o < 1.5\times10^{-3}$ cm. Of course, this value is strongly temperature dependent, primarily through the thermal equilibrium vacancy concentration. If inequality (17) is not fulfilled, grain growth will be unrestricted.

2.2.2. The "Chaudhari" approximation. It is interesting to note that the existence of an "equilibrium" grain size predicted by Chaudhari [1] also follows from equations (12) and (13). Indeed, assuming the existence of such a critical radius and thus setting V to zero and further assuming that the vacancy concentration is equal to its thermal equilibrium value (a tacit assumption in Chaudhari's paper [1]) we find that $dG/dr = 0$ if

$$r \cong \frac{r_o}{1-\frac{4\gamma r_o(1-\nu)}{E(\delta\beta)^2}} \tag{18}$$

This formula reproduces Chaudhari's result [1], which was recently revisited by Thompson and Carel [2].

2.3. *The kinetic approach*

Obviously, the two limit cases considered above do not give a full picture of grain growth in thin film. A detailed description of the evolution of grain size, and the accompanying development of the vacancy concentration and the tensile stress in a film deposited on a substrate can be obtained using a kinetic approach presented below.

2.3.1. Governing equations. In a kinetic approach, the evolution of the grain size can be investigated by considering the energy balance. By equating the energy released when the grain size increases by dr to the sum of the increments of the elastic energy and the energy of the vacancy sub-system, we obtain:

$$\frac{\gamma}{r^2}\mathrm{d}r = (1-\nu)\frac{\sigma}{E}\mathrm{d}\sigma + \frac{NkT}{c^{\mathrm{eq}}}(c-c^{\mathrm{eq}})\mathrm{d}c^{+} + \frac{V^2}{mr}\mathrm{d}t. \quad (19)$$

Here

$$\mathrm{d}c^{+} = \frac{\delta\beta}{r^2}\mathrm{d}r \quad (20)$$

is the increment of the vacancy concentration generated as a result of the reduction of grain boundary volume upon the grain size increment dr corresponding to the time increment dt. The last term represents the energy dissipation (per unit volume) within the time dt due to grain boundary motion; m denotes the grain boundary mobility assumed to be the intrinsic one. (This implies that the grain boundaries are considered not to be pinned at the surface [7].) Obviously, m represents some average mobility, the averaging being over the entire population of boundaries. The authors are aware of the fact that this is a fairly crude (though not uncommon) approximation, as individual boundaries possess different mobilities, depending on the boundary type, degree of coincidence, misorientation angle, etc. [7]. As a matter of fact, the form of the dissipative term in equation (19) can be seen as an operational definition of the average grain boundary mobility m. This averaging is in keeping with the global approach adopted in this model, particularly with regard to using a uniform, "mean-field", vacancy concentration and not keeping track of vacancy generation or annihilation sites.

Combining equations (19) and (20) one obtains

$$\frac{\gamma\mathrm{d}r}{r^2\mathrm{d}t} = (1-\nu)\frac{\sigma\mathrm{d}\sigma}{E\,\mathrm{d}t} + \frac{NkT}{c^{\mathrm{eq}}}(c-c^{\mathrm{eq}})\frac{\delta\beta\mathrm{d}r}{r^2\,\mathrm{d}t} + \frac{V^2}{mr}. \quad (21)$$

Neglecting the Chaudhari effect (i.e. setting $\sigma = 0$) and the vacancy effect introduced here (i.e. setting $c = c^{\mathrm{eq}}$), one obtains the standard grain growth equation of the type dr/dt = $zm\gamma/r$, with the numerical coefficient z being identified with unity.

The set of equations (21) and (13), with σ given by equation (6), provides a full description of the time evolution of the grain size, vacancy concentration and stress. A convenient non-dimensional form of this set of equations reads

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{1}{\chi^2}\frac{\mathrm{d}\chi}{\mathrm{d}t} - C, \quad (22)$$

$$\left[A + (1-B)C - \left(\frac{1}{\chi_{\mathrm{o}}} - \frac{1}{\chi}\right)\right]\frac{1}{\chi^2}\frac{\mathrm{d}\chi}{\mathrm{d}t} = -\left(\frac{1}{\chi_{\mathrm{o}}} - \frac{1}{\chi} - C\right)\frac{\mathrm{d}C}{\mathrm{d}t} + Q\frac{1}{\chi}\left(\frac{\mathrm{d}\chi}{\mathrm{d}t}\right)^2. \quad (23)$$

Here

$$C = c - c^{\mathrm{eq}},\ \chi = \frac{r}{\delta\beta},\ \chi_{\mathrm{o}} = \frac{r_{\mathrm{o}}}{\delta\beta},\ A = \frac{4\gamma}{\delta\beta E}(1-\nu),$$
$$B = \frac{4NkT}{Ec^{\mathrm{eq}}}(1-\nu),\ \text{and}\ Q = \frac{4(1-\nu)\delta\beta D_{\mathrm{v}}}{d^2Em}.$$

The time t in equations (22) and (23) is expressed in terms of d^2/D_{v}, i.e. is non-dimensional as well.

The set of equations (22) and (23) describing the evolution of the grain size and the vacancy concentration provide a full description of the system. (The corresponding variation of stress is then given by equation (6).) It should be noted, however, that the Chaudhari approximation—translated into the present kinetic approach—corresponds to suppressing equation (22) and setting C and dC/dt to zero in equation (23).

2.3.2. Numerical solutions. The set of equations (22) and (23) was solved numerically. In all cases, the solutions show a continual growth of the grain size with time. The maximum growth rate is observed at the very beginning of the process. A practically uninhibited, nearly parabolic, growth regime is observed at large times (Fig. 1). This behaviour is preceded by an "incubation" stage in which the grain growth rate is reduced, as clearly seen in Fig. 1.

The length of the plateau-like incubation stage depends on the values of the model parameters and the initial grain size, χ_{o}. An interesting feature found is that during the incubation time, the vacancy concentration, C, after a rapid initial growth, remains nearly constant (Fig. 2). The end of the incubation

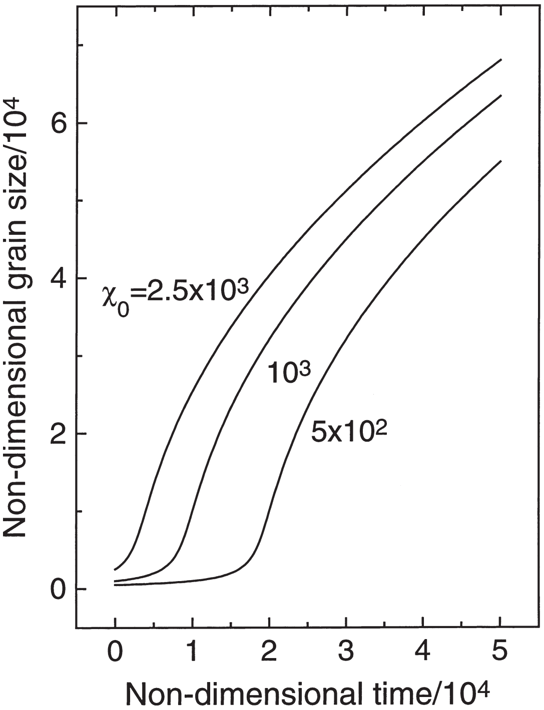

Fig. 1. Variation of the grain size with time for various values of the initial grain size. (All quantities are given in dimensionless units.)

period is signified by a precipitous drop of C and a peak in the time dependence of the grain growth rate, $d\chi/dt$ (Fig. 3). This makes it possible to clearly identify the incubation time, τ. Its significance can be interpreted as follows. Even though grain growth does occur during the incubation time, the magnitude of the grain size does not change substantially. For all practical purposes one can thus consider τ as the time of relative stability of the grain structure. Knowing the dependence of τ on the initial grain size, temperature and sink spacing, one can assess this time for a system of interest.

The variation of the grain growth curve χ vs. t, as well as the concomitant variation of the vacancy concentration C and the grain growth rate $d\chi/dt$ with the initial grain size χ_o can be followed in Figs 1-3. The parameter values ($A = 5$, $B = 5\times10^7$ and $Q = 10^{-4}$ were chosen to represent a typical metallic material, such as an fcc metal, at about half the melting temperature.)

The dependence of τ on $1/\chi_o$ is shown in Fig. 4. As can be seen, it is represented, apart from the very small values of $1/\chi_o$, by a straight line passing through the origin. By varying the model parameters A, B and Q, it was shown that this dependence can be represented by a simple formula:

$$\tau = \frac{B}{A}\cdot\frac{1}{\chi_o} \tag{24}$$

It is a very fortunate circumstance that an analytical

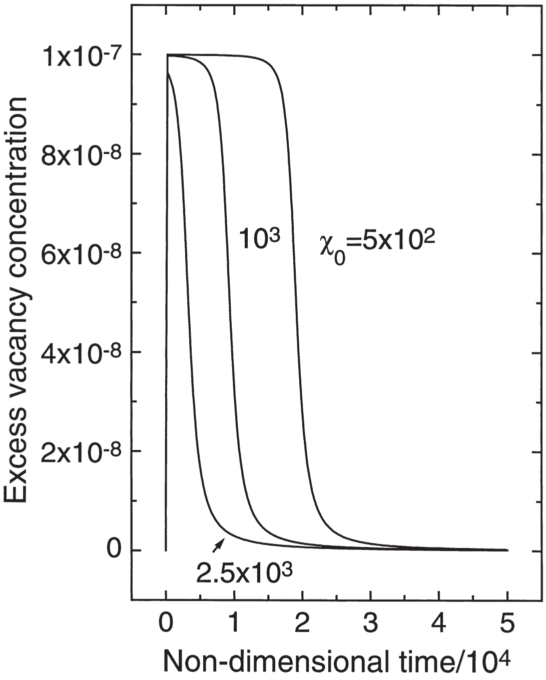

Fig. 2. Evolution of the excess vacancy concentration with the non-dimensional time for three different values of the initial grain size.

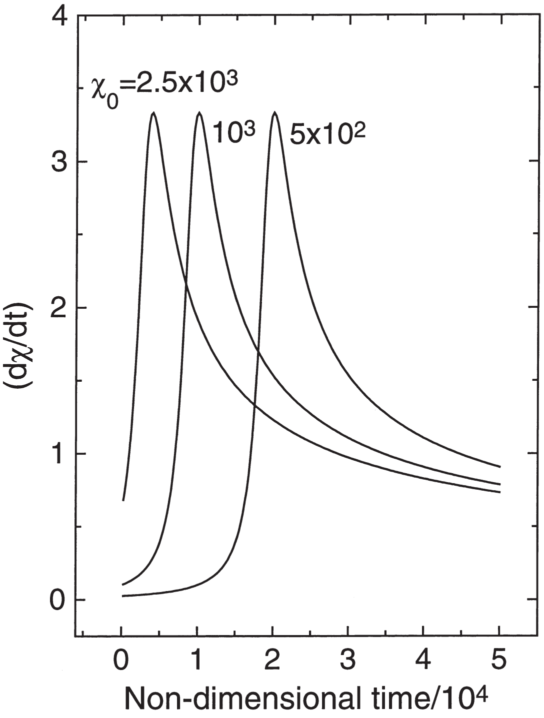

Fig. 3. The grain growth rate as a function of time for three different values of the initial grain size. (All quantities are given in dimensionless units.)

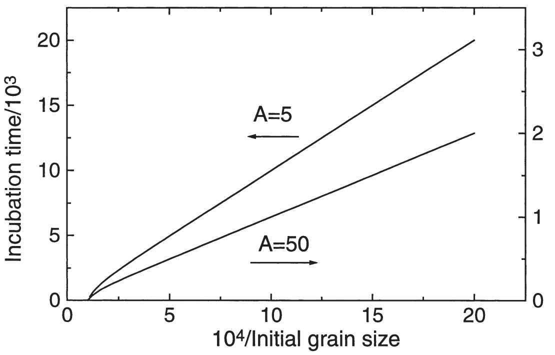

Fig. 4. The initial grain size dependence of the incubation time. (Note the different scales for the two different values of the parameter A used.)

formula representing the numerical results could be found. It should be mentioned that τ is not sensitive to the dissipation parameter Q. For example, a decrease of Q by a factor of 10 (from $Q = 10^{-4}$ to $Q = 10^{-5}$) leads to a hardly noticeable change of τ by less than 0.03%. An increase of Q has a larger, but still insignificant effect on τ. For $Q = 10^{-3}$ the value of τ is just 1% smaller than for $Q = 10^{-4}$. (This example corresponds to $\chi_o = 10^3$, the values of A and B being as in the above calculations.) By contrast, the value of χ_o at which deviations from the linear relation, equation (24), seen as a drop-off in Fig. 4, occur, does depend on Q. However, this dependence is not very strong either: as shown in Appendix A, this value of χ_o can be estimated as $(B/Q)^{1/3}$. We would like to stress that the temperature dependence of the dissipation parameter Q is not very strong as it enters through the ratio of the vacancy diffusivity and the grain boundary mobility—two quantities with similar activation energies, at least for sufficiently pure metals. The non-dimensional relation, equation (24), can be re-written as

$$t_{\text{incubation}} = \frac{(\delta\beta)^2 NkT}{\gamma r_o} \cdot \frac{d^2}{D_v c^{\text{eq}}} \tag{25}$$

expressing the incubation time $t_{\text{incubation}}$ in terms of the physical parameters of the material, temperature and the sink spacing d.

Equation (25) provides a means for the evaluation of stability of the grain structure of thin films against grain growth. The incubation time is proportional to the square of the quantity $\delta\beta$ that determines the "vacancy capacity" of grain boundaries. General grain boundaries are likely to have a larger "vacancy capacity". One can therefore expect that a system of general boundaries will be more stable than that of special boundaries, provided that the greater mobility of the latter does not outweigh this effect.

In addition to the incubation time τ or $t_{\text{incubation}}$, it is of interest to estimate the change of the grain size over the incubation time. As can be seen from Fig. 1, the increment of χ amounts to only a small fraction of χ_o. As shown in Appendix A, this increment, $\chi - \chi_o$, is approximately equal to A, which is much smaller than χ_o.

Finally, the tensile stress σ developing in the film can be calculated using equation (6). The results for the set of parameter values $A = 5$, $B = 5 \times 10^7$ and $Q = 10^{-4}$ and three different values of χ_o are shown in Fig. 5. An interesting feature of the evolution of σ is evident from the graphs: after a period of rapid growth (which roughly coincides with the period of constancy of C), a pronounced deceleration of growth is found. With decreasing χ_o this second stage of stress development corresponds to an almost horizontal plateau, while the stage of growth is described by a linear time dependence (cf. Appendix A). The "steady-state" of stress is associated with a drop of C observed in Fig. 2 and the growth of χ according to the equation

$$\frac{\sigma}{E}(1-\nu) = \frac{1}{2}\left(\frac{1}{\chi_o} - \frac{1}{\chi} - C\right) \tag{26}$$

that represents a non-dimensional form of equation (6). Obviously, in the limit of large time the stress is given by

$$\frac{\sigma}{E}(1-\nu) = \frac{\delta\beta}{2r_0} \tag{27}$$

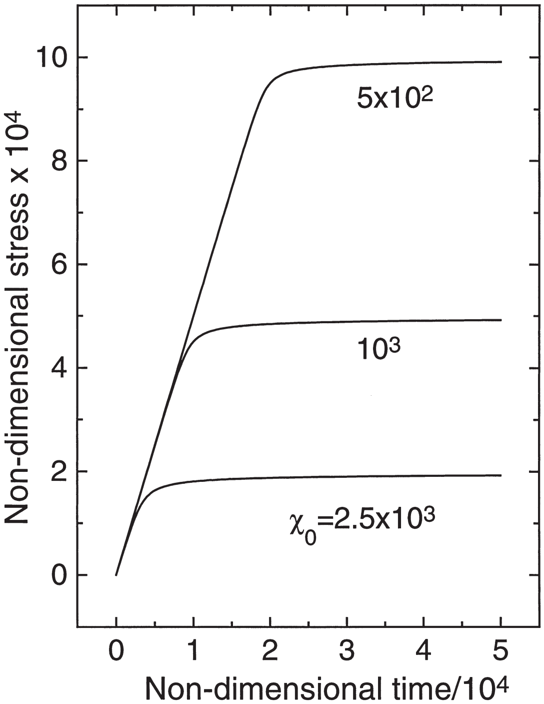

Fig. 5. Time dependence of the elastic stress for three different values of the initial grain size. (All quantities are given in dimensionless units.)

It is interesting to note that the incubation time expressed by equation (25) does not contain any elastic constants which suggests that elasticity is not an efficient inhibitor of grain growth in thin films. A weak dependence on the biaxial elastic modulus only enters through the dependence of the incubation time on Q discussed above. A slight decrease of $t_{\mathrm{incubation}}$ with increasing Q (or decreasing elastic modulus) reflects the fact that the incubation time in a less stiff material is reduced, i.e. inhibition of grain growth due to elasticity is smaller. The relative contribution of the elastic effect as compared to the effect of grain growth inhibition by vacancy generation becomes large with increasing initial grain size r_{o}. However, as both effects decrease with r_{o}, the predominance of the elastic one becomes apparent only in a more rapid than linear decrease of the incubation time with increasing r_{o} seen in Fig. 4. These considerations show that the effect of suppression of grain growth by elastic stress predicted by Chaudhari [1] only plays a subordinate role, the leading grain growth inhibition effect stemming from vacancy generation. As mentioned above, this observation means that the assumption of constancy of the film thickness is actually a redundant constraint that we henceforth drop without any significant loss of generality of the model.

Finally, we note that the Chaudhari case can be construed if a fairly artificial condition is used, that the vacancy concentration c is identically equal to the thermal equilibrium value c^{eq}. Dropping equation (22) and solving equation (23) in which $C = 0$ and $\mathrm{d}C/\mathrm{d}t = 0$ are set yields the solution shown in Fig. 6. (The initial radius, $\chi_{\mathrm{o}} = 0.1$, was chosen from within the range where grain growth locking due to the Chaudhari mechanism, i.e. by the elastic stress, is operative, viz. $\chi_{\mathrm{o}} < A/2$, cf. equation (18).)

3. DISCUSSION AND CONCLUDING REMARKS

It has been demonstrated that—despite the two factors inhibiting grain growth, viz. the development of elastic strain and, notably, the leading effect of vacancy supersaturation accompanying the loss of grain boundary area—grain growth occurs at all conditions. In other words, there is no critical initial grain radius r_{o} below which grain growth would be prohibited, contrary to the prediction in [1]. However, in a range of parameters of practical importance, the temporal behaviour of a polycrystalline thin film may exhibit an incubation period during which the grain size changes by only a small fraction of its initial value. It is in that sense that one can refer to the incubation time as a period of stability of grain structure. The magnitude of the incubation time is given by equation (25) which provides a tool for assessing the period of stability of a thin film with a given vacancy sink spacing against grain growth for a temperature of interest.

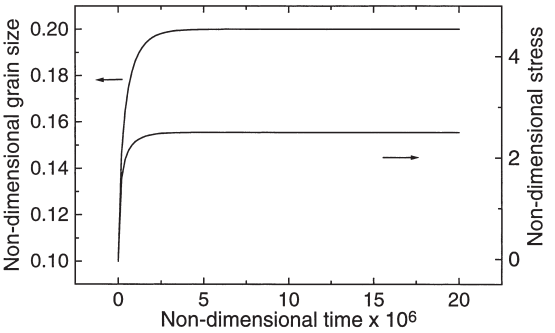

Fig. 6. Variation of the grain size and the elastic stress with time for the "Chaudhari case" for $\chi_{\mathrm{o}} = 0.1$. (All quantities are given in dimensionless units.)

The model is based on the assumption that the release of the excess free volume of grain boundaries during grain growth occurs by the bulk diffusion of the vacancies ejected into the bulk by migrating grain boundaries. An alternative channel through which the film may dispose of the excess free volume would be the grain boundaries themselves. For a general, "unsealed" film, vacancy transport via grain boundaries—straight to the surface—would be a mechanism for excess free volume reduction. Formally, for this case the structure of the model would not change. The excess vacancy concentration in the boundary would contribute to the Gibbs free energy of the system and would need to be removed to the surface by grain boundary diffusion in much the same way as in the above bulk vacancy generation process. However, there are reasons to believe that impurity contamination of grain boundaries at their intercepts with the film surface (selective etching at grain boundaries) will inhibit the free volume release through grain boundary "channels".

A global thermodynamic approach to the problem was taken here, with no detailed monitoring of the generation, diffusion and annihilation of vacancies. Instead, the model operates with the average grain size, the average grain boundary mobility and the average vacancy concentration. For example, such local events as "re-adsorption" of an individual vacancy emitted into the bulk at its "place of birth", the particular grain boundary it was generated at, were neglected. Similarly, no account was taken of grain size distribution whose evolution may involve local growth of the grain boundary phase despite its overall reduction during grain growth. These events will, of course, reduce the effect of vacancy supersaturation and the amount of grain growth inhibition predicted, but only in a quantitative, numerical sense.

To get a feel for the stabilisation effect predicted, particularly for orders of magnitude of the incubation time, we consider a typical face centred cubic metal, represented by gold, for selected values of the homologous temperature and vacancy sink spacing d. In this numerical exercise the initial grain size is fixed at 10^{-2} μm. Table 1 summarises the estimates for the incubation time made with the self-diffusion activation energy of 1.81 eV, the pre-exponential factor in the coefficient of self-diffusion of $10^{-5}\ \mathrm{m}^2\ \mathrm{s}^{-1}$ and

Table 1. Vacancy sink spacing and temperature dependence of the incubation time

d (μm)	T/T_m	$t_{\text{incubation}}$ (s)
0.01	0.2	1.7×10^{18}
	0.3	1.3×10^{7}
	0.5	2.1×10^{-2}
0.1	0.2	1.7×10^{20}
	0.3	1.3×10^{9}
	0.5	2.1
1	0.2	1.7×10^{22}
	0.3	1.3×10^{11}
	0.5	2.1×10^{2}

the grain boundary energy of 0.4 Jm^{-2} [8]. Furthermore, the grain boundary characteristics δ and β were taken to be 10^{-9} m and 2×10^{-2} [4, 6], respectively. Assuming that the vacancy sinks are associated with dislocations, the values of d in Table 1 correspond to the dislocation densities ranging between 10^{16} m^{-2} (for $d = 0.01$ μm) and 10^{12} m^{-2} (for $d = 1$ μm). For film thickness w smaller than the average dislocation spacing (and provided the film surface and/or the interface can act as vacancy sinks), d is to be associated with w.

An interesting feature of the incubation period is that, in addition to the relative stability of grain structure, stability of the vacancy concentration at a high level ($C_o \cong B/A$) is maintained. This unexpected effect may play an important role in various areas of physics and chemistry of thin films, particularly those where diffusion controlled processes and vacancy controlled chemical reactions, including oxidation kinetics, are of significance.

A final remark is due here. In considering the tensile stress emerging as a result of release of free volume associated with grain boundaries, the analysis was limited to the elastic strain range. However, as seen from the numerical results regarding the stress, Fig. 5, for the smallest initial grain size considered, the stress level may be high enough to induce plastic flow. Even though the maximum stresses are achieved towards the end of the incubation time, they may affect the stability of the grain structure. An analysis including plasticity leading to stress relaxation will be given elsewhere. However, as the elastic stress effect was shown to be of minor importance, inclusion of stress relaxation would not change the predictions of the paper with regard to grain growth kinetics.

In conclusion, vacancy effects in grain growth in thin films were considered. A kinetic approach used made it possible to give a full description of the evolution of the average grain size, the vacancy concentration and—for the case of constant thickness—the tensile stress in a thin film on a substrate. A simple expression for the incubation time, i.e. the time of stability of the grain structure of a thin film, in terms of the vacancy sink spacing, temperature and grain boundary characteristics was obtained. The magnitude of the elastic stress and the level of vacancy supersaturation, stable over the incubation time, were determined. It is hoped that experimental work needed for verifying these modelling results will be stimulated by the present article.

Similar considerations can be applied to grain growth in reinforcement particles in a composite, in lamellae of multilayers, etc. An analysis of grain growth in such elastically constrained systems will be presented elsewhere.

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APPENDIX A

A.1. Vacancy concentration during the incubation time

As follows from the numerical results presented in Section 2, the excess vacancy concentration $C = c - c^{\text{eq}}$ remains nearly constant, at a level C_o, during the incubation period of duration τ. From equation (22) it follows

$$\frac{1}{\chi^2}\frac{\mathrm{d}\chi}{\mathrm{d}t} \approx C_o \tag{A1}$$

yielding upon integration

$$\frac{1}{\chi_o} - \frac{1}{\chi} = C_o t. \tag{A2}$$

Using equations (A1) and (A2) and neglecting unity as compared to a large quantity B one then obtains from equation (23)

$$A - BC_o - C_o t = Q\chi^3 C_o \qquad \text{(A3)}$$

For $\chi_o < 10^3$ and $Q = 10^{-4}$, when C_o is small (usually ranging between 10^{-8} and 10^{-6}), the right-hand side of this equation is small compared to one. This can only be fulfilled over the entire incubation time if

$$C_o \cong \frac{A}{B + \tau} \cong \frac{A}{B} \qquad \text{(A4)}$$

A.2. Increment of the grain size during incubation time

Using equation (A2) one can estimate the grain size at the end of the incubation period. Denoting it by χ_{end} and using equation (A4) for C_o one has

$$\chi_{end} \cong \chi_o\left(1 + \frac{A}{\chi_o}\right) = \chi_o + A \qquad \text{(A5)}$$

In all exercises considered, A was much smaller than χ_o.