8.2.2 Tempering and Ostwald Ripening

Third Strategy: Tempering

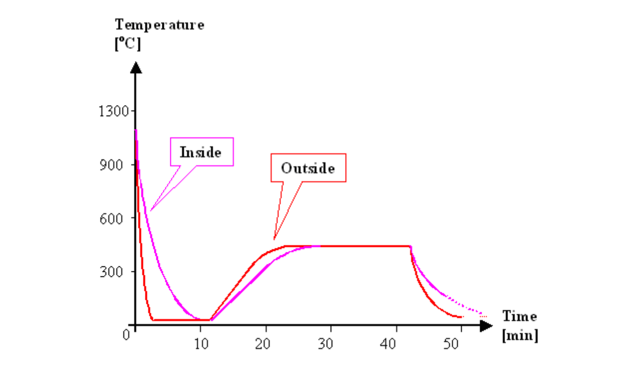
The third strategy was: Force the crystal to take a *special* way towards nirvana by **temperature profiling**. That's what we will do a lot; often in conjunction with the other strategies.

- Let's look at an example:

    1. Quench your steel with some suitable parameters (starting temperature, type of quenching fluid, volume of quenching fluid, temperature of quenching fluid, how long you keep it in the quenching fluid, ...). That's using the first strategy.
    2. Heat it up again to a typically low to medium temperature and hold it there for a while. Parameters are: Temperature, time, cooling down procedure (slow or fast)).

  Both points together mean you provided a *temperature profile* and that means you used the third strategy.
- Heating up again after some initial cooling is known as "**tempering**" your steel. We will look at some examples of tempering shortly, so I won't dwell on it here.

In other words, we subject our steel to a defined temperature vs. time treatment. The example above produces what was known as "**tempered steel**" in the 19th century and beyond, the best possible steel for demanding implements like swords or umbrelly spines.
The temperature - time profile in this case might look like this:



Temperature - time profile for "tempered" steel

Very schemantically; numbers are not too meaningful.

Temperature-time profiles can get quite involved. Sword blades from wootz steel, for example, may have been subjected to many intentionally performed hot-cold cycles.
Now why should one want to do this? Because it allows to engineer the density and size of cementite precipitates, among other things. And that is relevant for you, the ancient smith.

- Let's consider a simple but important example. You, the ancient smith, want to make a wootz blade with a "water" pattern. By definition this is done with hypereutectoid or high-carbon steel. The final steel crystal, as you know *now*, thus needs to precipitate *a lot* of carbon as cementite. If you don't use tricks, the primary cementite will encase the ferrite grains as shown before, resulting in useless brittle steel.
  You definitely need to prevent this. Moreover, you also need to induce the crystal into making *large* precipitates in certain places, so your blade will show the elusive "water" pattern when its finished (I'll get to this in due time).
- The crystal, as you know (the reader, not the ancient smith), also wants to make large precipitates in the pearlite - cementite two-phase region that we have at room temperature. It just does not succeed most of the time because the *primary* cementite nucleates and grows along the grain boundaries, while the *secondary* cementite produced pearlite or, worse, makes those brittle walls even thicker.
- So the first thing you need to do is to prevent cementite nucleation at grain boundaries at all costs. You do that by employing strategy No. 1. You select not just *any* high carbon hypereutectic steel but suitable wootz steel that does not only contain some other impurities at the right concentrations but also in a special spatial distribution. You either picked a very special steel or you got a brittle and useless blade. We can be rather sure that a lot of bad blades have been made, indeed—we just never read about those nor did they survive.
  I'll come back to that. For now let's just consider how one would go about making just a few and large cementite precipitates. There are two basic or "theoretical" options for doing this:

    1. *Nucleate* just a *few* precipitates, far removed from each other. Then let them grow until all the carbon is used

up. This way you will only have have a *few big* ones in the end.
The question, of course, is: "*how?*"

2. *Nucleate lots of small* precipitates and subject them to a kind of "grow big, winners take all" race. The losers, falling behind in growing, will be forced to stop growing altogether and must shrink instead, releasing their carbon atoms and feeding the more successful ones with it.
   The question, of course, is: "*how?*"

The *first* extreme is simply not feasible in crystal with defects, and thus certainly does not apply to all normal iron and steel crystals. Defects act as **nucleation centers** and if you have a lot of defects you will nucleate a lot of precipitates. That is especially true if you start with proper wootz steel that contains additional impurity atoms to induce nucleation of cementite everywhere and not at the grain boundaries. Sorry. You will alway nucleate lots of small precipitates at high temperatures.

It's just like the early American settlers. The were roaming the ~~crystal~~ the prairie as individuals or as twosomes, and nucleation of a settlement was easy. Plenty of good sites. Right at the edge of the forest, next to the little brook, in that protected shallow, or at the lake shore. Eventually, more people precipitated around some logwood cabin nuclei, forming small towns. No power in the world could have induced individual settlers in the USA to start with just a few sky scrapers in just two or three major places.
Sorry. Just forget option No. 1; it won't work. Except if you start with ultrapure iron where no nucleation places are available (put your settlers in a featureless and waterless desert). Then induce some defects for nucleation (dig a well and create an oasis). That will make sure that all your perambulating carbon atoms (settlers) will be found there and nowhere else after a while.
That's obviously just as impractical for making cheap steel in bulk as the making of ideal carbon steel discussed before.
Nevertheless we employ that strategy on occasion—for silicon products, of course.
But you, the ancient smith, couldn't even dream of doing it that way. You had no idea anyway what was going on in your steel. The same is true for your superiors up to and including your Gods. In the many revelations coming straight from some deity and recorded in some holy book, no practical advice for hard-working smiths or artisans was ever given.
You, the ancient smith, thus had to go with the second option.

Tempering and Ostwald Ripening

The *second* option might look at bit crazy at first. Why should some disadvantaged precipitate that couldn't grow fast enough for whatever reason, give up and start shrinking at some point, releasing its carbon atoms so that the big and important ones can get even bigger? It goes against ~~our~~ my and hopefully your basic feeling of taking from the rich and giving to the poor.

Well, the principle behind the second option was first written down by what we must assume was a closet materials scientist: **Matthew the apostle** He teaches: "For to all those who have, more will be given, and they will have an abundance; but from those who have nothing, even what they have will be taken away" (Matthew 25:29).
Mathew's principle is not just for the religious, it governs much of everyday life:

- Have you ever considered what there was before high-rise buildings covered large parts of Manhattan? Just look at Chinese cities today and you see how many small houses disappear and feed huge sky scrapers. Not exactly with the bricks they were made from but with their former share of the land, the electricity, the water, emissions, and so on.
- Have you ever been inside a major European cathedral? Odds are that it was built on the side of a big church that was erected on some old basilica, which has been build over an ancient chapel; cannibalizing each time the material from the older construction and other abandoned smaller buildings in the surroundings.
- Maybe more to the point: have you looked at the distribution of wealth in the USA lately? A few bank accounts have grown to humongeous size while most others shrank. Many are close to or below zero now.
- Ripe **Swiss cheese** contains only a few big holes. Young Swiss cheese contains many small ones. Guess what happens during ripening or ageing?

Matthew's principle is important in Material Science and Engineering. We scientists know it under a different name, however:

In science, Matthew's principle is called Ostwald ripening

- *Ostwald ripening* is a very common process inside materials, and we will soon see how it works for making wootz sword blades. If we exclude cathedral building, bank accounts, cities or other stuff that is *outside* of Material Science proper (Swiss cheese is inside), *Ostwald ripening* is a process that we understand very well; we can actually *calculate* what is going to happen.
I will not go into the mechanisms behind Ostwald ripening here. You can get a first taste form the science module, where the first part is not too difficult to grasp.
The long and short is that Ostwald ripening always happens in crystals. Exactly how depends on the circumstances, in particular the temperature - time profile—and that we can control to some extent. We will need to keep Ostwald ripening in mind when we now look at real steel.

Science Link **Ostwald Ripening**

Tempering and Nucleation

So far I gave you the impression that there is not much we can do about nucleation. Is that really true? Well, mostly but not quite. Crystals want to make a few big precipitates if the phase diagram calls for it, and for doing that they have two basic options outlined above.
Now crystals don't know a thing about the two options they have *in principle*, they're just doin' what comes naturally.
Their ***IQ*** rarely exceeds that of the people addressed in Annie's well-known song, which one could amend by the lines:

You don't have to know how to precipitate When you're plagued with too much carbon. You just let'em loose and they'll start to mate Doin' what comes naturally	Crystals are dumb in any shape They ain't had any learning. Still they're happy like an ape Doin' what comes naturally.

- The crystal starts making the first tiny precipitates at places where their *nucleation* is particularly easy (principle of supreme laziness) if you give it time. That is almost never somewhere inside the *perfect* crystal lattice but almost always at major big defects. When you are out in the street and in need of precipitating something out of your body, you look for a suitable place like the bathroom of Hotel to dumb the stuff - provided you have time. You also take your time and do whatever you do at leisure.
Grain boundaries, especially the juncture of two grain boundaries, are the corresponding great nucleation sites for the crystal, where it can dumb the surplus atom it doesn't want to have in its ~~body~~ bulk anymore, in style - if there is time. The precipitates grow leisurely.

Link Hub **Nucleation**

When needs get more pressing, meaning the driving force get larger, you settle for any bathroom, including those aromatic small cubicles distributed everywhere. Dislocations, or some small precipitates of some *other kind* correspond to that as far as the crystal needs are concerned. You do not loiter and precipitates grow quickly.
If the driving forces become overwhelming and the alternative to immediate precipitation is utter disaster, you settle for a dark corner or just about any place (just one foreign atom or even the perfect lattice). And you do it as quickly as possible.

So there is nothing much you can do about nucleation. You are stuck with the infrastructure or defect structure that's there. The key word is rather "driving force". Provide large driving forces and nucleation will happen in far more places then in the case of small driving forces. The result are many small precipitates that came into being rather quickly.

- Like always, there is a catch. You get a large driving force if you cool down quickly to some temperature well below some transformation temperature, e.g. our by now well-known 700 ^{o}C (1292 ^{o}F) for carbon steel. There is an urgent need now to have cementite precipitates but since you cooled down quickly, there was not enough time to make them. Nucleation will start all over but growth is sluggish since nothing moves very fast anymore at that temperature.
- Yes? You think, maybe, let's raise the temperature again, after we now have all these nuclei, so the precipitates can grow faster? Very good. That's a straight A for paying attention. The headline, after all, is temperature profiling. What it all amounts to is the "**golden rule**"

Control nucleation! **Control kinetics!**

- We are now at the core of Materials Technology, in particular iron and steel technology. Controlling *nucleation* means to control the starting configuration for the march to nirvana and the beginning of cooling. Controlling kinetics means temperature profiling.
  - With the starting configuration you can control nucleation in many ways; I'll get to that. You could, for example, *work with defects*. As mentioned before, it is often quite efficient to introduce intentionally a few suitable foreign atoms besides our omnipresent carbon.
    Of course, you move now from a *binary* system—just iron and carbon—to a far more complex system and only ~~God knows~~ Materials Scientists know, what else besides helping the nucleation of e.g. cementite, those foreign atoms will do with iron and steel. God probably knows too, but hasn't revealed it directly so far. Interestingly enough, as mentioned before, all those revelations in all those holy books never contained any hard scientific facts.
    The foreign atoms that you did not introduce *intentionally* but happen to be there without you knowing, might be just as efficient for nucleating cementite. And you may not need a lot to change the behavior of your steel. Concentrations far below 1 % might be sufficient.
    Wootz steel, for example, needs either a little vanadium (V), niobium (Nb), titanium (Ti), or possibly a few other "carbide formers" for being what it is, if Verhoeven is right (I do believe he is, up to a point).
  - Alternatively or additionally you can influence nucleation by controlling the "*driving force*" that pushes the crystal towards nirvana, as outlined above.
- We will now turn towards real steel more and more, and all the points made here and before will come into their own. Before we do that, however, we will see how nucleation and Ostwald ripening works at something *far simpler* than steel but of prime importance for sword bearers: the making of optimized aluminum **beer cans**.