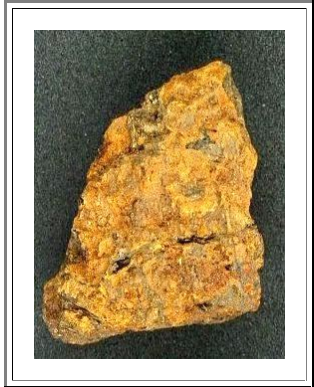## 8.4.2 Alloy Steels

General Remarks

Writing these modules, I found it surprisingly hard to find data or good metallographic pictures for the *plain carbon steel* of the preceding chapter.

- Well, there is a simple reason for that: There is practically no such thing as plain carbon steel - and probably never has been.
- Steel practically always contains other elements besides carbon too, which were added intentionally or unintentionally.

Unintentional elements are in particular Sulfur (**S**) and Phosphorous (**P**); but also **Sn**, **As** and **Sb**.

- All these elements tend to diffuse to grain boundaries where they might segregate; reducing the cohesive strength - the steel becomes brittle. If it does not happen right away, it might happen after some temper treatment; as a result we have (undesired) *temper brittleness*.

By now you should be sensitive to words like "tend" and "might", which indicate that things are not so simple and easy.

- Phosphorous, for example, is not *always* harmful. In properly treated steel, it *might* be beneficial, too, as shown below.
- Since the "**bog iron**" (German: "**Raseneisenerz**"), used for millennia to make iron and steel, contained relatively large amounts of **P**, it "might" have been crucial for the early smiths to keep the Phosphorous from segregating to grain boundaries. What bog iron looks like is shown on the right - we all have seen stones like that, but possibly not recognized what it was.
- However, if you were lucky, some other elements contained in *your* iron "might" have helped in this respect and you may never have noticed that you had a problem.

But generally, some elements, in particular Sulfur **S** (and **P**), are almost always *bad* news, and not easy to avoid.

- But fortunately, Manganese (**Mn**) is also quite ubiquitous - and it sort of "soaks up" the Sulfur (by forming immobile sulfides).
- We thus have a *first reason for adding something else*: To neutralize bad effects of unwanted, but hard to avoid **trace impurities**. But this, while being quite important, is nevertheless only a *minor* point for making **alloyed steels**, sort of a fringe benefit.
- So small wonder that you will always find **0.5 % -1 %** or so of **Mn** in practically any alloy steel (and in "plain carbon", too).

The *major* reasons for adding all kinds of elements to carbon steel are:

- **1.** Improved strength while maintaining good ductility and in particular workability ("Verarbeitbarkeit"). The key words in this context are **solution strengthening** and **precipitation hardening** ("Mischkristall- und Ausscheidungshärtung") while maintaining **weldability** ("Schweißbarkeit").
- **2.** Improved **hardenability**. The key is to enable martensite formation even at relatively low cooling rates so that it can occur in the interior of massive steel pieces , too. In German, hardenability is called "**Härtungstiefe**" (= "hardening depth"), which gives a better impression of what is meant: Even regions deep in the bulk, which by necessity cool down more slowly than surface near region, become "hard", i.e. experience *martensite formation*.
- **3.** Improved **corrosion resistance**. The key word is "**stainless steel**", resulting from rather large additions of Chromium (**Cr**).
- **4.** Stabilized austenite at low temperatures. In other words, we get (nonmagnetic) **austenitic steel** (with an **fcc** lattice) at room temperature (and somewhat below). It is almost, but not quite the same thing as point **3.** from above.

In addition, we should not forget that properties like **weldability**, and pedestrian concerns like *money*, are also part of the alloying game

All the obviously desirable features from above can be achieved to some extent by adding a suitable amount of the right elements.

- To make things complicated, most elements do several things from the list above, and a combination of two elements usually does not just produce the sum of the individual properties, but something new.

- In addition, improving one property by adding a certain element might easily produce problems with some other properties. You many have to compromise.
- And not to forget: As we have seen by alloying Iron with just Carbon: Many variations of properties are possible with just *one* element!
- In discussing, not to mention *making* alloyed steels, a certain amount of alchemy is in evidence, even today. And new discoveries and new steels will certainly come forth in the future, too.
- The link provides a short list of some alloying elements and what they are used for.

It is entirely impossible to touch all bases here. Let's just give the four categories from above a cursory glance and make a basic distinction at the beginning:

- We distinguish between

  - **Low-alloy steels**: We only add less than about **2** weight **%** of the major alloying element(s) (and usually keep the carbon concentration low)
  - **High-alloy steels**: We add a lot more than **2** weight **%** and possibly as much as **20** weight **%**.

- In between is "**medium-alloy**", but that already goes to far in this context.

Improved Strength and Good Workability

Here we are generally talking *low-alloy steels*, in particular with a rather low carbon concentration. The general idea is to avoid martensite formation, which is bad for welding and shaping, but still have good strength properties.

- If you want to *shape* a piece of material by any method (for car bodies you just press some sheet metal in a form), you must have some "workability"; in other words, you need some plastic deformation, i.e. ductility. Think of pure martensite as being like glass, and you get the idea.
- *Weldability* is a particular important part of "workability"; another one would be "hot pressability" (Heißpreßbarkeit") or "drawability" ("Ausziehbarkeit; Tiefziehbarkeit"). Just consider how you would make a car body, if those two properties are non-existent, and you have a good idea of how important "workability" is for mass production!

We clearly need strength (= "hardness") without martensite formation.

- This leaves us with all the basic mechanisms discussed in chapter **8** for strengthening.
- We thus add suitable elements to obtain:

  - *Solution hardening*. Except for nitrogen, which dissolves as an interstitial like carbon, all other suitable elements will always be of the substitutional solid solution type.
  - *Precipitation hardening*. Either by forming finely dispersed hard and small *carbides* of the alloying elements, or by influencing the cementite formation to occur in fine particles, or by producing precipitates of compounds of the alloying elements (e.g. borides, or intermetallic phases), or by all of the above.
  - *Grain size reduction*. You may produce small grains (i.e. from a martensitic transformation), and/or keep small grains small by keeping grain boundaries from moving (and thus grains from growing) by precipitating suitable elements there (without making the grain boundary brittle, of course). This will always lead to hardening, too.

It only remains to check the "easy" elements of the periodic table under all kinds of conditions. Let's do that for *solution hardening* first.

- What we find is that Carbon and Nitrogen have by far the biggest direct effect on the yield strength (owing to their being interstitials), and that Phosphorous *in solution* is very good, too (but, remember, very bad if segregated in grain boundaries).

- Then we have Silicon (**Si**), Manganese (**Mn**) Titanium (**Ti**) and Copper (**Cu**, not shown) and some others as still pretty good solution hardener. **Cu**, however, has drawbacks (including its prize), and **Si** causes problems here (also it is much in use for other purposes).

- This leaves **Mn**, **Ti**, and to some extent **Ni** and Vanadium (**V**) as alloying elements (we also had **Mn** to neutralize spurious **S**, if you remember).

- Complex - but not difficult. We had much the same picture before for Copper.

- In essence, we *understand* that part of steel alloying.
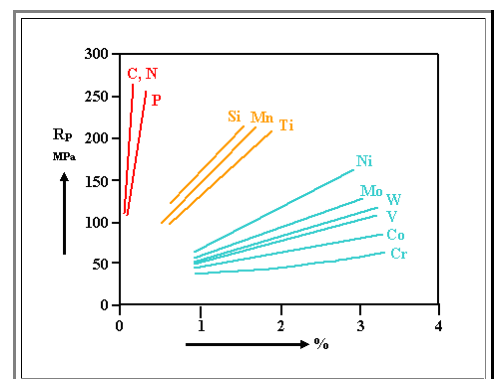
Precipitation hardening can be more efficient than solution hardening, and indeed, very small amounts of Boron (**B**; **0.005 %**), or about **0.1 %** of Niobium (**Nb**) or Vandium (**V**) will produce considerable increases in strength.

- Always provided that the heat treatment was right, the grain size is small, and so on and so forth.

- Just on example: Niobiumcarbide particle of about **1 nm** size will increase the yield stress from about **20 MPa** to **200 MPa**, at a concentration of about **0.1** weight **% Nb**, while "huge" particles with about **10 nm** diameter have practically no effect anymore!

- We understand that immediately, by looking at the mechanism of precipitation hardening. If a **1 nm** particle can stop a dislocation completely, a **10 nm** particle can do no more - but we have **1000** times fewer **10 nm** particles at a fixed solute concentration.

- We also understand why these **micro-alloyed steels** are rather recent developments: Try to optimize such a steel if you don't know what happens, can't see your precipitates anyway, and can't measure their size and other properties for some quantitative data. In other words, with no knowledge about deformation and dislocations, just optical microscopes, and without the whole bag of microanalytical tools, you are simple blind. The best you can do is go by trial and error following up some guesses.

Anyway, with some basic understanding and giving proper care to their needs, micro-alloyed steels may have much better strengths than "mild" carbon steels, with all other properties (exept the prize) being comparable.

To some extent, micro-alloyed steels are the steel industry's answer to the **Al** car-body challenge from **Audi**, because they allow to maintain the easy manufacturability and strength of a steel car body, while considerably reducing the weight (the sheet metal can be thinner).

Of course, you may now ask yourself a simple question:

- Why do I always add *carbon*, if I can get all kinds of hardening mechanisms from *other elements*, too?

- Good thinking. Take carbon-free iron, add sizeable amounts of elements like **Ni** and **Co**, and rather small amounts of, for example, **Al**, **Si**, **Mo**, or **Ti**. This gives you some solution hardening if nothing else happens.

- Keep out **P**, **S** and so on, make sure the grain size is very small and the grain boundaries not embrittled by segregation of the wrong elements.

- Upon cooling down this alloy, some relatively soft martensite will form (No carbon!). This is when you shape your piece of steel in the form it is supposed to have when it is finished.

- After that, you do some tempering, just right, to now form lots of very small *intermetallic precipitates* between the major elements and the minor elements.

Hardening mechanisms of maraging steel
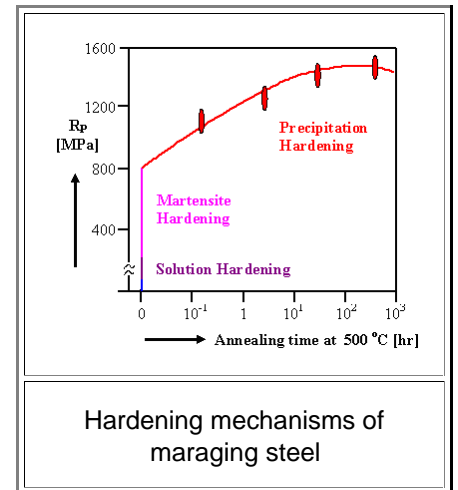
This puts some precipitation hardening on top of everything else and you end up with "**maraging steel**" (short for martensitic aging), being fantastically strong while still ductile - and being rather expensive.

- The picture above shows the total effect with an increase of the tensile strength to a fantastic **1500 MPa**! Even larger values have been achieved while still keeping a maximum elongation of **6 % - 8 %** before fracture!

- A maraging steel is what you use for landing gear of Jumbo jets, for ultra centrifuges (needed for making atomic bombs) or for golf clubs (needed for hitting little balls). Interestingly, if you enter "maraging steel" into Google, you will find either golf club advertisement, or stern warnings concerning trade restriction, but very little useful information. We have a real high-tech material here!

Improved Hardenability

Shaping a sword, a car body, or whatever by banging, pressing, stamping, rolling or drawing a piece of some rather soft steel into the desired shape, and then making it hard by heating and quenching, is actually a great way of getting strong (= hard) products with comparably little effort.

- So we want to keep this old-fashioned hardening method, known for millennia for plain carbon steel, but we also want to make the result less sensitive to the cooling rate. Remember, with plain carbon steel, you only get hard martensite in those parts of your work piece that cool down with cooling rates of about **1000 K/s**.

- There is no way to achieve this kind of cooling rate with anything thicker than a few **mm**! Therefore the only option left is to alloy the right elements to our plain carbon steel, hoping that this will lower the austenite - martensite transformation temperature. This then might produce the good *hardenability* we are after - which, remember, is not just a large hardness value, but hardness as deep as possible into the bulk of a massive sample.

- This brings us to an old piece of wisdom concerning of what is better: Being practical, or being theoretical? If you don't have a good *theory* here, you do not even know if that feat is possible at all. Even if you trust your luck, you have no idea of how much of what you should add. Good luck and all the time in the world to you practitioner!
- Well, the truth is that we know a lot about alloying and hardenability, but we really do not have a "final" theory yet, and a lot of what is known about hardenability did come from an empirically established data base.
  - Thanks to Walter **Jominy** (the Chief Metallurgist for Chrysler Corporation sometime before the war), there is at least a simple but accurate test to assess the hardenability of a given sample.
  - Just take a standard size sample, heat it to some high temperature, and then spritz water (at defined conditions, of course) at one end as shown below. The cooling rate will be different from one end to the other of the sample, and all you do after it has cooled down completely, is to measure the hardness along its length.
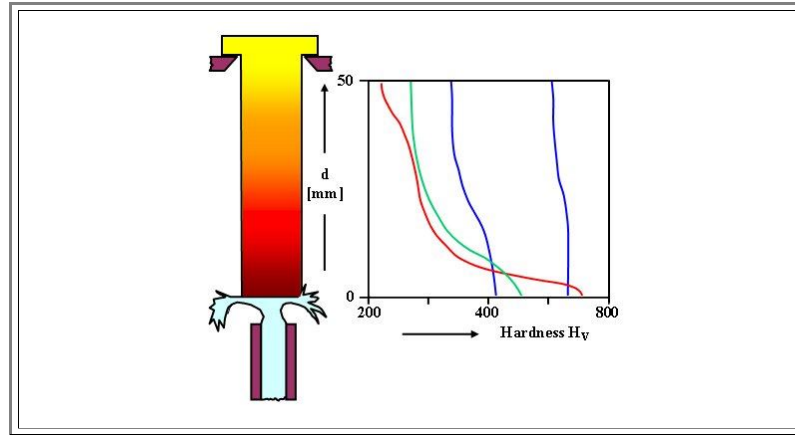

- What you might find is shown to the right of the test set-up.
  - Plain carbon steel with sufficient carbon (e.g. **0.8 %**) may become very hard in the region where the cooling rate was very high, but the bulk of the sample remains "soft" (red curve), while very mild steel with little carbon (e.g. **0.3 %**) just shows some hardening (green curve).
  - Now add some **Cr**, **V**, **Mn**, **Ni**, or **Mo** (or some other suitable elements), and if you do everything right, you may obtain the blue curves - steels with good hardenability and adjustable hardness.
- All you have to do now is to check what happened to the other **10** or so properties of supreme interest (ductility, weldabiliy, fracture toughness, corrosion resistance, ...).
  - If you are extremely lucky (and after **10** - **20** years of work), you may find a new kind of steel with properties just right for your purpose and better than anything else available so far.

Austenitic and Stainless Steels

- We all know it: Iron and steel **rusts**! What we probably do not know: Relatively pure iron ("wrought iron") rusts far less then steel.
  - In Delhi is a **1600** year old huge iron pillar (**7 m** tall, **6** tons in weight; see picture on the right) that does *not* rust. It was forged together from many pieces of wrought iron with low carbon content. Its "secret" has recently been unraveled: The relatively large amounts of **P** in the iron and in slag particles within the iron, catalyzed the formation of δ-**FeOOH** ("Misawite") and a layer of crystalline phosphates that together form a stable protective layer.
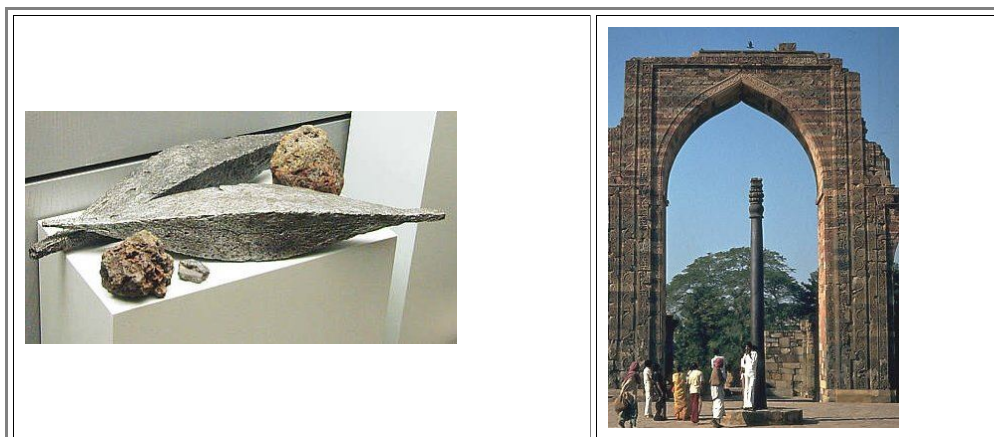
  - In the "Württembergisches Landesmuseuum" (which we encounter in "sword" conncections, too) and in many others, iron bars in the typical double-pyramid shape of the Celts as shown above are on display. Here si a picture:

- If you ever visit these museeums (the display above is from the museeum in Heidelberg), don't miss this part; you will experience some surprise: These wrought iron bars, about **2000** years old, look like new. There is hardly a trace of rust.

- But these are the exceptions to the rule: Iron and steel rusts! In the museeums mentioned above, you can also see the evidence for this fact: Most *steel* objects like swords are just lumps of rust.

In general, this is easy to understand: Since metals have too many electrons by definition, and Oxygen has too few, metal-oxides will form in air. The noble metals are just the (rather easy to understand) exception to the rule.

- The oxidation of a metal exposed to air will go on as long as oxygen can meet metal, i.e. as long as either one can diffuse through the oxide layers formed.

- **Stainless metals**, obviously not decomposing into oxides foreever, thus can only exist if the unavoidable oxide layer formed in air will be impenetrable to oxygen as soon as a certain (small) thickness has been reached.

- This is not all that difficult to achieve, after all, metals (and other reactive elements) like **Al**, **Si**, **Pb**, **Cu**, **Cr**, ... are quite stable in air (at room temperature), and, as we have seen, even some relatively pure iron does not rust.

Iron, plain carbon steel, and many alloy steels, however, do generally *not* form a stable oxide - they rust! And sooner or later our car body, sword, or cooking pot is just a piece of ugly iron(hydro)oxide.

- And there is nothing particular systematic that you can do. The method of choice, of course, is to *paint* the object, or more generally, to apply a protective coating, e.g. paint, **Zn**, **Cd**, or **Cr**, or if money is of no consequence, **Au**. But this will only help for some time if the object is mechanically stressed (i.e. *used*) because than the thin protective layer will sooner or later been worn off or develops cracks - rusting just starts later, as we all know.

The alternative is to *alloy* a sufficient amount of typically **Cr**, so that the surface *always* is covered with a stable **Cr_2O_3** layer.

- The minimum amount of **Cr** you must add is **13 %** (a number that can actually be calculated), but up to **25 %** or so are used.

- But now you have *high alloy steel*; and while it may not easily corrode, its properties may also be quite different from plain carbon steel.

Staying simple, you can get stainless steel by only alloying pure **Fe** (no carbon) with **Cr** and nothing else.

- But even then you will get something new: **Fe - Cr** alloys stay *ferritic* (i.e.. in the **bcc** phase) at *all* temperatures - they do not form **fcc** austenite at all. Well, no reason why they should, considering that this is no longer **Fe** with a little bit of something.

- The problem, however, is that now you have no possibility of using some kind of martensitic transformation for hardening.

So if you also want strength, weldability and so on, you start a whole new game of going through the periodic table in search of proper additional alloying elements.

- Adding some Carbon again will help; **0.6 %** is already enough to produce some martensite and thus hardenability. Simple **Fe - Cr - C** stainless steels, quenched and tempered, are indeed used for, e.g., ball bearings, kitchen knives or surgical instruments.

- We now have stainless steel, with a **bcc** lattice at room temperature (lossely still called "ferrite"), it is also "ferro"-magnetic (try your kitchen ware). But we can do more than that with high alloy steel containing a lot of **Cr**.

Besides having sufficient **Cr**, add some **Ni** (say **10 %**) and the ubiquitious Manganese (about **1%**).

- What you will obtain is a steel that is *still austenitic at room temperature* (i.e a **fcc** and **non-magnetic**)). It is not the stable phase at room temperature, but the transformation temperature is lowered and never takes place for normal cooling rates.

- This is mainly a result of the **Ni** addition; the transformation temperature goes rapidly down with increasing **Ni** concentration (from **914 ºC** at **0 % Ni** to **720 ºC** for **8% Ni**, or to **600 ºC** for **15 % Ni**.

Austenitic steels are materials quite different from regular steel.

- Not only are they stable in corrosive environments (thanks to stable **Cr_2O_3** on their surface) and non-magnetic.

- They are relatively tough but still more ductile than regular steel and thus are easy to work with because they can be pressed or drawn. They also have better creep properties (we will learn what that is in chapter **10**) A certain problem is that they work harden very rapidly, which makes them difficult to machine.

- You will find a lot of austenitic steel around you. Your kitchen sink will almost certainly consist of austenitic steel, but also the inside of your electron microscope, and much piping in your nuclear power plant.

Well, so much for steel in just two short chapters. Three final remarks are in order:

- **1.** I found it is impossible to do "steel" justice without including some of its history.

- **2.** It is even more impossible (excuse the oxymoron), to do steel justice without having gone through the "basics" first, as put down in chapters **2** to **7**.

- **3.** There is much more scientific stuff around steel (and any other alloy) that was carefully avoided here in order not produce system crash at this level. In particular there are things like *TTT-diagrams* ("temperature-time-transformation"), semiquantitative complicated diagrams that reveal , e.g., what will happen to a piece of alloy if it is cooled down with a specific cooling rate.

I hope that you understood the basic messages:

- **1.** Steel is just a collective name for an incredibly complicated set of materials with wildly different properties.

- **2.** But everything can be understood *in principle* by understanding the atomic mechanisms of "strength" (and "fracture"). There is *no mystery* anymore, and no magic is needed to produce a wide variety of products reliably.

- **3.** We are just in the transition period where development of new steel alloys (of Iron and other metals) switches from the (highly educated) "trial and error" method, to a development that is guided by scientific principles based on the theory of the atomic structure of the material.