

1. Basics of Segregation

Phase Diagram and Macroscopic Segregation

What is segregation? Wikipedia (English) offers nine different kinds of segregation. We have, for example, racial, religious, or sex segregation - but none of the nine is what I want to go into here. You need Wikipedia (German) to find it:

"**Segregation** in Materials Science: Separations of defects or impurities in a solid by diffusion" (my translation). That's it. Not a particularly good definition, and certainly not very helpful. Let's go for a better one:

Segregations produces a permanent non-uniform distribution of "minority" atoms in solid phases. It happens whenever there is a phase transformation

Just to be on the safe side, let's first make sure what is *not* segregation. Consider a phase transformation from some liquid L to a mixed phase $L + \alpha$. A state point inside the phase field of the mixed phase decomposes along a *tie line* into two state points at the phase field boundaries. You now have some α phase (typically at the container walls) and some still liquid L phase in equilibrium. Both phases do *not* have the *composition* of the system but whatever the phase diagram demands at the state point given. When salt water solidifies, the first pieces of ice do not contain any salt, the remaining liquid is saltier.

Now would be a good time to brush up on your [phase diagram background](#) if the text above wasn't crystal clear.

But let's go on. Even so the minority component of the system is now distributed inhomogeneously between the solid and the liquid phase, it is in equilibrium and we do *not* call this segregation. Segregation, as we like to define it, *only* takes place within one phase, not between phases! If the α phase would be austenite, for example, and the distribution of carbon *inside* the austenite at room temperature would be *permanently inhomogeneous* or non-uniform, we have *carbon segregation*. We also do not have equilibrium anymore.

Now let's look at segregation from a practical (and somewhat limited) viewpoint by listing the features and properties that are of interest to us.

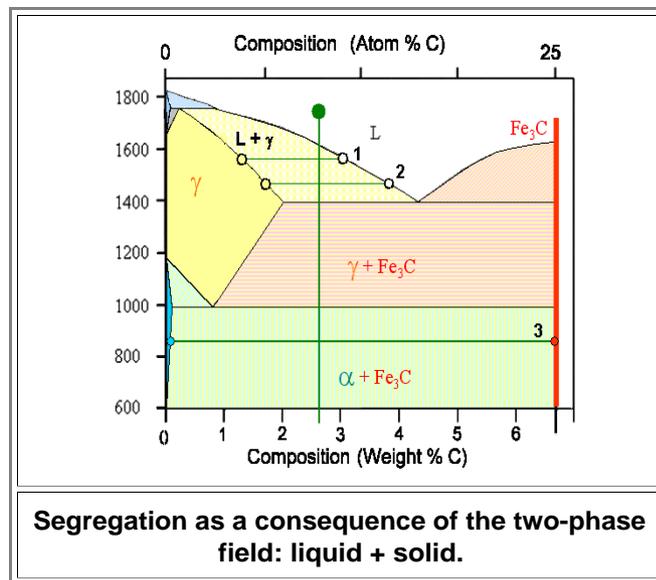
Let's keep it easy by considering for starters *only* segregation resulting from the liquid-solid phase transformation. Here is a list of some salient if sometimes trivial points linked to segregation:

1. Segregation happens while liquids *freeze*, implying that the liquid-solid phase boundary *moves* into the liquid.
2. Segregation concerns *primarily* the *atoms* of the minority component of a binary system, e.g. carbon in iron. However, the conveniently always "forgotten" other impurity atoms also contained at low concentrations in our "binary" system will also be distributed inhomogeneously in the solid right upon freezing.
3. Both the inhomogeneously distributed minority component *atoms and / or* the inhomogeneously distributed impurity *atoms* might nucleate inhomogeneously distributed *larger defects* like precipitates upon cooling. The typical wootz pattern is due to this "follow-up" effect, for example.
4. Segregation may happen at all moving phase boundaries but is most prominent at the *solid-liquid phase boundary* because the concentration of atoms is typically different on both sides of the boundary by necessity. The phase diagram shows and quantifies this.
5. Segregation only comes into its own if the system is *not* in equilibrium. The effects of segregation become more prominent the more the system deviates from equilibrium. Large deviations from equilibrium imply faster boundary movements; segregations effects thus become more prominent for large growth rates of the solid (= fast boundary velocities).
6. Freezing involves movements of the solid-liquid phase boundary into the liquid. While this movement is *primarily* driven by temperature *gradients*, segregation influences the movement and the shape of the phase boundary quite a bit. There is a feed-back loop! Segregation influences segregation.
7. Segregation influences the *stability* of the solid-liquid phase boundary and leads to various self-organized special structures or shapes of that boundary. These boundary structures might survive to some extent and can be seen in the microstructure like the grain morphology found at room temperature.
- 8.

8. Segregation influences the local *speed* of the solid-liquid phase boundary movement, and can even lead to periodic stop-and-go movements.
9. Segregation happens if atoms in the solid and the liquid cannot move fast enough to quickly establish equilibrium concentrations. In the *solid*, movement is restricted to diffusion and is thus only controlled by the temperature. In the *liquid*, movement of atoms takes place by diffusion *and* by convection, the flowing of the liquid. The convection strength and the flow pattern depends on many variables and influences segregation very much.
10. Segregation is difficult to deal with quantitatively. First, because there is a feed-back loop: segregation influences what is going on at the solid-liquid phase boundary, and what is going on there influences segregation. Second, because only a full three-dimensional treatment can do justice to segregations - and that is never easy. Third, because calculating the flowing of liquids is rather difficult, in particular if there is turbulent flow.

● In other words: it is almost hopeless! Well, not quite. Some basics can be readily understood, and the basic behavior of some real systems is also not too difficult to understand. In what follows, I'll go into that. But be warned: What kind of segregation takes place in *wootz steel*, leading eventually to the pattern on *wootz blades*, is not all that clear to me at present.

▀ For starters, let's look at some major points from the list above in some detail. First, let's find out (again) how a phase diagram shows and quantifies the difference of the atom concentration in different phases. Of course, we take our old friend, the iron - carbon phase diagram for illustrating this point. We start, for example, with a composition of 2.7 % carbon, and a temperature well within the liquidus part as shown below.



Now we lower the temperature of the system with some *rate*, e.g. 0.001 °C per minute, or 100 °C per minute, or whatever we like. As long as we do brain work, there are not restrictions for the **cooling rate** employed. If we would do a real experiment, very slow cooling rates tend to be extremely boring (even to [graduate students](#)), and very fast cooling rates are simply impossible.

● Whatever we do, sooner or later we hit the line separating the fully liquid phase (L) from the two-phase region L + γ. A little further down we reach the state indicated by "1". The state point then decomposes into the two state points shown.

What we will find in *equilibrium* is: a little bit of the γ austenite phase, and a lot of the liquid phase. With the [lever rule](#) we could deduce how much, exactly, "a little bit" and "a lot" would be, but that is not all that important here.

● Important is that the phase diagram tells us that inside the L + γ field the composition of the liquid and the solid *must* be quite different. The solid at state point 1, for example, has about 1.3 % carbon, the liquid around 3 %. Those are the nirvana or equilibrium values for these phases at the chosen temperature. The fact that the carbon concentration must and will be different in the two phase is *not* what we call segregation. It is, however, the reason or cause for segregation to happen as soon as we deviate from equilibrium. The larger the difference in the two concentrations, the bigger the possible segregation effects. It is therefore useful and customary to use the ratio of these two numbers to define an (equilibrium) **segregation coefficient k**, sometimes also called **partition coefficient** or **distribution coefficient**:

$$\text{Segregation coefficient } k = \frac{C(\text{Solid})}{C(\text{Liquid})} = \frac{C_S}{C_L}$$

- Since the liquid typically contains the higher concentration of the atoms in question, we have typically $k < 1$. For non-equilibrium, we define an **effective segregation coefficient** k_{eff} that is always closer to unity than the equilibrium one.

Now let's see how segregation works. We start from a perfect equilibrium situation at point 1 and lower the temperature until we arrive at state point No. 2. We have now about equal amounts of solid and liquid and still different equilibrium concentrations of carbon in the two phases. However, the carbon concentration in the two phases are now also *different* from what they were in state No. 1!

- The solid phase and the liquid phase now need *larger* carbon concentrations compared to what they had in state 1 to be in equilibrium. The segregation coefficient also changes somewhat but not *all that much*. If we want to keep *equilibrium*, the carbon concentration in the parts already crystallized while in state 1 now *must go up* since in equilibrium the concentration has to be the same everywhere. How could that happen? At state point 1 you usually find a layer of the solid coating the walls of your vessel. When you go to state point 2, you add another layer but with a different composition. How can the two concentrations equilibrate? You guessed it: by *diffusion*! Carbon from the carbon-rich melt keeps diffusing into the crystallized parts until the right concentration is achieved everywhere. The carbon concentration in the liquid then will be automatically at the correct value, too.

The key point is: *This will take some time*. It will actually take a lot of time - until hell freezes over or until the end of time, whatever comes first, if you go for absolute perfection. If you are practical and only request that the actual concentrations should be very close to, but not necessarily *exactly* at the equilibrium concentration, it still takes some time - but now you might be able to wait for it.

- How much time it takes to stay sufficiently close to equilibrium at every temperature depends mostly on the magnitude of the *diffusion coefficient* of carbon in γ -iron at the chosen temperature. If we look at trace impurity segregation, the diffusion coefficients of the various *impurity atoms* also come into play. For our example, they tend to be far smaller than that of carbon. At high temperatures the diffusion coefficients are large and it may not take very long to get close to equilibrium. However, since diffusion coefficients decrease *exponentially* with decreasing temperature, waiting times at lower temperatures get *exponentially* longer. Before I come back to what that implies, let's cool down our sample a bit more.
- Eventually we hit the line separating the $L + \gamma$ phase from the *austenite* (γ) + cementite (Fe_3C) phase mixture. The system decomposes into austenite and cementite, and the carbon concentration in the austenite changes once again. This "once again" must happen once again by *by diffusion*. As we go down the temperature inside the $\gamma + \text{Fe}_3\text{C}$ phase field, the concentration of carbon in the austenite and the *amount* of Fe_3C cementite changes. Eventually we hit the line separating the (γ) + (Fe_3C) phase from the final *ferrite* (α) + cementite (Fe_3C) phase mixture known as *pearlite*. The system decomposes into ferrite and cementite as shown above for one example state, and the carbon concentration in the ferrite changes *by diffusion* as we go down the temperature as before. In the end, at room temperature (not included in the drawing above) we have ferrite and cementite. If we managed to maintain *equilibrium* at all times, the concentration of carbon and impurities in the two phase is what it should be and uniform. Let's emphasize this:

What we *don't* have in equilibrium is *segregation*!

- True. If we manage to have equilibrium for the final structure at room temperature, there is no segregation because the relevant atoms (carbon and some minor impurities in this example) are uniformly distributed. *However:*

What we *don't* have in almost all circumstances is *equilibrium*!

- Achieving equilibrium for our example here involves to move a lot of carbon atoms around all the time. To do so requires *extremely* slow cooling rates even for practitioners, and infinitely slow cooling rates for purists. In other words: It can't be done under most circumstances. Some remainder of the effects taking place at the three phase transformations involved are bound to be permanently present at room temperature. For slowly diffusing impurities (like vanadium) the final inhomogeneous distribution will tend to be more strongly related to the distribution right after freezing than for quick moving atoms (like carbon).

So let's consider the other extreme. We go to some state, e.g. state No. 1 within some short time, not maintaining equilibrium all the time. Then we cool down extremely rapidly "freezing in" whatever we had as solid. Since we are only interested in the solid, that can be done most easily by just *decanting* the mix. Quickly pour off the liquid. This keeps not only the solid at whatever composition it had at that moment in time, it also allows a direct look at the *morphology* of the solid-liquid interface. That's how the [picture in the backbone](#) was obtained.

- The solid we obtain will have about the composition indicated by the phase diagram for the temperature at which we decanted the mix. This is neither the composition of the original liquid nor what we would expect at room temperature. For our example it would not even have the right structure ($\alpha + \text{Fe}_3\text{C}$ or pearlite) but would be austenite. That won't really happen because you just can't cool down that fast. In other words; it is not all that easy to assess what happened during freezing. What's left at room temperature is always different from what there was at freezing, and it is not always very clear what kind of changes occurred during (rapid) cooling.

In real life we will be somewhere between the two extremes. We will cool down too fast for achieving near-equilibrium "everywhen" and everywhere, but since we solidify all of the original liquid, the average or *global* composition of the solid will be the same as that of the original liquid. That is not true for the *local* composition. The parts that solidified first (close to the container wall) will have a lower concentration, the last parts to solidify will have a higher concentration. We have *macro* segregation, in other words.

- This just rehashed with some more details what I already stated in the backbone about "[macroscopic segregation](#)" in the extremely simple lead (Pb) - tin (Sn) system. The Fe-C system considered here is far more complex. It has two more phase transitions besides the liquid-solid "freezing". That doesn't make it easy to deal with but it doesn't add something qualitatively new either. Knowing about cooling rates, etc., we even could calculate the global concentration variations.

Before I go into this, let's summarize:

- Segregation effects arise because we have mixed phases in equilibrium. A segregation coefficient can be defined to assess the magnitude of the effect.
- Segregation effects tend to become more severe for small segregation coefficients since larger concentration differences need to be equalized.
- Segregation effects tend to become more severe for larger deviations from equilibrium, always going with larger cooling rates, because less time is available for equalizing concentration differences by diffusion.

- That much is obvious for *macro segregation*, as we call concentration differences or *gradients* on scale that is just a bit smaller than the sample size. You have macrosegregation if the concentration in a 10 cm sample changes on a scale of centimeters.

What about [micro segregation](#), or concentration gradients on a micrometer scale and thus typically much smaller than the sample size? Or even worse, for scales in between "macro" and "micro" that become important, for example, for wootz steel.

- Same thing in principle - but for far more complex reasons! In order to get a grasp on this topic, we first need to look at the *morphology* of the solid-liquid interface *and* on the way it moves. For doing this, I must first discuss a few basics about the *currents* flowing through a *moving* liquid-solid phase boundary during solidification.

Currents Through the Solid-Liquid Interface

One key to (micro) segregation phenomena is the *morphology* or the "shape" of the interface. I bet that if anybody would ask you what the interface between the liquid and solid part of some freezing concoction would look like, you would tend to say: "Probably planar, just like the interface between some liquid and gas. If I pour some water into a pot, its interface to the air is just a simple plane. Why should it be otherwise, when it starts to freeze? I've actually seen that happen, and the interphase (note the clever spelling!) between some ice on a lake and the water is usually quite planar.

Not to mention that you, personally, emphasized many times that interfaces want to minimize their area. Between a liquid and a solid contained in some pot or vessel, nothing beats a planar interface, give or take a little global curvature, with respect to minimal area."

- Good arguments. You are absolutely right - as long as we consider systems at, or not too far from equilibrium. But now we consider systems *far from equilibrium*. Those systems are *always* characterized by the fact that there are large current (densities) of something flowing through, towards, or away from the interphase. Why? Because the system *always* wants to get into equilibrium. Since it is far off equilibrium, something needs to change. But you only can make changes if something suitable moves from here to there - and that constitutes a *current* of something! Here are some examples of currents that we have [used before](#):

- Water* flows through a 3/4" pipe, trying to establish equilibrium. Nirvana will be obtained if as much water as possible is "downhill" or at low pressure. That's why it flows! The water current is as large as it can be, given the constraints. As much water as possible will flow, and the strength of the current will never decrease from the possible maximum values "just so".
- Electrical current* flows through a wire, trying to establish equilibrium. Nirvana will be obtained if as many electrons as possible are at low potential or voltage. That's why we have electricity. The current density is always as large as it can be given the constraints. ... (see above)

- **Carbon atoms** flow from the surface of your steel into the interior, trying to establish the concentration needed for equilibrium. That's why they are doing this. Nirvana will be obtained if the concentration is the equilibrium concentration everywhere. The carbon atom current density is always (see above).
- **Heat**, meaning energy, flows from some hot part to some cold part, trying to establish equilibrium. Nirvana will be obtained if the temperature is the same everywhere. And so on.

As soon as equilibrium is reached, there are no more currents. That also implies that the currents are large at the beginning, getting smaller as the system moves closer to equilibrium, but never smaller as they could be.

▶ If you ponder that for a while, you realize that there are **two** kinds of currents that must be flowing through, towards, or from a liquid-solid interface during freezing:

1. A heat or energy current
2. A current of atoms.

● **Heat**, a form of **energy**, needs to flow through the interface and eventually **out** of the system for two reasons:

1. Freezing involves that the system **cools down**. That means that the thermal energy contained in the system at high temperatures must be taken out. Remember that **temperature** is just another word for energy! During freezing the still liquid part is naturally at a higher temperature than the already solidified part - heat energy thus must flow from the liquid **through the liquid-solid interface** into the solid, and from there through the walls of the container (and possibly the air) into the environment. How much energy flows out per second determines the cooling rate: how fast the (average) temperature goes down.
2. Freezing liberates energy called the "**heat of solidification**". This energy is produced right at the interface, where the solidification takes place. It needs to be removed in addition to the system energy given by the temperature. Once more, it eventually has to flow from the interface to the outside. When heat of solidification is produced, it invariably raises the energy level around the interface and thus the temperature. That's why you cannot solidify something arbitrarily fast.

● The **heat current density** j_H , i.e. how much heat flows out per square centimeter and second, is exclusively determined by the temperature gradient dT/dx or how much the temperature changes per length unit, and the **thermal conductivity** κ of the materials. In three dimensions we have $\nabla T(x, y, z)$ (use [this link](#) for the meaning of the "napla" operator ∇) for the temperature gradient, and the fundamental equation writes

$$j_H(x, y, z, t) = -\kappa \cdot \nabla T(x, y, z, t)$$

From a mathematical point of view this is exactly the same kind of equation as the one we used for describing **diffusion**. Well, why not? We have the same underlying physical phenomena, after all. The only difference is that something a bit more abstract than particles flows: energy!

In principle we should also write the thermal conductivity κ under the napla sign for reasons explained below. We also need to consider everything as a function of temperature and thus time.

● **Atoms**, or more precisely, impurities and alloying atoms, need to flow towards, "through", and away from the interface because the equilibrium concentration in the solid and the liquid is, as a rule, not the same. What the respective concentrations will be at some temperature **T** is given by the phase diagram as outlined above. Looking at [phase diagrams](#) for a while makes clear that the only exceptions to the rule are **eutectic** (or eutectoid) points.

Here are a few points of interest:

- Atoms of the host materials (the majority component) do not need to flow through the interface. In principle they hardly need to flow at all. All that needs to happen is that the atoms of the liquid in contact to the solid "freeze", i.e. arrange themselves orderly and fitting to the crystal surface they are next to. This takes entropy out of the system and thus releases energy, the "heat of solidification". In other words: Upon freezing, you get back the investment in energy (the "heat of melting") that was necessary to make a big jump in the entropy when turning an ordered crystal into an unordered liquid.
- Currents of atoms are thus not necessary in a **pure** substance that freezes. However, there is no such thing as a pure substance and even small concentrations of some impurity atoms can have large effects linked to segregation as [shown here](#). Also, the atoms in the liquid usually move quite a bit because of convection. The melt is not just sitting there but moves around in loops and eddies.
- In binary compounds, the freezing of an atomic layer next to the solid-liquid interface always (except at eutectic points) contains too many atoms of the "junior" partner or alloying element. The surplus atoms must move out into the liquid to establish equilibrium - we need a particle current from the solid into the liquid. Same thing for impurity atoms.

In equilibrium, the concentrations of alloying (or impurity) atoms should thus decrease suddenly at the interface by an amount given by the segregation coefficient **k**. As long as equilibrium is **not** reached, we will have a **concentration gradient**, i.e. a gradual and not a sudden decrease of the concentration from the

value in the solid to the value in the liquid.

We know already that the particle (= atom) current density j_A , i.e. how much atoms flow out per square centimeter and second, is exclusively determined by the concentration gradient dc/dx , or how much the concentration changes per length unit, and the **diffusion coefficient** D of the atoms. In three dimensions we have $\nabla c(x, y, z)$ (use this link for the meaning of the "napla" operator ∇) and the fundamental equation writes

$$j_A(x, y, z, t) = - \nabla \{D(T(x, y, z, t)) \cdot c(x, y, z, T(x, y, z, t))\}$$

That is our old [diffusion equation](#) or Fick's first law, except that we now have the diffusion coefficient under the Napla sign since it is no longer constant but depends on the temperature, which in turn depends on the coordinates and the time t . In the liquid, for example, diffusion is always much faster than in the solid.

To make things a bit more complicated or realistic, it is necessary to realize:

- Our two basic equations are linked. A heat current changes the local temperature and thus diffusion coefficients. Particle currents change the local atom concentration and thus the composition and therefore the melting point (or more generally, the phase transition temperature). Changed melting points change the ratio of liquid to solid, and so on.
- While diffusion is the *only* way to move atoms in a solid, that is *not* true for a liquid. The liquid may also move atoms by *convective flow*, i.e. it flows around. **Convective flow** is essentially driven by density gradients in the liquid that are caused by temperature gradients via thermal expansion.
- The total surface area of the solid-liquid interface can and will change in many ways (as we shall see in the follow-up module). As a simple example, solid crystals might form inside the melt and grow, adding more interface area.

What a mess! Let's see if we remember what we wanted to learn about? Ah - yes: *segregation!* Well, just use the two equations above, add boundary conditions, and specify them for whatever you have in mind. Then solve them, deriving the concentration and distribution of some impurity at room temperature, and you have segregation covered.

Before you now rush off, firing up your computer to do this, let me give you a piece of advice: *Forget about it!* Simulating crystal growth is far beyond the ken of most if not all people. I certainly couldn't do it. With present-day computers experts can do a lot for some "simple" problems, but in the words of one such expert (Jeffrey J. *Derby*, Department of Chemical Engineering & Materials Science University of Minnesota):

The complete modeling of crystal growth from first principles is impossible.

We need to take a different approach to get closer to understanding segregation. To do so we need to keep in mind: it is the interface and all the the currents tied to it that determine what will happen.

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