Origin of copper precipitation strengthening in steel revisited

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Abstract

Evaluation of the various sources of strengthening of ferritic steels by body-centered cubic (bcc) Cu alloy precipitates using the usual models eliminated misfit and modulus mismatch as the sources. The strengthening was attributed to the details of forcing a dislocation through a bcc Cu precipitate.

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1. Introduction

Precipitation strengthening in steels from copper rich body-centered cubic (bcc) precipitates, since the early paper of Russell and Brown [1], has generally been attributed to a difference in modulus between the precipitate and iron base solid solution matrix. A shear or Young’s modulus for the precipitate appropriate for face-centered cubic (fcc) copper has been assumed [1,2]. There is of course no direct measurement of the moduli or elastic constants of bcc copper. Ab initio calculations for bcc Cu [3] have predicted that at a temperature of 0 K the modulus \( C' = (C_{11} - C_{12})/2 \) is either zero or negative. Many years ago Zener [4] calculated a negative \( C' \) for bcc Cu and pointed out that bcc Cu thus is structurally unstable. Zener [4] also pointed out that low \( C' \) leads to large amplitude thermal vibrations and high vibrational entropy that may stabilize the bcc structure at elevated temperatures. If \( C' \) is negative, \( G_{[110][111]} \), the shear modulus on the primary slip plane in the slip direction for bcc metals, is also negative [5].

\[
G_{[110][111]} = 3C_{44}C'/(C' + 2C_{44})
\]

Misfit strengthening due to a lattice misfit between the bcc Fe matrix and the bcc Cu precipitates has been considered very small because the atomic volumes of bcc Fe and fcc Cu corrected for reducing the coordination number from 12 to 8 are very close. However, when Cu is dissolved into Fe there is an increase in atomic volume. This was observed many years ago by Norton [6] and more recently by Ma et al. [7] who extended the solid solubility by ball milling. We may expect that the average atomic volume in the precipitate is actually larger than that calculated from fcc Cu.

Many atom probe analyses of the precipitates in Fe base Cu alloys going back to the early work of Goodman et al. [8] and current research by Isheim and Seidman [9,10] have shown that the precipitate is a mixture of Cu and Fe. The core regions of Cu-rich 3 nm average size precipitates in a steel specimen with 1.3 at pct. Cu directly aged at 490 °C from the solutionizing temperature contained 64 ± 1 at.% Cu and 33 ± 1 at.% Fe. Nickel added to the steel to prevent hot shortness of the steel from Cu also segregated to the precipitate interface.

Thus the source of precipitation strengthening by bcc Cu precipitates needs to be re-examined because the calculations of the precipitation strengthening by the modulus effect are not correct, the misfit effect may not be
negligible as has been assumed, and there are additional sources of strengthening as discussed below.

When the precipitate radius is not large compared to the dislocation core radius the dislocation core cannot be ignored in discussing the origin of precipitation hardening. This is especially true for bcc metals because of the core asymmetry. Harry and Bacon [11,12] used many body potentials to simulate $\{111\}$ screw dislocations in Fe and bulk bcc Cu and in bcc Cu precipitates by molecular dynamics. They computed the energy vs. distance as a screw dislocation travels through a bcc Cu precipitate and determined a value for the strengthening from the slope. Traverse of the precipitate by the screw dislocation was predicted to transform the structure to an fcc-like structure. This will be discussed in more detail later in this paper.

Ab initio computations of the lattice and elastic constants of bcc copper were recently done at Northwestern University by Liu and Asta [12]. These, to be published separately, are used in the present paper.

2. Lattice constant and atomic volume of bcc copper

Using the full potential linearized augmented plane wave (FLAPW) method, Wang and Sob [4] computed the lattice and elastic constants of bcc Cu. They obtained at absolute zero temperature 0.280 nm for the lattice constant $(0.01098 \text{ nm}^3 \text{ atomic volume})$, however, “$C'$ vanishes or is even negative”. Using empirically derived interatomic potential values and molecular dynamics simulation, Harry and Bacon [11] calculated a lattice constant of 0.296 nm $(0.01297 \text{ nm}^3 \text{ atomic volume})$ for bcc Cu at zero pressure, which is substantially larger $(3\% \text{ linearly or } 10\% \text{ by volume})$ than the values computed from fcc Cu or by Wang and Sob. Harry and Bacon computed a positive value, 96 GPa, for $C'$.

However, according to their method of computation, when the lattice constant reaches 0.2885 nm, “one of the $\Gamma$–$N$ phonon branches becomes imaginary due to a shear instability”.

The atomic volume of bcc copper computed by Liu and Asta [12] at 0 K is $0.01209 \text{ nm}^3$. This is $2.6\%$ larger than the value calculated by Wang and Sob but $7\%$ less than the atomic volume calculated by Harry and Bacon.

The experimental atomic volume at room temperature for bcc Fe and for bcc Fe–Cu alloys measured by Ma, Atzmon and Pinkerton [7] are plotted in Fig. 1 along with the value computed by Liu and Asta for bcc Cu [12]. The latter was extrapolated, using the thermal expansivity for bcc Fe, to 0.01216 nm$^3$ at room temperature. The data set fits into a smooth curve. A small positive deviation from linear relationship (Vegard’s rule) is observed, which is reasonable since the Fe–Cu system has a positive (repulsive) pairwise interaction energy. A very large negative deviation from Vegard’s rule is obtained with the Harry and Bacon value, while the value predicted from fcc Cu $(0.01181 \text{ nm}^3)$ gives a huge positive deviation from Vegard’s rule.

The elastic constant, $C'$, of bcc copper at absolute zero was calculated for three different atomic volumes by Liu and Asta [12]: those of fcc Cu, bcc Fe and a value in between. The computed values of $C'$ for bcc copper were slightly negative for all three volumes, approximately $-13 \text{ GPa}$. There is no computed value for $C'$ at room temperature. It depends on the temperature coefficient for $C'$, the difference in temperature coefficients for $C_{11}$ and $C_{12}$, which are not known. Of course, when $C'$ is negative, $C_{12}$ must be larger than $C_{11}$. If $C_{12}$ has a more negative temperature coefficient than $C_{11}$ the curves will cross at some temperature and $C'$ will become positive. The composition of the bcc precipitates is approximately 1/3 Fe. $C'$ must increase with Fe content of the precipitate, increasing the likelihood that $C'$ of the precipitate is positive at room temperature. But whether positive or negative, $C'$ is small.

3. Precipitation strengthening

The increase in tensile yield stress observed on aging a binary Fe–1.67 at.\% Cu alloy quenched from 1000 °C and aged to maximum yield stress at 475 °C was 365 MPa [13]. In a low C steel containing 1.35% Cu, 0.8% Ni and 0.5% Mn plus Nb for grain refinement by NbC, the increase in yield strength from precipitation was approximately 350 MPa [14]. These correspond to a shear yield stress increase of approximately 200 MPa using the von Mises criterion.

With small weak closely spaced precipitates, gliding dislocations shear the precipitate rather than bypass
them. As a first approximation, the precipitation strengthening is related to the force on the appropriate dislocation segment of length \( L \) needed to shear the precipitate by a distance of one Burgers vector, \( b \).

\[
\Delta \tau b L = F
\]  

(1)

In Eq. (1) \( F \) is the strength of the precipitate against shear. The applied stress is increased until shearing takes place thereby determining \( \Delta \tau \), the increase in flow stress due to the precipitates. The dislocation moves through the precipitate in steps of \( b \). The \( F \) values for each step are not equal. It is the maximum value of \( F \) that determines the flow stress; \( F \) in Eq. (1) is the maximum value. \( L \) is the spacing between neighboring precipitates. Eq. (1) neglects that the dislocation bends when it impinges on the precipitate and when a precipitate is completely sheared a slip area is swept out until the dislocation impinges another precipitate. This is the basis for the general Friedel–Brown–Ham equation [15,16] for weak precipitates that are sheared rather than by-passed.

\[
\Delta \tau = \frac{2}{bL(T)^{1/2}} \left( \frac{F}{2} \right)^{3/2}.
\]  

(2)

In this equation \( F \) is again the strength of a precipitate and \( T \) is the dislocation line tension usually taken to be 1/2 \((Gb)^2\). The derivation of this equation starts with a force balance between the dislocation line tension and the force necessary to shear the precipitate, \( F \), when the angle of bend of the dislocation impinged on the precipitate is at its critical breaking value. Since the publication of the Brown and Ham chapter [16] Eq. (2) is generally used to compare with experimental results when the precipitates are sheared by glide dislocations.

### 3.1. Misfit strengthening

To evaluate the possible role of misfit stresses in precipitation strengthening, the following equation from Brown and Ham [16] that is derived from Eq. (2) is used.

\[
\Delta \tau = 4.1G(a_0)^{3/2}f^{1/2}(r/b)^{1/2}
\]  

(3)

In this equation \( \Delta \tau \) is the shear yield stress, \( G \) is the shear modulus, \( a_0 \) is the lattice parameter, \( f \) is the volume fraction, \( r \) is the particle radius and \( b \) is the Burgers vector. The lattice constant for a precipitate of 2/3 Cu and 1/3 Fe from Fig. 1 is 0.2891 nm. With \( d \) for iron of 0.28665 nm, this gives \( \Delta d/dL = 0.0085 \) and \( \varepsilon_0 = 0.0057 \). The volume fraction of precipitate was found to be 0.014 from the three-dimensional atom probe investigation [9,10]. \( G \) for iron is 80 GPa and \( r/b \) is taken to be 2.5. The computed value for \( \Delta \tau \) is small, 26 MPa. Thus misfit stresses do not make a significant contribution to the experimentally observed increase in yield stress in bcc Fe from bcc precipitates containing Cu.

### 3.2. Chemical strengthening

When a dislocation shears a precipitate bond switching takes place. Extensive shearing on many slip planes such as during ball milling essentially dissolves the precipitate forming a solid solution, a metastable bcc solid solution in this case. Zhe and Asta [12] computed a positive formation energy of 0.25 eV per atom for the hypothetical intermetallic FeCu with the B2 structure.

Friedel [15] gives a formula for \( F \), the force that is required to shear a spherical precipitate.

\[
F = \left( \frac{\Delta U}{b} \right) \left( \frac{2r}{b} \right)
\]  

(4)

In this equation \( \Delta U \) is the change in energy per atom for one slip step, in the present case due to bond switching. The maximum number of atoms entering the interface per slip step is when the dislocation is in the center of the spherical precipitate. While Friedel used Eq. (1) to determine an estimate of \( \Delta \tau \), we will use \( F \) from Eq. (4) with Eq. (2). Since a Cu atom at the interface is one half in the precipitate and one half in the matrix \( \Delta U \) is assumed equal to 0.125 eV or 1/2 the formation energy per atom. With this assumption, \( \Delta \tau \) computes to about 75 MPa. This is an overestimate since the precipitate contains less than 1/2 Fe and there is no evidence for ordering. The conclusion is that chemical hardening cannot make a major contribution to the increase in yield stress.

### 3.3. Modulus difference strengthening

The equation for precipitation strengthening for the difference in modulus between the precipitate and matrix derived by Russell and Brown [1] is

\[
\Delta \tau = 0.8 \frac{Gb}{L} \left[ 1 - \frac{G^2}{G_1^2} \right]^{1/2} \sin^{-1} \frac{G_1}{G}
\]  

(5)

In this equation \( G \) is the appropriate shear modulus of the matrix and \( G_1 \) is the appropriate shear modulus of the precipitate. The appropriate shear modulus is \( G_{110}^{[111]} = 3C_{44}C'/(C' + 2C_{44}) \). [5] This is 60 GPa for bcc iron. Concerning the precipitate modulus, however, the results of the ab initio calculations for \( C' \) in bcc Cu at 0 K are negative [12] as already discussed. Preliminary computations for bcc Cu–Fe solid solutions predicted \( C' \) to slowly increase with Fe content becoming \( 0 \) at near 50% Fe [12]. Since the temperature coefficient of \( C' \) is not known but must be small, either positive or negative since it is half the difference between the temperature coefficients of \( C_{11} \) and \( C_{12} \), \( G_1 \) is also small whether negative or positive. With \( G_1 \) being small the arc sin term in Eq. (5) is small and a small value for \( \Delta \tau \) is predicted. It is unlikely that the modulus difference is the source of the precipitation strengthening in this system.
3.4. Dislocation core–precipitate interaction strengthening

When the precipitate radius is not large compared to the dislocation core radius the structure of the dislocation core cannot be ignored in discussing the origin of precipitation hardening. This is especially true for bcc metals because of the core asymmetry. Harry and Bacon [11] used many body potentials to simulate precipitations in Fe and bulk bcc Cu and in bcc Cu precipitates by molecular dynamics. Even though there is concern about the potentials that they used, there is nevertheless qualitative validity to their findings.

Their atomic scale simulations of a (111) screw dislocation moving through pure Cu nanoscale precipitates predicted that regions in the dislocation core become close to the fcc structure inside the Cu precipitate. As the precipitate increases in size, the atomic structure of the dislocation core approaches closer to the fcc structure. Harry and Bacon suggest that a dislocation moving through a bcc Cu precipitate transforms the bcc structure to one resembling locally the fcc structure (such as the 9R structure). The simulation gave the interaction energy decreases from 0 well outside the precipitate and must escape in order for plastic flow to continue, or the Orowan process must become active. The final conclusion is that much more theoretical work is needed before the origin of precipitation strengthening from bcc “Cu” precipitates in Fe base alloys is well understood.

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References