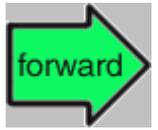




TTT Diagrams



1. The Basic Idea

How Fast Do Phases Change?

Science

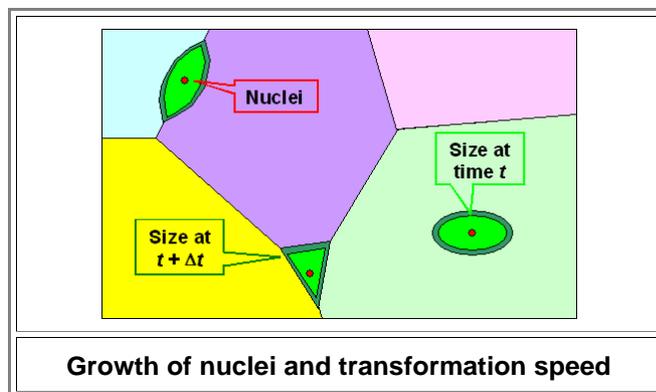
First I need to point out that what follows is mostly based on the very good book "[Engineering Materials II](#)" from **Michael Ashby** and **David Jones** since one can't do much better than these guys. Second, in this module I will stay qualitative, just introducing the basic ideas and how they connect. Details will be found in the follow-up modules.

For starters, let's consider how *fast* a phase transformation takes place. Imagine, for example, some pure iron that was kept at a temperature of 1000 °C (1830 °F) and thus has assumed the γ austenite phase or fcc structure. Now you cool it to a temperature somewhat below the transformation temperature of 914 °C (1677 °F) for pure iron, where the α ferrite phase or bcc structure is stable. What you expect is that bcc nuclei form and grow. Keeping your sample at the chosen temperature, meaning that you perform an **isothermal experiment** (isos = same, equal in Greek) we ask ourselves this question: How long does it take to transform 100 % austenite to 10 %, 20 %, ... 90 %, 100 % ferrite?

- The answer must come from two obvious inputs:
 - It depends on how fast a ferrite nuclei grows.
 - It depends on how many nuclei there are.
- Let's first look at how fast a given nuclei will grow.

How Fast Do Nuclei Grow?

Let's look at some phase γ of some material that is about to transform to some other phase α . The very first step is always to form tiny nuclei of α that are able to grow. Refresh your memory [here](#) if necessary. Let's see what these nuclei do:



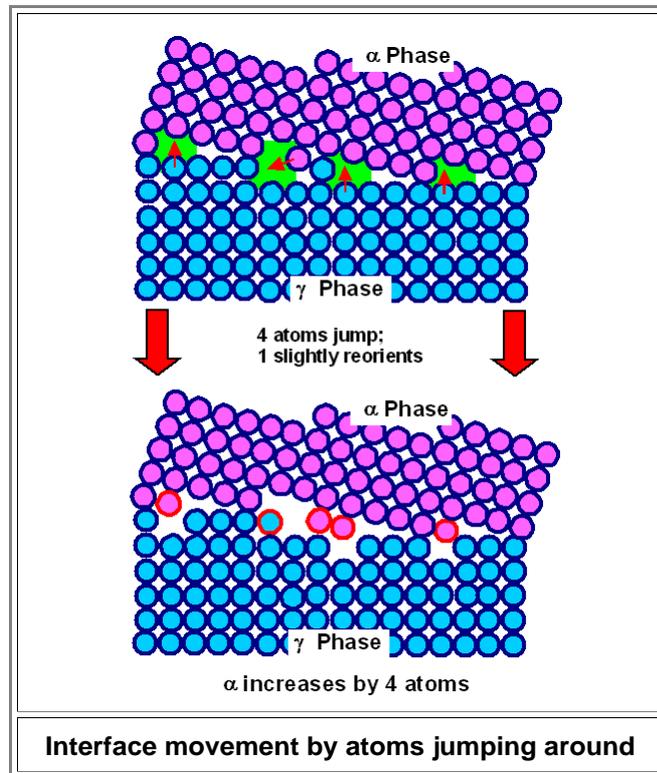
Shown are three tiny red nuclei: in the grain, on a grain boundary and on a grain boundary junction. Some time t has passed since their formation, and they have grown to some (light green) size with a shape that is determined to some extent by the crystallographic orientation of the grain and the conditions at the grain boundaries.

- A little bit later - at the time $t + \Delta t$ - the precipitates are a little bit larger (dark green) and the total amount of transformed volume is a little bit larger, too. The essential and simple conclusion is:

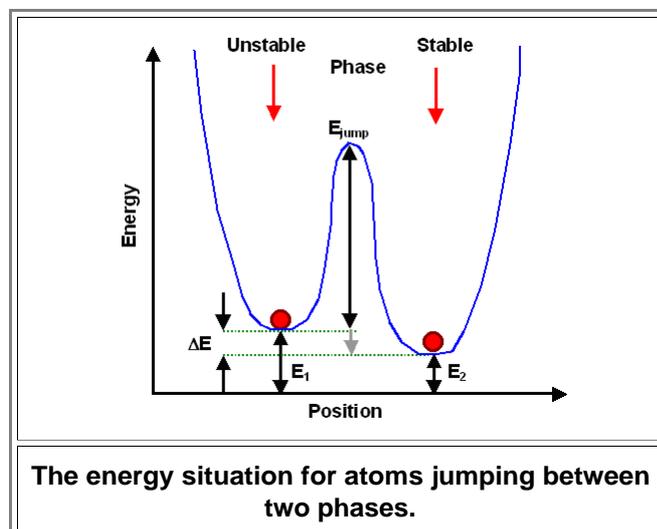
**The rate of the transformation
is proportional to the velocity
of the interface between the phases**

That is so clear that no more needs to be said. Of course, precipitates of different morphology might grow faster than others, and for a given precipitate some corner might move faster than some other part - but it is equally of course that I mean the *average* interface velocity in all cases.

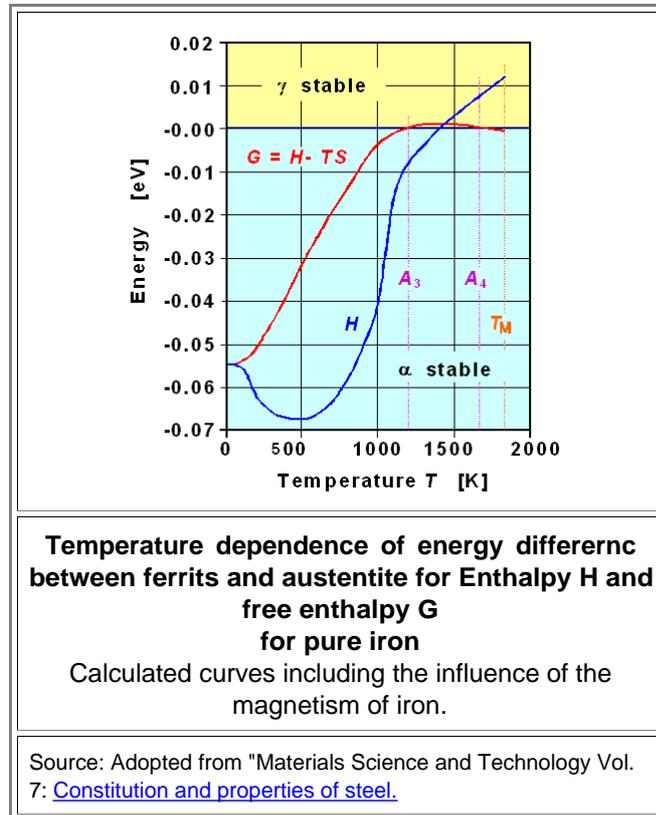
- So what determines interface velocities? That's actually an easy question. All you need to remember is that nothing happens if atoms don't move. If a phase boundary (that's what we have here) is to move, the atoms in or near the boundary need to jump to a different position. It's easy to illustrate this with a variant of an old picture:



- The upper figure shows four atoms about to jump, the lower picture the result. This is just a variant of the old figure illustrating how grain boundaries can emit and absorb vacancies. It serves equally well to demonstrate how phase boundaries move in principle (emitting and / or absorbing vacancies in the process).
- The decisive thing is that all those atoms still haven't learned about thermodynamics etc., and don't know how they are supposed to jump. That's why they just jump more or less at random. Depending on conditions, it just so happens that a few more jump from blue to mauve than from mauve to blue, leading to a net increase of the mauve part. Why does that happen? Because the energy on one side is a bit lower than on the other side.
- Whatever phase is the stable one at some temperature happens, by definition, to have a lower free enthalpy (or energy for short). An atom at the boundary that "wants" to switch from one phase to another one has to overcome an energy barrier and the situation looks - schematically - like this:



- You have seen [similar figures before](#). Once more, you can just as well use a figure like that to illustrate how vacancies jump around. The energy needed for a jump, by the way, is [around 1 eV](#). The guys in the valley on the left jump occasionally to the valley on the right, and vice versa. However, since the guys on the right see a somewhat lower energy barrier, they jump more often to the right than the one on the right jump to the left. Bingo! We have a *net* flux of atoms from right to left. It is the same basic situation we encountered when we looked at the [atomic mechanism of diffusion](#).
- You should have no trouble realizing that the *net* jumping rate - number of jumps from left to right *minus* number of jumps from right to left - must be tied to the difference ΔE in the energy between left and right. And that difference has a name: *driving force*!
- So how large are the driving forces? Tiny, actually, if you compare them to other energies - for example the energy needed for a jump, always around about 1 eV. Here are the data for pure iron:



- Austenite (γ phase) only exists because the atoms gain a puny **0.001 eV** relative to staying in the α phase! Well, yes, it's not a lot - but then there are a lot of atoms and it sums up. If you funnel off 0.1 cent at every money transaction occurring at a bank because you programmed the computer to round (0.1 - 0.4) cents down to 0, and (0.6 - 0.9) cents up to 1, and send 1 cent to your account for 0.5, you get 1 cent for about 10 transactions, or a cool 1000 \$ for 1 million transactions. That doesn't take much time in a major bank and chances are good that nobody will notice. Not that I want to give you ideas. This little scam has already been done.
 - In any case, the difference in energy between austenite and ferrite will increase with decreasing temperature. It is small close to the transformation temperature (A_3 in the figure above) and gets larger as the temperature goes down.
- For iron we now have numbers. For anything else there might be numbers too, but we don't need to know them. All we need to know is:

The driving force for a phase change below the transformation temperature *always* increases with decreasing temperature

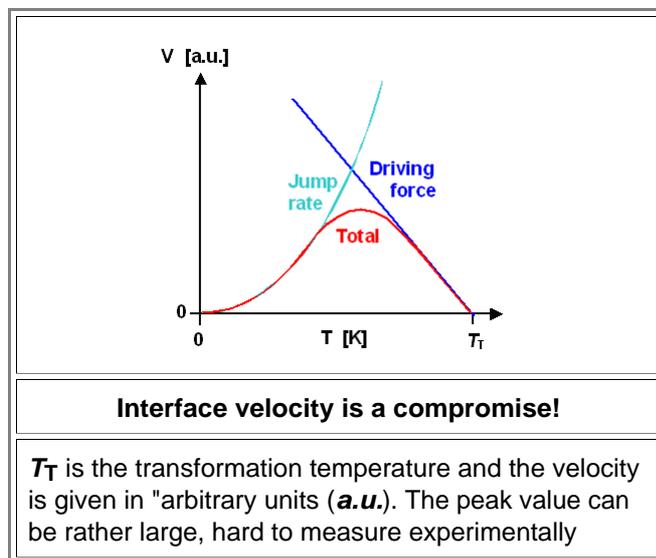
- What that means is that with *decreasing* temperature, the ratio between the two individual jumping rates, and thus also the *net jump rate*, *increases*. From a net jumping rate point of view, the interface velocity will thus *go up* with decreasing temperature.

Does this mean that the interface velocity simply increases with decreasing temperature? Well - no! Ask yourself a question that you can relate to much easier: Let's assume that more dollars per time unit jump into your bank account than jump out. "Jumping rates" are then just a measure of the amount of money flowing in or out (on average). If the jumping rates are as pictured above, you will feel very good because your balance goes up. Now look at the *speed* with which you balance goes up. It is certainly proportional to the *relation* of the jumping rates - but unfortunately also to the *magnitude* of these rates. 10.000 \$ going in per week and 1000 \$ going out give the same relation as 10 \$ going in and 1 \$ going out - but the speed your balance goes up with is quite different for the two cases. Even if nothing jumps out any more, so you have the biggest possible net jump rate, you're not going to be too happy if only a few dollars jump in.

In other words: If the atoms getting more sluggish, not much will happen anymore. If they stop jumping altogether, nothing will happen at all. We know that jumping rates of vacancies *go down (exponentially) with temperature*, and that's also true for atoms jumping in interfaces. That can only mean that from a jumping rate *magnitude* point of view, the interface velocity will *come down* with *decreasing* temperature

Now we have a little puzzle: With decreasing temperature we expect that

- the interface velocity goes *up* because of an increasing driving force, and that
 - the interface velocity goes *down* because of decreasing jump rates.
- How does one solve a problem like that? By compromising! The simplest way to see what is going to happen consists of making a little drawing:



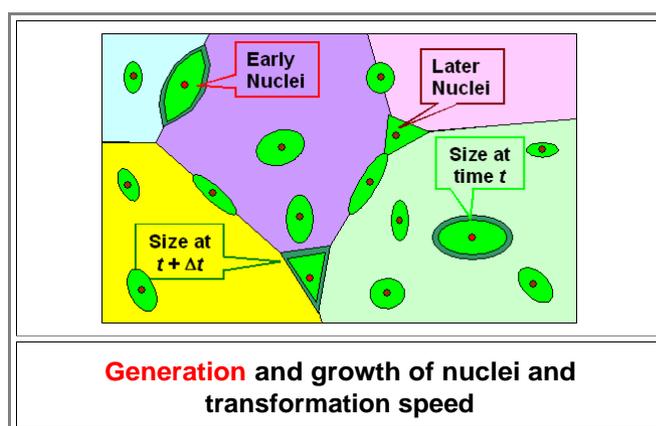
At high temperatures the driving force dominates what happens. At low temperatures it is the jump rate (also known as *diffusion coefficient*). In between, it is in between.

The final conclusion is clear: As far as interface velocity is concerned, it peaks at some temperature well below the actual transformation temperature T_T . If you keep your sample just a few degrees below the transformation temperature *or* at very low temperatures, it will take a long time before the process is over.

Details, of course, depend on many things. We will deal with that in the next module in this mini series.

How Many Nuclei Will There Be?

Now let's look at the *second input*. How many nuclei will we have? Schematically, it will be like this:



▶ We simply need to realize that after the first few nuclei came into being (the ones [shown above](#)) and commence growing, more nuclei are generated and grow as time passes by. What we need to assess is how many nuclei are generated per cubic cm (cm^3) and second (s).

● In the Science Module "[Nucleation](#)" this is covered in some detail. What we must recall is that nuclei need to have a [critical size](#) before they are able to grow, and that this critical size depends on two parameters:

1. [Homogeneous](#) vs. [heterogeneous](#) nucleation. Heterogeneous nucleation, e.g. at grain boundaries or dislocations, is easier. It therefore comes with a smaller critical size compared to homogeneous nucleation in a perfect part of the crystal.
2. [Supersaturation](#). The critical size decreases with increasing supersaturation of the point defect / impurity atoms that want to precipitate. Since the supersaturation increases with decreasing temperature, nucleation gets easier with decreasing temperature.

▶ We may in good conscience expect that the generation rate for nuclei is small close to the transition temperature (small supersaturation) but increases quickly with decreasing temperature.

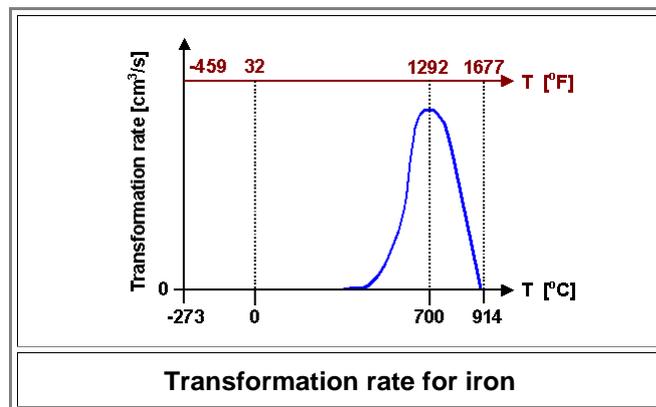
● Alas! If it gets too cold, not much will happen anymore, just as in the case of the interface velocity. I do not need to dwell on this; it follows exactly the same line of arguments given for the interface speed.

▶ I even will refrain from plotting the generation rate for nuclei vs. temperature. As long as we stay *qualitative*, the curve looks just as the one shown above for the interface velocity. *Quantitatively*, with numbers, the curves are different, of course.

Transformation Rate and TTT Diagram Principles

▶ In the beginning of this module the question was: how fast do phases change? In other words: we want to get a handle on the **transformation rate** of a phase.

We have already figured out that the transformation rate must be proportional to the interface velocity of the growing phase *and* to the number of nuclei which is given by their generation rate. We have also qualitative curves for that, and since they look the same we can safely assume that a transformation rate curve would look about the same, too - something like this:

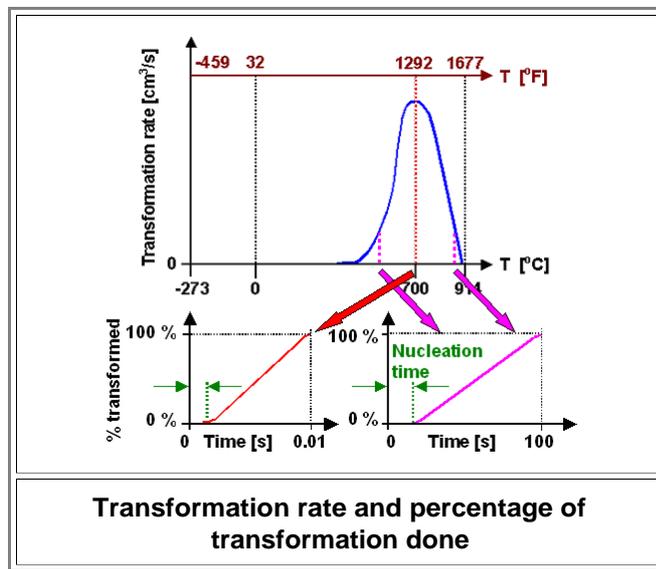


● This is already a *semi*quantitative curve. On the temperature axis are the proper numbers for pure iron. I can do this because I know where to find the data. We note two points:

- Nothing much happens right below the $\gamma \rightarrow \alpha$ transformation temperature of 914 °C (1677 °F) or at temperatures below about 400 °C (752 °F)
- The maximum transformation rate occurs at 700 °C (1292 °F)

▶ Fine. Now we have some idea about the transformation rate. That's highly interesting of course. Or is it? No - it isn't, really. What you, the ancient or modern smith are really interested in, is to what extent a transformation has actually taken place *after* some time of working with the material.

● Well, if you have the rate you just need to "sum up" (or integrate) to get the total. How much has transformed after some time t ? Multiply the rate by t and you got it (provided the rate is constant). This is shown below - plus one more thing we need to consider now.

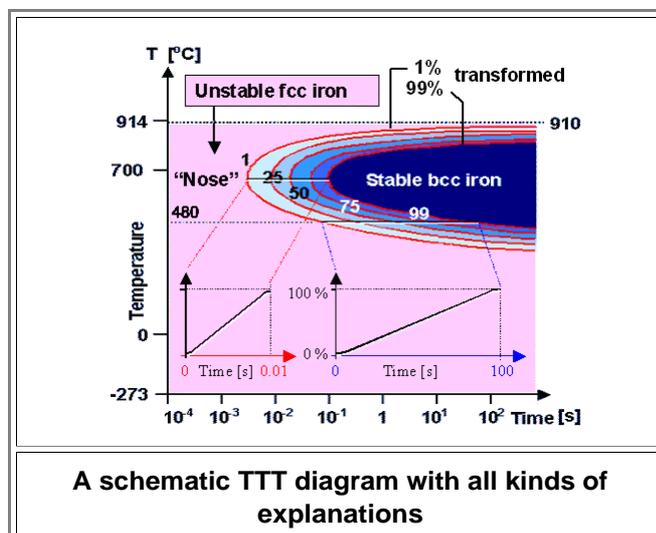


Transformation rate and percentage of transformation done

- The two curves below the old transformation rate curve show how much percent of the material has transformed to the new phase after some time t for two different transformation rates. One rate (belonging to the red dashed line in the curve above) is the maximum, the other ones (dashed pink lines) are much smaller. Looking at the time scales we see that it takes *much* longer to transform everything for the smaller rates. Well, big surprise! Yes, but it is important to realize that the times needed for 100 % transformation can be very different, far more so than the figure might suggest. That will necessitate *logarithmic scales* in figures to come.
- One more thing we need to consider now: the fact that transformation doesn't start right away when the chosen temperature is reached. You must produce some nuclei first. That takes some time (the "nucleation time" in the figure above), and it takes more time at very high or very low temperatures for the reasons considered above.
- ▶ Now we are done! All that remains to do is to redraw the whole thing for the percentage transformed. That will turn the transformation rate scale into a time scale. We take the time scale to be logarithmic, and turn the whole figure around by 90°.

We have produced an isothermal time - temperature - transformation diagram!

- Here is what it looks like:



A schematic TTT diagram with all kinds of explanations

I admit that the figure is a bit overloaded but we need to get a few terms and conventions straight. Let's suppose that we have a piece of pure iron that we cooled down suddenly from a temperature above the fcc $\gamma \rightarrow \alpha$ transformation temperature at **914 °C** (1677 °F) to **700 °C** (1292 °F). What is going to happen to this piece of iron is something we can find out if we move in the TTT diagram along the **700 °C** to the right (or up the time scale).

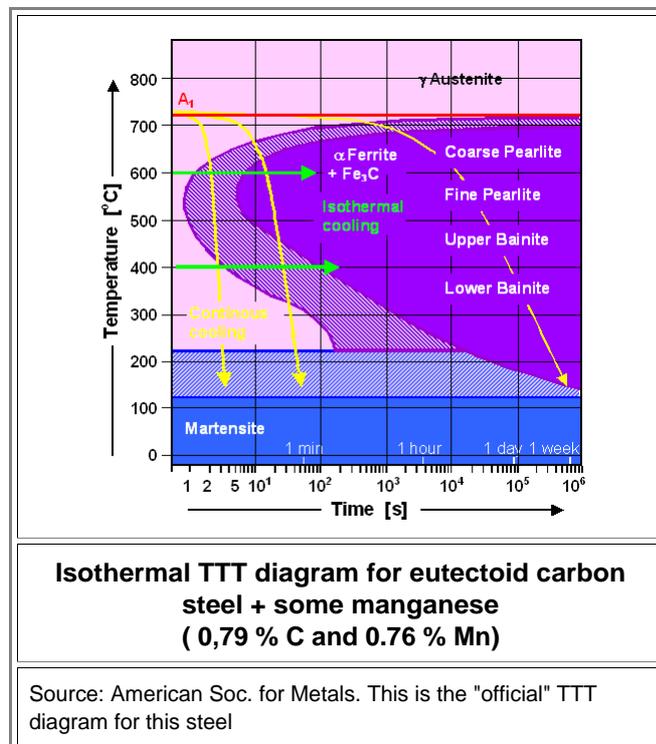
- We start in the pink fcc γ region, but after a few milliseconds (10^{-3} s) of generating nuclei, we hit the "nose" of the (blue) α region. In a TTT diagram the first line denotes always that 1 % has now been transformed. The last line gives 99 %, and the lines in between with 25 %, 50 % and 75 % are usually not shown. We do not use 100 % (or 0 %) since, as in real life, it might take forever to finish the last 1 % of a given task.
- After about a tenth of a second (10^{-1} s) the transformation is practically finished. The diagram on the lower left shows this, it is directly taken from the figure above the TTT diagram and usually not included.
- If we repeat the experiment at a temperature around **480 °C** (900 °F), we hit the 1 % transformation line after about a tenth of a second, and the transformation is finished after about 100 seconds. It takes far longer than at **700 °C**. This is why we need to use a *logarithmic* time scale. So be careful when extracting numbers. The length of the line from start to finish is only about twice as long as the one at **700 °C**, but the amount of time needed is about 1000 times longer. That's what logarithmic scales do to you. There is a reason, after all, why you always hated logarithms. If you are a mature male you also hate (very much so) that moment when your doctor sticks his finger into a very personal orifice that I won't name to check some very male gland. Well, it's good for you. So are logarithms.

If all of this is clear, we can now look at a real TTT diagram without all the frills and explanations given above, and progress a bit about how to use it.

Getting Real: The TTT Diagram

Here is the "official" isothermal TTT diagram for eutectoid *carbon steel*. It is not all that different from the unofficial TTT diagram for the pure iron above, except that the $\gamma \rightarrow \alpha$ transformation temperature is now at **723 °C** (1333 °F). Look up the [phase diagram](#) if you wonder about this.

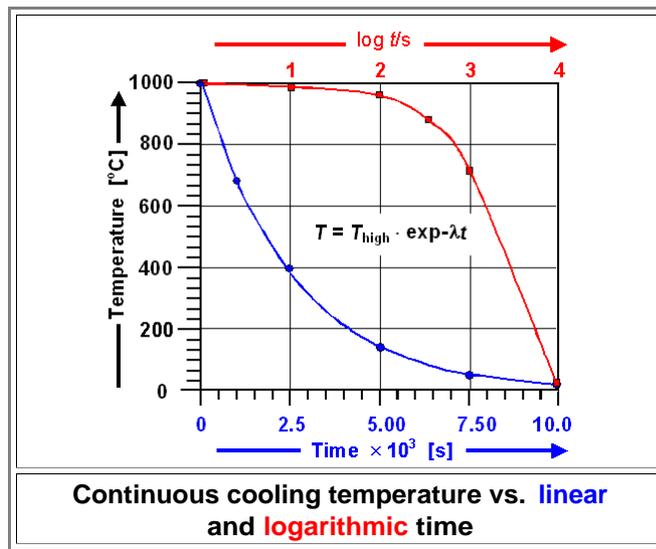
- As before, we have an austenite region, stable above the transformation temperature **A₁** at **723 °C**. Instead of only α ferrite, we now have ferrite *and* cementite (Fe_3C) inside the "nose". In addition, we have the martensite region at low temperatures.



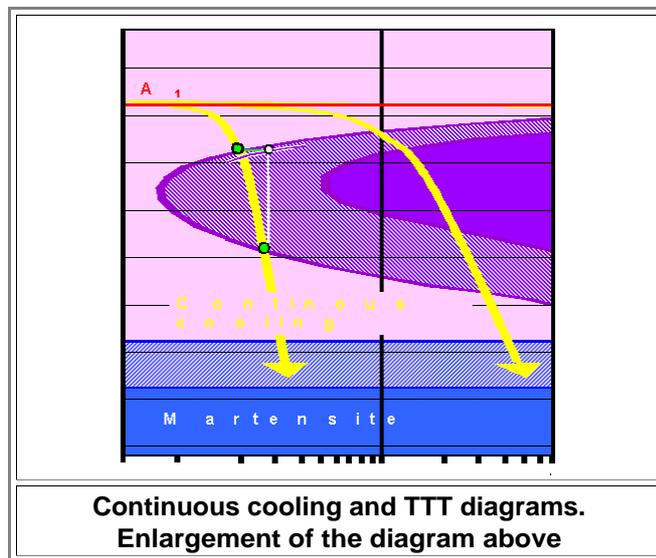
If we follow isothermal lines like the green ones, nothing new emerges. However, when we make or process steel, we usually do not keep it at some constant temperature for a very long time but let it cool down "naturally" or, as we call it, *continuously*. Naturally occurring **continuous cooling** would follow the yellow lines. Now you should have two questions:

1. Those yellow lines do not look like the diagrams for natural cooling we [had before](#). I would expect an exponential decay following the [simple relation](#) $T(t) = T_0 \exp(-\lambda t)$. I did pay close attention to the [beer module](#), after all. So, how come?
2. If those yellow lines signify anything - what is it? How can I use a TTT diagram that was made for predicting what happens if you keep the *temperature constant* ("isothermal") to say anything about what happens if you *cool continuously*?

Good questions; almost. The first one is easy: It's logarithmic, man! That distorts a typical exponential decay curve like this:



The answer to the second question is a bit more difficult. Isothermal TTT diagrams indeed do *not* really show what will happen if you run some temperature profile "through" them. What really happens is shown below:



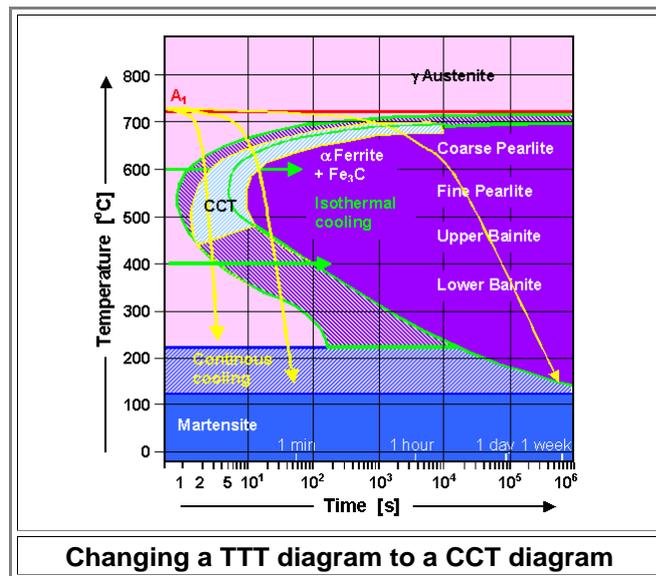
This is just an enlargement of the [figure above](#). To see what happens, let's assume that the left cooling curve, when it hits the nose of the TTT diagram (upper green point), would stay at *constant* temperature for the time it takes it to leave the nose (lower green point). It would follow the green line up to the white point. There it would end on a curve that represents only a small amount of transformed material.

What will be *really* transformed must be even less since the temperature during that time interval goes down, after all.

Far less material thus will be transformed than indicated by the positions of the yellow lines inside the nose.

Does that mean that we cannot use isothermal TTT diagrams to predict what will happen during continuous cooling? Yes, that is exactly what that means. We need to use **Continuous Cooling transformation** or **CCT** diagrams!

- Now I have good news: CCT diagrams do not look all that different from TTT diagrams! Push the upper part of the "nose" a bit down and to the right - and you are done! That's what it looks like:



The difference between the isothermal TTT diagram and a CCT diagram, that is valid for continuous cooling that follows (approximately) some exponential decay law, seems to be minor. I need to make two points to this:

1. It looks like a minor difference but, since we have a logarithmic time scale, this can be deceiving. So if you look for *quantitative* data, wanting to extract *numbers* from these diagrams: be careful!
2. If you use these diagrams only for *qualitative* reasoning, you don't need to bother distinguishing between TTT and CCT. They all look roughly the same anyway.

- People use these kinds of diagrams for both purposes; they are absolutely essential to metal technology. On occasion, however, some confusion is produced. The pictures above, for example, can easily lead you astray. So let's look at what you need to know when "reading TTT or CCT diagrams not to get wrong ideas.

In the pictures above the thermal history of the sample was given by temperature-time "pathways" in the form of green or yellow lines with an arrowhead. In the case of continuous cooling (yellow lines), the pathways always end around room temperature because that is what your sample does.

- The uninitiated then tend to assume that whatever is found at the *end* of the pathway arrow is what you will find in your sample. That is *wrong*.

If there are 1% and 99% lines, what you will find is whatever you encountered at the point where the pathway arrow crosses the x% line of some phase "nose". At this point x% of the material is transformed and that means that phase-change wise not much else is going to happen from then on - always provided that no other phase change is lurking at some lower temperature, of course.

All that is going to happen after you cross the final 99% point is:

- The last 1% are transformed. On occasion that might take a long time - but that is of no consequence.
- Grains grow larger.
- Supersaturations are reduced.
- Ostwald ripening commences.

That is all important and needs to be considered - but the phase or phase mixture doesn't change anymore.

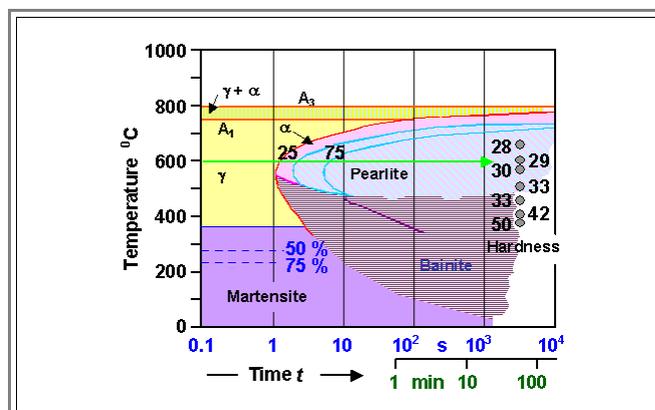
- That two out of three yellow pathway arrows hit the martensite region in the figure above thus *doesn't mean anything*. These arrows were well inside the 99% transformed area in the ferrite + cementite field and are not going to transform into a metastable phase at lower temperature.

The third yellow arrow belongs to a sample that has not completely transformed its austenite to ferrite + cementite. The remaining austenite then is going to transform to martensite.

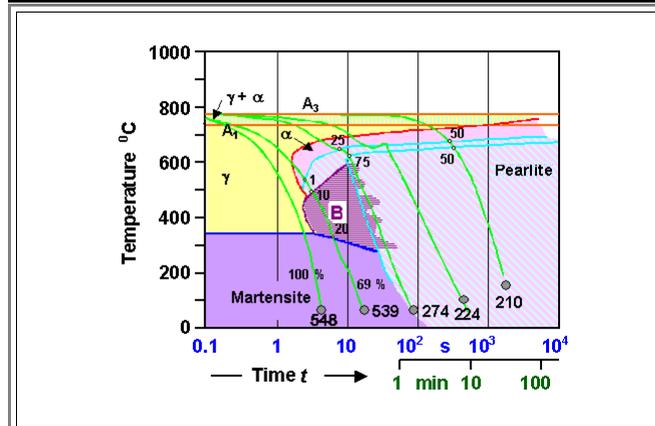
So why do I extend the martensite field all the way to the right of the nose? Obviously all pathways coming down there must have crossed the 99% transformation lines? Simply because there will be pathways not yet considered, where this is not the case.

It is just easier to keep the TTT diagrams a bit "open", hoping that the user knows how to deal with it.

We will see a bit better how this works in the next examples. Shown are actual and somewhat more involved diagrams for 0.44% carbon steel:



TTT Diagram for 0.44 % carbon steel



CCT diagram for 0.44 % carbon steel

Source: After "Einführung in die Werkstoffwissenschaften"; ed. W. Schatt, 7th edition 1991.

- Some new features and additional information appear in both diagrams.
 - First**, we now have **ferrite region** in front and above the pearlite nose. Well - why not? We have hypo-eutectoid steel here, so between the temperatures **A₃** and **A₁** you need to form some primary ferrite before whatever is left transforms to secondary ferrite and pearlite (look it up yourself!)
 - Second** the (approximate) Vickers Hardness is given that you end up with following various pathways. You can do that because you will obtain a defined structure with a defined hardness if you follow a given cooling pathway. Of course, you **know** that for isothermal annealing you will eventually go down to room temperature, essentially "freezing in" the high-temperature structure since nothing much changes anymore.
 - Third**, Bainite is drawn in - even so it is **not** a proper phase. There is **no transformation** from pearlite into bainite and means that you can't give a transformation percentage boundary. That's why I made it fuzzy in some parts. In old times, making a **drawing** was far more difficult than it is today. You actually had to **draw** it with ink on a piece of paper, so people tended to draw a clean line, hoping that everybody would know that this is overdoing it a bit.
 - Fourth**, the CCT diagram contains some **numbers** at the points where the cooling curve crosses (phase) lines. These numbers give the degree of transformation in percent. It's just not possible to have a CCT diagram where one line gives the same transformation percentage for all cooling lines crossing it somewhere. For example, if you look at the second green cooling curve from the left, you see a "1" at the point where it leaves the ferrite region, diving into the pearlite part, a "10" where it leaves the pearlite part, and a "20" where it leaves the bainite region. That means that 1%, 10 % and 20 % have transformed to ferrite, pearlite and bainite, respectively, strongly insinuating that the remaining 69 % must be martensite. Of course, in those rather busy diagrams there is just not enough room to write in all the numbers, so only a few or none are given, hoping that the reader knows how to interpolate or to guess what it should be.
- In the next module of this series I'm giving you some idea about how one calculates TTT and CCT diagrams.



TTT Diagrams

