



# TTT Diagrams

## 4. Experimental Construction of TTT and Phase Diagrams

### The General Principles

Science

How do we get those complicated TTT or CCT diagrams as shown in the preceding parts? We can calculate them [in principle](#)—but not in reality. We need to measure them, just like the [phase diagrams](#) describing what we get in *equilibrium*. I have *not* told you how to measure phase diagrams way back; we now look at all of this in one fell swoop.

The basic idea is to measure a property that changes noticeably when phase changes occur. All you need to do is to run your sample through a temperature range, recording the actual temperature and the property in question. We can do that in several modes:

- Changing the temperature *very slowly*, giving enough time to establish equilibrium all the time. That will give us phase diagrams.
- Changing the temperature *rapidly* with **various** rates. That will give us CCT diagrams.
- After an initial rapid drop to some pre-set temperature, we keep that temperature *constant*. That will yield TTT diagrams.

Writing this down is far easier than doing it, of course. There are plenty of technical problems. For instance:

- Waiting for equilibrium can take far too long at low temperatures to be practical. Phase diagrams at low temperatures are therefore a bit tentative on occasion.
- For phase and TTT diagrams the temperature of your sample should be the same everywhere. This is easier to achieve with small samples. Measuring whatever you measure, however, is always more difficult with small samples.

What properties do we measure? There are essentially *two* properties that indicate phase changes quite nicely in all kinds of materials:

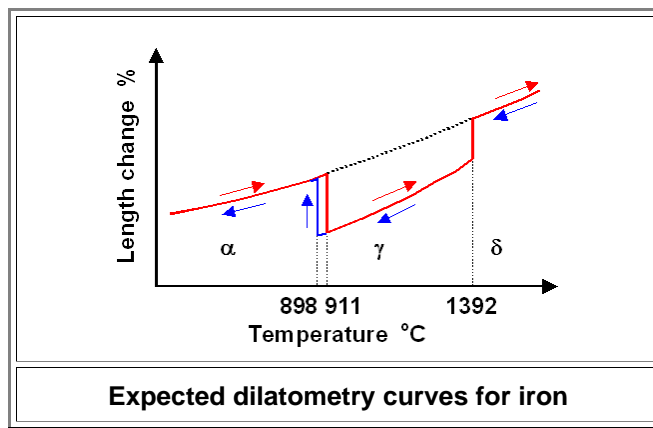
1. The *specimen size*. Different phases of the same materials typically have different densities. A given amount of material thus occupies different volumes for different phases. Iron, for example, contracts when it switches from a (not closely packed) bcc crystal to a closely packed fcc crystal. On top of these phase-change induced length changes is always the basic thermal expansion. This method is called **dilatometry**.
2. The **specific heat capacity c..** This is simply a measure of how much heat = energy it takes to increase the temperature of a standard sample by 1 K (= 1 °C or 1.8 °F). Phase changes consume or release additional heat (our "old" [heat of melting](#) or [heat of solidification](#) ) and thus announce their occurrence. This method is called **thermoanalysis**. Since it is mostly done by comparing the specimen under investigation to a standard specimen, it is better known as **Differential Thermo Analysis** or **DTA**

### Dilatometry

The principle is clear. You measure dimensional changes of your sample as a function of temperature. Usually you use an elongated sample like a rod, and you measure only its change in length.

There are many ways to measure length changes very sensitively, even at high temperatures. I won't go into that except to mention that with optical methods or with piezoelectric sensors you can measure length changes as small as nanometers. So, if you did acquire a (not so cheap) state-of-the-art dilatometer, the quality of your results depends mostly on the quality of your sample.

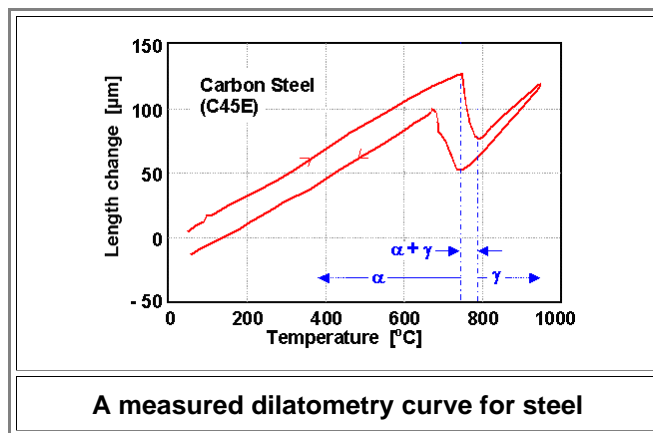
Here is what you can expect for pure iron and a perfect sample for slow heating / cooling rates:



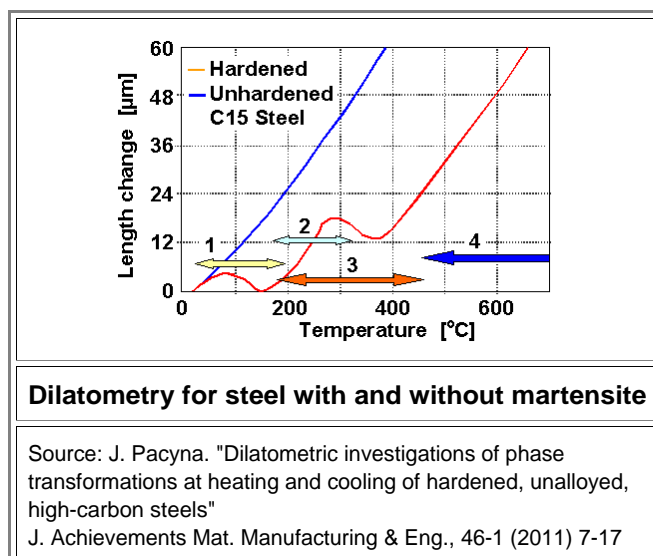
- As the temperature increases, the length of the specimen increases smoothly due to thermal expansion. At the  $\alpha \rightarrow \gamma$  transformation temperature of 911 °C (500 °F), however, the specimen gets suddenly shorter. This mirrors the change to the more closely packed fcc lattice. Further temperature increase produces again a length increase due to thermal expansion and a sudden "jump up" in dimension when the structure changes back to the bcc phase now called  $\delta$ .

Reducing the temperature produces the old curve for high temperatures but a somewhat retarded dimensional change at medium or low temperatures because nucleation for the new phase takes time and the growth needs some driving force. Of course, if one would cool down extremely slowly, all dimensional jumps would be at the same temperature in principle. In reality, you just can't spend the time required for equilibrium at medium or low temperatures.

Now let's look at what one *really* gets:



- Not too bad but not ideal either. The data are a bit more complicated than what we expected for pure iron. One of the reasons for this is that here we have *steel* (0.45 % C) and not pure iron. The phase changes in both directions then occur over a range of temperatures, indicating the mixed phase  $\alpha + \gamma$ . Here is an example of a dilatometry measurement where a lot is going on:



- Compared are two specimen of the same steel (0.15 % C). One ("unhardened") was slowly cooled; the other one ("hardened") was quenched so that martensite was formed. The unhardened sample only elongates due to thermal expansion when heated, but the hardened sample shows a quite different behavior, contracting twice in the process

A detailed analysis yielded the following data:

In **region 1** the first negative effect occurs. What happens is that the carbon contained in the martensite starts to precipitate. It is doing that by first forming very small **transient** or unstable carbides like- $\text{Fe}_5\text{C}_2$  ( $\chi$ ),  $\text{Fe}_{2.4}\text{C}$  ( $\epsilon$ ) and  $-\text{Fe}_2\text{C}$  ( $\eta$ ). This is quite similar to what was going on in the Al-Cu system that we [looked at before](#).

The second negative dilatation effect occurs in **region 3**. Here the sample shrinkage is related to the formation of regular cementite  $\text{Fe}_3\text{C}$  that nucleates and grows independently from the transient carbides. The process starts at a temperature of about 200 °C (392 °F) and continues up to a temperature of about 425 °C (800 °F), while the transient carbides shrink. All this carbide formation reduces the dimensions because all carbides pack carbon and iron more densely than martensite.

However, while cementite forms in **region 3**, the retained austenite turns into ferrite and cementite (in the structure of lower bainite). This happens predominantly in **region 2** and leads to a volume increase. This effect overcompensates the the shrinkage due to cementite formation for a while, and in total we see the volume increase before it comes down again.

In **region 4** carbon precipitation is finished and we have normal thermal expansion. It is a bit slower than in the unhardened sample because the many very small carbide precipitates start to rearrange themselves into larger aggregates by some kind of [Ostwald ripening](#).

Of course, you don't get this interpretation just by looking at the curves for a long time. You need, e.g., supporting information from some kind of microscopy.

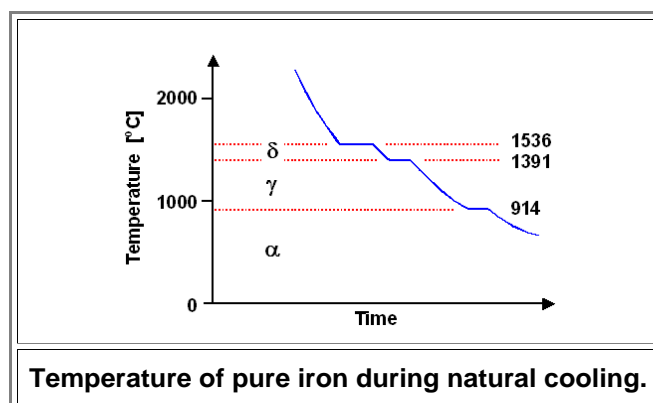
Much more could be said to dilatometry but the examples given must suffice.

### Differential Thermo Analysis

Why do we need thermoanalysis when we have dilatometry? Simple: dilatometry doesn't always work. For example, two different phases might happen to have about the same density and then would not show up in dilatometry. Also, you need sizeable samples with a defined geometry (typically a rod) to get good results.

- For thermoanalysis, small samples in any shape might be good enough. The procedure can be simple, too. You can get good data already by just measuring the temperature of your sample as it cools down naturally in some cold environment.

For pure iron you will get curves like this one:



- Whenever a phase change occurs the temperature stays constant for a while since heat is released. You have witnessed that many times when the outside cools down and water begins to freeze. The temperature of the water plus the ice will stay at exactly 0 °C ( 32 °F) until all water is solid—no matter how cold it is. Solidification releases the "**heat of fusion**" or "heat of solidification", which must be transported out of the system. We learned all about that in the [segregation module](#).

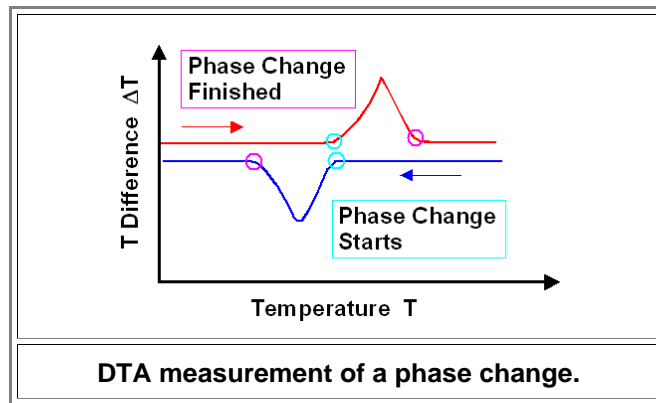
Going in reverse, meaning heating instead of cooling, you need to supply exactly the same amount of energy to melt the material, but now we call it "**heat of melting**".

**All** phase changes release or consume energy during cooling or heating, respectively, at the temperature where the phase change occurs . The reason is deeply entrenched in the [second law](#). On the way to lower temperature you (the crystal) want to lower your entropy; the thing to do is to get more orderly. A phase change happens at some temperature  $T_{PC}$  if that helps in that respect, and typically gets rid of a lot of entropy  $S_{PC}$ . The energy going with that is  $\pm TS_{PC}$ . Heating up you need to "pay" this amount of energy, cooling down you get it back.

So just keeping track of the specimen temperature while it is heated or cooled will give you some ideas about the phase changes occurring. But we can do better than that:

1. We do not just heat up or cool down "naturally" but in a controlled oven. In other words, we have a slowly increasing or decreasing and fully controlled environment temperature.
2. We measure the temperature of the sample *and* simultaneously the temperature of a reference sample that does not show phase changes in the temperature range considered. What we plot is the difference  $\Delta T$  of the temperature of the two samples. This is far more pronounced than the direct change in temperature

- The temperature difference  $\Delta T$  is small except when a phase change occurs. If heat is released or needed for a phase change during cooling / heating, the actual sample will stay hotter / colder than the reference sample for a while, and  $\Delta T$  shows a negative / positive peak, roughly like this:



Nowadays, with fully automated equipment and computerized data analysis, DTA branched into several more sophisticated techniques that I will not go into. Suffice it to say that we can determine experimentally the diagrams we need. But don't forget: Even with highly sophisticated equipment, you still need many samples with different compositions that you must run through your analytical tools before you can construct a phase diagram. For TTT and CCT diagrams you need many samples of the same kind with the same microstructure for starters.

- Somebody needs to make these samples, pre-characterize them, run them through the dilatometer and / or thermoanalyzer, look at the microstructure after analysis or in between, and compile the data. Time to look for a [graduate student](#).



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