9. Real Steel

9.1 Some General Remarks

9.1.1 Things Get Complicated

Properties and Microstructure Reconsidered

So far I have mostly looked at an *ideal* iron - carbon *alloy*, called **plain carbon steel**, with just an occasional glance of what else might be in there. This is not realistic. In ancient steel, there is *always* something else in there - essentially the more prominent elements of the periodic table in some form or other *and* inclusions of slag particles, charcoal, "pebbles", and whatever else was around. Whatever is in there got inside by circumstances and certainly *not* by intention. Aristotle, after all, had proclaimed that <u>steel is especially pure iron</u>, so why should you add something? Even if you, the ancient smith who had fortunately never heard of Aristotle, dunked your red-hot iron in all kinds of revolting stuff including <u>goose shit</u>, you didn't do it in order to get some element inside the steel crystal lattice. You believed in the working of some magic that somehow relates to goose shit or whatever, or you simply did it because somebody (your master) had told you that this is what one does. Just think of all the revolting stuff people eat just because somebody (typically parents) told them that this is what one does, and you see how powerful tradition can be. My wife (from NYC), for example, eats slime that's is *still alive!* inside some closed (for good reasons!) <u>nacre</u> shell!

Times have changed. When we make modern steel, we add all kinds of alloying elements *intentionally*. But mostly we also have some stuff in there that we do not care about. The only question is if we *know* that some unintentional stuff is in there, and how we make sure that we can tolerate it. We need to distinguish a bit more closely between the various things our iron / steel might contain and define a few terms:

- Alloying elements are there because we added them intentionally.
- **Dirt** atoms in concentrations around 0.x % are there because they happened to be around in one of the processes involved in making the steel. We don't want them but we know they are there. We tolerate a certain amount of dirt especially sulfur (S) because it costs money to make really <u>clean iron</u> and steel. You do it, however, if you must.
- Trace elements are always unintentionally in there. Their concentrations is low some ppm to below the
 detection limit and we typically neither know nor care about that.
- Inclusions, in contrast to atoms, are *pieces* of something (slag, charcoal, tiny stones, ...) that somehow made it inside your steel. Inclusions are much larger than atoms and in most of steel history were simply part of your solid raw iron / steel. They are always there if your steel was *never* liquid. This was a huge problem for ancient steel makers and it is still a (small) problem today. The Celtic iron from the 5th 1st century BC shown below, while possibly rather pure, is sure to be full of slag and charcoal inclusions.



Celtic "trade" iron from Pleidelsheim, Germany

Source: Special exhibition dedicated to the Celts of the first millennium BC <u>"Baden-Württemberg State Museum of Archaeology" and the "Württemberg State Museum", 2012/13, Stuttgart, Germany</u>

The periodic table contains about 90 elements that you can find out there, if mostly in disguise, i.e. tied up in some compound. You can also just buy most of them, something that is much easier to do. Some elements are very rare and thus not likely to be unintentionally incorporated in your steel. That is one reason why many of those 90 elements are only found in very low concentrations in your steel, <u>ppm</u> or much lower. You need sophisticated equipment to detect them.

It is very likely that a very low concentration of something does not influence the properties of your steel very much - but you never know for sure. <u>Boron</u> (B), for example, will be felt at concentrations as low as 0.0003 % (3 ppm).

- But many elements are ubiquitous enough and thus might make it into your steel. Assuming that we always have some carbon around, we have, expanding on the above a bit, the following basic possibilities:
 - 1. The element in question is present in a *extremely* low concentration, say below 10 <u>ppm</u> or 0.001 at%. You need sophisticated equipment to detect it. It is very likely that it causes *no problems* and *no benefits* since it does not noticeably influence the properties of your steel. However, you never can be quite sure as long as you didn't look into it. 1)
 - 2. The element is present in what we call a **low concentration** above 100 ppm or 0.01 at% and up to the usually 1 wt % or 2 wt%. It *mostly* causes you all kinds of *problems* but might be good in special circumstance. Sulfur (S), phosphorus (P) or oxygen (O) comes to mind.
 - 3. The element is present in low concentrations and is (almost) always *good* for you. **Manganese** (Mn) is the example for this. We might have been lucky because some manganese is contained naturally or we added it intentionally for example in the case of "micro-alloyed steel".
 - 4. The element is present in a low concentration and noticeable but mostly *not doing all that much*. Small quantities of elements like nickel (Ni) or chromium (Cr) are in this category.
 - 5. The element is present in a **high concentration**, from 1 % to above 10 %. Then it is (almost) *always* intentionally in there and thus must be doing something beneficial.

Point 1 - 4 covers what is called low alloy steels, point 5 leads over to high alloy steels.

As you see, steel science is difficult. Very difficult. What we learn from all of the above is that just knowing the concentration of some element doesn't tell you how it might change properties. And I'm meaning <u>all</u> relevant properties, not just the basic "strength" stuff that I mostly discussed so far. And whatever it does in principle will very much depend on processing. And on what else is in there. And on the temperature and the environment.

Nowadays we may know the exact composition of a steel down to trace elements in the <u>ppm</u> or even <u>ppb</u> range - but that does not tell us all that much about its properties. The properties, as you know by now, depend on the <u>microstructure</u>, which depends on the compositions <u>and</u> the processing, or everything you or somebody else ever did to your steel.

To make things even more complicated we must now also consider **steels without carbon** or more properly, steels with very low carbon concentrations. The link will tell you far more about that than you ever wanted to know. These " *designer steels*" are always modern steels and their number and market share is rapidly growing. Don't mix that up with old-fashioned *wrought iron*. It is low in carbon, yes, - but it is not steel!

Link Hub

Major Steels

You can already appreciate that with only a little carbon you cannot produce much cementite. Hardness thus must come from something else. I will come to that.

Of course, over the last 150 years or so, when something akin to steel science was born and thrived, a lot of data have been collected and refined into knowledge and rules. But that only helps to some extent, because there is almost no rule without exception. Sulfur in steel is always bad? Yes, but there are some steels where sulfur (S) is added intentionally because it makes machining easier. Even evil phosphorous is used in modern so-called weathering steel and some others. Another example is oxygen. It is decisive for making your steel. You blow it through your molten raw stuff in order to take out you whatever you don't want, but you typically don't want it in the solidified product 1.

So, once more, steel science and engineering is difficult. Very difficult. Thank God! It gives us scientists and engineers something to do for making a living. If systems are very complex, then there is also a lot you can do.

Look at *modern* alloy steel; iron with alloy elements that we put in there *intentionally*. *I*, a *modern* steelmaking scientist have an incredibly large selection of <u>alloying elements</u> and processes up my sleeve, from which *I* can choose. That's why there are thousands of different iron alloys out there today, all of them we call "steel". And that's why there will be many more to come, just wait. The parameter space involved is still largely unexplored. In contrast, *you*, the *ancient* smith *and* steelmaker (almost the same thing) had only very limited options. Worse, you had not much leeway in exercising these options either.

Your first option was to choose among the few kinds of steel available two thousand or three thousand years ago.

- 1. You had essentially wrought iron or a mild carbon steel, always with some additional dirt in there. Your steel was never liquid, so it always contained slag inclusions.
- 2. You had essentially a phosphorus (or arsenic) steel with some other dirt in there. Your steel was never liquid, so it always contained slag inclusions.
- 3. You had essentially a carbon phosphorus steel with some other dirt in there. Your steel was never liquid so it always contained slag inclusions.

- 4. You had "wootz" steel that had been liquid once. It had a high ("hypereutectoid") concentration of carbon and contained some dirt, but hardly any slag inclusions. Some wootz kinds also contained traces of strong carbide formers like vanadium (V) that were not distributed homogeneously.
- 5. You had some weird stuff.

Your second option was how you processed your steel. Not much choice here either. Temperatures were restricted and not precisely known, and thermal treatment consisted of natural cooling or some kind of quenching. Your third option was which God you prayed and made sacrifices to. It might have helped your spiritual well being but did very little towards improving your steel.

At this point you must become aware once more that what I have summarily called slag inclusions are objects of prime importance for all ancient smiths making iron and steel objects including sword blades, from all steel other than wootz steel. Inclusions are the major reason for all this folding and hammer-welding; I'll get to that. But let's assume that we know that it is the microstructure, including *slag inclusions*, that determines the properties in

the end. Let's think about this for a minute. Do we (I include myself) really know how the properties of steel depend on the microstructure?

Let's say we know the exact composition of a steel and its microstructure. That allows you and me (in principle) to make some educated comments or guesses about its *hardness* and *ductility*, allright. But how about the following properties:

Weldability; the possibility to join two peaces by simple liquid or torch welding without compromising mechanical strength at the weld seams? Weldability is a very important property. If a steel cannot be welded, forget it for the car industry.

Corrosion resistance, or how fast does it rust? Under normal conditions? In salt water? I don't have to explain the importance of that property.

- <u>Creep resistance.</u> That doesn't mean that the steel resists to be being used by (insert creep of your choice). It means that it deforms plastically and very slowly under a stress that is far lower than the yield stress and thus shouldn't do anything. We are talking long term behavior here, a tricky business.
- Fatigue resistance. Can steel (or any material) get tired and collapse? You bet! Fatigue happens if small oscillating strains (vibrations in other words) occur long enough in your steel. I'm talking small stresses and strains here once more, that should be well contained in the elastic region of the stress-strain diagram. Accordingly, the microstructure should not change - but it does, leading eventually to fracture. I have mentioned fatigue (and creep) before but now you know that these properties, like all properties, must somehow be tied to the microstructure. In both cases the properties and thus the microstructure changed under conditions where we wouldn't have expected that.

The list would go on for at least 20 more points if we look seriously at all important properties. The link gives some more examples.

Then you repeat most of the list but for some *temperature* other than room temperature. Is fatigue more pronounced at high temperatures?

The answers to the many questions hinted at above must be hiding in the microstructure. There simply is nothing else. My colleagues and I (mostly my colleagues, to be honest) indeed do know a lot about how all these properties depend on the composition and the microstructure. Not yet all there is to know, but a lot. I give you a taste treat in two advanced modules about creep and fatigue. I will not say much about corrosion - yet. It's too painful, see below. Not only for the owner of fine steel products but also for Materials Scientists. While we do know a lot about corrosion, it's not nearly as much as we would like to know.

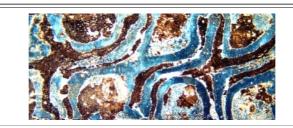
Advanced Links

Illust. Link

Steel

Properties

Creep **Fatigue**



Different corrosion in parts of a pattern-welded sword.

Source: Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany. Used with permission.

- Some smith around roughly 500 AD made a complex pattern-welded sword from two kinds of steel. One of these steels was phosphoric steel (I'll get to that shortly), the other one carbon steel. Look at what you get after only a millennium and a half! The carbon steel is almost gone whereas the phosphoric steel was rather corrosion resistant under the conditions encountered.
 - And that is even a well-preserved artifact. Most of those swords, originally looking like <u>that</u>, are now only a vague orange colored spot in the earth.
- Of course there are a lot of basic rules about properties and microstructure. Most of them were found empirically and explained later, if at all. I will give you one important rule as example:

<u>Pearlite</u> is bad for weldability and corrosion resistance. <u>Martensite</u> is worse.

Tough luck! Our main ingredients for increasing hardness cause severe problems regarding other properties. So we need to do something about that by alloying the right elements besides carbon. That's essentially why we do extensive alloying. As far as only hardness is concerned, just working with (clean) iron and carbon would already do a good job.

The good news thus is: With proper alloying you can cure some problems of your steel.

- However, there is still no such thing as a <u>free lunch</u>.
 - The *bad news* is: There is no super steel that gets only good grades with respect to all the 20 plus properties of interest to you when you consider a product. One size doesn't fit all.
 - To some extent this is clear. Super steels cannot exist because quite often some requirements on your list are contradictions in terms. You just cannot have a steel that is easy to press into some shape (so it must have a low yield stress) and very hard (requiring high yield stress) at the same time. It's just like demanding a round square, esoteric science or theo logy.
 - Good grades in all non-contradicting properties are not possible either; in particular if one of those properties is called "costs count", i.e. if the <u>great cost issue</u> raises its ugly head.
- The message is clear: you must compromise! You might be looking all your life for that gorgeous person with a Noble prize in physics, a lot of money, a friendly and honest disposition, and so on, but you are most likely better off to compromise when looking for a partner (especially if you are a physicist).

You might be looking all your life for that supersteel either. Going for the best compromise is smarter.

- That's why there are far more than 1000 types of steel out there that you can buy. In a few years from now there will be even new types steel science and engineering is still far away from having made everything that has some value for somebody. Development of new steel types is more and more based on <u>solid science</u> including a lot of computing. That does not preclude that on occasion some "tinker" <u>comes up with a big surprise</u>.
- You realize of course that we are now deeply in non-crystalline organic waste, to say it politely. How do we make a catalogue listing that many types of steel in a systematic fashion? How do we **categorize steels**? It's like categorizing the many different types of wine or living beings. "Red, white, rosé", or "animals, plants, fungus" comes to mind and gives an easy start and some trouble. Under which wine heading would you list champagne or "Schillerwein" a German specialty where you mix red and white grapes? Are viruses living beings and if so, which heading covers them?
 - The real trouble, of course, starts after the first level of the system. The next level of listing wines, for example, may contain identifiers like grape type (e.g. Lemberger, Pinot Noir, Zinfandel, Primitivo, ..) or region: Württemberg, Napa valley, California, Bordeaux, Rioja, ...). It's not overly helpful. I bet you don't know what a Lemberger grape is (my preferred variety) or that Zinfandel and Primitivo are just two different names (USA and Italy, resp.) for the same grape. Giving the sugar content (or words for it like "dry" or semi-dry") and so on comes next, plus lots of entertaining descriptions ("steely with a hint of flint"). And you know what: It doesn't tell you much about how some wine will agree with you don't have extensive prior experience with wines and the classification system.
- Historically, wine was only categorized by its origin. The same is true for steel. Where it was made (or who made it) told you how it was made and what kinds of properties and quality to expect. "Sheffield steel" or "Krupp Stahl" said it all. Some areas or producers just produced better wine or steel than others, and nobody knew exactly why this was the case.
- Categorizing steels is almost as bad as listing wines. I won't even attempt it here.
- This Hyperscript, however, claims to encompass everything remotely interesting to swords, and that must include some way to classify steels. I therefore give you the basics about categorizing steels in a basic module.

It is basic and not advanced because is contains absolutely nothing that is difficult. It just is awful, illogical, wretched and complicated - even so no politicians and lawyers were involved.

Basic Link

Categorizing steel

Getting Closer to Real Steel

In a general and somewhat trivial way we distinguish between the unwanted evil impurities called *dirt*, and the wanted good ones that we then call *alloy elements*. There are thus two reasons why you have foreign atoms in your iron or steel:

- 1. They originate almost exclusively from *making* your steel and *processing* it without conscientiously adding alloying elements.
 - What you find in your finished product then goes mostly back to what you filled into your smelter. The concentration of some element in your steel may change during processing, quite a bit in fact, so what you have in the end depends on both variables.
- They originate only to a small extent from making your steel and mostly by being deliberately introduced by you.
 It is clear that this demands powerful real-time analytics. You must know at all times what is in your steel so you can take out what needs to be taken out and insert the right quantities of what needs to be inserted. You also need to know how to do this.
- The first point, of course, relates to iron and steel making for the first 3.500 years or so, the second point to the way we do it for the last 100 years or so.
- I will get back to modern steel making, but for now let's look at the old-fashioned way. Both kinds of elements, the badies and the goodies, then come almost exclusively from the ingredients used in the making of the steel, including the ingredients used for optimizing slag. I'll get to slag in the fullness of time.
- In ancient times you stuffed unclean ore and unclean charcoal into your smelting furnace. You had no choice, you simply didn't know better. You might have had an idea that cleaner is better, though. Remember? All that was known about the "theory" of steel is that **Aristotle** had proclaimed around 350 BC that steel was <u>especially pure iron</u>.
 - So you may even have treated your ore before you used it, removing some of the unwanted stuff, but nonetheless your ingredients were never very clean. In our modern times we still stuff unclean ore and "coke" into our huge blast furnaces. Not because we couldn't make clean ore and carbon but because it's impossible to get clean carbon and pure iron ores in huge quantities for very little money. Coke in this case means rather clean carbon and is not something you drink or stuff up your nose. I'll get to coke in the fullness of time, too.
- Whatever happens inside your blast furnace (and that's a rather complex story we are going to tackle in the next chapter), you cannot reasonably expect that pure iron will come out. Nevertheless, our forebears did produce admiringly clean wrought iron in their primitive "bloomery" furnaces. They could do that because they made very clever use of the iron-carbon phase diagram without having the slightest notion of what that might be. Their stuff always contained slag inclusions, however.
- By the way, the **silicon** (Si) production of today follows the same basic ideas we use for making iron. You throw dirty silicon "ore" (actually silicon oxide or **silica** (SiO₂), otherwise known as quartz sand) and dirty coal / coke into a furnace. You even add some more dirt in the form of (special) wood chips because that makes the product better just like the special plants put in the crucible when making wootz steel. The only difference to iron making is that you don't set the mix on fire. You run some heavy electric current through it. It's necessary for some <u>particular reason</u> but the effect is the same. Things get rather hot.
 - What you get is surprise <u>dirty silicon</u>. There is a lot of dirty silicon (also called "metallurgical grade silicon") made every year; well above one million metric tons. Most of this metallurgical grade silicon goes you guessed it into steel or aluminum as <u>alloying element</u>. An amazingly large part is also used to make <u>silicone</u>, a polymer that has many uses, some of them associated with outstanding properties of people like <u>Pamela Anderson</u>.

 By the way (once more), you noted (I hope) that silicon, silicone, and silica are about as different as romanic, romantic, and Rome, or "Smelting", "melting" and "gelding". Unfortunately this is not always known to journalists, translators or museum people.
 - A small part of the metallurgical grade silicon, about 25.000 tons per year or 2 % of the total, is converted to the ultra-clean and quite expensive <u>single-crystal silicon</u> that ends up in computer chips, solar cells, or micro-mechanical devices like the "heart" of your beamer or the movement sensors in your i-phone.
- Only a small part of the total iron / steel production of old ended up in a superior sword. The product then is expensive and so on, but also demonstrates the top technology of the time. That's what motivated my (amateur) interest in swords, remember?

It also motivates my (professional) interest in solar cells. While we can make an enormous number of computer chips from one ton of ultraclean silicon, one ton won't get us very far if we want to make square miles of solar cells with silicon. That's why there are large efforts under way to learn how one could make good solar cells with dirty

Attention! I'm getting fundamental; veering off the topic! and cheap "metallurgical grade" silicon. It will be rather exciting for the initiated to watch if the silicon guys can do what the steel guys managed to do 2000 years earlier by cunning, and about 150 years ago by evolving into Materials Scientists and Engineers. They either learned how to live with dirt or how to remove it cheaply.

I'm absolutely sure we will succeed with silicon, too. We are already at the "break even" point now (2012), i.e. producing your electricity with solar cells cost just as much as in the old-fashioned way. That can be roughly compared to the point in time when mass-produced steel had its "break-even" with the dominating cast iron. Just wait an other 20 years and solar energy will be far cheaper than running power plants with coal, oil, or gas. Yes, you are right - the sun doesn't shine at night; in my country quite frequently we do not even see her during the day. I know that. All I have to say is: trust your scientists and engineers to find a solution. Don't trust your bankers, oil companies, power plant owners and related politicians to find a solution. And keep the latter from hassling the former.

In particular, do kick your economist in the rear when he tells you that the solution will be to write some numbers on paper (called CO_2 emission certificates). I guarantee that they will work just as well as the papers pronouncing fledgling dot.com companies to be more valuable than, let's say, Mercedes; the papers that promised to yield far more then 20 % a year by bundling mortgages yielding around 3 %; or the papers stating that Greece is a healthy economy ready to join the euro. Not to forget, of course, all the papers stating that a crisis that resulted from overspending, can only be overcome by more overspending.

So trust my colleagues and me in particular. If it makes you feel better, you could send me large amounts of money and I will send you a paper stating in many fancy words that the energy crisis and the financial crisis is now over *for you*. Don't miss this opportunity! I will serve only the first 1000 applicants, the rest will have to live with both crisis' forever after.

Dianzhong Li, Xing-Qiu Chen, Paixian Fu, Xiaoping Ma, Hongwei Liu, Yun Chen, Yanfei Cao, Yikun Luan & Yiyi Li, in the article "Inclusion flotation-driven channel segregation in solidifying steels", published in: Nature Communications 5, Article number: 5572 in Novemebr 2015, report the observation that "Channel segregation, which is featured by the strip-like shape with compositional variation in cast materials due to density contrast-induced flow during solidification, frequently causes the severe destruction of homogeneity and some fatal damage " is caused by oxygen precipitation and occurs for oxyen concentrations above 0.001 wt%. "This study uncovers the mystery of oxygen in steels, extends the classical macro-segregation theory and highlights a significant technological breakthrough to control macrosegregation" is claimed by the authors.