# 8.4 Steel

8.4.1 Plain Carbon Steels

Some Preliminary Remarks

- The "**Iron Age**" lasted a long time. It actually should be called "*Steel* age", because *pure* iron is not only difficult to make, but has only limited limited use as a structural material.
  - **Steel** and **cast iron**, both **Fe - C** alloys or compounds, and not just *iron* made the difference to the bronze tools and weapons in use before the iron age. Note, however, that bronze products were used for a long time parallel to steel products.
  - The beginning of the iron age in Northern Europe dates to about **800 BC**; one could debate if it ever really ended. The industrial revolution in the **19th** century has one of its deeper roots in the discovery of how steel could be mass produced; and the car industry, for example, is still perfectly impossible without steel but quite possible without Silicon. The computer, of course, is perfectly impossible without **Si** - but does this mean that we are now in the **Silicon Age**?
- Iron technology was invented in the Mediterranean about **1500 BC**; present day knowledge ascribes its discovery to the **Hethites** from what is now Turkey.
  - India and China also mastered iron technology in ancient times. It appears, however, that the Hethites were earlier by several hundred if not **1000** years. The Japanese, of course, had and still have a heavy cult around their steel swords for a longe time, and there was some early iron techology in Africa, too.
- In the "Hyperscripts of AMAT", a growing number of modules deals with the history of iron and steel; in particular with the ancient paradigm of this material: the **(magical) sword**. These modules will give you an idea of what iron technology meant to our ancestors, and why your conception about it is probably totally wrong. Available are:
  - A short history of Iron and steel

    - In German.
    - In English (the newer and occasionally updated version).
  - Myths around making a sword (In German; not for the faint of heart)
  - The Ring of the Nibelung (In German; Wagner's opera in the context of forging Siegfrieds sword).
  - Damascene Technology (In English; contains many links to other sources).
  - An early (magical) sword (In English; shows the original and its reconstruction).
  - Magical swords (In German; What makes a sword magical - how is a Japanese sword made?).
- In this module, however, we will look at steel from a *scientific point of view*.
  - This is not easy: Steel is an extremely complicated material with an amazingly large number of variants; and new discoveries are still being made.
  - Here we will only look at some *basics*; this involves cutting corners and being at bit imprecise at times. To simplify things, we will treat carbon steels, alloy steels, and cast iron separately; even so this does not make much sense for many *real* steels.

The Iron - Carbon Phase Diagram

- The Iron - Carbon Phase Diagram is one of the most important diagrams of mankind - but not part of public education.
  - Here is the important part:
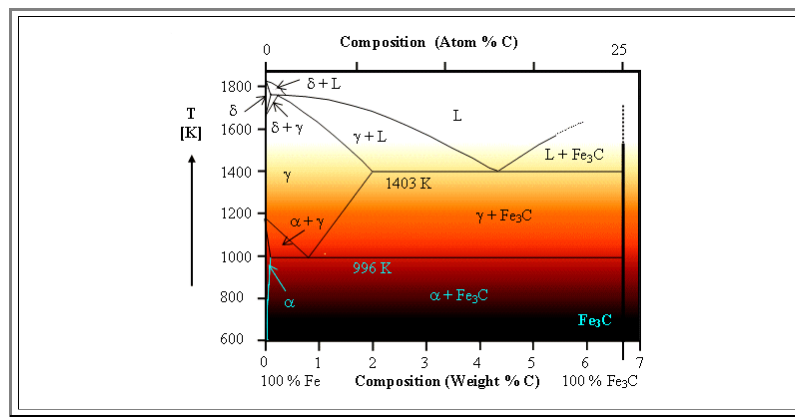
▶ What we see is:

🔵 The color a smith sees at the temperature given (sort of). Notice the "bright cherry red" at the **996 K** boundary

🔵 Absolutely *pure* iron changes from the α-phase (which has a **bcc** lattice) to the **fcc** γ- phase just below **1200 K** (**1180 K**, to be precise). Around **1700 K** it changes to the **bcc** δ-phase; at **1800 K** and some it melts.

🔵 There is no β Phase ??? Well - β -ferrite is simply non-magnetic α - ferrite; here we can just forget about it.

▶ The situation is quite different with a little bit of carbon - somewhat more than **0.1** weight **%**, say. Around the melting point tricky stuff is going on, which we will not consider any more.

🔵 *Below* **996 K (= 723 ºC)** the iron cannot dissolve all the **C** and we have some mixture of α-iron and **Fe₃C**.

🔵 *Above* **996 K**, however, the γ-phase can keep quite a bit of **C** in solid solution up to a maximum of **2%** at **1403 K (= 1130 ºC)**.

🔵 At about **0.8 % C**, we have an eutectoid composition at a temperature of **966 K**, and around **4.5 %** we have a true eutectic composition at **1403 K**.

🔵 The diagram extends only to about **6.7 % C**; at higher **C** concentration nothing of interest will be found. This means we are actually considering the **Fe - Fe₃C** phase diagram.

🔵 If you wonder why so much happens with so little carbon, don't forget: At **6.7** weight **%**, every fourth atom in the soup is a carbon atom; we have **25 atom %**!

▶ All important true phases have (old) names; these are

- **Cementite** (German: **Zementit**). The stoichiometric **Fe₃C** phase. It is a compound with a complicated lattice; it is rather hard and brittle.
- **Ferrite** (German: "**Ferrit**). The α-phase with the **bcc** lattice. If you want to be precise, you call it α **- ferrite**.
- **Austenite** (German "**Austenit**). The γ-phase with the **fcc** lattice.

▶ Just to get you used to the facts of life concerning iron and steel, there are some more old-fashioned names still very much in use, and absolutely de rigeur for everybody who calls herself a materials scientist:

- **Pearlite** (German: **Perlit**), the two-phase mixture obtained right below the eutect*oid* point at **0.8 % C** concentration - we will encounter it quite soon and excessively.
- **Ledeburite** (German: **Ledeburit**); the two phase mixture obtained right below the eutect*ic* point at **4.5 % C** concentration; we will not have much dealing with that because it should not exist in equilibrium at room temperature.
- **Martensite** (German: **Martensit**); a kind of metastable version of *austenite* + carbon; but with a tetragonal lattice and different mechanical properties; this will exercise us a great deal.
- **Bainite** (German: **Bainit**); a mixture of α **- ferrite** supersaturated with carbon and *cementite*, but in a (non-equilibrium) structure quite different from *pearlite*.

🔵 If you wonder why there are so many strange names, consult the link.

▶ Considering **cast iron**, the important part is the eutectic at around **4.4 % C**.

🔵 At that concentration, casting at about **1400 K** is easy; and the temperature is so low that it was easily achieved in ancient times.

🔵 But cast iron contains a lot of *carbon* (mostly in the form of *graphite*; which is not directly evident from the phase diagram), is brittle, and while employed in huge quantities, not what we are after. What we *are* after is *steel*.

Considering *steel*, the important part is the eutectoid reaction at about **0.8 % C**.

- If we cool this composition from a temperature larger then **996 K** ("bright cherry red"), it will completely ("congruently") solidify into a **Fe - Fe₃C** eutectic, i.e. a mixture of α-iron (i.e. **bcc** iron with a tiny bit of dissolved **C**) and cementite (i.e.**Fe₃C**).

- This mix is shown on the right; it is called "**pearlite**" (German: **Perlit**); the black lamellae are the **Fe₃C** parts; their thickness is a few **µm**. The name comes from the pearl-like luster of this material.
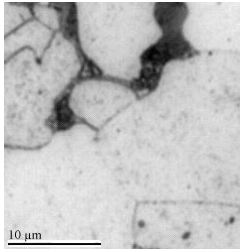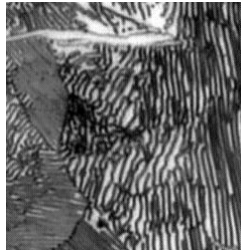

What do we get if we cool a composition somewhat poorer ("hypo") or richer ("hyper") in carbon than the eutectoid composition?

- At high temperatures just before the phase change takes place and for less carbon then **0.8 %** at the eutectoid point, we will have a **hypoeutectic** mixture of ferrite with practically no carbon and austenite with the eutectoid composition.

- Below the eutectoid temperature, the ferrite just stays ferrite, but the austenite turns into pearlite. We expect islands (= grains) of pearlite with its typical laminar structure embedded in ferrite.

- Conversely, if we have too much carbon, i.e. **hypereutetectic** steel, we expect island (= grains) of pearlite embedded in cementite.

That is different from an *eutectic* reaction, where both components need to solidify. Here nothing needs to solidify, we have some grain structure with α and β grains, and the α grains could remain unchanged.

- We won't go into more details here, but you can look at an [illustration of the solidification](#) and phase change process in an illustration module.

What the structures (= [Gefüge](#)) you get look like is shown in the pictures below.

Ferrite and blackish Pearlite grains at **0.1 % C**	Ferrite and more blackish Pearlite grains at **0. 4% C**	Pearlite and (white) cementite at **1.3% C**.

Interestingly, cementite seems to be black for hypoeutectice steel and white for hypereutectic steel. Six sources ignore
the obvious problem with pictures like these. The resolution of the apparent paradox (probably) is as follows: Both, ferrite
and cementite are "white". The black part comes from the *boundaries* between ferrit and cementite (a simple optical effect
at high magnifications).

Now there is a first complication: If we start well above the eutectoid temperature of **996 K**, the composition of the α **+** γ, or the γ **+ Fe₃C** phase mix has to change according to the lever rule as the temperature decreases.

- It only can do so by *diffusion in the solid state*. But this is a relatively slow process, so we might expect that what we will get, will depend on the *cooling rate*. Only for very slow cooling will we obtain the "equilibrium" structure shown in the phase diagram.

What kind of mechanical properties do we expect? We have, after all, some kind of composite made from a relatively soft and ductile material (ferrite) and a hard and brittle material (cementite).

- As far as Youngs modulus is concerned we could use the [rules derived for compound materials](#).

- But we are more interested in properties like hardness, yield stress, ultimate tensile strength, and maximum strain. The latter is a kind of direct measure for ductility. Since all these properties are "defect sensitive" (as we learned in chapter 8!), simple rules cannot exist. We only can make educated guesses.

We certainly would expect that an increasing cementite concentration would lead to an increase in hardness but to a concomitant loss of ductility (it becomes hard and brittle).

- Let's see what we get. Some essential mechanical properties are shown on the right. Since not only the carbon concentration, but also other structural details determine what you get, the graphs give a whole ranges of properties for structures somewhere between "annealed" and "normalized".

- "Annealed" and "normalized" refer to different standardized heat treatments designed to give comparable structures with respect to grain size and shape, and dislocation density.

- "Annealed" is as close to equilibrium as possible. We have large grains and small dislocation densities. "Normalized" means that some heat treatment was used so that the history of the material (it might have been heavily deformed, for example), is essentially wiped out, but grain sizes are small and we are far from equilibrium.

The first graph shows the yield stress R_P (German: Fließgrenze) and the ultimate tensile strength R_M (German: maximale Zugfestigkeit).

- We see that both increase with increasing carbon content, but the more important parameter R_P sort of tapers off and remains constant around **0.5 % C**

The second graph gives the maximum elongation that can be achieved in a tensile test and the impact energy or fracture energy (German: Zähigkeit).

- The maximum elongation is a fairly direct measure of ductility; we see that the ductile behavior gets worse in a rather linear fashion with increasing carbon content.

- It is pretty close to zero as soon as there is no longer a contingent matrix of ductile α- ferrite.

- The impact energy is a fairly direct measure of "brittleness". Low energy means easy fracture - the material is brittle.

- It decreases steeply, tapers off around around **0.5%**, and reaches a relatively constant low value for hypereutectic steels. Essentially, the fracture toughness than is determined by the fracture properties of the cementite, which now forms a continuous skeleton with embedded pearlite grains [1].
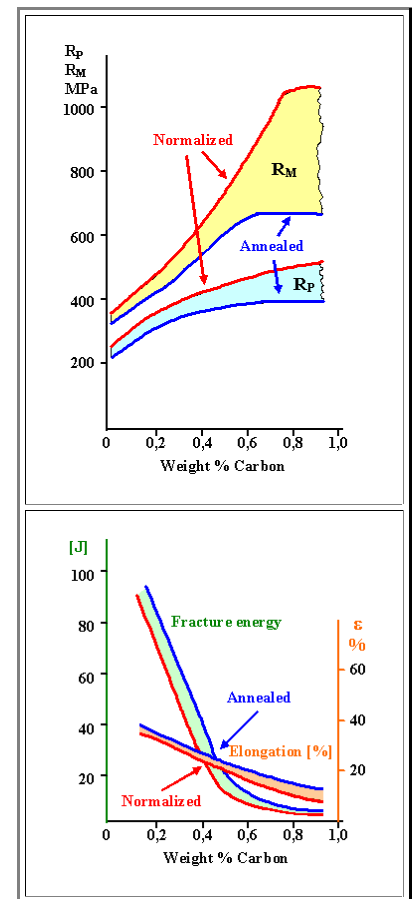
Kinetics of the Eutectoid Phase Change

So much for the *simple* part. Iron-carbon compounds or **plain carbon steels** now become difficult for two major and related reasons:

1. The phase diagram from above does not show the *real* equilibrium structure - **FeC₃** called *cementite* is *not* the phase with the absolute minimum of the free energy; that is actually *carbon*.

- However, **FeC₃** is metastable; it simply forms before pure **C** (= graphite) can develop; and it may take a long time before all **FeC₃** is decomposed into **C**.

- The real, i.e. true equilibrium phase diagram of **Fe** and **C**, however, looks a lot like the **C - FeC₃** from above. Just take out the vertical line for stoichiometric **FeC₃**, substitute "**C**" for "**FeC₃**" everywhere, and shift the horizontal lines downwards a few **K**; leaving everything else the same (except for the "**L + graphite**" liquidus line, which goes up much steeper). If you can't imagine this, look it up in the link.

- This has some consequences for **cast iron** (it is essentially the reason why we find pure graphite and not just cementite in cast iron as already mentioned above)

2. The solubility of carbon in austenite is much larger than in ferrite. At temperatures somewhat higher then the "magical" **996 K**, austenite can easily accommodate any carbon concentration around the eutectoid concentration of **0.8%**.

- Passing the eutectoid temperature during cooling now requires a radical change. Practically all the homogeneously dissolved carbon now has to go to the inhomogeneously distributed cementite - by diffusion, there is no other way.

- This simply takes time, and if that time is *not* available, because the austenite is **quenched**, i.e. *rapidly cooled* (really rapidly at this point, with at least **1000 K/s** for hypoeutectics), something *new* happens.

- The carbon stays in place - more or less - and this necessarily prevents pearlite and ferrite formation. Instead, a new lattice type is found, called "**martensite**". It is a body-centered tetragonal lattice; essentially a **bcc** lattice elongated somewhat in one direction.
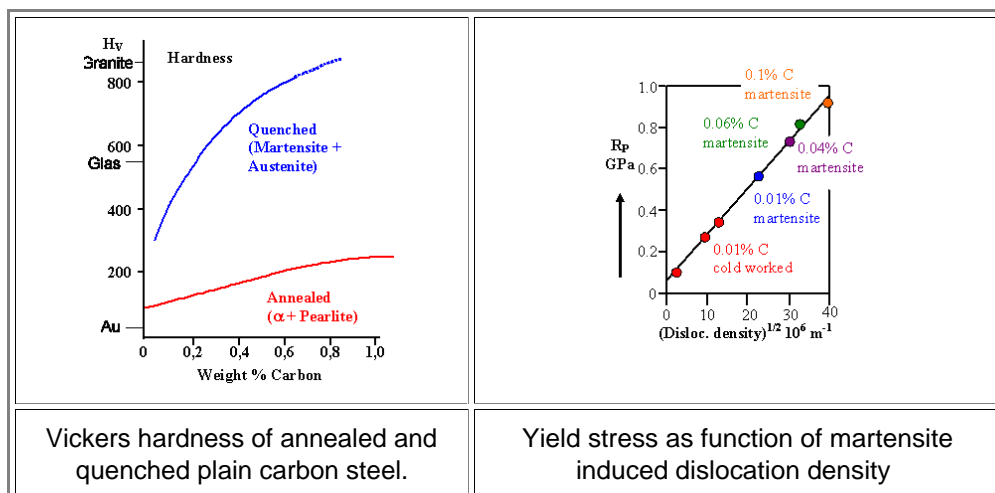
- The transformation from the *fcc* austenite lattice to the *tetragonal* martensite lattice does not need long range diffusion (as, e.g., the transformation from the austenite lattice to pearlite).
  - It takes place by a *shear process* (involving special dislocations); and all transformations of that kind are called **martensitic transformations**. There are many martensitic transformations in materials science.
- It looks like martensitic transformations are easy - if you don't have to move atoms around, it could just happen!
  - Not so: Changing from one lattice type to another one will (almost) always involve a volume change. If there is no moving around of atoms, if nothing can "give", such a transformation will then automatically produce a lot of stress and strain, and thus requires plenty of energy. Martensitic transformations therefore are *difficult*; they only happen if there is a large driving force.
  - As a corollary, martensitic structures are rarely equilibrium structures; they are metastable at best. But that does not mean that they can last a long time at normal temperatures.
- The pictures below illustrate what happens and what it looks like.

| The martensite shear transformation | Martensite "needles" or lathes in austenite (Magnification **×1000**) |
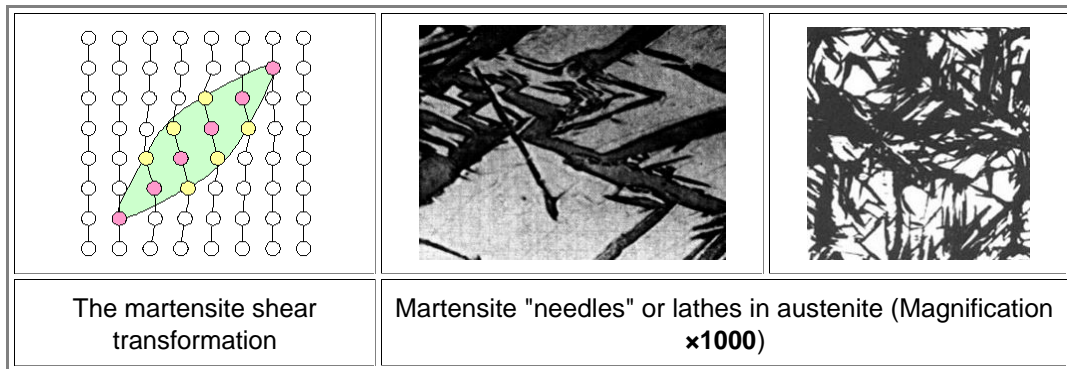
  - Looking at the schematic representation of the shear transformation; it is clear that the process is not easy, stores a lot of elastic energy, and tends to make thin needles or plates (called "**lathes**").
- Pure martensite is soft and ductile. However, we don't have pure martensite; we have martensite with interstitially dissolved carbon - and this is an extremely hard and brittle substance.
  - Hard martensite is of not much use by itself - but it is the key to things like "magical swords" or high strength steels
- Look at the Vickers **hardness** diagram below to get an idea of how much better the edge of a Japanese swords - pure martensite - will be, compared to a regular decent steel.
  - If you want to know what "*hardness*" means in some detail - look up the link above. For steel, the Vickers hardness H_V is pretty much the same thing as the yield stress R_P; we have in a good approximation

$$R_P \approx 3.2 \cdot H_V$$

- So in all the diagrams here or in books, you can always substitute hardness for yield stress and vice verse at least qualitatively. For numbers you have to watch out what kind of hardness (usually Vickers or Brinell) is given

| Vickers hardness of annealed and quenched plain carbon steel. | Yield stress as function of martensite induced dislocation density |

- Why is martensitic steel so *hard*? A better question is: Why is the *yield stress* so high, because this addresses basic mechanisms we learned about in chapter **8**?
  - Above we said because carbon containing martensite is hard - but that is a bit of a tautology.
- Do we need new mechanisms for raising the yield stress of a given material that we did not address in chapter **8**?
  - As you would guess: Not really! Martensite formation simply generates a high density of dislocations since a lot of (local) plastic deformation is needed to accommodate the martensite "lathes"

- Indeed, if we plot the yield stress (or hardness) versus the root of the dislocation density introduced by various martensitic structures, we obtain exactly the straight line we would expect from the discussion in chapter 8.3.4
- While this kind of knowledge is not (yet) very helpful if you actually *make* steel; it simply proves that we understand what is basically going on - and therefore also what can go wrong.

Steel Making Now and Then

So, if you were an ancient smith and you would quench your red-hot sword blade in cold water, you might on occasion find that the edge of the sword is now extremely hard, while the interior is still tough, but far softer.

- What has happened then is easy to see - for us: Only the surface near parts will cool down fast enough for martensite formation. The inner parts simply will stay hot longer and just produce pearlite with ferrite or cementite.

But this will only work *on occasion*. Why it does not always work, you don't know. Your best guess would be that some magic is involved, or that some goods need to be in a good mood on quenching day, if things are to work out.

- Because what you ancient smith - living sometime between **1500 BC** to **1850 AD** - can't know, is that what you get also depends very much on the exact carbon content (which, whatever it was when you started, you changed a lot simply by forging the blade in your fire).
- Even worse: What you get also depends a lot on all the other elements that your raw steel will contain in some small amounts. And on the temperature you quench from. And on the temperature you quench to. And on the liquid you use, not to mention if you agitate it it or don't. And on the clay, or whatever you use to coat parts of the blade.
- And no god, priest, nobleman, politician, philosopher, general, or feuilleton writer ever told you anything helpful for about **3000** years of steel technology; notwithstanding all the sacrifices, spells, offerings, prayers, tithes, etc. that you made or were forced to make, and their ever-present air of general superiority.
- For all you know, and for all the bullshit they did tell you (try Aristotle): Some of your products might be good, some might be bad. And nobody really knew why.

Thank ~~god~~ scientists and engineers, *we* don't have to slit the throat of some living being anymore so that some macho or tussy up in the heavens or down in the netherworld feels obligated to help us to produce good steel on occasion. *We* know almost everything there is to know about martensite formation in plain carbon steels. Not yet *everything* there is to know, but enough to turn martensite into full scale use for special steels. In particular we know *three* major tricks that help us to produce a wide variety of steels reproducibly and reliably:

- **1.** We can produce martensite with rather *low* cooling rates, too. All we have to do is to add some suitable elements (which will bring us to the next subchapter dealing with alloy steel). This will allow us to produce *homogeneous martensite* even in bulky steel. That's nice, but still not of much use.
- **2.** We can **anneal** the material in a well-defined way; i.e. heat it up again. Since martensite is only metastable, we can expect that at enhanced temperatures we will get some change to the stable cementite + ferrite mixture. If we do it right, we will retain some of the hardness of the martensite while gaining some of ductility of low-carbon steel.
- **3.** During cooling, we can keep the steel at some medium to high temperature for a while (this process is called **tempering** (from German)) - and produce yet another structure.

For the second point, all that needs to be done is to get the carbon in the austenite mobile again, so it can form cementite and ferrite.

- Obviously, you want to stay below the eutectoid temperature for this; **300 ºC - 600 ºC** is what you use.
- You won't get pearlite + ferrite, however. You rather end up with small **FeC$_3$** (= cementite) particles in α-ferrite. Your grain size is also smaller, because you retain the small grain structure of the martensite.
- What you are doing now is optimizing precipitation hardening. The fine **FeC$_3$** particles make dislocation movement difficult (which gives a high yield stress and hardness), but do not completely prevent it (which keeps the material ductile).

But don't "over-temper"! If the cementite particles get too coarse, you loose hardness without gaining much ductility anymore.

- If you do it *just right*, you end up with **tempered steel**, a synonym for the ultimate combination in strength, hardness, toughness - you name it - for a good part of the **19th** and **20th** century.

By now you got the idea: The exact structure of the cementite - α-ferrite mixture is of prime importance. We have all the strengthening mechanisms discussed in chapter **8** in combination; in addition we keep microcracks from happening or spreading. What you get will depend sensitively on the carbon concentration, and in particular at the heat treatment (cooling and annealing / tempering).

- Very slow cooling gives an equilibrium structure with largish grains [1] of pearlite and ferrite. For low carbon concentrations (say **0.1% - 02 %**) we get mediocre strength properties of this "mild" steel. However, the material is easy to work with and it can be welded! That's why your car body and much else is made from this basic kind of steel (however, with a few more alloying elements thrown in).
- Rapid cooling plus tempering gives "tempered steel". The ultimate in strength for plain carbon steel, but not easy to work with; it is also not weldable.

How about rapid cooling to some intermediate temperature; and slow cooling after that? Followed by some tempering or not?

⬤ You get the idea once more. There are innumerable possibilities for plain carbon steel; and then we have the whole periodic table for alloying - but essentially we understand what is going on.

The "*rapid cooling to some intermediate temperature and slow cooling after that*" suggestion is actually a good one. It produces yet another characteristic mix of FeC_3 - α-ferrite, called "**Bainite**".

⬤ The picture below shows some transmission electron microscope pictures of the structures discussed:

Pearlite	Bainite	Tempered martensite
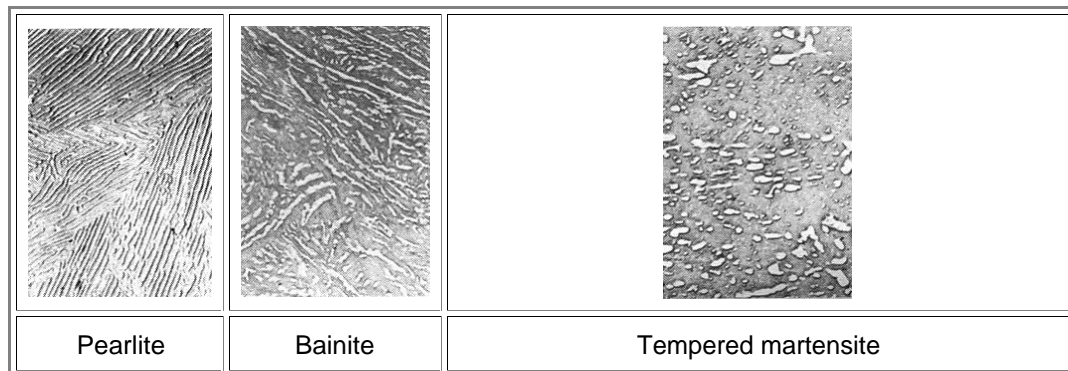
⬤ Pretty much the same mixture of **Fe** and **C**, but different structures and *very* different properties

As promised, we only did some basics - there is much, much more to plain carbon steel!

Now we look at all that stuff from a "distance" and realize that what we do when we make plain carbon steel is just what some ancient smiths did: We used "damascene technology": We always produced an intimate mix of "soft" and "hard" iron. But there are differences:

⬤ We do it on a much finer scale and in far more tricky ways. We also understand what we do. We don't need magic of any kind or help from above (or below).

⬤ We also know how to define and measure the properties of the steel we make. We do not have to cut through live people to assess the quality (as the Japanese did).

But for many kinds of the steel we can make, we have essentially the same problem as our elders: We cannot *cast* everything we want.

⬤ While we can easily achieve the needed temperatures, just pouring some liquid **Fe - C** mix in a form will not give the structure we need. Maybe some additional heat treatment helps, but if not - then you bang your material into shape like all smiths before you

⬤ If you can't cast it, you also will have a hell of a time to weld it. After all, welding means to liquefy portions of your material and then solidify again. If the structure at the seam is not what you need, you have a problem.

This is the main reason while car bodies, to give one example, are not made from very strong steel.

⬤ If instead of pressing sheets of the stuff into the right shape and then weld everything together you would have to bang it out of some big lump of steel with a hammer, you and I and most everybody else would not be driving a care.

⬤ So be glad we have **mild steel** and understand its properties perfectly. Otherwise, the parts of society mentioned above would do what they always do and did: *They* drive a car, and *you and me* do the banging - as **slaves**.

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[1] Pearlite is not a phase, it is a mixture of two phases. However, given its distinct structure and its appearance in "*grains*", it is often treated as if it would be a true phase. Since grains can only be formed by true phases, purists sometimes use the word "nodule" instead of grain.