# 6.1.3 Reading Phase Diagrams: Mixed Phases and Boundaries

The next rule we need to learn is about **two-phase regions**. What happens there?

- At a first glance something quite strange. While we still can define a proper location in the phase diagram, and draw it as a point or small circle called a "**state point**", it doesn't make much sense anymore.

- Our system, after all, contains *two* different phases and that's why it decomposes into *two* state points, always positioned on the boundaries separating the two–phase region from the one-phase regions to its left and right.
  To understand this, we look at an example. We take two steels: a low carbon one (around 0,35 %) and a "eutectoid" one (around 0,8 %) or "*composition 1*" and "*composition 2*", respectively.
  This is drawn into the phase diagram below, where I also have added some additional information.

Now fire up your brain smithy and heat both steels to a temperature of about 1200 K (927 °C, 1701 °F), where you let them sit for a while. This state of being is symbolized by the green and red state points in the phase diagram.

- At the high temperature where we start our two steels, we have plenty of vacancies running around. The carbon interstitials run around extremely fast too, and our two steel crystals achieve nirvana with respect to their carbon distribution rather quickly.
  The carbon atoms then are uniformly dissolved into the fcc crystal structure that the iron always assumes at that temperatures, no matter what kind of structure it might have had before we heated our steel. The crystal goes for nirvana and even tries to get rid of all the grain boundaries and dislocations that might be in there.

- The crystal will work hard at doing this but it will not be totally successful in your or my lifetime. Nevertheless, unwanted defects will be removed to some extent during the time you wait, and we will have relatively large austenite grains with few dislocations.

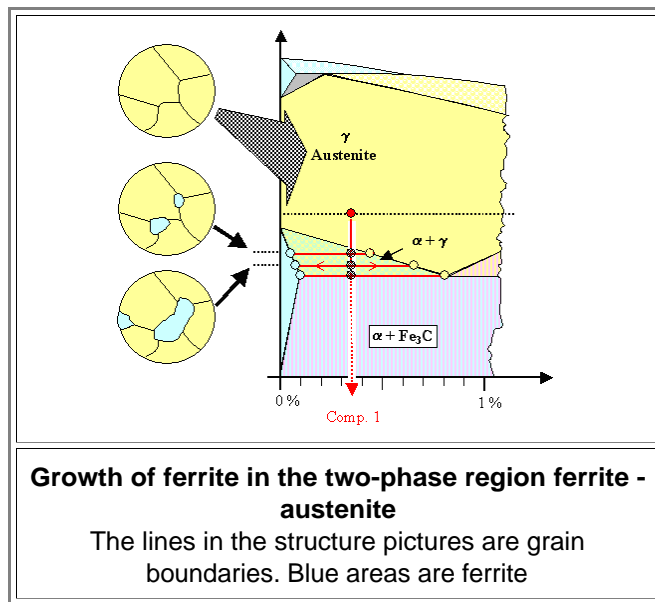**Cooling two different compositions from about 1200 K**.
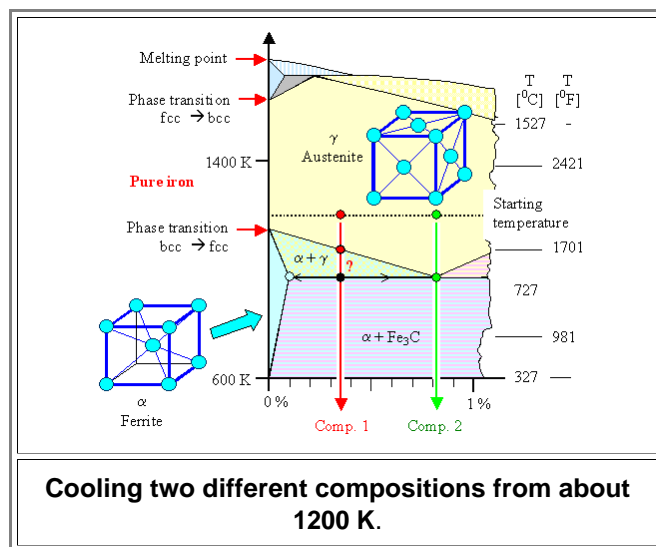
Now an evil person—you, the smith—takes the steel pieces out of the fire where they were happily approaching nirvana.

- Their temperature starts to go down, and that means that our red and green state dots move down the vertical line with some "speed" that is given by the cooling conditions. As long as they stay in the yellow area that marks the austenite phase, they don't care all that much about getting colder. As long as their state dots are in austenite phase region, they are close to nirvana.

- Sooner or later the red *composition 1* steel will come to a critical temperature (second red state point) that separates the pure γ phase from the mixed α + γ phase region; soon after that it comes to a second critical temperature (black point) separating the α + γ phase region from the α + Fe$_3$C phase region.

- The *composition 2* steel too will have come to that critical temperature by then. As soon as steel No 1 gets inside the blue-yellow triangle that marks the region where we have a mixture of the α phase and the γ phase, it needs to assume that "state", whatever it is. Nirvana now means you must be α + γ, so that's what the steel is endeavoring to be.
  There is no choice now but to **decompose** into some parts that are still γ = fcc, and some parts that must change into α = bcc.

But how can that be? There is no α phase with a carbon concentration like that of our two steels. It there must be an α phase, it must have far less carbon inside than what *composition 1* brings along.

- Well, crystals go through whatever it takes to obey the second law. The carbon is expelled from the parts that assume the α phase, and the remaining γ phase must take the surplus. That is not as tricky as it sounds. Illustrated it looks as shown below

Growth of ferrite in the two-phase region ferrite - austenite
The lines in the structure pictures are grain boundaries. Blue areas are ferrite

As soon as a phase transition to the mixed α + γ phase becomes necessary (we still call it a phase transition even so, technically it is a transition from *one* to *two* phases), small specks or nuclei of ferrite start forming at some good nucleation points. That means grain boundaries, of course, or even better, the **nodes** of grain boundaries as shown.

The carbon is redistributed. Very little remains in the ferrite, most is now in the austenite.
How much precisely? Exactly as much as the two new blue and yellow state points *on the boundaries* between the mixed α + γ phase and the neighboring phases to the left and right will have.
The phase diagram even tells us *how much* of α + γ we will need. That relates to the *length* of the red horizontal lines in the figure above to the left and right of the black state point; I'll come to that shortly

So the **rule for two-phase regions** obviously must be:

> **In two-phase regions the state dot will always decompose into two state dots. These are situated at the intersection of the horizontal " tie-line " with the boundaries separating the two-phase regions from the one-phase regions**

The **tie-line** is simply the horizontal line defining a constant temperature.

The mind now boggles a bit and thus is very receptive to new little theorems:

1.	**For a binary system there are never more than two phases in a mixed phase region**
2.	**To the left and right of a two-phase region there are always one-phase regions**

Now that's a relief! Complicated structures like mixtures of ferrite, austenite and cementite are now forbidden!

- Those are not obvious little theorems, by the way; they are actually rather hard to prove. They come out of a more general theorem called **Gibbs' phase rule**.
  I will not go into the intricacies of Gibb's phase rule here; consult the science module if you are interested.
  I will point pout, however, that the geographic maps you know also go with a major theorem that you probably don't know. It also says something about how many different areas you can find.
  Here is the key word: "Four color theorem".
  Use the link if you want to know.

Back to two–phase regions, knowing now that there are no three-phase regions. What you, dear reader, must have been wondering about if you looked at the picture (otherwise do it now), is that during its travel through the two-phase region *the actual composition of the steel must change all the time!!!*.
The ferrite regions must get larger, the austenite region must shrink, and both of them must change their carbon concentration *all the time* while the temperature goes down. That's what the phase diagram states. And that's what *must* happen for nirvana!
Evidently that implies that a *lot of atoms need to move*.

- That's exactly what it means. If the temperature is high enough long enough, so all those atoms can move, either with the help of vacancies or by direct diffusion in the interstitial lattice, your steel can cope. It might feel a bit harassed by being put through this ordeal but it only needs sufficient time to move a lot of atoms about. Doing that it establishes closeness to nirvana once more.

Now comes your great moment to show that dump piece of inanimate matter who is the Boss!

- *You*, the ancient (or modern) smith **quench** your steel, meaning you cool it very rapidly, typically by throwing the red-hot piece into cold water.
  Your steel hates you now but can't do much about it. Nothing in there can move anymore after the short time it takes to get down to just a few hundred centigrade.
  That is true at least for the outer parts because the inside of a big piece of iron always will stay hot far longer than the outside, of course. There is only that much you can do with *quenching*.

The structure you find now at room temperature might be quite different from what your steel had in mind for its nirvana state, or at least for some second-best state.
Your work piece may even shatter into fragments because large stresses built up that exceed the fracture stress at some point. If it doesn't fracture, it might bend into weird shapes because dislocations react to the stress, move around, and cause plastic deformation.

- Why should stress build up? Because the cold parts on the outside contract (the opposite of thermal expansion) and "squeeze" the hot parts inside so much that a lot may happen. "Squeezing" is, of course, just another word for exerting stress on the inside.
 We definitely must expect plastic deformation to take place during quenching, and possible even fracture

> **Here is a first reason for the "soft"
> steel core inside sword blades.
> It can easily "give" and thus keeps
> the blade from fracturing during a quench.**

You noticed, I hope, that I have started discussing what you, the smith, *can* do, in contrast to what the steel *wants* to do. I'm starting right now to move from the *science* of "happy" metals close to nirvana, to the *technology* or *engineering* of metals. That typically means that we need to make them unhappy but useful. Sometimes I wonder if women feel the same way about men.

- Before we go deeper into this, I will explore what happens to steel No. 2 with the ***eutectoid composition*** of 0,8 % carbon.
  You know the rules by now. You do it. I help you by providing a suitable picture in the next figure.
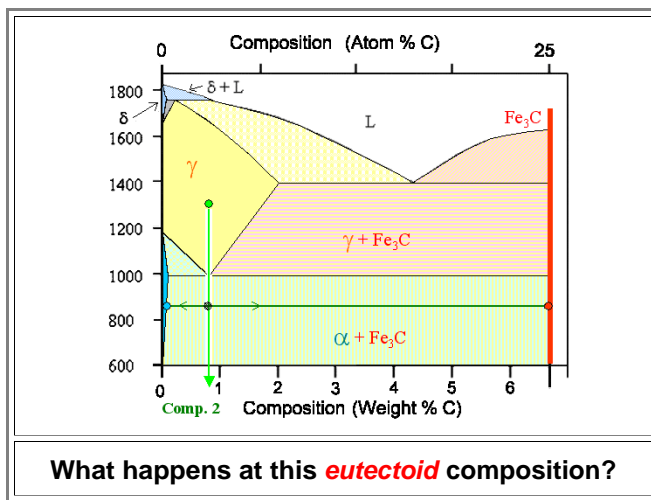
What happens at this *eutectoid* composition?

"Well, upon reaching about 1000 K, the steel enters the two-phase α + Fe$_3$C region and must decompose into the phase to the left (α or ferrite) and the phase to the right (Fe$_3$C). Right?" *Right! Good answer.*

- "And what exactly is Fe$_3$C in this context?" *Good question!*
  In our phase diagram it is shown as a solid vertical red line at 6,7 wt% carbon. What's so special about the "magical" 6,7 % carbon?
  Look at the scale above! It happens to be exactly 25 atom %, and that's what counts.

- In other words, we have a composition with exactly *one* carbon atom for *three* iron atoms. If you have that, you can actually form **iron carbide**, a chemical compound with the chemical shorthand **Fe$_3$C** and the name "**cementite**".

- The properties of cementite, or iron carbide, or Fe$_3$C, or whatever you want to call it, relate to the properties of pure iron (Fe) or pure carbon (C) just as much as, for example, table salt (NaCl) relates to pure sodium (Na) or pure chlorine (Cl): *Not at all!*

Cementite by itself is some hard and brittle stuff. Its name was introduced by **Osmond** and **Werth** in 1885, when they realized that at high temperatures steel contained what we now call ferrite and austenite, and that at low temperatures there were "cells", somehow *cemented* together by some carbide that they aptly called *cementite*.

- You're getting a bit woozy now; I'm getting tired, too. But before we take a break with our favorite liquid poison, you must realize two important things:
  1. You don't yet know all there is to know with respect to the iron-carbon phase diagram; e.g. that all of the above contains a *big lie*. Continue with the science link if I haven't reached your yield point yet.
  2. You did realize a major truth about plain carbon steel: It's iron with just a little bit of carbon in it (something like 0,3 % - 1,5 %), Yes, but did you realize that carbon steel *cannot* be a uniform smooth substance at room temperature?

  The phase diagram insists that it is a mixture of relatively pure and soft iron (the ferrite) and something rather alien: hard and brittle cementite, a crystal with a rather complex crystal lattice. We are forced to conclude:

Science link

Phase diagram

Steel is a composite material on a microscopic scale. It is a mixture of hard (cementite) and soft (ferrite) components.

- Steel in its most simple form as **plain carbon steel** already consists of hard cementite and soft ferrite pieces if you look at it with a microscopic. It's already a kind of "*damascene*" material even if it appears to be perfectly smooth and uniform to the unaided eye.