7.2.2 Mixed Blessings

What Could happen

- Carbon steel is composed of something soft and ductile: ferrite, and something brittle and hard: cementite. Even readers given to the bulk intake of beer during reading non-fiction (or fiction, not that I blame them) got that by now. Steel is a kind of **composite material**; a material made by somehow joining two different materials.
    - On a *microscopic* scale steel is thus exactly what the various "damascene" techniques of joining hard and relatively brittle with soft and ductile steel are supposed to do on a *macroscopic* scale. It is always assumed that this brings out the best of both materials, and that the product would now be hard and ductile and not soft and brittle

Why?

- Why shouldn't it be soft and brittle?

- Whenever we make a *composite material* it contains a least *two* phases, in contrast to a chemical compound, which is a one-phase material. An ideal composite material is made from at least two uniform materials that have different properties. The composite material will have properties different from that of its "parents" but there is no reason why it should always inherit the "*good*" properties of its parent.
    - Why should it combine just the best of the parents? Just look at your kids. Some of mine are actually female, do not like beer and red wine, and never showed any interest in the science of steel!
      To be sure, composite properties of materials will be determined to a large extent by the properties of the parents. But how they come out in the end is also determined by the (micro) structure of the composite, very much so.
      This is easy to see for a composite with parents that are hard & brittle and soft & ductile.
    - If you don't see this right away, do a little (brain) experiment. Build two walls or houses
        1. The first wall you make with hard and brittle rocks or cinder blocks that are held together by some kind of rubbery mortar or glue. You also might fill the interstices of a (yielding) wooden framework structure with (unyielding) bricks.
        2. The second wall you make with soft rubber bricks that are held together by hard and brittle mortar. You also might encase (yielding) iron rods into (unyielding) concrete.

      Which wall will be rather hard but will yield elastically or plastically to some pressure without breaking, and which one will be brittle and break immediately into pieces if forces exceed some limit?
      Right. *Structure* (in the case of kids called upbringing or nurture) matters just as much as the *properties* passed on from the parents (in the case of kids called genes or nature). This is illustrated below.
      By the way, did you note that I have just settled the old "**nature or nurture**" debate?

Advanced Link

Composite Materials

Wood - brick composite

Brick - mortar composite
Warped old houses in Lüneburg, Germany.

A picture of *all* steel reinforced concrete constructions still standing after experiencing what the two houses above went through.

A lot of houses like the ones above survived heavy bombing during WW II - warped, bent and damaged, but standing - while concrete buildings either stayed unwarped as before or collapsed completely.

We want hard but ductile steel. Our ingredients so far are soft and very ductile ferrite, comparatively hard and somewhat brittle pearlite, and really hard and fully brittle cementite. We want to combine these ingredients in such a way that we emulate wall structure No 1 and never get No. 2. So let's see what that implies:

- *Hyopeutectoid steel:* We need to embed the comparatively hard and somewhat brittle *pearlite* into a matrix of soft and ductile ferrite, just as shown in this picture. Good ductility at medium hardness can be expected
- *Eutectoid steel:* You have little choice here. From what we considered so far you get pearlite all over, as seen in these pictures. Good hardness and reduced ductility should result.
- *Hypereutectoid steel:* You definitely want the really hard and fully brittle cementite distributed *in* the pearlite like in this picture od wootz steel. What you don't want are closed shells of cementite around the pearlite as shown here since this must lead to rather hard but completely brittle steel. But that is what you will get if you don't pay close attentention.

These microstructures then might bring out the best of the *three* phases we have at our disposal: hard - but not brittle. The question now is how to make them. As you know by now, the crystal itself is not going to be overly helpful in this business.

Mother nature knows how to deal with question like this.

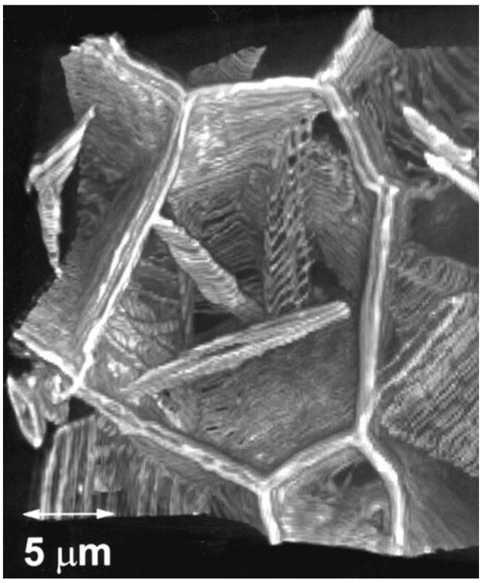
Nacre, a compound material of soft proteins and hard **calcium carbonate** ($CaCO_3$), not only gives mother-of-pearl its luster but also its *strength*. It consists of hard and brittle calcium phosphate platelets embedded in a soft matrix of proteins and thus comes pretty close to the first type of wall constructed above.
Nature uses that principle quite a bit. We also find in bones, for example, except that instead of calcium carbonate you have variants of **calcium phosphate** (knon as **apatite**) in **bone**. The proteins are mostly collagen.
Calcium phosphate, by the way, is a chemical compound you are very familiar with. You imbibe (dissolved) calcium phosphate in one form or other when your drink milk or eat milk products. It comes in several variants, e.g. as $CaHPO_4$ or "hydroxyapatite" ($Ca_{10}(PO_4)_6(OH)_2$). Your tooth enamel is made from the stuff, just with less protein. All variants are hard and brittle.
Fresh bones are rather tough and flexible. I avoid the word *ductile* here because the crystalline part is not ductile at all, i.e. its dislocations can't move, and the organic part is not crystalline, so there is no plastic deformation or ductility *by dislocations*. That doesn't mean that organic or amorphous material cannot deform plastically at all, only

that the mechanism is completely different from that of crystals.
You know that. Breaking that turkey wishbone after Thanksgiving is far easier if you let it dry for a few days. The soft and flexible protein (mostly collagen) stuff in between the hard bone stuff ("hydroxyapatite") then has decayed and the formerly tough and somewhat flexible bone becomes quite brittle and easy to snap.

- Isn't that great? Now we start to understand the principle behind the *damascene* technique or **composite steel** as I will call it from now on, the mixing of different steel variants.
  - Well—not really. In the case of nacre and many technical composite materials, the focus is primarily on optimizing Young's modulus or the **stiffness** of the material, together with the fracture toughness.
    Composite materials like nacre or carbon-fiber-reinforced plastic (***CFP***) have a far larger effective Young's modulus compared to the "parent" protein or plastic, respectively. It is primarily the stiffness of the composite material that has improved. It also doesn't fracture as as easily as the very stiff but brittle "parents" phosphates or carbon, respectively.
  - In composite steel we *cannot* change Young's modulus or the stiffness very much because we still have mostly iron. Use this link if you forgot this. So making better swords by using composite steel techniques must have some other rationale behind it.
- If we now look at the hardness of composites and not at *Young's modulus*, we first need to recall that hardness for metals is

  1. just another word for "yield stress", and
  2. the yield stress is the stress that enables dislocations to move.

  - Cementite is brittle and that translates to: dislocation movement in cementite is impossible. It follows that pearlite must be harder than ferrite because the cementite in there cannot but act as an insurmountable barrier for dislocations, and that will make their movement more difficult.
    While dislocations cannot move across the cementite lamellae in pearlite, they can go around—it's just *harder* to do (pun intended). So even eutectoid pearlite is still ductile to some extent.
- Now let's look at hypo- and hpyereutectic steel or, as we just learned, at pearlite embedded in ferrite or pearlite with primary cementite, respectively.
  - Hypoeutectic steel is simple. The primary ferrite grains are soft, dislocations can move easily. The hardness of hypoeutectic steel will be some average of the hardness of ferrite and that of pearlite. What you get will also depend somewhat on structure parameters like grain size, of course
  - The hypereutectic case is trickier. If we embed something reasonably hard but still ductile like pearlite in something very hard and brittle like cementite, the resulting composite would be very hard—but it would also be *completely brittle*. This is so because the dislocations in the pearlite grains still could move but never could get out of the grain. It's just like your rubber brick wall made with brittle mortar.
- We will get exactly this undesirable situation if the *primary* cementite in hypereutectic steel does indeed nucleate at the grain boundaries and then grows to envelop the grain into a brittle cementite shell. Unfortunately that's exactly what hypereutetic steel does if left to its own, nirvana-seeking devices. Here is a remarkable picture showing just that:

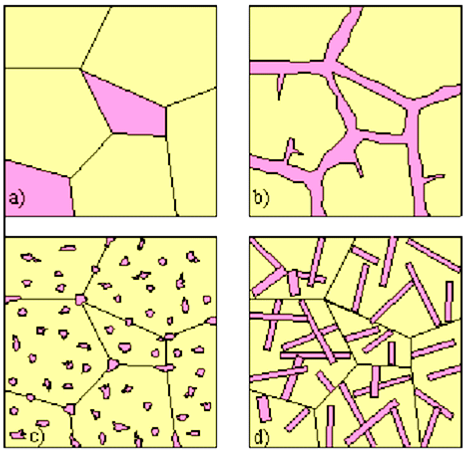


Three-dimensional rendering of cementite completely enclosing a pearlite grain.

Source: The Naval Research Laboratory: 75 Years of Materials Innovation; Bhatka B. Rath and Don J. DeYoung; JOM, 50 (7) (1998), pp. 14-19; by permission

  - This is a three-dimensional computer reconstruction of one-half of a hypereutectic steel grain, showing *only* the cementite. It reveals the three-dimensional morphology and connectivity of the cementite plates masking the grain boundaries and shows a few lath-shaped cementite particles with the the "zebra" pattern typical for pearlite.
    The grain is completely encased in cementite. In addition some pearlite structures are visible inside the grain. It is not all pearlite because some of the *secondary* cementite re-enforced the primary cementite at the grain boundary.
  - How do you get a picture like this? Take a picture of the (defect etched) surface, polish off 0.2 µm material, take another picture. Repeat 150 times. Then process the individual pictures and feed them into a computer that assembles the final compound picture (after it was fed with proper software for doing this). Obviously a task for graduate students who will love it.

- Four letter words come to mind now. Why? Because what this means is that you, the ancient smith attempting to make a *wootz blade*, have a *big* problem now. Considering that **wootz steel** with roughly 1,5 % - 2 % carbon is *hypereutectic*, actually very much so, you are in big trouble. The stuff you are supposed to work with tends to be very hard but is totally brittle. You just as well could make a blade from glass.
  - Turning wootz steel it into a hard but very flexible and tough material, as it is reported to be, obviously needs more than just to let it cool down slowly. The trick is, quite obviously, to distribute the considerable amount of cementite that the phase diagram requests for hypereutectic carbon steel in such a way that good properties emerge.
- Just to make sure that you know what I'm talking about, the next figure *schematically* shows some possible ways of distributing a certain amount of cementite in a matrix of austenite (or the final pearlite).



Four principally different ways of distributing brittle cementite

The matrix could be *austenite* at high temperature or *pearlite* at lower temperature. What is shown is:
a) Austenite / pearlite grains and cementite grains. This pretty much *never* happens
b) Austenite / pearlite grains in a cementite shell. That's what tends to happen. It is clear that this structure is brittle and breaks easily.
c) Lots of little roundish (roundoid?) precipitates ("spheroids") of cementite. That's what you find in wootz steel.
d) Lots of little platelets / needles of cementite.

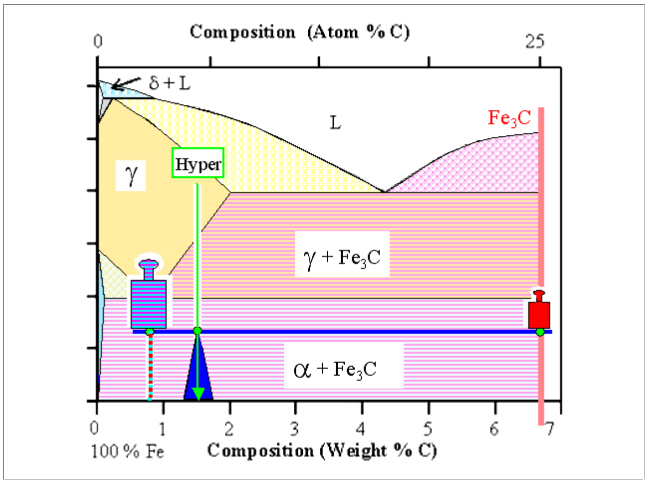
  - The matrix *could* be austenite at high temperature or *pearlite* at lower temperature.
    It better be austenite at high temperature, however! Because if you cool below the transformation temperature, the remaining austenite just transforms into pearlite but leaves the *primary* cementite intact. It is thus essential to control the structure of the *primary* cementite already at high temperatures; to do so at low temperatures is far more difficult or impossible.
    In other words: if you start the transformation to pearlite with a "bad" structure (like b), it is far more difficult or impossible to turn it into one of the more desirable structures at the lower temperature.
- Let's look at that in more detail. What we *might* find at room temperature in full accordance with the phase diagram are structures like:

1. Just a random mixture of ferrite (yellow) and cementite grains without any pearlite. This is a conceivable structure but never found. The principle of supreme laziness is very much against such a structure.
2. Pearlite grains (yellow) separated by cementite walls. That's what the crystal would produce if left to its own devices; the picture above illustrates that rather nicely. But why? Why does the crystal want to make this bad (for us) structure? We shall see.
3. Lots of small cementite particles embedded in large *ferrite* grains. Not something likely to occur either.
4. Lots of cementite particles - small, large, mixed, whatever - embedded in large *pearlite* grains. That's what we would like have to some extent. The hard and brittle stuff completely embedded in the softer but still hard and still ductile stuff. *Wootz steel* will fall in that category.
5. Long and interconnected cementite needles in pearlite (like a glass fiber network contained in epoxy). Not likely to occur, even so there are recent reports about "cementite nanowires" in wootz blades.
6. Stacks of thin cementite platelets embedded in pearlite. Variant d) in the figure above could be seen as a schematic drawing of this case or number 5 just above since in a two-dimensional drawing you can't tell if longish objects are needles or platelets seen "edge on".
7. *Your* proposal. I'm sure you can come up with something.

- If you have a good memory, you notice that we are getting close once more to discussing optimization of your product. What structure would we like to have? Why? And what do we have to do in order to obtain it?

The Lever Rule

- Before we look ever deeper into those questions, we need to clear up one last point about phase diagrams. Here, as in the various drawings shown all along, we mixed all kinds of phases—ferrite , austenite, cementite, pearlite—in some ratio. What ratio exactly?
  - The time has come to produce the *last rule* for reading phase diagrams. You will now learn *how much* of each phase we have in a two-phase region. This is not directly given by the composition. Knowing that you have, for example, 1,6 wt% carbon in iron, doesn't tell you how much of that carbon will be in the austenite or the liquid, respectively, at 1600 K. In other words. Just knowing the concentration of a component doesn't tell you how much of it you will find in the coexisting phases.
  - The phase diagram will tell you that. Here comes the simple **lever rule**:



Lever rule illustrated for a composition with 1,6 wt% carbon

- Let's look at an example of a 1,6 % hypereutectoid carbon steel. That means that we have 1,6 g of carbon in a little less than 100 grams of iron.
  In the mixed phase of ferrite + cementite that we expect at room temperature, *how many* grams of iron or cementite, respectively, do we have?
  - Well. Let's do a little math: We have 100 grams altogether. Pretty much all of the 1,6 g of carbon is tied up in the cementite or Fe_3C. So every carbon atom in there ties up three iron atoms for cementite formation. In grams that would be…?
  - OK, enough math—you know where that would end. There is a much easier way: Look at the phase diagram and use the *lever rule*. What that means is easy to understand, just look at the picture above.
    Imagine that at the composition you're considering is the pivot of a seesaw, with the beam extending to the state points of the two phases the system must decompose into (pearlite and cementite in this example). Balance the seesaw by putting the weights with the proper ratio (= ratio of the two beam lengths) on the beams, and you have the weight ratio of the two phases in the composition.

  - Just looking shows that for 1,6 % carbon steel we need about *seven* times more pearlite than cementite. That's why the *primary* cementite is not so prominent in the picture we had before; we simply do not need very much.

- The time has come to tackle the big questions, alluded to above and before:

What structure is optimal for sword making?

If I know what I want,
how can I make it?

- Of course, that are not just the basic question for hypereutectic steel but for just about *any* steel in the context of sword making.
  - Let's generalize a little bit and consider that your customers did not only want swords from you and your colleagues, but also knives, dinner plates, and tankards for beer. As time progressed and people got more civilized, they wanted also wine glasses, bicycles, Mercedeses, solar cells, yachts, cell phones, power plants, machine guns, wrist watches, airplanes and artificial knee joints; not to mention pace makers, viagra, and Wagner operas.
    The two questions above then apply to just about everything that is made by scientists and engineers.
    Replace "sword" by "product" and you have the **Materials Science and Engineering mission statement**.