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Critical sizes for the stabilization of coherent precipitates

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On growth of a precipitate beyond a critical size \( r^* \), interfacial misfit dislocation loops are energetically stabilized. In the case of precipitation in (small) finite crystals, the energy of both the coherent precipitate and the dislocation loop are altered with respect to bulk crystals. Thus, as the crystal (domain) size approaches nanoscale, the critical size \( r^* \) is expected to be altered with respect to bulk crystals. In the current investigation, finite element simulations are performed to study the variation of critical size \( r^* \) with crystal/domain size and it is shown that below a critical domain size, the coherent precipitate is stabilized. Important findings include: (i) strain energy versus precipitate-size plot shows change in curvature for large precipitate sizes and (ii) coherent state is stable in two distinct regimes of precipitate sizes. Further, a phase diagram showing the stability regions of the coherent and semi-coherent states of the precipitate is drawn. © 2014 AIP Publishing LLC.

I. INTRODUCTION

A precipitate with a small misfit with the matrix tends to be coherent in order to minimize the interfacial chemical energy. Global energy minimization dictates that on growth beyond a critical size \( r^* \), an interfacial misfit dislocation loop becomes favourable. Such an interface with interfacial misfit dislocations is termed as semi-coherent. The value of \( r^* \) depends on the strain energy stored in the precipitate of radius \( r_p \) \( (E_C \) or \( E_{\text{strain}}^\text{ppt} \) (Ref. 3) and the energy cost for a dislocation loop \( (E_d) \) of radius \( r_d \) (Ref. 4)

\[
E_C = \frac{8\pi^3}{3} \frac{f_m^2 G}{p_{\text{m}}} \left( \frac{1 + \nu}{1 - \nu} \right),
\]

\[
E_d \approx \frac{G b^2}{2(1 - \nu)} r_d \left[ \ln \left( \frac{8r_d}{nm} \right) + 1 \right],
\]

where \( G \) is the shear modulus, \( \nu \) is the Poisson’s ratio, \( f_m \) is the lattice misfit between precipitate and matrix, \( b \) is the modulus of the Burgers vector and \( 1/c_{\text{m}} \) is the core cut-off radius (usually in the range of \( b \) (Ref. 3) to \( 5b \) (Ref. 5)). The core energy is usually about 10% of the total energy. The abovementioned equations assume that the matrix (domain) is infinite. It is also seen that strain energy function (Eq. (1)) has a positive curvature for all values of \( r_p \). Critical size \( r^* \) is given by2,3,7

\[
r^* = \frac{b}{8\pi \varepsilon (1 - \nu)} \left[ \ln \left( \frac{8r^*}{b} \right) + \frac{3 - 2\nu}{4(1 - \nu)} - 1 \right],
\]

where \( \varepsilon \) \( (\varepsilon = \frac{(1 + \nu)f_m}{3(1 - \nu)} \) (Ref. 8)) is the strain parameter of the constrained system (i.e., of the precipitate). The equation for \( r^* \) (Eq. (3)) is derived based on the criterion that energy released on loop formation is equal to the strain energy of loop (when the precipitate size is \( r^* \)).

The interfacial dislocation loop can form at the interface by many mechanisms (e.g., climb of interfacial loop, punching-in of shear loops, expansion of a loop inside the precipitate, trap of external loops, etc.), which depend on the local microstructural conditions present in the sample. The semicoherent interfaces are more glissile as compared to the coherent interface and this transition of the interface may play an important role in the change of the shape of the precipitate (e.g., the precipitate may go from a spherical to cuboidal).9

Finite element method (FEM) has proved to be an important tool in the study of dislocations,10-12 precipitation,13,14 and coherent to semi-coherent transition in precipitates.15 The morphology of precipitates13 and stress state of the system16 during phase transformation has been analyzed by FEM. Dislocations in finite domains have also been investigated using FEM.17,18 FEM has the following advantages in the context of precipitation and coherent to semi-coherent transition in precipitates: (i) stress state of the semicoherent precipitate can be computed,15 (ii) effect of multiple dislocation loops can be studied,19 and (iii) microstructural effects on the strain energy of precipitates and also on \( r^* \) can be investigated. Additionally, FEM has also been successfully used to simulate the precipitation in epitaxial films.14 In addition to FEM other techniques like \textit{ab initio} density functional theory has recently been used for the study of coherent to semi-coherent transition of precipitates.20 The authors (Sampath and Janisch20) have pointed out that “A wide variety of literature is available for coherent interface calculations, whereas for semi-coherent interfaces it is rather limited.”

The current manuscript is intended to make the following important contributions to our understanding of the coherent to semi-coherent transition of precipitates in finite crystals (including nanoscale crystals/domains). (1) Change in the energy landscape \( (E_{\text{loop}}^\text{strain} \) versus \( r_p \) plot) due to finite domain effects. (2) Effect of domain deformations (due to precipitate) on coherent to semi-coherent transition. (3) Determination of regimes of stability of coherent precipitate.
(vis-à-vis the semi-coherent precipitate). (4) Variation of critical size ($r^*$) with domain size and the determination of critical domain size at which coherent state is stabilized. Towards this end, a model system has been considered (for material properties): the γ-Fe precipitate (with 2 wt. % Cu) in the Cu-γFe matrix system and analyses are carried out using FEM. In the current work, the focus is on understanding the basics of precipitates (with misfit strains) in domains with confined geometry (thus highlighting the difference between bulk domains and nanoscale domains). Hence, the conclusions drawn are expected to be applicable to other systems as well.

The assumptions made (“ideal features” of the model) are as follows. (1) Domain is assumed to be cylindrical and precipitate is assumed to be spherical (in the Cu-γFe system the precipitate becomes cubic only after the interface becomes semi-coherent). The effect of spherical domain is considered in the supplementary material.21 (2) The precipitate is positioned at the centre of the domain (which is the highest energy position and hence in practice precipitates may energetically prefer to be positioned off centre). In the case of precipitation, nucleation may be preferred at the surface, which has also not been considered in the ideal model. (3) Multiple nuclei may form leading to more than one precipitate in the domain—this aspect has been ignored. (4) As comparison is made between the energy of a coherent and semi-coherent precipitate of a given size to determine critical size, the interfacial energy is a constant additive term to the strain energy of the system, and hence is not considered in the computations. In future works, some of the assumptions used in the current work can be relaxed, thus taking into account deviations from ideality found in practical situations. However, it is noteworthy that some of the fundamental aspects discovered from these simulations will express themselves in practical cases as well.

II. FINITE ELEMENT METHODOLOGY

A schematic of the numerical model used to simulate the stress state of the spherical γ-Fe (with 2 wt. % Cu) precipitate in Cu-2 wt. % Fe cylindrical matrix is shown in Figure 1. Isotropic material properties used in the simulations are (i) lattice parameter of the precipitate ($a_p$) = 3.56 Å, (ii) lattice parameter of matrix ($a_m$) = 3.615 Å, (iii) modulus of Burgers vector ($b$) = $\sqrt{2}a_p/2 = 2.519$ Å, (iv) shear modulus of precipitate ($G_p$) = 108.84 GPa, (v) shear modulus of matrix ($G_m$) = 55.27 GPa, (vi) Poisson’s ratio of precipitate ($\nu_p$) = 0.2729, and (vii) Poisson’s ratio of matrix ($\nu_m$) = 0.3236.22 The values of $G$ and $\nu$ are obtained by Voigt average of the single crystal data.22 The use of isotropic material properties is suitable for easy comparison with available analytical expressions.

To explore the effect of anisotropy on the critical sizes ($r^*$ and $r_1$), three cases are considered (corresponding model is as in Figure 1(b)): (i) a special case, where the material y-axis is parallel to the axis of the cylinder ($\theta = 0^\circ$); (ii) the y-axis is at an arbitrary angle to the axis of the cylinder ($\theta$ is chosen as $10^\circ$ for comparison with other results); and (iii) another special case, where $y$-axis is perpendicular to the axis of the cylinder ($\theta = 90^\circ$). A 3D numerical model (Figure 1(b)) is used for the simulation of the system with anisotropic material properties. The anisotropic elastic material properties used in the simulations are $C_{11}^m = 170.19$ GPa, $C_{12}^m = 122.18$ GPa, $C_{44}^m = 76.15$ GPa, $C_{11}^p = 228.92$ GPa, $C_{12}^p = 134.77$ GPa, and $C_{44}^p = 116.26$ GPa (superscript “m” refers to the matrix and “p” refers to the precipitate). The domain size (R) is kept constant at 160 b. It is to be noted that the orientation of the loop changes with the material axes, due to restriction imposed by crystallography.

A brief outline of the simulation methodology is presented here. The reader may consult the work of Kumar et al.15 for further details. The stress state of the coherent precipitate, in a domain of radius “R,” is simulated by imposing stress-free strains (eigen-strains) in region P (marked in Figure 1) corresponding to the lattice misfit present at the interface between the precipitate and the matrix. The value of the misfit strain is calculated as: $(a_p - a_m)/a_p = -0.015$. These eigen-strains are imposed as thermal strains in the finite element model. The elastic strain energy of the growing precipitate is obtained by increasing the radius of the precipitate ($r_p$) in the numerical model.

The stress state of an interfacial misfit dislocation loop is simulated by imposing eigen-strains in region D (marked in Figure 1) corresponding to the insertion of a disc of atoms in the precipitate. The strain is calculated from the formula

$$\varepsilon_f = \frac{a_{[110]} + b - a_{[110]} }{a_{[110]} + b} = \frac{1}{2}, \quad (4)$$

where $a_{[110]} (= 2$ b) is the lattice spacing along the [110] direction. It is important to note that the structure and energy of the core of the dislocation loop is neglected in the present study. Details of validation of this FEM model for the simulation of an edge dislocation can be found elsewhere.15,23
The 2D domain is meshed with 4-noded bilinear quadrilateral elements of mesh size \( b \times b \). Displacement boundary conditions are imposed as in Figure 1(a) and axisymmetry is along the \( y \)-axis. The length of the symmetrical-half of the cylindrical domain is 400 \( b \). The length is chosen such that the free-surface effects from the flat surfaces are negligible (i.e., the domain behaves like an infinitely long one). Simulations of the stress state and the computation of the strain energies are performed by assuming linear elasticity theory and the finite element model is implemented using ABAQUS/Standard FEM software (Version 6.81, 2008). Inset to Figure 1(a) shows the orientation of interfacial misfit dislocation loop with respect to the crystallographic directions/plane. To simulate the effect of anisotropy, a 3D model as shown in Figure 1(b) is used, wherein 8-noded hex elements are used. Displacement boundary conditions are imposed in accordance with the symmetry of the system.

The critical size \( r^* \), is determined by plotting the strain energy of the coherent (\( E_C \)) and semicoherent (\( E_{SC} \)) precipitate as a function of its radius \( r_p \). The value of \( r^* \), corresponds to the cross-over of the two curves. Special attention is paid to the nature of these plots (and further to the intersections of these curves beyond \( r^* \)), in comparison to such plots for large scale domains. The abovementioned process is repeated for various values of the domain radius \( R \) (model shown in Figure 1(a)). The critical domain radius \( R^* \) is determined from the plot of \( r^* \) versus \( R \); where \( R^* \) is the radius of the domain below which the \( E_C \) and \( E_{SC} \) curves do not intersect (i.e., there is no \( r^* \)). In case of bulk domain, Kumar et al.\(^\text{15}\) compared the finite element simulation results for strain energy of the coherent precipitates, with isotropic and anisotropic material properties. The strain energy variation with the radius of precipitate compares well with theoretical expression (Eq. (1)), for the domain with isotropic material properties. Kumar et al.\(^\text{15}\) have shown the utility and advantage of the finite element methodology by considering an example of a spherical precipitate in a thin disc.\(^\text{15}\)

\[ \text{III. RESULTS AND DISCUSSION} \]

Figure 2 shows the stress state of the system (plot of \( \sigma \) contours) in the absence (Figure 2(a)) and presence (Figure 2(b)) of an interfacial misfit edge dislocation loop (for \( R = 120 \, b \), \( r_p = 80 \, b \)). The Fe-2 wt. % Cu precipitate region (shaded in grey) is under tensile stress state and the region of the matrix near to the precipitate is under compressive stress state. The stress state reverses near the interfacial misfit dislocation loop (giving compressive stresses in the precipitate region and tensile stresses in the matrix region, as shown in Figure 2(b)). Domain deformations (with deformation scale factor 10) due these stresses are to be noted.

The strain energy of a precipitate of fixed radius \( r_p \) in a finite domain is lower than that of the same precipitate in an infinite domain due to two factors: (i) reduction in the volume of strained material and (ii) domain deformations. Figure 3 highlights these effects, wherein the strain energy of the coherent system with a precipitate of radius 30 \( b \) is plotted with domain radius \( R \). It is seen that the energy of the system decreases steeply with a decrease in domain radius \( R \) below 160 \( b \) (~403 Å); wherein nanoscale effects become prominent.

Figure 4 shows the variation in the strain energy with the radius of the precipitate \( r_p \) for system without \( E_C \) and with \( E_{SC} \) misfit dislocations loop. Plot of Eq. (1) is also shown for comparison. A domain of size 160 \( b \) (~403 Å) has been considered for the illustration of finite domain effects. It is seen that for small precipitates the system behaves like

\[ \text{FIG. 2. Plot of the FEM simulated } \sigma \text{ stress contours in a symmetrical half of the domain: (a) corresponding to the formation of a coherent precipitate of } r_p = 80 \, b \text{ and (b) semi-coherent precipitate with an interfacial misfit dislocation loop. Domain radius } R \text{ is } 120 \, b \text{ and the region shaded grey corresponds to the precipitate. The stress plots are in the deformed configuration (deformation scale factor = 10). The undeformed domain is marked with a dashed line.} \]

\[ \text{FIG. 3. Reduction in the strain energy of a coherent precipitate (of fixed radius 30 b) with decreasing domain size "R." Percentage reduction in energy for a domain of size 60 b is also marked (point P). Nanoscale effects become prominent in the region shaded grey.} \]
an infinite one and the FEM results match reasonably well with the theoretical equation (as seen in inset to Figure 4).

For larger sizes of the precipitate, finiteness of the domain and domain deformations play an increasingly important role. This results in two important effects: (i) change in the curvature of the E-rp plot after a certain rp (labeled as r_p^mfl) and (ii) decrease in the energy of the system with increasing rp, beyond a certain rp (labeled as r_p^max). These two aspects do not have analogues in infinite domains. Another important feature to be noted in Figure 4 is the double intersection of the curves (a) and (c). The first of these corresponds to the usual r^* and the second intersection, which has been labeled as r_p^C. This has not been described in literature. Beyond, r_p^C is a second region of the stability of the coherent state. The reason for the existence of this second regime of stability of the coherent state is as follows. For a given domain size (R), as the precipitate size (rp) approaches R, the system can lower its energy considerably due to domain deformations and hence there is insufficient strain energy (the "matrix" part of the domain is limited in volume) to accommodate a misfit loop. To visualize this effect better, one can consider the entire domain to be the precipitate—in which case there will be no strain energy in the system (and hence no critical size). The energy of the semi-coherent state is lower for precipitate sizes between r^* and r_p^C.

Figure 5 shows the variation of normalized critical sizes ((a) r^*/R and (b) r_p^C/R) with domain size. In the region enclosed by curves (a) and (b), the semi-coherent state is stable. This is similar to a phase diagram where the regions of stability of the coherent state and semi-coherent state have been delineated. As the domain size (R) decreases, r^*/R and r_p^C/R approach each other and at R = 80 b the curves (a) and (b) in Figure 5 converge. The E versus rp plot for R = 80 b is shown in inset (of Figure 5). It is seen that energy curve for the coherent precipitate becomes tangential to the curve for the precipitate with a misfit dislocation loop (i.e., there is no intersection). For R < 80 b, the E-rp plot for the coherent precipitate is always lower than that for the semi-coherent precipitate (i.e., the coherent state is stabilized for all rp). The value of R = 80 b has been labeled as R^*, which is the critical domain size below which a coherent precipitate is stabilized for all rp. The r^* and r_p^C values have been normalized with "R," to accommodate for the fact that there is an increase in r_p^C due to the increasing domain size (i.e., the coherent state become stable when the precipitate size approaches that of the domain). It is to be noted that (i) r^* need not be normalized, as r^* tends to 47 b—the value for bulk domains, (ii) normalized r_p^C (i.e., r_p^C/R) tends to 0.85—the value for bulk domains, and (iii) to plot both these quantities on the same graph the normalized values have been used.

The results can be summarized as follows: (i) R > 80 b, E_SC < E_C for rp ∈ (r^*, r_p^C), (ii) R = 80 b, E_SC > E_C for all rp except for one rp (where r^* = r_p^C), and (iii) R < 80 b, E_SC > E_C for all rp.

The important points to be noted from the Figure 5 are (i) r^*/R increases with decreasing R and (ii) r_p^C/R increases with increasing R and tends to saturate. These observations can be understood as follows. As the domain size (R) decreases, the energy of the system decreases (Figure 3) and hence the precipitate will begin to dominate for rp values approaching R. The r^* with increasing R (this effect is amplified in the plot due to a decreasing R in the denominator). Finite domain effects (reduction in strain energy with increasing rp) will begin to dominate for rp values approaching R, and hence r_p^C will increase with increase in R. As mentioned before, normalization of r_p^C with R restricts this unbounded increase and r_p^C/R tends toward saturation.

The results of the simulation with anisotropic material properties are summarized in Table I. The results obtained with isotropic material properties are also shown in the table for comparison. The energy of the system (E_C and E_SC) are compared for a size of the precipitate (rp) of 60 b (>r^*). The energy of the system with and without the dislocation loop is
lower for the case with anisotropic material properties. It is seen that there is minor quantitative change in the results (r* and r^2) in the anisotropic model, with respect to that for the isotropic model. For the “anisotropic model,” r* remains constant with a change in angle of the material axis (h). This is to be expected, as the free-surface effects play a lesser role in the determination of r* as compared to r^2. The increasing value of r^2 with “h” is also to be expected, as with increasing “h” a reducing portion of the loop retains its proximity to the free-surface (as explained previously, r^2 arises purely due to free-surface effects). It is important to note that, there is no qualitative change in the behaviour of the system on the introduction of the anisotropic material properties. This is noteworthy, given the fact that, h = 90° represents a geometry, which is vastly different that, when h = 0°. Keeping above discussions in view, we can infer that all the interesting features displayed by the system (which gain prominence in nanoscale domains), can be studied using isotropic material properties.

IV. SUMMARY AND CONCLUSIONS

(1) In finite domains (single crystals), the strain energy of the coherent precipitate (EC) is altered with respect to that in infinite domains due to two factors: (i) reduced amount of strained matrix and (ii) domain deformations. In such situations, the standard theoretical equations cannot be used to compute the energy of the coherent or the semi-coherent precipitate (with a misfit edge dislocation loop). A salient feature of the strain energy versus radius of precipitate (rp) plot is the change in curvature beyond a certain size of the precipitate (i.e., the EC-rp plot develops a point of inflection).

(2) Critical size for coherent to semi-coherent transition (r*) is also altered in finite domains. An additional feature (with no analogue in infinite domains) is the existence of two critical radii (r* and r^2), and hence two separate regions of stability of the coherent precipitate (rp < r* and rp > r^2). A phase diagram showing the stability regions of the coherent and semi-coherent states can be drawn by plotting the r*/R and r^2/R curves with “R.”

(3) As the size of the domain is reduced below a critical value R*, the coherent state is fully stabilized (i.e., the coherent precipitate is stable for all rp < R*). At this value of R* (which is in the nanoscale regime), the lower (r*) and upper (r^2) critical radii curves merge.

Investigations have been performed using finite element method considering material properties (and misfit) corresponding to the Cu-γFe as a model system. In spite of the results being obtained for a specific set of material properties and certain idealized geometry of the domain and the precipitate; the essential features of the results are expected to be valid for other precipitates/matrix combinations and even certain other geometries. Exact analyses of these situations can be based on the understanding gained form the current simulations and can form scope for future studies.

21See supplementary material at http://dx.doi.org/10.1063/1.4878435 to study the effect of domain shape on coherent to semi-coherent transition in finite domains.