

## Heterogeneous nucleation of microcracks in strained metals

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A THEORY of non-homogeneous nucleation of microcracks in metal crystals subjected to one dimensional state of strain is presented in the paper. Investigated are the conditions of formation of vacancy clusters at the grain boundaries, the considerations being based on an analogy with the process of heterogeneous nucleation of vapour deposits on solid substrates. Atomistic approach is adopted and the problem is analysed via the petit canonical ensemble; the entire problem is reduced to the determination of the partition function of a two-dimensional gas consisting of particles of various dimensions. From the partition function (internal energy contributions being disregarded), the free energy of the system is determined. Minimum of that energy yields then the surface density of critical aggregates. The final result of the paper has the form of an equation for the microcrack nucleation rate at the grain boundaries of the strained crystal, based on kinetic considerations. The hypothesis proposed constitutes an essential extension of former papers of the author.

W pracy buduje się teorię niejednorodnego zarodkowania mikroszczelin w kryształach metali znajdujących się w jednoosiowym stanie odkształcenia. Zbadano warunki powstawania odpowiednich zgrupowań wakansji na granicach ziaren w oparciu o analogię z procesem heterogenicznej nukleacji kondensatów par na ciałach stałych. Wybrano podejście atomistyczne i zanalizowano postawione zagadnienie poprzez mały ansambl kanoniczny, sprowadzając problem do wyznaczenia sumy statystycznej dwuwymiarowego gazu, złożonego z cząstek o różnych wymiarach. Z sumy statystycznej, wyznaczonej przy pominięciu wewnętrznych wkładów energetycznych, otrzymano energię swobodną układu. Minimum tej energii prowadzi następnie do powierzchniowej gęstości agregatów krytycznych. Końcowym rezultatem pracy jest równanie na prędkość zarodkowania mikroszczelin na granicach ziaren odkształconego kryształu, wyprowadzone na podstawie rozważań kinetycznych. Zaproponowana hipoteza stanowi istotne rozszerzenie poprzednich prac autora.

В работе дана теория неоднородного образования зародышей микротрещин в кристаллах металлов, находящихся в одноосном деформированном состоянии. Исследованы условия возникновения соответствующих группировок вакансий на границах зерен, причем используется аналогия с процессом гетерогенной нуклеации конденсатов паров на поверхности твердых тел. Предпочтение отдано атомарному подходу, с точки зрения которого поставленная задача проанализирована при помощи малого канонического ансамбля. Таким образом задача сводится к определению статистической суммы двухмерного газа, состоящего из частиц различных размеров. Статистическая сумма определяется пренебрегая внутренними слагаемыми энергии и позволяет вычислить свободную энергию системы. Минимум этой энергии приводит к поверхностной плотности критических агрегатов. Конечной целью работы является вывод уравнения для скорости зародышеобразования микротрещин на границах зерен деформированного кристалла, основанный на кинетических рассуждениях. Предложенная гипотеза является существенным расширением результатов, полученных ранее автором.

### 1. Introduction

IN EARLIER works [1, 2], a theory was constructed of formation of nuclei of vacancy clusters in a single crystal metal subject to uniaxial strain. Treating the vacancies as molecules of a perfect gas and assuming an analogy with the process of formation of a new phase in a vapour-liquid system, the nucleation rate equation was derived. On the basis

of energy considerations, the change of the activation energy of the vacancy motion ( $\Delta U$ ), due to the crystal elongation, was also found in the form:

$$(1.1) \quad \Delta U = aR_0^m \left\{ 1 - (1 + \varepsilon)^{-m} - \frac{m}{n} [1 - (1 + \varepsilon)^{-n}] \right\},$$

where  $a$ ,  $m$ ,  $n$  are positive material constants,  $\varepsilon$  is the linear strain of the crystal, and  $R_0$  is the lattice constant.

The aim of the present paper is to investigate the microcrack nucleation rate in a polycrystalline material subject to uniaxial strain. This extension of the earlier hypothesis constitutes a further step in finding a proper model of the fracture mechanism.

It is known that the vacancy clusters are formed much more easily on the grain boundaries than within the grains. Thus one of the ways which can bring us closer to the early stage of real fracture mechanism consists in investigating the process of heterogeneous nucleation of the microcracks from dispersed vacancies. The considerations are based on assuming an analogy with the process of vapour condensation on a substrate. On the other hand, if the supersaturation is high, nucleation theory predicts a very small size for the critical cluster. Since in our case such conditions may be encountered [3], the treatment of heterogeneous nucleation requires an atomistic rather than a thermodynamic approach. Consequently, for the analysis of the problem, the description of vapour deposits on a substrate, carried out on the basis of statistical mechanics and proposed by D. WALTON [4], T. N. RHODIN [5], and V. HALPERN [6], was chosen. This approach based on the equilibrium distribution of different clusters is equivalent to the kinetic treatment made by other authors [11, 12].

## 2. The equilibrium density of clusters

Let us consider a sample of a polycrystal subject to uniaxial strain. The assumptions regarding the model of the actual body and the process considered may be listed as follows:

- i. The crystal has a simple cubic lattice.
- ii. Dislocation density is negligibly small everywhere except on the grain boundaries.
- iii. Grain boundaries are free from preferential adsorption sites.
- iv. Only single advacancies (adsorbed vacancies) are mobile along the grain boundaries. They cannot migrate into other grains across the boundary.
- v. Only single advacancies may desorb directly from the boundaries; the desorption from clusters already formed, is disregarded.
- vi. Nucleation and growth of aggregates occur only by the addition of single advacancies due to surface diffusion. Direct impingements of single elements from the vacancy vapour on the clusters are negligible.
- vii. The decrease of advacancy concentration around the growing aggregates is not taken into account.
- viii. There exists only one orientation of the clusters. This assumption can be removed without changing the essential procedure [4, 5, 6].
- ix. A quasi-stationary state of the process is established.
- x. The process is considered to be isothermal.

Let us now consider an internal region of the crystal containing a grain boundary.

The system vapour-advacancies-vacancy aggregate is in metastable equilibrium when the phase equilibriae are established: advacancies  $\rightleftharpoons$  aggregate and vapour  $\rightleftharpoons$  aggregate as well as the adsorption equilibrium vapour  $\rightleftharpoons$  advacancies [7].

Under the assumptions summarized above, the problem has been analysed via the petit canonical ensemble and reduced to that of calculating the partition function of a two-dimensional adsorbed gas composed of different aggregates. From the partition function, calculated with disregard of internal energy contributions, the free energy of the system has been determined. The minimum of this energy leads then to the density of the critical clusters. Finally, from kinetic considerations, the nucleation rate is found.

The partition function has the form:

$$(2.1) \quad Z = \sum_i \exp\left(-\frac{E_i}{kT}\right),$$

where  $E_i$  is the energy of state  $i$ ,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature, and the sum is taken over all possible configurations of the  $N$  advacancies on the grain boundary.

Let  $N_0$  be the density of discrete adsorption sites per unit area of the grain boundary ( $\approx 10^{15} \text{ cm}^{-2}$ ),  $N_1$  — the number of single advacancies per unit area of the boundary,  $N_i$  — the equilibrium surface density of clusters of  $i$  advacancies, and  $\varepsilon_i$  — the potential energy of an aggregate of size  $i$ .

Assuming that  $N_0 \gg \sum_{i=1}^n N_i$ (<sup>1</sup>), which means that the fraction of the unit area of the grain boundary, covered by the aggregates of various classes, is negligibly small,  $N_i$  aggregates can be distributed over  $N_0$  positions in

$$\binom{N_0}{N_i} = \frac{N_0(N_0-1) \dots (N_0-N_i+1)}{N_i!} \approx \frac{1}{N_i!} N_0^{N_i} \text{ ways,}$$

and its contribution to the partition function is

$$(2.2) \quad \hat{T}_i = \frac{1}{N_i!} N_0^{N_i} \exp\left(\frac{N_i \varepsilon_i}{kT}\right).$$

The total contribution to  $Z$  of all the aggregates is the product of all the terms (2.2)

$$(2.3) \quad \hat{T} = \prod_{i=1}^n \frac{1}{N_i!} \left[ N_0 \exp\left(\frac{\varepsilon_i}{kT}\right) \right]^{N_i},$$

and the partition function is the sum of all these products over all possible distributions

$$(2.4) \quad Z = \sum_{k=1}^n \prod_{i=1}^k \frac{1}{N_i!} \left[ N_0 \exp\left(\frac{\varepsilon_i}{kT}\right) \right]^{N_i}.$$

The most probable distribution of aggregates of different sizes corresponds to the minimum of free energy  $F$ . This, owing to the relation

$$(2.5) \quad F = -kT \ln Z,$$

(<sup>1</sup>) Eliminating of this convenient assumption leads to more complicated formulae without changing the procedure [5]. For small clusters, the error seems to be negligible.

leads to the maximum of  $\ln Z$  with the condition:

$$(2.6) \quad \sum_{i=1}^n iN_i = N.$$

Thus the problem is reduced to the solution of a system of two Eqs.: (2.6) and

$$(2.7) \quad \frac{\partial}{\partial N_j} \left[ \ln Z + \ln \lambda \left( \sum_{i=1}^n iN_i - N \right) \right] = 0,$$

where  $\ln \lambda$  is the Lagrangian multiplier.

Applying the method of the maximum term [8], we replace the sum (2.4) by the largest component  $\hat{T}$ :

$$(2.8) \quad \ln \hat{T} = \sum_{i=1}^n \left[ -\ln N_i! + N_i \left( \ln N_0 + \frac{\varepsilon_i}{kT} \right) \right].$$

Now assume that  $N_i \gg 1$ , so that we can use Stirling's formula,  $\ln N_i! = N_i \ln N_i - N_i$ . We then have

$$(2.9) \quad \ln \hat{T} = \sum_{i=1}^n \left[ -N_i \ln N_i + N_i + N_i \left( \ln N_0 + \frac{\varepsilon_i}{kT} \right) \right].$$

Formal differentiation performed in the Eq. (2.7) the Eq. (2.9) being taken into account, leads to

$$(2.10) \quad \frac{\partial}{\partial N_j} \left[ \ln \hat{T} + \ln \lambda \left( \sum_{i=1}^n iN_i - N \right) \right] = -\ln N_j + \ln N_0 + \frac{\varepsilon_j}{kT} + j \ln \lambda = 0.$$

Hence

$$(2.11) \quad N_j = N_0 \exp \left( \frac{\varepsilon_j}{kT} \right) \lambda^j,$$

and putting  $j = 1$ , we can find  $\lambda$ :

$$(2.12) \quad \lambda = \frac{N_1}{N_0} \exp \left( -\frac{\varepsilon_1}{kT} \right).$$

Substituting (2.12) into (2.11), we have

$$(2.13) \quad N_n = N_0 \left( \frac{N_1}{N_0} \right)^n \exp \left( \frac{\varepsilon_n - n\varepsilon_1}{kT} \right).$$

This distribution is valid for all aggregate sizes, so it holds also for the density of critical clusters  $N_{n^*}$ . Moreover,  $E_{n^*} = \varepsilon_{n^*} - n^* \varepsilon_1$  is the net gain in potential energy when the cluster is formed from  $n^*$  advacancies. This is the binding energy of a cluster of  $n^*$  vacancies, formed on the grain boundary, relative to that of  $n^*$  free advacancies. Consequently, the density of critical clusters may be written in the form:

$$(2.14) \quad N_{n^*} = N_0 \left( \frac{N_1}{N_0} \right)^{n^*} \exp \left( \frac{E_{n^*}}{kT} \right).$$

### 3. Nucleation rate

To apply Walton's approach to our problem, we have slightly to change the definition of the critical aggregate. In classical nucleation theory, this is an aggregate with equal probability of growth or disintegration. Here, we define the critical cluster as the aggregate with probability of growth  $\leq 1/2$  which, after catching one additional element of the mother phase, attains the growth probability  $\geq 1/2$ . Thus the nucleation rate  $J$  is the rate of promotion of critical clusters, containing  $n^*$  vacancies, to the smallest stable clusters (nuclei) by a single advacancy capture

$$(3.1) \quad J = N_{n^*} w_{n^*}^v,$$

where  $w_{n^*}$  is the capture rate of single advacancies by a cluster of size  $n^*$ .

The mean lifetime of an advacancy on the grain boundary before desorption is:

$$(3.2) \quad \tau_a = \frac{11}{\nu} \exp\left(\frac{E_a}{kT}\right),$$

where  $\nu \approx 10^{13}$  is the atomic vibrational frequency, and  $E_a$  is the adsorption energy of a single vacancy.

If we denote by  $P_p$  the incidence rate of vacancies, the equilibrium advacancy population  $N_1$  can be expressed as

$$(3.3) \quad N_1 = P_p \tau_a = \frac{P_p}{\nu} \exp\left(\frac{E_a}{kT}\right).$$

The incidence rate may be approximately written

$$(3.4) \quad P_p = \nu c,$$

where  $\nu$  is the average velocity of a vacancy within the grains, and  $c$  is the current volume vacancy concentration in the strained crystal ( $\varepsilon > 0$ ).

The average velocity of a vacancy may be represented in the following form [2]:

$$(3.5) \quad \nu = \nu R_0 \exp\left[-\frac{(U_m - \Delta U)}{kT}\right],$$

where  $R_0$  is the lattice constant,  $U_m$  is the activation energy of motion of vacancies, and  $\Delta U$  is the decrease of this energy given by the Eq. (1.1).

On the other hand, the initial ( $\varepsilon = 0$ ) concentration of vacancies is given by the known formula

$$(3.6) \quad c_0 = \mathcal{N} \exp\left(-\frac{U_f}{kT}\right),$$

where  $\mathcal{N}$  is the total number of atomic sites per unit volume, and  $U_f$  is the activation energy of formation of a vacancy.

Due to the strain, the energy of vacancy formation will be lowered. If we assume that this energy decrease is  $\Delta U$ , then the current vacancy concentration can be written in the form:

$$(3.7) \quad c = \mathcal{N} \exp\left[-\frac{(U_f - \Delta U)}{kT}\right] = c_0 \exp\left(\frac{\Delta U}{kT}\right).$$

Combining the Eqs. (3.4), (3.5), and (3.7), we obtain for the incidence rate the following equation:

$$(3.8) \quad P_p = \nu R_0 c_0 \exp \left[ -\frac{(U_m - 2\Delta U)}{kT} \right].$$

The capture rate  $w_{n^*}$  can be calculated from kinetic considerations. When advacancies diffuse over the grain boundary with a mean velocity  $v_d$  and  $b_{n^*}$  is the capture width of the critical aggregate (equal to the diameter or the periphery of the aggregate [9, 10]), then

$$(3.9) \quad w_{n^*} = b_{n^*} N_1 v_d.$$

The average migration velocity of a single advacancy over the grain boundary is approximately

$$(3.10) \quad v_d = \nu d \exp \left( -\frac{E_d}{kT} \right),$$

where  $d$  is the distance between adsorption sites, and  $E_d$  is the activation energy for surface diffusion.

From (3.9), (3.10) and (3.3), we have

$$(3.11) \quad w_{n^*} = b_{n^*} P_p d \exp \left( \frac{E_a - E_d}{kT} \right).$$

Substituting (2.14) and (3.11) into (3.1) and taking into account (3.3) and (3.8), as also putting  $N_0 \approx 1/d^2$ , we finally obtain the microcrack nucleation rate in the loaded crystal:

$$(3.12) \quad J = (R_0 c_0)^{n^*+1} d^{2n^*-1} b_{n^*} \nu \exp \left[ \frac{(n^*+1)(E_a - U_m + 2\Delta U) + E_{n^*} - E_d}{kT} \right],$$

where  $\Delta U$ , as a function of strain  $\varepsilon$ , is given by (1.1).

#### 4. Conclusions

The proposed mechanism of microcrack nucleation explains to some degree the beginning of the process of fracture and the nature of formation of small cracks. Once the growing nucleus of a microcrack has reached the size of the order of a Griffith crack, its further growth can follow the existing continuum hypotheses. On the other hand, however, the idealized structure assumed for our considerations constitutes a very approximate model of a metal. Consequently, the nucleation rate equation derived here presents merely a theoretical result, and only further investigations can show whether it may find practical applications.

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Received November 16, 1972.