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Short communication

Stabilization of nanostructured materials using fine inert ceramic particles

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Abstract

Modified versions of the Zener drag equation were obtained by evaluating a non-random distribution of incoherent ceramic particles in a nano-crystalline material. Analytical investigation of particle-boundary correlation indicates that the limiting grain size would be proportional to $f_V^{-1/3}$ for f_V larger than 2.96%. The limiting grain size can be obtained by a combination of random and non-random Zener drag pressure in the case of volume fractions smaller than 2.96%.

Keywords: A. Grain growth; B. Grain size; Nanostructures; Fine ceramic particles

1. Introduction

Nanostructured materials are thermodynamically unstable due to the presence of a large fraction of interface boundaries. Stabilization of the fine grained structure is of critical importance if the unique structures and properties of nanostructured materials are to be retrained. The distribution of inert ceramic particles in a nano-crystalline (NC) matrix and thus the effect of Zener drag can be employed as a useful method for stabilization of grain size [1–4]. Experimental investigations reported the marked effect of second phase particles on the stagnation of grain growth in NC materials [5–7]. In spite of its name, Zener never published any paper on this effect and his contribution was made through a personal communication to Cyrile Stanley Smith [8]. However, the effect has become known under Zener's name, and in the last 60 years since its discovery, several extensive modeling and simulation studies have been completed. These studies have focused chiefly on the effects of particle shape, volume fraction, coherency, distribution, particle correlation with the boundary.

Several studies, experimentally [9,10] or theoretically [11–15], have shown that the number of particles correlating with boundaries is much higher than the value estimated using a random approach. The assumption of a random distribution of precipitates at grain boundaries does not seem to be representative of the real materials. Specially in NC matrixs, the presence of a high amount of grain boundary phase causes a non-random distribution of particles. Within the framework of this paper it is our intention to firstly explain the classical Zener relationship and then by means of some changes in the stated assumptions, obtain a modified equation for NC materials.

2. The drag pressure due to a random distribution of particles

For a volume fraction f_V of random distributed spherical particles of radius r, the number of particle per unit volume (N_V) is given by

$$N_V = \frac{3f_V}{4\pi r^3} \tag{1}$$

The number of particles intersecting unit area of boundary is then

$$N_S = 2rN_V = \frac{3f_V}{2\pi r^2} \tag{2}$$

The drag pressure caused by the particles on unit area of the boundary is given by

$$P_Z = F \cdot N_S \tag{3}$$

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where F is the maximum restraining force of a particle intersecting a grain boundary of specific energy γ.

$$F = \pi r \gamma \tag{4}$$

and hence

$$P_Z = \frac{3 f_Z \gamma}{2r} \tag{5}$$

The driving pressure for growth (P_g) arises from the curvature of the boundaries and is given by

$$P_g = \frac{2\alpha\gamma}{D} \tag{6}$$

where D is the grain size and α is a geometrical constant of about 0.37 [16].

Grain growth will cease when $P_g = P_Z$, i.e.

$$D_Z = \frac{4\alpha r}{3 f_V} \tag{7}$$

was obtained by Zener [17], assuming a random distribution of spherical particles intersecting macroscopically planar boundary, in the situation where the particle size is much smaller than the initial grain size ($r \ll D_i$, Fig. 1a). Similar relationships can be obtained considering different points of view [18–20].

3. The drag pressure due to a non-random distribution of particles

3.1. Particles correlation with boundaries

A non-random distribution of particles may occur as a result of several factors for example planar arrays of particles in the rolled materials, the precipitation of particles onto pre-existing low or high angle boundaries, or inhomogeneous nucleation of crystallites on the surface of particles in casting methods.

As the grain size is reduced in a poly-crystalline material, the ratio of grain boundary to lattice phase increases. In the case of a distribution of sub-micro particles in a NC material, one can assume that all the particles are in contact with the boundaries. For nano-particle distributed NC materials, even for smaller particles than an initial grain size ($r < D_i$), all the particles would be in contact with boundaries as the grain growth starts. Accordingly, the number of particles intersecting unit area of boundary cannot be obtained by Eq. (2).

Assuming spherical grains of D diameter, the number of grains per unit volume is given by

$$N_D = \frac{1}{(4/3)\,\pi (D/2)^3} \tag{8}$$

Considering boundaries are shared between two grains, the surface area of boundaries is then

$$S_V = \frac{N_D \cdot 4\pi (D/2)^2}{2} = \frac{3}{D} \tag{9}$$

The number of particles intersecting a unit area of boundary can be obtained by

$$N'_S = \frac{N_V}{S_V} = \frac{D f_V}{4\pi r^3} \tag{10}$$

For incoherent spherical particles the pinning pressure (P'_Z) will be given by

$$P'_Z = F N'_S = \frac{D\gamma f_V}{4r^2} \tag{11}$$

Considering the driving pressure for growth (Eq. (6)), the limiting grain size can be obtained

$$D_{Zl} = \frac{1.72r}{f_V^{0.5}} \tag{12}$$

The result is similar to the limiting grain size obtained by Humphreys who considered all the particles lying on the vertices [16], Anand's estimation of subgrain size in a quenched steel [9] and the result of the computer simulation of Srolovitz et al. [21] and Moelans et al. [22].

Though Eq. (11) was obtained using an analytical approach, it may be encountered some difficulties when considering the assumptions and results together. Inter-particle spacing for a homogenous dispersion of spherical particles in a matrix is obtained by

$$L = N_V^{-1/3} \approx \frac{1.61r}{f_V^{1/3}} \tag{13}$$

At any volume fraction, Eq. (12) predicts limiting grain sizes larger than inter-particle spacing, so some particles have inevitably been detached from the boundaries, which is in contradiction to the initial assumption stating all the particles are in contact with grain boundaries.

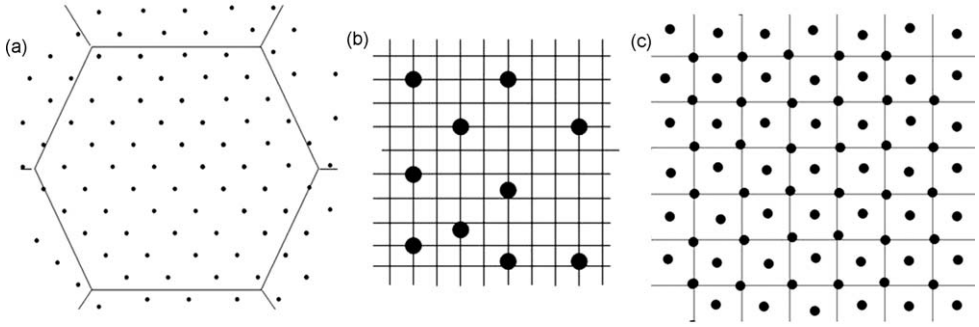

Fig. 1. Correlation of particles with boundary in (a) random, (b) non-random and (c) combination of random and non-random distribution.

3.2. Particles correlation with corners

In the case of NC materials, it is reasonable to assume that all particles lie on quadruples, because in these positions the particles, by removing the maximum boundary area, minimize the energy of system (Fig. 1b). This represents the situation in which all particles are in boundary corners but not all the boundary corners are occupied by particles; hence grain growth will actually continue to occur until all the grain corners are pinned.

When studying grain growth in a dispersion of Fe_3C in Fe, Helman and Hillert found that most of the particles were situated in the grain corners at inhibited grain growth [23]. Using the estimation of Hillert [24], there are 24 grain corners in each grain but each corner is shared between 4 grains. There would thus be enough particles to fill all the grain corners in a material if there are on the average 6 particles per grain volume, thus

$$\frac{N_V}{N_D} = 6 \Rightarrow \frac{D}{r} = \frac{\beta}{f_V^{1/3}} \tag{14}$$

where β = 3.6.

Computer simulation by Hazzledine and Oldershaw [12] and Anderson et al. [25] indicated in relationships similar to Eq. (14), differing only in having a slightly different β value. However, this type of relationship can be validated for volume fractions larger than a critical value where $10^{-1} > f_{V_{crit}} > 10^{-2}$ [16,26].

Because the line representing Eq. (14) intersects the line representing Eq. (7) at about $f_V = 0.1$, Hillert suggested that the limiting grain size will be controlled by Eq. (14) for f_V larger than 0.1 [24]. The reason why the particles should be located in quadruple point was not discussed by the aforementioned authors. However, it seems to be reasonable in the case of NC materials.

For f_V smaller than $f_{V_{crit}}$, stagnation occurs at a grain size larger than one predicted by Eq. (14), so one should use Eq. (7) and the obtained limiting grain size is larger than inter-particle spacing. Since the growth was started from a nanostructured matrix, one can assume that a fraction of particles occupies the boundary corners and the remaining fraction is distributed in the matrix (Fig. 1c). Indeed, this would be the case when a combination of random and non-random distribution of particles takes place.

Instead of intersecting Eqs. (14) and (7) in order to find the $f_{V_{crit}}$, we used a rather more accurate estimation which was employed by Humphreys to find changes of drag pressure via initial grain boundary size for a given f_V and r [16].

Considering cubic unit cells of D length, there are $1/D^3$ cubics per unit volume. Each cell has 8 corners. Since each corner is shared between 8 unit cells, the number of boundary corners per unit volume in a material of grain size D can be obtained approximately by $8 \times (1/D^3)/8 = 1/D^3$ and thus the fraction of particles lying on these sites is given by [16]:

$$x = \frac{1}{N_V D^3} = \frac{4\pi r^3}{3 f_V D^3} \tag{15}$$

The number of corner-sited particles per unit area of boundary is then

$$N_C = x N_V D \tag{16}$$

and the remaining particles

$$N_r = 2 r N_V (1 - x) \tag{17}$$

Thus the total number of particles per unit area of boundaries is $N_C + N_r$. Using Eq. (3) the pinning pressure is

$$P_Z = \pi r \gamma (x N_V D + (1 - x) 2 N_V r) = \frac{2\alpha\gamma}{D} \tag{18}$$

Considering the driving pressure for growth (Eq. (6)), the limiting grain size can be obtained

$$\frac{3 f_V}{4r} D^3 - \alpha D^2 + \frac{\pi r}{2} D - \pi r^2 = 0 \tag{19}$$

Eq. (19) was solved by MATLAB software for $10 < r < 200$ nm and $0.001 < f_V < 0.22$ (Fig. 2). Hunderi calculated that the interaction of particles with various position of a boundary induces different pressures. While obtaining Eq. (19), however, the drag pressure caused by the presence of particles at grain boundaries, triple lines and quadruples is assumed to be identical.

There is a considerable departure from Zener-analysis of the stagnation of grain growth at $0.02 < f_V < 0.19$, in the direction of an increased particle drag compared with Zener estimate. At volume fractions larger than 0.19, for a random distribution of particles, the intersection of grain boundaries and particles increases and thus, Eq. (7) would predict similar values to Eq. (19). One can see that at volume fractions smaller than 0.02, there is a negligible difference between Eqs. (19) and (7). It can be rationalized studying the effect of f_V on x (Eq. (15)) and thus on P_Z (Eq. (18)). The reduction of f_V to very small values would increase grain size which affects Eq. (15) by the power of three, thus x tends to zero. Accordingly, those parts of Eq. (18) according to the non-random particle distribution, i.e.

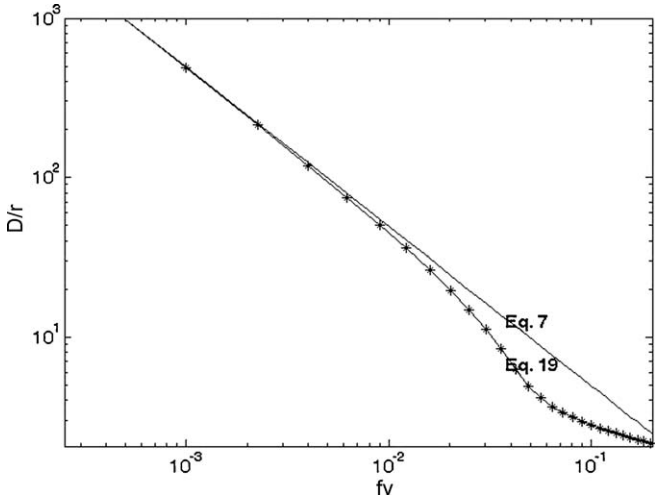

Fig. 2. Comparison between normalized grain size vs. volume fraction obtained by Eqs. (7) and (19).

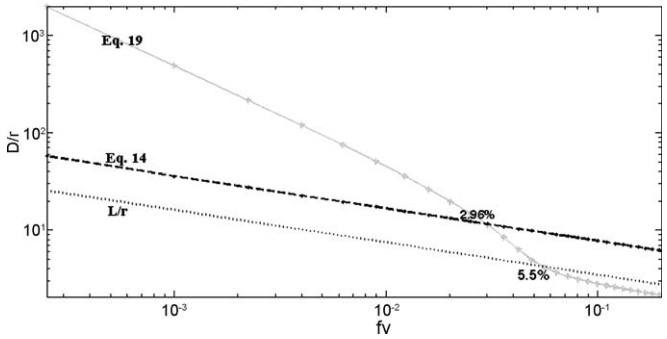

Fig. 3. Intersection of normalized grain size obtained by Eqs. (14) and (19).

$\pi r\gamma \times (xN_V D - 2xN_V r)$, would become negligible and Eq. (18) would change to Eq. (3).

Normalized grain size obtained by Eq. (19) has an intersection with L/r of $f_V = 5.5\%$ (Fig. 3). This intersection occurs at $f_V = 16.9\%$ when the Zener equation is used. Since the limiting grain size smaller than the inter-particle spacing cannot logically be stabilized, thus Eqs. (7) and (19) cannot be used for f_V larger than 16.9% and 5.5%, respectively.

In the case of NC materials, Eq. (19) has an intersection with Eq. (14) at 2.96%, which indicates that limiting grain size will be controlled by Eq. (19) for f_V smaller than 2.96% and by Eq. (14) for f_V larger than 2.96%.

4. Conclusion

Non-random distribution of particles in a fine grained matrix was observed in several experimental investigations. Thus the classical Zener equation cannot be used for NC materials when all or most of the incoherent ceramic particles are correlated with grain boundaries or corners. Considering all the particles correlate with boundaries, one can deduce a normalized grain size proportional to $f_V^{-1/2}$. In a better estimation, particles are in contact with corners, which predicts a limiting grain size proportional to the inter-particles spacing, i.e. $f_V/r \approx f_V^{-1/3}$. However, this type of relationship has not been validated for the total range of volume fractions, and therefore a relationship based on the combination of random and non-random particle distribution was obtained for the small values of f_V.

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