

## 8.2 Outwitting the Second Law

### 8.2.1 Strategies for Winning

#### States and Microstructure

Now let's outwit the [second law](#). We need to do this because we definitely don't want to have the **microstructure** that the crystal wants to make. In its unwavering adherence to the second law it is going for the best nirvana **state**, and we don't like that. Before we go on, let's define two terms a bit more precisely:

1. What, exactly, is a nirvana **state** for binary compositions like iron and carbon?

The first answer is simple: It is the **state** you find in the [phase diagram](#) for a given composition and temperature. So far I have used the expressions "**nirvana**" and "**nirvana state**" more or less indiscriminately; they meant essentially the same thing. But meanwhile you have learned a thing or two and it is time to be a bit more discerning. We now use the term "**nirvana state**" to indicate that the crystal has assumed the proper basic **structure** necessary for nirvana, indeed, but not necessarily nirvana itself.

It is easy to illustrate the difference between nirvana and a nirvana **state**. For example, if **you** want to achieve (temporarily) nirvana, your nirvana **state** means that all the things required for nirvana are at hand, e.g. leisure, beer, red wine, good book, attractive and willing person of the right sex, and so on. Having all that, i.e. being in a nirvana **state**, is a necessary prerequisite for achieving nirvana but does not yet constitute nirvana. How far you get nirvanawise depends on how all those ingredients interact with each other and with you. In other words: the details (called microstructure) of the nirvana state also matters quite a bit.

So a crystal must first be in a nirvana state if nirvana is to be achieved later. It then can be close or not so close to nirvana proper, depending on what the microstructure of the nirvana state looks like.

Let's look at some basic possibilities for crystals:

- The nirvana state of a binary composition like iron and carbon consists of either one phase or a mixture of two phases, [never more](#). The [phase diagram](#) shows you which one of the two it will be for any given [state point](#). The nirvana state of iron with 1,3 wt% carbon at 1100 K, for example, is  $\gamma + \text{Fe}_3\text{C}$  or in words: austenite plus cementite. [Look it up](#) yourself.
- If the nirvana state consists of just **one** phase, nirvana proper calls for a single crystal without any defects except the [required point defects](#); essentially vacancies and the dissolved atoms of the second constituent (e.g. the carbon in iron). For example, a ferrite polycrystal full of dislocations is in a nirvana **state** but has not yet achieved nirvana.
- If the nirvana state consists of **two** phases, nirvana proper calls for two single crystals with the phase boundary area as small as possible.

We know already that achieving nirvana proper is an elusive goal for most materials. Achieving the nirvana **state**, however, is possible, and that must always be the first step on the way to nirvana.

2. What, exactly, is a **microstructure** or simply **structure**?

Easy. It's nothing but the exact arrangement of the atoms described in terms of [defects](#). Describing a microstructure thus may entail entries like:

- Average grain size and grain shape (round or elongated?)
- Nature, size and distribution of precipitates.
- Density and distribution of dislocations.
- Kind, concentration and distribution of dissolved point defects (uniformly distributed or enriched around grain boundaries?)
- Presence of metastable phases (e.g. martensite).
- Presence of nanocracks, inclusions of something else (slag in steel).
- ...

The list is long and in practice not so easy to compile. Generally speaking, the longer and more detailed it is, the larger is the deviation from the (always simple) nirvana structure.

Now comes an important point: We can express the difference or "distance" of the **actual** microstructure from the **nirvana** microstructure in numbers (with unit energy). The larger the distance, the larger the need or drive for the crystal to do something about it. That's why we call this distance: [driving force](#)! We need to write that down in big letters:

## The driving force for change is the difference in energy between two alternatives

- You are right. It should actually be called driving *energy* but for historical reasons it's called driving *force*. Knowing the driving force of a crystal will give us a good idea about what the crystal is going to do if we don't interfere. It's like knowing how your opponent is going to employ his troops in the upcoming battle. That will certainly help you to win the fight.

### Strategies and Tools

For our sword blades we want certain microstructures. There is no such thing as "one microstructure fits all". What kind of microstructure is best for you blade depends very much on what kind of steel you start with, and what kind of (carbon steel) blade you want to make. Let's look at three examples:

- Modern blade from uniform steel*. You want small grains and very small precipitates in medium carbon steel; not too many dislocations. That ensures that your steel is quite hard but still ductile enough not to fracture completely or to suffer heavy damage at the edge on impact.
  - Wootz steel blade with "water" pattern*. You need to start with high-carbon "hypereutectoid" steel that must have been molten once (no slag residues, no microcracks, etc.). You need to control nucleation of the cementite and you need to form very large precipitates arranged in some pattern. Possible but not easy.
  - Japanese katana*. You need at least two different kinds of steel, both as uniform as possible. The softer one could contain coarse grains and precipitates, and the harder one must be able to develop martensite (I'll get to that).
  - Pattern welded blade*. You need at least two kinds of steel, three are even better. Two must "look" differently after etching so a pattern can develop, their microstructure actually doesn't matter all that much. Two different kinds of carbon concentrations will not be good enough; different phosphorous concentrations (I'll get to that) might do the trick. The microstructure of the third kind (used for the edge) should be like that of the modern blade from above or the hard steel of the katana
- Lots of different microstructures; none of them close to the nirvana structure. We now need to discuss strategies for making the desired microstructures. Before we look at this, however, I'm going to make an important statement:

## There is no such thing as plain carbon steel!

Only with very modern technology can we make something that comes close to an ideal *binary* composition made from only *two* kinds of atoms like iron with a defined amount of carbon *and nothing else*. The problem is that making such a "perfect" carbon steel (or any other binary composition) is always very expensive and mostly pointless. So it's rather rare.

- In order to make an **ideal carbon steel** you would have to start with extremely pure iron. Next you alloy it with some defined amount of ultrapure carbon—but what for? You would get "ideal" carbon steel with some specific properties indeed—but are those the properties you want? If you can make ideal binary carbon steel, you can do that with most of the other 90 elements of the periodic table, too. Chances are that some other combination will give you better steel than what you can get with carbon. There is no reason whatsoever that from 70 or so possible alloy elements, carbon should happen to be the best.

We can only justify taking this ultra-expensive route for special applications where we need specific properties that we cannot get in cheaper ways. Even then we compromise. We don't start from *ultrapure* iron, just from relatively pure iron. We may not want carbon in there but tolerate a little bit. Then we add small amounts of other elements to achieve the properties we want. That is not only done, it is a growing part of modern steel making. The catchwords are [High Purity Steel](#) and [High-Strength Low-Alloy Steel](#) or *HSLA* steel.

Making large quantities of cheap steel thus forces us to work with non-ideal carbon steel that also contains relevant quantities of other elements. In fact, many of today's steel do not rely on carbon as the main alloying element at all. You the ancient smith, however, had no choice. You had to work with what you could make or get.

- This is a very important point. We are now moving, ever so slowly, from being Materials *Scientists* to being Material *Engineers*. We must work with what we have or can afford.

# The difference between Materials Scientists and Material Engineers is: Money

● **Money matters** to Material Engineers. Not only does a Material Engineer project leader make far more money than a Materials Scientist professor, the former must be aware of the costs of what he is doing, on return on investment, impact on the environment, and so on. He cannot focus on making ideal steel, he typically must make *cheap* steel—in bulk!

● So *real* steel always contains other impurities besides carbon, some added intentionally, some unintentionally. As long as there is not a lot of this stuff around, the iron - carbon phase diagram still is (approximately) valid with respect to the *nirvana states* one should expect.

It is the *microstructure* that is sensitive to small amounts of impurities. This is good because it is mostly the microstructure we want to optimize for our purpose since there is not much we can do about the nirvana state (I'll get to the important exception shortly). Impurities thus are an important part of our arsenal for fighting the crystals tendency to be a softie.

By the way, did you note that I'm not saying that Materials Engineers *never* make expensive and almost ideal materials, They do—whenever money can be made and there is no alternative.

● If we look at *silicon* (Si) instead of iron, we need to make ideal (and expensive) silicon since some products we make from silicon *only* work if we use extremely perfect silicon. That means we need [single-crystalline silicon](#) with (almost) no defects in the crystal, except for some painstakingly selected foreign atoms that we *need* in well-defined small concentrations. Silicon crystals are far more perfect than the best we could ever do with iron, and about as close to nirvana as a crystal can ever get.

Yes—it's expensive. Very expensive. Luckily, the products we make from this *expensive* perfect silicon are very small: microelectronic components like micro processors or the memory in an USB stick. So we get a lot of products and thus cash out of very little silicon.

Making a microprocessor out of a slice of perfect single-crystalline silicon requires to make changes to the silicon, This, as always, requires to move atoms around.

How is it done?

Well, employ the strategies listed below (plus a few special tricks). I'm talking basic Materials Engineering here when I now talk about strategies for optimizing microstructure, not just sword blade making.

Times are a'changing. Right now we need "perfect" but inexpensive silicon *in bulk*—for making huge amounts of **solar cells**. A real challenge for Materials Science and Engineering. As you will see (on roof tops), we are up to the job!



But back to the topic: strategies for making the desired microstructures. Here are the basic strategies and tools we have at our disposal. In simple cases one strategy may suffice but in most cases you must use combinations.

## ● Strategies:

1. **Stop** at the right moment whatever the crystal is doing at high temperatures. For doing that you cool it quickly; a process called "**quenching**". There might be two effects:
  - The crystal retains more or less the microstructure it had at the high temperature.
  - The crystal switches to a "desperation" microstructure that does not need much atom movement to come into being, just large driving forces.
2. Use *violence*. Change the structure by massive **deformation** induced from the outside.
3. Force the crystal to take a *special* way towards nirvana by **temperature profiling**. Change the temperature in some specific way, allowing only those things to happen that should happen.
4. **Optimize the composition**. Make sure you have the right proportions of the main ingredients and the proper *seasoning with impurities*.

## ● Tools:

1. **Cold liquid**. Throw your hot steel in it and you have quenching.
2. A **hammer** or any kind of press, rollers, ..., for inducing plastic deformation.
3. A controlled heat source for **tempering**. Your hearth, an oven or crucible, a powerful Laser, a torch, friction - whatever works.
4. **????** You need to add or remove this and that and there is no particular tool describable in just a few catch words.

I will go through all of that in more detail in what follows. Here we just note that strategy number 4 is actually very powerful but the tools that go with it are a bit vague. In particular for you, the ancient smith. While nowadays we can quantify and understand the "this and that" bit, you, the ancient smith, could not. The only tool you had at your disposal was the ability to pick the ["right"](#) kind of iron or steel from a rather limited supply. The material you started with had then some composition that you could not change all that much any more. The only exception is what is known as "**carburizing**" or "**de-carburizing**" at high temperatures, increasing / decreasing, or more generally, changing the

carbon concentration somewhat in surface-near regions.

In essence: it is not so much the smith but the people who made his steel who employed strategy No. 4 - knowingly or unknowingly. It is a major strategy and I will come back to it later to some extent when I go into the making of steel. Now let's look at strategies No. 1 and 2 in a more superficial way before I go into more details. Strategy No. 3 will exercise us a lot in what follows, so I will not say anything to that right here.

### First Strategy: Quenching

After the crystal assumed the proper nirvana *state* at high temperatures, it will start to work on the microstructure. Precipitates will grow (in a two phase state) until there is only one (or a few) large one, or shrink (in a one phase state) until there is none; grains will grow, getting larger and fewer; dislocation will gradually disappear, and so on. The quenching strategy exploits the fact that some *intermediate* structure that the crystal assumes on its way to the nirvana structure may suit our needs better than an earlier or later structure. It's like preferring teenagers to children or adults for some purpose that I have yet to find out.

For stopping whatever the crystal is doing at some particular temperature and point in time, we simply make use of the fact that not much can happen anymore if *atoms can't move*. All it takes to keep atoms from moving are low temperatures. Just look at the [numbers](#) again to appreciate this.

For steel and most other common metals, room temperature is often (but not always) cold enough for preventing atoms to do something.

At room temperature a *carbon* interstitial (or other interstitials like nitrogen (N) atoms) makes roughly one jump per second. Within a whole year they can move about one micrometer at best. That's not a lot but enough to cause some trouble on occasion, as we will see.

The movement of all other atoms - either by [vacancy or by interstitial diffusion](#) - is so sluggish at room temperature that they're not doing much anymore during your lifetime. The *iron* atoms thus do not move noticeably during one year at room temperature. However, if many years have passed; for example thousand or two thousand years, things may not be so clear anymore.

Very old glass, an [amorphous solid](#) (the opposite of crystalline order on the atomic level, and not the nirvana state) may have crystallized (nirvana state) just a bit after 2000 years or so because its atoms are moving ever so slowly. We notice that because the glass turns "milky".

The structure of very old steels may have changed a bit, too. It's not so easy to tell because we don't know what the microstructure was 2000 years ago, and we have hardly any specimens to investigate, anyway.

So what you can do as a first option is to "*freeze in*" some desirable microstructure that might exist at high temperatures by cooling down real fast - for example by dropping your hot steel in cold water. That process is called "*quenching*". You can control the **cooling rate** somewhat by quenching into **water** (fast), **oil** (not so fast) or **brine** (slow), and of course by the temperature of your quenching liquid.

What strategy No 1 obviously needs is a certain control of the *cooling rate*. How many degrees does your sword blade cool down per second? Cooling rates are thus measured in degrees per second, for example in °C/s; the same as K/s

Quenching your work piece is not as easy as it appears. First of all, you just can't cool down a solid piece of steel (or anything else) arbitrarily fast. The best you could do (if money is no concern) is dropping your hot steel blade into liquid helium at 4 K (- 269 °C, -452 °F). Even better would be to let *somebody else* drop it because what you get is a very cold sword blade and a major explosion when all that liquid helium turns instantaneously into gas.



#### Quenching a steel bar at one end

The bottom sits in (originally) cold water. While is cold enough to appear black, most of the rest is still red hot.

Source: Alexander Kilpert; Internet; with friendly permission.

- No matter how you quench, the part in touch with the coolant will always cool down far more rapidly than the rest; see above. Same thing for the inside in comparison to the outside. The earth has been put into a really cold place some billion years ago but is still rather hot inside. You can try a little experiment with a hot potato if you have doubts about that. Take it out of the boiling water, hold it under running cold water for a few second until the outside feels right for eating, and then bite into it. You will suddenly and painfully understand what I mean. In other words: it is *impossible* to cool down a big piece of steel with the same cooling rate everywhere. During quenching the outside will always be colder than the inside, until all parts eventually have reached ambient temperature. What you will get during quenching *without fail* is therefore a **temperature gradient** inside your steel, a change of temperature with position. That's not so good for what we have in mind. We want to freeze-in a certain microstructure and that will only work as desired for the outer parts of a work piece that can cool down real fast. In the inner parts it is hot much longer, and we must expect the microstructure deep in the steel to be different from that on the outside. Too bad - and not much you can do. But the unavoidable *different* cooling rates (in scientese we call it *differential* cooling rates) in different parts of your blade can also be useful, as you might know if you know anything about the Japanese art of making sword blades. I'll get to that.
- To make things worse, quenching also has a few side effects that may turn it into a dangerous medicine. You might get the desired microstructure alright—but in a blade that has shattered into several pieces or bend into a distorted shape. The reason for that is that quenching *always* induces massive mechanical stress, directly tied to the temperature gradient. I will get to that, too, in due time. Moreover, If you really rush the crystal by cooling it *very* quickly, it might not be able to produce the nirvana state, never mind the microstructure. It then changes its strategy for achieving nirvana, which was: i) assume the nirvana state, ii) optimize the microstructure. Instead it might do crazy and unexpected things like forming *martensite*. I'll get to that later.
- Despite all the problems listed above (three times "I will get to that later!"), quenching *is* a major way to process steel. But the unavoidable differential cooling rates do put limits to this strategy, and as you just learned, it isn't quite as easy as it appears on first sight.
- In other words: you can cool quickly but the iron crystal will fight back. How it does that we will see in what follows.

### Second Strategy: Hit It Hard!

- The second strategy is the simple and time-honored strategy most men use whenever they are supposed to do something but are out of their depth: Resort to violence!



**Sword, plowshare, whatever: beat it hard!**  
*"Let Us Beat Swords into Plowshares"*, Sculpture by Evgeniy Vuchetich in front of the UN building in NYC;  
 The other way around is [here](#).

Source: Internet at large

- Destroy the structure that your crystal assumed at some temperature and some point in time by banging it hard with a hammer.  
Or run it through a rolling mill, a press - anything that induces massive plastic deformation and perhaps some micro-cracking.

▶ If you hit your sword blade-to-be hard with a hammer, something *must* happen inside the crystal. At the very minimum you induce [plastic deformation](#), generating a lot of [dislocations](#) and running them through the crystal.

- Look at [how its done](#) again: a dislocation moving through a crystal produces a shape change and thus plastic deformation. Already a little bit of violence produces [a lot of dislocations](#)!  
Besides plastically deforming your work piece, you also may fracture the *brittle cementite* inside by banging on your steel - [here](#) is the picture showing that.

The havoc wrought by banging your steel with a hammer at temperatures not too high should influence the final structure at room temperature. It does - and we will have to look at that a bit more shortly.

But don't forget: If you bang your steel *above* the transformation temperature for forming austenite or one of the mixed phases with austenite (around 1000 K (727 °C; 1341 °F), or if you heat it after banging beyond that temperature, the structure produced by banging will get lost during cooling, provided there is enough time. Above a transition temperature, the steel loses its "memory" of what was done to it before, to put it in simple words, and moves determinedly and quickly to the new nirvana state, forgetting all that has happened before.