back

Smelting Science

6. Getting Serious About Smelting Iron

Boudouard Equilibrium

In iron smelting we need to reduce iron oxides to elemental iron. For doing that we need some reducing agent that loves oxygen even more than iron does (i.e. has a stronger affinity to to oxygen than iron) and is thus able to divorce the iron from its (much loved) oxygen. This is not an amiable divorce but a violent affair.
The reducing agent will be carbon, and the necessary violence (= energy needed) comes from thermal energy, i.e. we need high temperature. The high temperature is provided by burning carbon (C), using up all the oxygen (O) in the process. The carbon dioxide (CO_2) produced will react with hot carbon to carbon monoxide (CO) according to

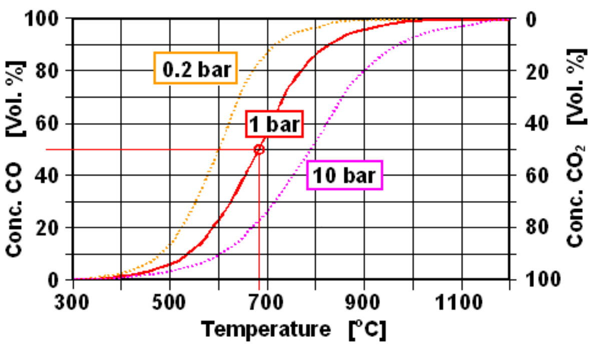
$$C + CO_2 \Leftrightarrow 2\,CO$$

- This is now a proper *equation* , in contrast to what I presented in the backbone ! There is now a double arrow ($\Leftrightarrow$) and not just a single arrow ($\Rightarrow$) denoting just "chemical shorthand". Since it is an equation you can read it backward just as well (if a = b we also have b = a). Then the carbon monoxide reacts with the carbon to form carbon dioxide.

$$2\,CO \Leftrightarrow C + CO_2$$

- This is actually the reaction that produces soot, fine carbon particles. Mostly annoying but also quite useful on occasion.

So what the hell do we have? First everything turned to monoxide, than back to dioxide, than to monoxide again, ...? Of course not! We will get an equilibrium with fixed concentrations of **[CO]** and **[CO_2]** ([...] means concentration of ...). **Octave Leopold Boudouard** (1872–1923) investigated what you get if an inexhaustible supply of carbon (i.e. [C] = const = "1") is in equilibrium with CO_2 and CO at the temperature ***T*** and some (constant) total pressure of the gases. The results are then often referred to as Boudouard equilibrium curves:



Boudouard equilibrium curves

- 1 *bar*, the old-fashioned (but sensible) unit of pressure equals about the normal air pressure we experience; it equals 100.000 Pa or "Pascal", the official (but stupid) pressure unit nowadays.

What do these curves tell us? Quite a bit

- Any point on the *red* 1 bar curve gives you the precise relation between the concentration of CO and CO_2 that you will find at the corresponding temperature *in equilibrium*. A 1:1 relation, for example, will be found at about 680 ^oC as shown by the thin red lines.
- Temperatures above 680 ^oC favor CO, below CO_2 prevails. Above 900 ^oC there is practically only CO around, below 500 ^oC you have practically only CO_2
- Points in the diagram corresponding to actual or measured concentration that are *not* on the red line denote a system *not* in equilibrium. The curve then tells you if your system is too hot or too cold for this kind of concentration.
- Looking at the lines for pressures different from 1 bar tells you that the equilibrium concentration of CO at a given

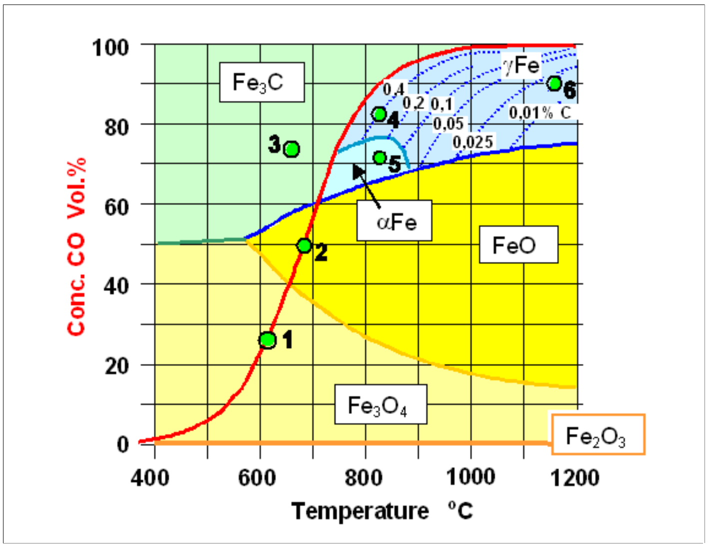
    temperature increases with decreasing pressure and decreases with increasing pressure

  - What kind of pressure do we have inside a smelter? Well, we are always close to atmospheric pressure of 1 bar. In the atmosphere we have oxygen and nitrogen, and bot gases contribute to the total pressure by their *partial pressure* (the pressure you would have if you take out anything else). In the oxygen-free zone of the smelter we still have the nitrogen, so the partial pressure of CO and CO_2 together is only about 0.4 bar. That is the pressure that counts for the Boudouard equilibrium, so we are somewhere between the 0.2 bar and the 1 bar curve. That is good because it means we get the necessary CO already at somewhat lower temperature but in what follows we use the 1 bar curve since it is close enough.

- This is nice but not very exciting. After all, we want to make iron. That happens because the carbon stuff reduces iron oxides somehow. Moreover, after having made iron, all the carbon stuff around can interact with the iron, carburizing it to some degree. What can we say about that?

Baur-Graessler Diagram

- The questions from above are answered to some extent by what are known as Baur-Graessler diagrams. The idea is to calculate the equilibrium conditions for all the reactions that can take place between iron and its compounds and carbon and its compounds at some temperature ***T***.
  That is not easy. Baur and Graessler actually calculated something far simpler than what is shown below. Nevertheless, when they did that around 1903, they had to make a lot of assumptions and their result was actually not very accurate. What we call a Baur-Graessler diagram today evolved from the work of many people and does get things right for ideal situations and *equilibrium*. It does not show what is really going on in a smelter but gives clear hints on what should be going on in "ideal" situations.
  Here it is:



Baur-Graessler Diagram of iron smelting

- The first thing to notice is that *two* diagrams were merged into one plot. First we have the **red** Boudouard equilibrium *curve* from before. Then we have the regions or *phase fields* where iron or its compounds are stable given a certain temperature and carbon monoxide concentration. If we have always total and perfect equilibrium in the sub-system "carbon and its oxides" the states of the system would be found *only* on the red line.
  But now we also look at the equilibrium of the solid phases given by their colored phase-fields. The lines separating these fields separate the respective stable phases. If a line is crossed by changing conditions, some reaction changes the phases accordingly.
  - Moving from point 1 to point 2 *slowly* by increasing temperature and thus CO concentration, changes Fe_3O_4 magnetite to FeO wüstite according to:

$$\mathbf{Fe_3O_4 + CO \quad \Leftrightarrow \quad FeO + CO_2}$$

    You are moving across a phase boundary and a phase transformation needs to occur. Moving from point 2 to point 1, i.e. the other way around, proceeds by the reverse reaction. And we have equilibrium all the time. Think of moving from - 5 ^{o}C to + 5 C^{o}in the system H_2O "water". Moving across the boundary at 0 ^{o}C will produce a phase change from solid to liquid water. If you do it very slowly, you will have the solid below 0 ^{o}C and the liquid right above that temperature .

Now consider a *quick* move from 1 to the temperature of point 2. The same thing happens as when you move *quickly* from - 5 ^{o}C to + 5 C^{o} across the boundary at 0 ^{o}C in the system H_2O "water"! The ice will *not* turn into water instantaneously. This particular transformation process, like *any* transformation process, takes some time. And as long as we have a mix of water and ice, the system temperature will be fixed at 0 ^{o}C, no matter how hot it is somewhere else.
In other words: As long as a phase transformation is not complete, the system is stuck at the boundary line for however long it takes to finish the phase transformation. You actually cannot change the temperature everywhere as you like. The liquid water might be at 5 C^{o}, yes, but the ice pieces floating in it are certainly not.

- This applies directly to the Baur-Graessler diagram above. If you move from one colored area to another one by changing the temperature and / or the CO concentration (and it doesn't matter if you are on the Boudouard equilibrium curve or not in this case), you will be *stuck at the boundary* for however long it takes to finish the reaction.
  If, for example, you start in the wüstite field and then go "up" to make some iron, you will be stuck on the blue line as long as there is still wüstite around. While you are stuck there you will produce iron - but *always* with a low carbon concentration.
  We also know that iron smelting in a bloomery *never* uses up all the wüstite in the system. That is easy to see since the slag produced always contains large amounts of wüstite, so it was always there. What follows is the *credo of iron smelting theory* :

Bloomeries can only produce wrought iron and never steel!

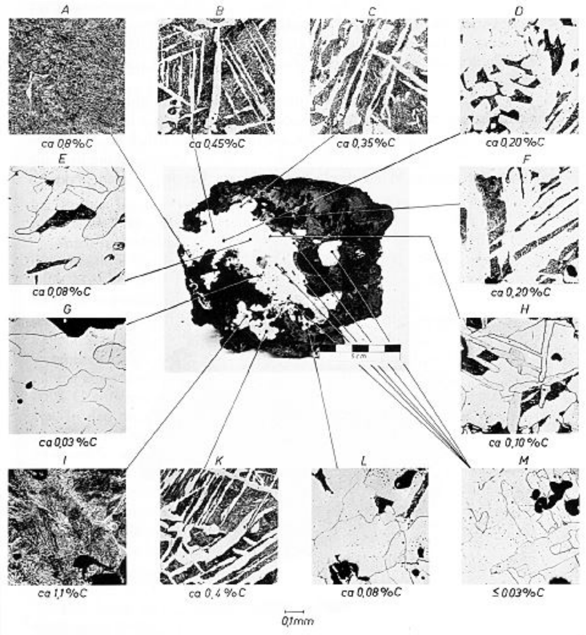
- You run across this credo whenever you read something about the history of iron and steel. Nobody doubted that mankind (in the West) made for millennia *only* wrought iron in the bloomeries. Steel was produced in a second step by "carburizing" the primary product "wrought iron" somehow, for example in in the hearth of a smith.
  And now we have proved that. There is only one little problem left:

Is it true?

Smelting "Ferrum Noricum"

Much of the above I owe to a detailed discussion in a very informative book1), dealing with Ferrum Noricum, the famous steel of the Romans made in what now is Austria. In this book you do not just find the *theory* of bloomery smelting but also *experiments* . The authors were scientists. And science *never* relies on theory, revelations, dogmas or credos alone. Science insists that you prove your theory by experiments.

- So **Harald Straube** and colleagues build a bloomery type smelter, following as closely as possible the constructions they had found by digging up 2000 years old remains of the smelters run by Celts and Romans. Then they smelted some iron. This is what they got:



Modern attempt at making Ferrum Noricum
Large picture

- I need not spell out that this was quite a surprise. The bloom was a far cry from being wrought iron only; it was in effect everything from wrought iron to almost cast iron and whatever is in between. "The results of the experiments and the conclusion drawn from the results differ considerably from the hitherto held notions about the metallurgy of a bloomery" writes Prof. Straube. He continues by developing a hypothesis of what might have happened. How he explains the findings and if he is correct or not is not important here. Important is that he has proved by an experiment that you can make all kinds of steel in a bloomery.
    - Prof. Straube, in essence, concedes that one can make steel in a bloomery but believes that is the exception and that the making of wrought iron is the rule. In this he is wrong as I believe. I base this on the fact that all those people out there who have run a bloomery in recent times, tend to make blooms similar to the one above and rarely homogeneous wrought iron.
- I'm not to saying that old iron masters did not make a lot of wrought iron in their bloomeries. Wrought iron, after all, is far more useful than steel for most everyday applications. All I'm saying is that you must take some care to run your bloomery "just right". More to that in the backbone.

What Went Wrong?

- So the theory is wrong? No, it isn't! It is quite correct for a system that adheres to the rules. Part of the rules are that you can neglect a lot of things that are there but *assumed* not to be important. There are usually good reasons for those assumptions but not certainties. As it turned out by experiment, what is going on inside a running smelter is simply far more complex than envisioned. Since nobody has ever looked closely inside a running smelter, there is no other choice: we can only assume what is going on. Nobody has ever looked inside a running sun either (nor is that likely to happen anytime soon) but physicists are fairly certain of what is going on there. They looked at the output of *assumed* processes - the various kinds of radiation coming out in the case of a sun - and compared that with observations. If you always get complete agreement with the predictions based on your assumptions or *model*, you tend to hold it for correct.
    - All *we* need to do now is to make a better model for a bloomery - in the form of a lot of coupled differential equations, for example. The old guys like Boudouard, Baur, Glaesser could have done that too, it just wouldn't have helped them. They could *not* have done the necessary math to come up with solutions. There is only that much what you can do with a pencil and paper.
- I have a good idea of what would need to be added to the bloomery model expressed in the Baur-Glaesser diagram to make it closer to reality. Going into that would not only be far too technical; it is also a waste of time because my ideas might be wrong.
  So let's finish this by simply stating that with some dedicated work, scientist and engineers would certainly be able to come up with a working model of a bloomery expressed in math or a computer simulation (same thing).
    - "Dedicated work", however, is just an euphemism for "lots of money". Since understanding the working of a bloomery is not all that interesting to most, getting that money is difficult, not to mention getting the people who could do it (not me), who typically have more rewarding work to do.