4. Size and Density of Precipitates

The Basics

▸ We have a supersaturation of point defects, we have some heterogeneous nucleation - finally we can make our precipitate. Two (related) questions should now occur to you:

1. How large will those precipitates be (on average, of course) and what determines their *size*?
2. How many will I find in a given volume or in other words: what kind of precipitate *density* will I get?

● Looking at energy balances, as in the preceding modules, will not do the trick here. If you just minimize the energy, you will *of course* end up with exactly *one* spherical precipitate, with a size that is just right to accommodate *all* the point defects that were supersaturated in your crystal. You can't have a better surface to volume ratio that that.

● Equally *of course*, that is *not* what you will find in iron or steel at room temperature (or in most other crystals) if you wait less than a sizeable fraction of the age of the known universe (about 14 billion years, by the way). Remember: if nothing moves, nothing happens.
The typical situation we have is:

1. At high temperatures our point defects - vacancies, impurity atoms, whatever - can move vigorously and thus can go places. On the other hand, the supersaturation is low; definitely lower than if you have the same concentration at lower temperatures.
2. The mobility of point defects is described by their diffusion coefficient $D(T) = D_0 exp-(E_D /kT)$; the average distance they covered after a time t is given by the diffusion length $L = (Dt)^{1/2}$.
3. At low temperatures, the supersaturation is high but movement is sluggish.
4. Nothing moves at room temperature.

▸ So how large can a precipitate be? There is an easy general answer: it can at best be so large as to contain all the point defects that had a chance to reach it. In other words:
All the point defects that were contained in a sphere with radius "total diffusion length" L_{to} determine the maximal size of a precipitate.

● Note that the answer to the second question from above is also clear now. We have one precipitate in a volume of about (L^3_{to}) and thus a precipitate density of $1/(L^3_{to})$.

▸ All that remains to do is to calculate L_{to}. For that we need to know the temperature profile $T(t)$, the way the specimen cools down with time.

● Then we calculate the diffusion coefficient at some temperature, see how far a point defect could go in some small interval around that temperature for the time the specimen stayed in that interval, repeat the procedure for other temperatures, and add everything up.
In other words; we *integrate*!
It is easiest to do that for L^2_{to}; we can always take the root when we are done.

▸ Quite generally, the (square) of the average distance L or **total diffusion length** that a diffusing object covers during cooling down in three dimensions is given by

$$L^2_{to} \ = \ 2D \cdot t \ = \ \int_{t' = t_0}^{t' = \infty} D(t') \cdot dt'$$

● The diffusion coefficient $D(T)$ is always given by $D(T) = D_0 \cdot exp–(E_D /kT)$ with E_D = migration energy with typical values of **(0.5 - 2.5) eV.**

● The most simple way of cooling is to put the specimen into some cold environment. The temperature profile then follows proper beer-froth dynamics (get a beer and look it up!) or $T(t) = T_0 \cdot exp–(\lambda t)$. T_0 is the starting temperature, and λ the "decay parameter".
While the "decay parameter" λ is most convenient for the equations, the **temperature gradient** $[dT/dt]_{t = 0} = –\lambda T_0$ is easier to grasp. To give an example: If we cool down from **1800 K** with a gradient of **–100 K/ s**, we have a decay parameter $\lambda = 1/18 \ s^{–1} = 0.055 \ s^{–1}$.
Another convenient way for looking at cooling-down dynamics is to define a "**cooling half-time**" $t_{half} = 1/\lambda$; i.e.

the time it takes to cool to about half the starting temperature. $1/\lambda$ actually takes you to **0.37 T_0** - but what the heck. If you are a stickler for correctness or just anal-retentive, you must go with $t_{half} = (1/\lambda) \cdot \ln(0.5) \approx 0.69/\lambda$. Combining the two, we can express the cooling half-time in terms of the temperature gradient as

$t_{half} = T_0/[dT/dt]$

Here is the illustration for all that:

Exponential decay of temperature and various parameters to describe it
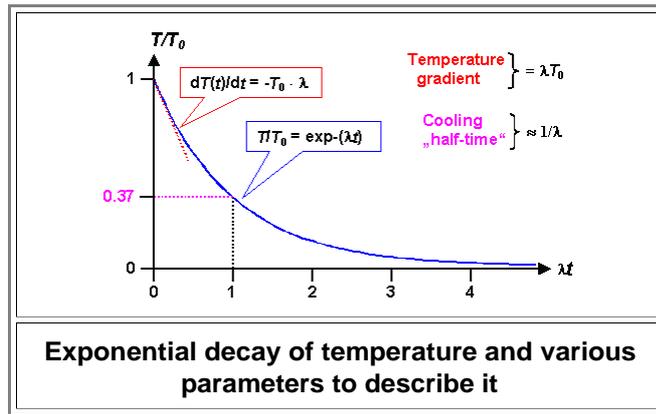
⬧ Writing out the integral by inserting the [basic equation](#) for $D(T)$ and the exponential decay function of the temperature from above, we get a little beauty:

$$L^2 = 2D_0 \int_{t_0}^{\infty} \exp - \left(\frac{E_D}{kT_0 \exp-(\lambda t)} \right) dt$$

⬧ The integral is a little math beauty because it looks neat, approachable and easy to conquer. It's like female human beauties. Behind the comely surface often hides a strong mind, and conquering is not all that easy either. Strangely enough, those humans who have no problem with the integral (few and mostly male) typically have problems conquering that female beauty.
Our little math beauty is not easy to do but needs to be **wooed** by suitable substitutions and approximations.

🔵 What one gets for the total diffusion length L_{to} after a rather lengthy exercise in calculus is

$$L_{to} = \left(\frac{2D_0 \cdot kT_0}{\lambda \cdot E_D} \right)^{\frac{1}{2}} \cdot \exp - \frac{E_D}{2kT_0}$$

⬧ That is an easy function to plot for some bandwidth of parameters.
Shown below are curves for diffusion energies from **0.5 eV** to **2 eV**. Cooling rates from **1 K/s** to **50 K/s** and a $D_0 = 10^{-5}$ cm^{2}s^{-1} are assumed.

Total diffusion length and cooling down
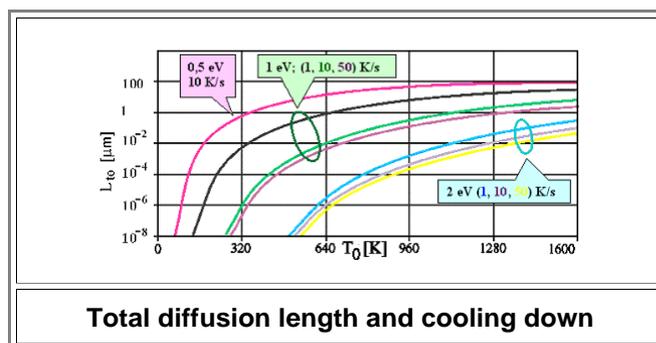
🔵 Of course, diffusion lengths below 10^{-4} **µm = 1 Å** are meaningless for atoms and just shown for completeness.

What we see quite generally is:

- The cooling rate matters less than the migration energy.
- Most everything happens at high temperatures.
- **1 µm** is already a large distance under many circumstances.

🔵 We knew that already to some extent. But now we have *numbers* for *all* kinds of circumstances.

Let's look at a few numbers for possible precipitate sizes. For simplicities sake we assume that the volume is L^3_{to}, that all the impurity atoms contained in that volume end up in a "cube" precipitate, and that the size of one "particle" is **0.3 nm³**. That's what we get for the size of the precipitate-cube in nanometer:

L_{to}	10 nm (0.01 µm)	100 nm (0.1 µm)	1.000 nm (1 µm)	10.000 nm (10 µm)
Conc. impurity	Size of precipitate [nm]			
10^{-6} (1 ppm)	0,1	1	10	100
10^{-5} (10 ppm)	0,215	2,15	21.5	215
10^{-4} (100 ppm)	0,464	4,64	46,4	464
10^{-3} (0.1 %)	1	10	100	1.000
10^{-2} (1 %)	2,15	21,5	215	2.150

🔵 Only in the two red cases the size of the precipitates surpass **1 µm**, making them just about visible in a light microscope.

Looking at carbon steel or "low-alloy" steel, containing fast-diffusing carbon in the 1 at% range, and slower diffusing stuff in the 0.01 at% to 1 at% range, we can expect to find carbon precipitates (Fe_3C or cementite) in the µm range and thus visible in a light microscope. Everything else should be far smaller, however, and thus had to escape the attention of early steel scientists, who could not yet command electron microscopes.

The Great Simplification

The total diffusion length L_{to} is quite important for many things related to iron and steel, and that's why I want to dwell on it a bit longer. I will get more specific for the atoms diffusing around in *iron* and *steel*, and more simplistic in how to look at the situation.

🔵 For that it is beneficial to rewrite the equation for L_{to} by introducing parameters that are more easy to relate to. My choice is:

- The "cooling half-time" $t_{half} = 1/\lambda$ or $\lambda = 1/t_{half}$.
- The diffusion length L_0 for a time $t_1 = 1s$ at the starting temperature T_0. That is just the square root of the diffusion coefficient and directly obtainable from diffusion data. We then have $L_0 = (D(T_0) \cdot t_1)^{1/2} = (D_0 \cdot t_1)^{1/2} \cdot exp-(E_D/2kT_0)$. This gives us $(D_0)^{1/2} exp-(E_D/2kT_0) = L_{to}/(t_1)^{1/2}$

🔵 Inserting this in the equation above yields

$$L_{to} = L_0 \left(\frac{2t_{half}}{t_1} \right)^{1/2} \cdot \left(\frac{kT_0}{E_D} \right)^{1/2}$$

$$= 1{,}41 \cdot L_0 \left(|t_{half}| \right)^{1/2} \cdot \left(\frac{kT_0}{E_D} \right)^{1/2}$$

$$= L_0 \cdot g(t_{half}, T_0, E_D)$$

While this may still look complicated, it makes estimations of L_{to} very easy for all the atom where you have some Arrhenius diagram of their diffusion behavior. All we need to do is to make a little table for typical values of the number $g(T_0, E_D, t_{half})$ by using values typical for iron and steel for some parameters. Don't forget: if we have an Arrhenius plot, we also have the migration energy E_D. So let's look at the parameters.

- Looking at typical migrations energies E_D for atoms moving around in iron, we find

  - Values close to **1 eV** for the interstitials carbon (C), nitrogen (N) and oxygen (O).
  - Values roughly around **1.5 eV** for most substitutional atoms.

  Taking E_D = **1 eV** and **2 eV** thus covers most everything.

- Looking at typical T_0 temperatures for iron, we can take the melting point of pure iron at around **1800 K** as an upper limit, and the "working " temperature off a smith at around **1000 ºC** (**1832 ºF**) as a lower limit - in the form of **1300 K**, of course. This gives us kT_0 values of **0.16 eV** or **0,11 eV**, respectively.

- For cooling half-times we might pick **36.000 s** (**10 hr**) **3600 s** (**1 hr**), **360 s** (**6 min**) and **36 s**, again covering most practical situations in between the two extreme values.

Now we can come up with two tables for the values of the factor $g(t_{half}, T_0, E_D)$ that (with interpolations) cover pretty much every cooling-down event.

$g(T_0$= 1.800 K, E_D, $t_{half})$				
E_D t_{half}	**36.000 s**	**3600 s**	**360 s**	**36 s**
1 eV	106	34	11	3
2 eV	75	24	7	2

$g(T_0$= 1.300 K, E_D, $t_{half})$				
E_D t_{half}	**36.000 s**	**3600 s**	**360 s**	**36 s**
1 eV	90	28	9	3
2 eV	64	20	6	2

What the numbers mean is clear. An atom that moves a certain distance L_{to} within 1 second at one of the two temperatures given, will go for a distance that is larger by the number in the table for the conditions indicated.

- Let's look at an example. From the Arrhenius plots in the "diffusion in iron" module you can see that within **1 s** carbon in iron covers roughly **50 µm** at 1800 K, and **10 µm** at 1300 K. It's migration energy is close to 1 eV. Looking at the table you realize that *carbon* covers **53.300 µm = 53 mm** for sluggish cooling from the melting temperature, and still **150 µm** for extremely fast cooling. If the starting temperature is 1300 K, it moves **900 µm** or **30 µm** for the extremes in cooling, respectively.
  The same exercise for *manganese*, starting with **70 nm** or **2 nm**, respectively, and a migration energy of 1 eV, gives **5.25 µm** or **140 nm** for the extremes and 1800 K, and **128 nm** or **4 nm** for 1300 K cooling.

- Yes, I know it is not quite that easy. Cooling relatively pure iron from the melting point at 1800 K to room temperature involves a bcc- fcc phase change at high temperatures and a fcc- bcc at around 1.000 K, with the carbon moving much more sluggishly in the fcc austenite phase; this is clearly visible in the Arrhenius plot. So we overestimate the total diffusion length L_{to} somewhat - but who cares? We only get orders of magnitude anyway. The consequence of this little exercise are obvious and dramatic, no matter how you look at details:

> # The carbon concentration in iron / steel will equilibrate over macroscopic distances at least in the order of 0.1 mm if you heat it *just once* to 1000 ºC

- It doesn't matter how you cool down, and in most cases equilibration occurs over much larger distances. Provided, of course, the carbon is atomically dissolved and can move freely in all directions

- In other words: banging together thin sheets of low carbon / high carbon steel for damascene pattern welding won't do you much good. You don't get a compound material but a rather uniform material with an medium carbon content. I have stated that before but now we are one step more quantitative. I'll come back to this topic later again.

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