



4. Segregation at High and Ambient Temperatures

The Rules of the Game

After I have introduced you to the influence of segregation *on* the final microstructure, I will now concentrate on macro and microsegregation of constituents and impurities *in* the final microstructure.

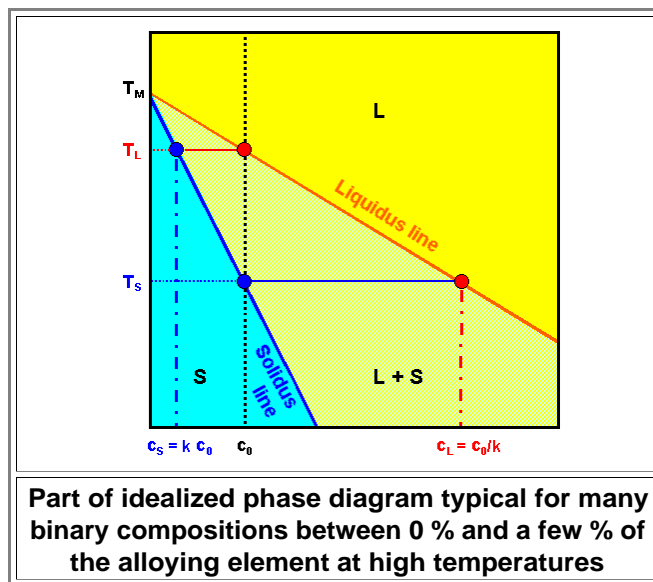
For simplicity in writing, I consider a melt that consists primarily of one constituent (e.g. 98 % iron), one alloying element (e.g. 1.95 % carbon) and some trace impurities (e.g. the rest of the periodic table with together 0.05 %). We also assume that the influence of the trace impurities on the melting point is negligible in comparison to the influence of the alloying element.

The simple way to look at this is to start with a few basic definitions plus simple truths:

1. In a solid-liquid *equilibrium*, most elements prefer to remain in the melt and thus have a **segregation coefficient** $k < 1$ that can be deduced from the respective phase diagram. The (equilibrium) segregation coefficient of carbon in iron is thus $k_{C \text{ in Fe}} = 0.6$ as a look on the iron - carbon [phase diagram](#) demonstrates. Some elements might prefer the solid to the liquid and then have segregation coefficients $k > 1$. This, while not uncommon, is rather the exception. It must be expected that the equilibrium segregation coefficient of the alloying element in some binary composition changes if some more elements are added. But as long as the concentrations of additional elements are low, it should not change very much.
2. Full equilibrium is *only* maintained for interface velocities $v \approx 0 \text{ mm/s}$. For noticeable interface velocities, we define an **effective segregation coefficient** k_{eff} that moves towards unity for increasing interface velocities v . This means that global segregation effects get smaller for increasing v ! This is clear: A very rapidly moving solid-liquid interface will freeze the melt "as is"; there will be no difference in composition between solid and liquid anymore.
3. **High temperature segregation** is the term I will use for the difference between the *nominal* concentration of alloy elements and impurities and the *actual* concentration *right after solidification*. High temperature segregation depends pretty much *only* on the speed $v(x, y, z, t)$ of the solid-liquid interface at some point in space and time, and the various concentrations of alloying elements and impurities in the melt. While the alloying element may influence $v(x, y, z, t)$ to some extent (via supercooling and so on), trace impurities don't. For high-temperature segregation, however, it doesn't matter *why* the interface has the velocity it has.
4. **Room temperature segregation** is the term I will use for what kind of non-uniformities are left in the concentration of of alloying element and impurities *and / or* caused by high temperature segregation. In other words: At room temperature the concentration profile of alloying elements and impurities will not be the same as at high temperature since diffusion tends to equilibrate any differences on a scale given by how far atoms can diffuse until it gets too cold to move. Local high concentrations of some atoms at high temperatures may increase the probability for nucleating precipitates or other large defects, *causing* an inhomogeneous distribution of those defects that does *not* mirror their high temperature segregation. Carbon in iron, for example, might be distributed homogeneously at high temperature but precipitate very unevenly because the cementite precipitates nucleate at inhomogeneously distributed or segregated impurities.

Now let's look at the most simple situation where a melt cast into a mould crystallizes close to equilibrium, implying a planar solid-liquid interface that moves slowly from the outside of the mould to the inside.

1. The relevant portion of the phase diagram for an alloying element with a segregation coefficient $k < 1$ (the rule) looks, slightly idealized, like this:



● This could be, for example, a part of the [iron -carbon phase diagram](#). The blue area then would stand for the (bcc) δ -phase (or austenite, if one moves to somewhat higher carbon concentrations).

▸ As long as we can approximate the liquidus and solidus line by straight lines with slopes m_S and m_L , simple geometry tells us that:

$$k = \frac{\text{segregation coefficient}}{\text{segregation coefficient}} := \frac{c_S}{c_L} = \frac{m_S}{m_L} = \text{constant}$$

● For some global or nominal concentration c_0 , we then can define the concentrations $c_S = k c_0$ at the temperature T_L where first freezing will begin, and the concentration $c_L = c_0 / k$ at the temperature T_S where freezing is completed.

● This implies that the very first parts to solidify will have the alloying element incorporated with a concentration $c_S = k c_0$, and that is lower then the nominal concentration c_0 ; always assuming equilibrium, of course!

High Temperature Macrosegregation

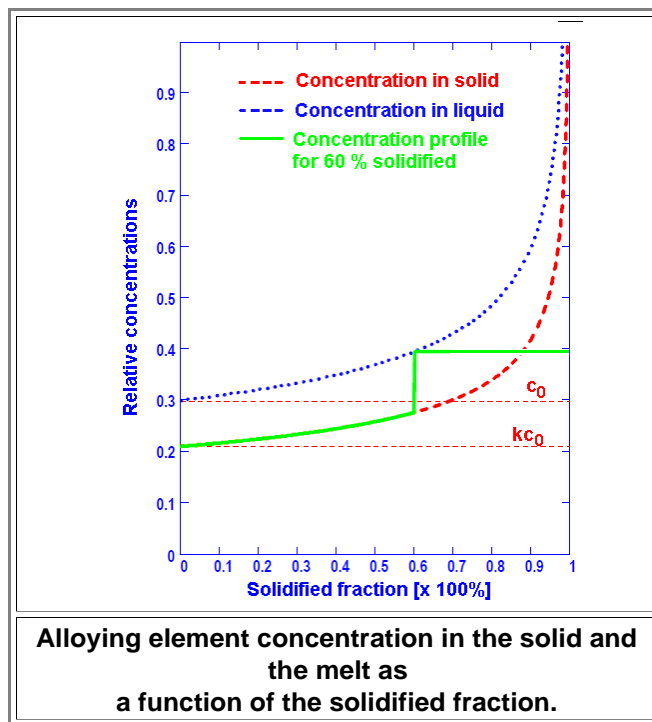
▸ If we would remain at or very close to equilibrium at all times, there would be no segregation at all. The unavoidable differences in concentration between parts that solidified early and those that crystallized late would be equilibrated by diffusion in the solid already at high temperatures. We must therefore deviate from equilibrium to some extent if we want some high-temperature segregation.

There are many ways of modelling this; one simple model was introduced by **E. Scheil** in 1942 [1](#).

● Scheil simply assumed that there is no diffusion in the solid, and arbitrarily fast diffusion in the liquid. In other words: the solid is forced to preserve whatever concentrations the alloy element (and the impurities) have right after solidification, and the liquid has a uniform concentration everywhere and at all times.

Turning off diffusion in the solid prevents equalization of the concentration in the solid, and thus assures that segregation effects at high temperatures are preserved at low temperatures.

This is not realistic at all for room temperature segregation, and not too good for high temperature segregation either! However, with diffusion coefficients "fixed" in this simple way, a mathematical analysis is possible, resulting in curves like the following one (I spare you the derivation and the equations):



The figure illustrates what one would expect for some concentration $c_0 = 0.3$, and a segregation coefficient of $k = 0,2/0,3 = 0,67$ typical for carbon in iron. The green curve gives an example for the calculated concentration profile in the solid and melt after 60 % of the total has solidified.

The first part to solidify has an alloying element concentration of $kc_0 = 0.2$. With increasing fraction of solidified material the concentration in the melt and solid increases; first slowly and then rapidly. The curves, however, diverge (running up to infinity) for 100 % or complete crystallization. That is obviously nonsense and simply reflects the shortcomings of the model. So we must ignore the prediction of the model for a high percentage of crystallization.

The model, however, describes the basic trends for the first two-thirds or so of "normal" high temperature crystallization rather well. As long as we look at *average* quantities, it even doesn't depend very much on the nature of the crystallization front. Planar, cellular, dendritic - it makes no difference for *averages* taken over areas and times large enough.

The **Scheil model**, in other words, describes **macrosegregation**. There are several other models with increasing sophistication but they all describe *only* macrosegregation at high temperatures.

All models give some ideas about the influence of the segregation coefficients and atom movement (by diffusion and /or *convection*) in the melt. The larger the difference of the segregation coefficient to unity, the larger the segregation effects. That is not only true for the alloying element but also for the trace elements that follow the same basic equations - as long as they are incorporated as single atoms.

We can abuse the Scheil model or the other models to some extent also for larger deviations from equilibrium and thus larger interface velocities v . All we need to do is to replace the equilibrium segregation coefficient k with the "effective" segregation coefficient $k_{eff}(v)$ that depends on the interface velocity and approaches unity for large v

That leads to a little paradox: macro segregation effects are only present for non-equilibrium but seem to get *smaller* in all macrosegregation models if the deviations from equilibrium get *larger*, since the effective segregation coefficients are then closer to 1!

Well, yes, the effects of *macro*segregation do tend to get smaller for larger interface velocities as outlined [above](#).

More important, however, is that the effects of *micro*segregation get *larger* for larger interface velocities!

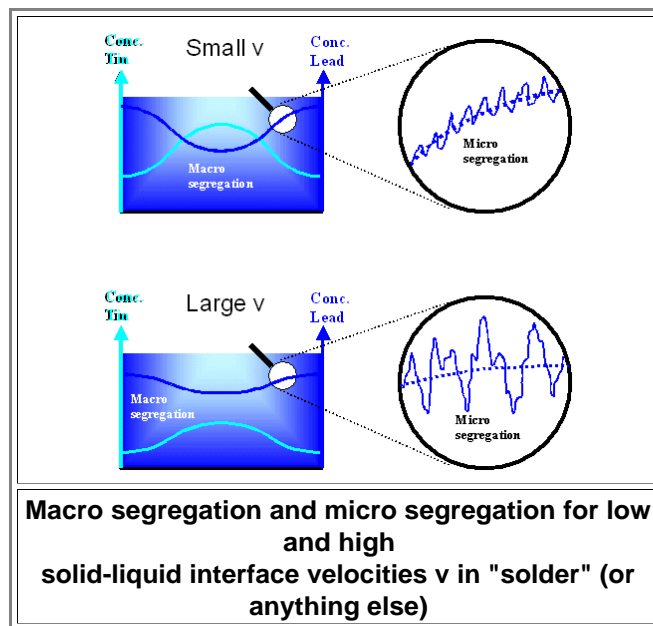
So let's look at high temperature microsegregation now. It is far more exciting than macrosegregation but also far more difficult to understand and model.

High Temperature Microsegregation

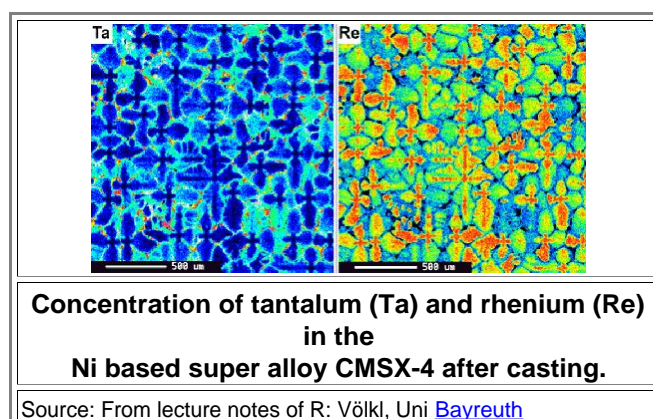
The easiest way to consider microsegregation is to ponder the following points.

- The *average* interface velocity v_{av} , together with the effective segregation coefficients $k_{eff}(v_{av})$ that go with v_{av} , govern macrosegregation, and thus the *average* concentration of alloying elements and impurities in the crystal at high temperatures right after solidification. v_{av} may change with time but in a smooth way.
- The *actual* interface velocity $v(x, y, z, t)$ may vary from point to point at some given time and (in a non-smooth way) for a given point in time. Averaging over suitable large areas and time intervals, however, must give v_{av} .
- The *actual* interface velocity $v(x, y, z, t)$, together with the effective segregation coefficient $k_{eff}\{v(x, y, z, t)\}$, governs the *local* concentration and thus also the *local deviations* from the average concentration.
- Deviations of the *local* interface velocity $v(x, y, z, t)$ from the average velocity v_{av} , or what we call the *fluctuations* of the interface velocity, get *larger* with increasing average velocity.

- In a very schematic way, this can be illustrated by enlarging on the [figure in the backbone](#):



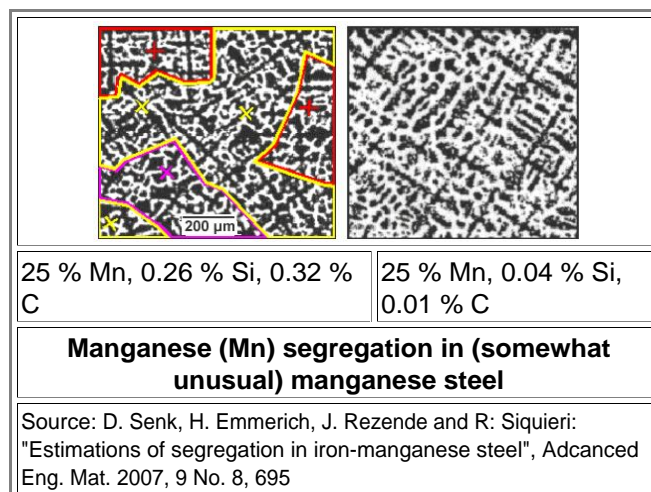
- On the *left* the variation of the lead and tin concentration due to **macro segregation**, coming right from the phase diagram, is shown schematically. That is the figure in the backbone. On the *right* we look at just the lead concentration in a small region (millimeter or smaller) The concentration fluctuates more or less periodically around the average values (dotted line) given by macro segregation, due to **micro segregation** effects. Increasing the growth speed *decreases* macrosegregation effects, but *increases* microsegregation
- It is clear by now that the average interface velocity v_{av} and its fluctuations Δv are the decisive parameters. It is also clear that during casting, v_{av} and Δv cannot be controlled directly. In other words: there aren't any buttons somewhere on the apparatus that you can turn to a desired value of v and Δv , ensuring that these values are now firmly established until further notice.
 - As far as the fluctuations Δv are concerned, it's even worse. They will tend to increase with increasing v_{av} , but not in a simple straight-forward way. For example, when you crank up the interface velocity, dendritic growth will start at some point, and fluctuations get much larger. The local growth speeds at the tips of the dendrites can be rather large for a while in comparison to v_{av} , for example.
- Obviously, what I would need to do now is to establish all the reason for velocity fluctuations, followed by some general fluctuation theory that is then applied to microsegregation. I'm not going to do that here, for the simple reason that I don't know of such a general theory. I will give you my *personal* "theory" for that topic in [this link](#); and I will have much to say about the topic in the [next module](#) of this series. Here we simply assume that dendritic growth will cause some fluctuations and only look in a more empirical way at what that can do to microsegregation.
 - If we have dendritic growth, the dendrites, by definition, grew considerably faster for a while than the solid they are attached to. It is thus clear that the liquid in between the already solidified dendrite arms will tend to be enriched with alloy /impurity atoms that have an (effective) segregation coefficient < 1 . The dendrite itself will be enriched with atoms that have segregation coefficients > 1 . This happens, indeed, and can be observed (with some luck) at room temperature. The picture below shows particularly nice examples.



- The pictures were taken with an SEM in the EDX mode. Colors encode concentrations of the elements named in the picture, and there is always a precise scale relating colors to numbers. I omitted that scale; it is sufficient to know that the concentration increases going from dark colors (black, blue,...) to bright colors (... , yellow, red). We look on top of dendrites oriented perpendicular to the viewing plane. It is clear that rhenium (Re) is enriched in the dendrites, tantalum (Ta) in the space in between. Just for fun, here is the composition of that super alloy:

Composition of the super alloy CMSX-4										
Element	Ni	Cr	Co	Mo	W	Ta	Re	Al	Ti	Hf
Conc. (wt%)	61.7	6.5	9.0	0.6	6.0	6.5	3.0	5.6	1.0	0.1

- Looking at the composition you get an idea that "super" alloys are not only super with respect to their properties, but also with respect to their complexity. So, next time when you are in an airplane look (with your brain) at the turbine blades made from superalloys in those jet engines. They are the ones that must take the highest temperatures in there, and thus are most prone to failure. You better give credit to the guys who developed super alloys to a point where they *never* fail! No airplane, to the best of my knowlegde, has ever crashed because turbine blades failed.
- If you now start thinking that your next sword should be made from a super alloy - forget it. Except if you plan to go to hell, where you might be induced to wield your sword at temperatures above 1.000 °C (1.832 °F). Because that's what super alloys are good for: providing mechanical strength (and corrosion resistance and so on) at very high temperatures.
- How about dendrite caused microsegregation in steel? Pretty much the same thing - in general. As for details, what kind of steel are we talking here? There are many hundreds if not thousands of steels that have sufficiently different compositions to give different segregation behavior *in detail*. Here are two examples:



- These are EDX pictures as above, but with concentrations coded in a grey scale instead of in a color scale. Concentration increase from black to white. The view is in the direction of dendrite growth. In the right-hand picture areas with more or less identical dendrite orientation (marked by crosses) are outlined; this might define (roughly) the grain structure. The left-hand picture essentially shows just one grain. In both examples the interdendritic areas are enriched in manganese. There is not much difference between the two steels with respect to room-temperature manganese microsegregation but with respect to carbon segregation (see below).
- Allright, now let's pause for a minute and recapitulate what we have achieved so far:
 - Good:** We have a good if rather qualitative ideas on how the interface velocity v and *high temperature* segregation hangs together, and how that ties in with the microstructure.
 - Mediocre:** We do not yet fully understand what we will find at room temperature, but we have hunches. In fact, I tricked you: the pictures above already show room temperature segregation!
 - Bad:** Despite a lot of effort, we have not yet encountered a layered distribution of impurity atoms that we seem to need in order to [explain wootz steel](#) and the enticing wootz swords made from it. Dendritic growth is just not all there is to microsegregation! The "banding" of cementite precipitates as required for wootz patterns is actually *not* a direct segregation effect, notwithstanding claims to the opposite.

- Before I tackle the really difficult third point in the [next module](#) of this series, let's finish this module by looking at a few essentials of *room temperature* segregation.

Room Temperature Microsegregation

So we have a freshly crystallized material at a temperature still close to T_M , with some inhomogeneous distribution of alloying elements and impurities, and some microstructure related to this. What is going to happen if we now let the material cool down to room temperature?

- A first and simple answer is: It all depends on:

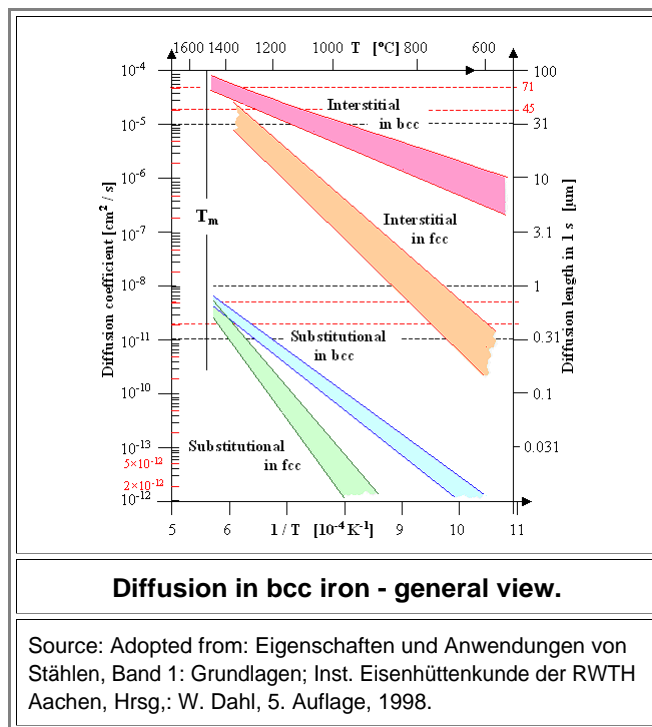
1. **Diffusion**. If anything in the segregated distribution of atoms is going to be different at room temperature from what it was at high temperature, then some atoms are no longer where they were before and thus must have *moved*. Neglecting violent processes like [martensite formation](#), atoms can *only* move by *diffusion*. The maximum distance they can cover within the time t is given by their [diffusion length](#) $L = (Dt)^{1/2}$; D is the [diffusion coefficient](#).
Note that atoms dissolved in the crystal matrix might redistribute by diffusion without noticeably changing the microstructure
2. **Phase transformations**. When a phase transformation occurs, the microstructure changes. This need not concern the distribution of alloying elements and impurities very much, but it often does. When γ -iron or austenite transforms to α -iron / ferrite and Fe_3C cementite, the carbon in the austenite has no choice but to redistribute a lot. It just cannot stay wherever it was; it must *diffuse* to the cementite that is forming. For low-carbon iron, you may have four phase transformations before the room temperature structure is reached (look at the [phase diagram!](#)), so a lot could happen.
3. **Precipitation**. So far we have assumed that all those segregated alloying elements and impurity atoms are atomically dissolved in the matrix of the host element. This might be the case right after solidification but the concentrations involved might exceed the solubility limit at some lower temperature. We must thus expect that some atoms will need to precipitate during cooling down.
This is definitely true for the [vacancies](#) (and possibly self-interstitials) that are also present (but not segregated) at high temperatures. They need to disappear completely.
For precipitation to happen, we need [nucleation](#) *and* diffusion.

- In short: A lot can and will happen - but in the background there is *always* diffusion as the decisive enabling *and* limiting factor. So one way to look at room temperature segregation is to consider how far the atom of interest can move during the cooling-down time in the given matrix.

I covered that already rather exhaustively in [this module](#). From a practical point of view, and with carbon steel in the back of our minds, we are well advised to differentiate between [interstitial atoms](#), typically fast diffusers, and [substitutional](#) atoms, typically slow diffusers. The first quantity to consider is the [diffusion length](#) L , the average distance between start and stop of a "[random walker](#)". The essential equations going with it were:

$L = a \cdot (N)^{1/2}$	$a = \text{length of step} \approx \text{lattice constant}$ $N = \text{number of steps}$
$L = (D \cdot t)^{1/2}$	$D = \text{diffusion constant}$ $t = \text{diffusion time considered}$

- The second version allows us to have an axis showing the diffusion length after 1 second in the typical [Arrhenius plot](#) of diffusion coefficients.
Here is the relevant picture for diffusion in iron taken from [this module](#):



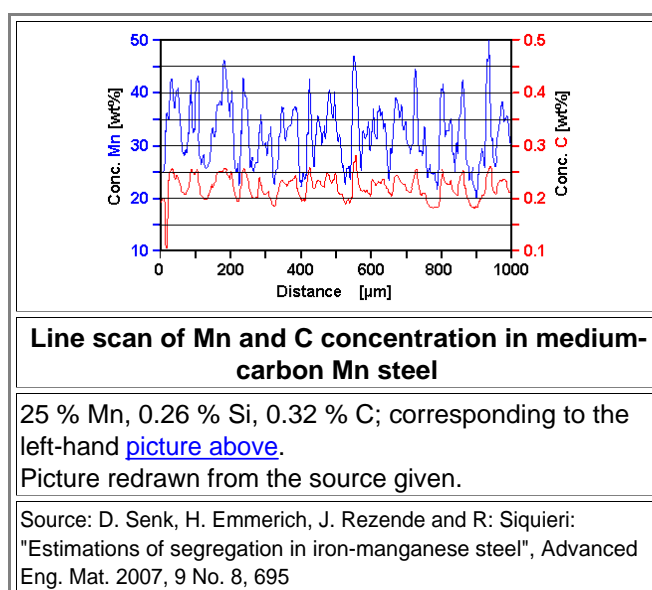
What we take from that picture (or the more detailed ones) is the 1-second diffusion length L_1 at the temperature T_0 of interest. I don't need to tell you that the diffusion length goes with the **square root** of the time, so after two seconds it is not twice of what it is after 1 second, but only $2^{1/2} = 1.41$ times larger. Of interest here is the melting temperature of iron / steel around **1500 °C**.

What we see is that for interstitial **carbon** (C) in bcc iron we have an $L_1 \approx 70 \mu\text{m}$ at **1500 °C**, in fcc iron it is around **30 μm**. Carbon will cover distances of many micrometers within the first second after solidification. Substitutional **manganese** (Mn), on the other hand, will have moved less than **0.5 μm**.

During cooling the movements become sluggish and essentially stops long before room temperature is reached. I have showed in [considerable detail](#) how one can compute the total diffusion length L_{to} and come up with some estimates of what is going on. What we need to know are the diffusion data of carbon and manganese and how fast the specimen cooled down.

Let's apply this to the segregation shown in the above pictures for manganese steel. Before I do this, however, let's look at two more sets of data from [this paper](#):

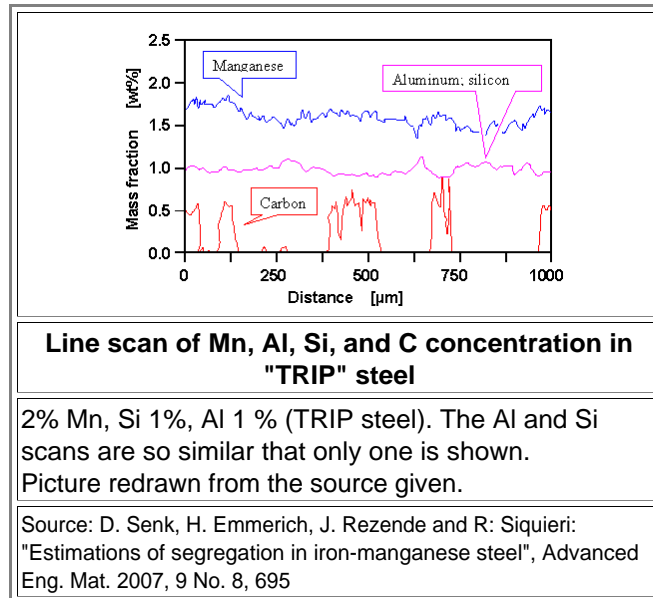
The paper provides "line scans" of concentrations. For a "line scan" you just move your probe along a line across the sample and record the concentration of the elements you are interested in. The spatial resolution of the line scan is a few μm. The pictures above are just a lot of line scans with color-coded concentrations. Here is a "line scan" of the manganese (Mn) and carbon (C) concentration in a manganese iron sample with medium carbon level.



What do we see? Let's list the important points:

- The average concentrations estimated from the line scan are not exactly as specified. That is most likely due to macrosegregation plus some uncertainty in calibrating the equipment.
- The concentration fluctuations indicating segregation are "in phase" for Mn and C. Wherever the Mn concentration is high, the carbon concentration tends to be high too, and vice versa.
- Concentrations change on a scale of about 10 μm or less.

Here is the same kind of picture for a "TRIP" steel with low manganese concentration and very low carbon concentration (not specified).



What do we see here ? Let's list the important points:

- The average Mn concentration estimated from the line scan is not exactly as specified. That is most likely due to macrosegregation plus some uncertainty in calibrating the equipment. Al and Si, however, are at the right value, and this might give a hint that the segregation coefficient is close to 1 (it is, actually) so their average concentration does not change very much in the specimen.
- The concentration fluctuations indicating *microsegregation* are "in *antiphase*" for Al and Si. Where ever the Mn concentration is high, the Al and Si concentration tends to be low; and vice versa.
- The carbon concentration of carbon is "in phase" with the Mn concentration but in a rather peculiar way with very strong amplitudes.
- Concentration changes for Mn and C change are on a scale of about 10 μm or less.

Note that all the segregation pictures and data shown so far were taken at *room temperature* and thus show *room-temperature* microsegregation, or what is left from the primary *high-temperature* segregation occurring during casting. The pictures are remarkable and go a long way towards explaining the "water" pattern in wootz steel. Let's analyze them in the light of what must have happened during cooling down.

First, we need to realize that the melting point of the Fe - 25 % Mn alloy is about 1400 $^{\circ}\text{C}$ (2552 $^{\circ}\text{F}$) and that it solidifies into fcc austenite that stays stable to almost room temperature. Carbon thus *might* be atomically dissolved throughout.

The interesting question is: How far can carbon (and Mn, Al, Si, ...) "go" during the cooling of the samples. In other words, What do we get for the total diffusion length L_{to} for cooling rates of 100 K/s at the surface and 1 K/s in the center of the cast?

Switching from cooling rates to the more convenient "*cooling half-time*" t_{half} , the time it takes to cool to about half the starting temperature as defined in the link, gives $t_{\text{half}} = 1400 \text{ s}$ or 14 s , respectively

The 1 s diffusion length of carbon at 1400 $^{\circ}\text{C}$ (2552 $^{\circ}\text{F}$) is *around* 10 μm in the fcc austenite phase. Consult the tables *made for that purpose* we find that we need to multiply this number by a factor of roughly 20 for the large cooling half-time, and by about 2 for the small one.

We thus find that the total diffusion length for carbon is somewhere between the extremes of $L_{\text{to}}(\text{C}) = 200 \mu\text{m} - 20 \mu\text{m}$. Now this is very strange.

Whichever way one looks at it, one conclusion is unavoidable:

There is no way that *atomically* dissolved carbon shows segregation effects on lengths scales smaller than about 30 μm

- This leads to another unavoidable conclusion: The carbon shown in the line scans above is *not* atomically dissolved! It must be precipitated, there is no other logical explanation
- In the [high-manganese case](#) where I suspected that "carbon thus *might* be atomically dissolved throughout.", this is probably not the case. Inspecting the proper *ternary* phase diagram would give the answer but it's not so interesting, so I won't bother.
The interesting thing is the [second figure](#) with the peculiar carbon distribution. It is now important to note that element analysis with a scanned electron beam (i.e. [EDX](#) and its brethren) cannot distinguish between atomically dissolved atoms and atoms in a precipitate. Whenever the electron beam hits a Fe_3C cementite particle, carbon would register at 25 %. However, since the volume probed by electron beam is much larger than that of typical precipitate (typically more than $10 \mu\text{m}^3$) it almost never hits *only* a cementite particle, but always a mixture of particle(s) and iron. It then registers the average of the carbon concentration in the volume probed - and we get numbers that fluctuate very much between close to zero (there is almost no carbon in the ferrite iron) and relatively large values.
- That's quite obviously what we see in the line scan of the low-carbon TRIP steel. The interesting part of what we see, however, is;

**Carbon precipitation occurs at areas where the manganese concentration tends to be a bit above the average.
The average distance between cementite-rich regions is 100 μm - 200 μm .**

- That implies that carbon precipitation does not happen everywhere and uniformly but mostly in "special" places. There the precipitate density is high, while in between it is rather low. The reason for this peculiar kind of room-temperature segregation is the high temperature segregation of some slow diffusing atom tied to the formation of dendrites. These atoms obviously provide the nuclei for carbon precipitation; it is prone to start wherever the concentration is highest.
It is quite possible that the original manganese distribution caused the nucleation of the final carbon segregation by precipitation, since it belongs to the so-called "[carbide formers](#)". Since the manganese concentration varies on a scale given by the dendrite size, it can be relatively coarse.
- ▶ Now to the climax: That's exactly how you would describe the cementite distribution for wootz steel! What we learn here for the making of wootz blades is:
 - The pattern of carbon precipitation at room temperature can be inhomogeneous on a rather large scale of 100 μm or so.
 - The scale observed relates to the size of dendrites formed during solidification and the total diffusion length of carbon. Both get larger if the temperature gradients were small and slow solidification took place.
 - Inhomogeneous or segregated cementite distribution at *room* temperatures is *always* caused by high-temperature segregation of carbide forming alloying elements.
- OK - now we know the secret of wootz blades, sort of? No, we don't! One major ingredient is still missing. This will be the topic of the next module in this series.

1) E. Scheil, Z. Metallkunde, 34, (1942), 70-72.

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