3. Supercooling and Microstructure

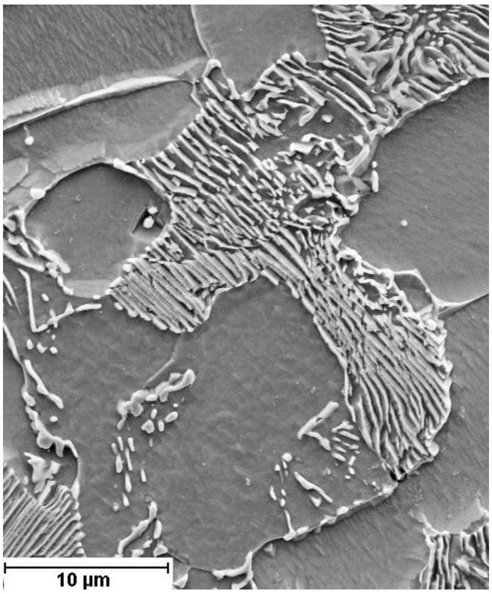
Segregation and Microstructure

Wen we look at the microstructure of a piece of iron or steel at room temperature, we see the result of all the processes that took place in the making of that sample. The microstructure encodes the whole history of that piece of material.
In human history, some events may not have left any traces whatsoever. Just think of all the major pieces of art that existed some thousand years ago somewhere on this planet, and about which we know exactly nothing. They are gone without leaving a known trace - just like your great-great-....great-grandfather and many other events that influenced what you are now.
Same thing for iron and steel. Things that happened at high temperature may not have left obvious traces at room temperature. Nevertheless, some piece of iron existing now came into being by something that happened in the past, exactly like you. In your case you can even date that event with some precision (your birthday minus nine month), in the case of iron, it is more difficult. Taking a close look at your structure (bodily and mental) or the iron microstructure, allows to infer many - but never all - things that happened to the specimen in questions after it came into being. How much we can learn, and how sure we can be about inferences we make, depends to some extent on how closely we look.

- Considering steel only, histories might be found somewhere inside the "parameter space" defined by extremes like:

  - The steel was never ever liquid, lived through several thermal histories (heating and cooling) and was shaped mainly be forging. That is true for most old steel objects.
  - The steel was liquid (just barely), cooled down slowly, and then was used for forging as above. This -roughly- covers wootz steel.
  - The steel was liquid, cast in a form, cooled down relatively fast, and is used pretty much "as cast". That's how some "raw" steel is made today.
  - The steel was liquid, is cast continuously into a "band" and subjected to some deformation by rolling as it cools down. That's how huge rolls of steel bands are made today, used, e.g., to form the body of your car.
  - The steel was liquid, cast in a form, cooled down at some defined rate, and subsequently subjected to heat treatments and some forging. That's the major way for making high-quality steel parts.

  Even if we would start from always the same composition - iron with 0.8 % carbon, for example - the microstructures we find could be very different. There are many microstructure pictures in this Hyperscript to illustrate this (find them!), here is just one example:

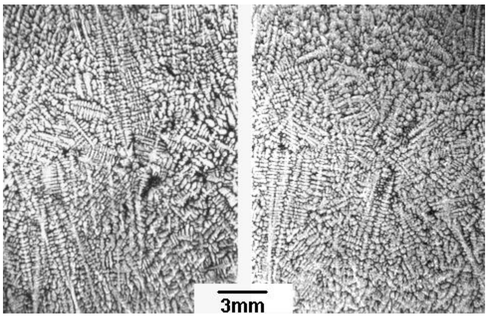


Microstructure of ≈ 0.3 % carbon steel

This is an SEM picture, taking by one of my students after elaborate specimen preparation. It shows grains of ferrite and pearlite. The cementite lamellae are nicely visible. (Go to the beginning of chapter 7 for the meaning of the terms). No dendrites are visible, even at low magnification.

- What you don't see in this example are the dendrites that figured so prominently in the preceding module and that I linked to *segregation*, causing constitutional supercooling.
  I don't know the history of that particular piece of steel but am sure that it was once liquid and then was cast. Dendritic structures may or may not have been there when it first solidified. It they were there, they have been wiped out by the phase transformation to γ + cementite and pearlite during cooling, and possible forging in between.

However, a *steel* microstructure might also look like this:



Dendrites in 9% nickel steel

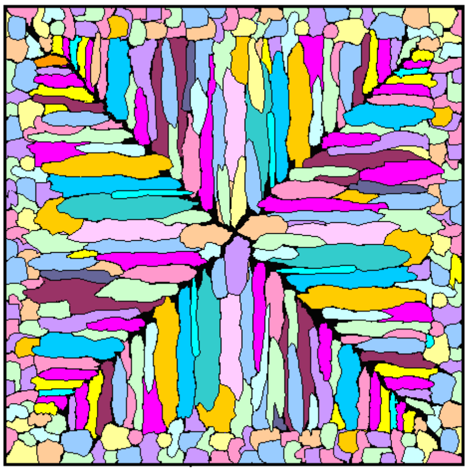
Source: J. Muramaya and T. Kunitake. "Internal Cracks in Cast Steel With 9% Ni for Cryogenic Applications" , Handbook of Case Histories in Failure Analysis, Vol 1, K.A. Esakul, Ed., ASM International, 1992

- Notice the huge difference in scale between the two pictures! The top picture would only cover the "dot of an i" in the lower picture.
  Clear dendrites with sizes of millimeters are visible, and that is not unusual for other steels, too. These dendrites may have been formed because of constitutional supercooling and thus are a result of segregation. In other words, and to make myself perfectly clear: Segregation phenomena often influence the final microstructure. They survive at room temperature in this case because in Fe - 9% Ni the liquid solidifies pretty much directly into austenite that might survive all the way down to room temperature. The phase diagram of Fe - Ni, in other words, is quite different from that of Fe - C.
  In other words: If you see dendrites at room temperature, you produced them during solidification. If you don't see them, it *could* mean that there weren't any - but you cannot be sure.
- When we discuss segregation, we must make a clear distinction between:

1. The influence of segregation on the final microstructure.
2. Macro and micro segregation of constituents and impurities in the final microstructure

Casting a Pure Metal and Microstructure

So let's first look at the microstructure. To make things simple, I will first consider a *pure* metal. There is then no segregation because there is nothing that could segregate. In other words, let's look at the very basics of what is going on during **casting**
Let's pour some pure liquid metal into some cube-shaped mould. Then we cut the cast cuboid, about in the middle, and look at the microstructure by examining the surface after proper preparation to reveal defects like grain boundaries. What we will find might look like this:



Very schematic figure of grain structure after casting a *pure* metal

- Colors symbolize different grain orientations. A real picture taken with a microscope does not really show the crystal orientation; at best you see the differences in reflection caused by this. It therefore looks rather monochromatic, as illustrated below.

On the outside we have a fine-grained structure consisting of small equi-axed crystals know as **chill crystals**. Equi-axed means that all axes are about the same length or simply that the crystals look about the same in every direction. The chill crystals would be smaller than shown above, but my artistic skills are limited. They also would look rather different for moulds that conduct heat very well (e.g. metal moulds) or very badly (e.g. "sand casting" moulds).

- After the chill layer, we find large grains, elongated in the direction perpendicular to the wall of the mould. Obviously they start growing from all four sides of the cube-shaped mold at the same time and stop when the hit their colleagues from the other sides. The black background at the diagonals, where those grains run into each other, symbolizes that you might find some holes and other coarse defects there. That might happen, for example, because some tiny droplets of liquid find themselves trapped between already solidified parts there. When they finally solidify they must shrink and have no choice but to leave a pore behind.
  Below is a real picture; it shows a detail from the micro structure of *pure* copper (Cu) as shown in the backbone . Both types of grains are clearly visible: The chill layer and the larger elongated grains are growing in a radial direction here. We do not see anything that looks likes dendrites - but that that doesn't mean that there weren't any! Can you figure out why? No? Then look here.

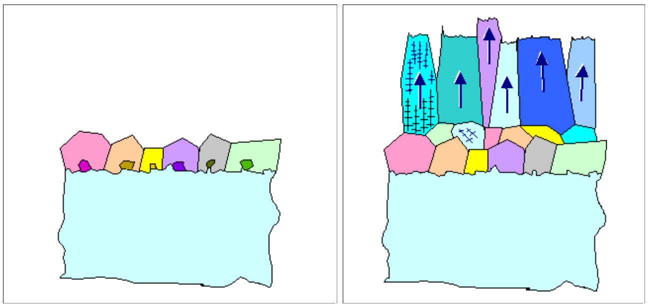
Detail of continuously cast pure copper bar (83 mm diameter)

Source: German Wiki; http://commons.wikimedia.org/wiki/File:Cu-Scheibe.JPG?uselang=de

- Note also the *striations* (vague lines roughly parallel to the perimeter) that may or may not indicate varying concentrations of some impurity (i.e. micro segregation). In this case it is rather clear that they are just artifacts from turning the piece on a lathe (look at the center of the big picture to see why).

What has happened? At the moment the hot liquid touches the cold mould wall, temperatures in the liquid drop rapidly and *"normal" supercooling* might occur despite an abundance of nucleation sites on the mould wall. Nucleation might be easy but is just not fast enough to counter the outflow of heat and thus the supercooling of the melt. This happens most easily if the temperature of the melt is just above the melting point. Then not much energy has to flow out of the system to lower the temperature to a value below the melting point, making supercooling easy. From what I ascertained in the preceding module, we must expect dendritic growth whenever the liquid is supercooled; it doesn't matter for what reason. And that is indeed what we often find for non-pure materials like binary (or more complex) alloys. With luck, we can make the original dendritic structure visible at room temperature as in the steel example above.

- It is thus likely that upon contact of the melt with the cold mould walls, crystals nucleate and grow as dendrites - in all directions. This happens for some time, leading to a confusion of dendrites of various length and directions that obstruct each other, break off, allowing new ones to nucleate and grow and so on.
  What is going on is limited by nucleation. You just can't start new crystallites fast enough to account for the ones stopping because they run into obstacles. That implies that the amount of heat of solidification produced in this early phase cannot keep up with the amount of heat that flows out of the system - supercooling results.
  However, if we look back at the preceding module, it is the quotient or relation of the temperature gradient ***G*** and the interface velocity **v** that decides if there is supercooling. Only if ***G*/v** is smaller than some critical value, interfaces are not stable, indicating supercooling. So what you get depends on the kind of mould, the temperature of the mould, how much the liquid is overheated (hotter than the melting point), and so on.
- While all this happens the mould heats up - quickly in the case of a metal mould, slowly in the case of a ceramic mould - and the temperature gradient driving the heat removal comes down. Supercooling is less severe and growth - still dendritic - slows down some. The initial confusion of all kinds of dendrites has solidified into the small-grained chill layer as the space in between the dendrites must eventually solidify, too. Since dendrites oriented perpendicular to the mould walls can grow faster in the interior than inclined ones, the large elongated crystallites start to develop. They all must be oriented in such a way that fast growing crystal directions (usually <100> directions for cubic crystal) are perpendicular to the solid-liquid interface. The elongated grains seen at room temperature may have originated form a bunch of dendrites with about the same orientation in all directions. In the next grain the dendrites had about the same orientation in growth direction but a random orientation in the other directions. We then have **small-angle grain boundaries** between the dendrites in a grain, and large-angle grain boundaries between the grains.
  This is schematically indicated in the figure below:



Very schematic figure of grain structure after casting
Colors symbolize different grain orientations, arrows the fast growth direction of the dendrites in a grain; typically a <100> orientation.

Very first moment after "impact".
Formation of the chill layer without supercooling.
Small grains grow rapidly from primary nucleation sites (indicated by darker colors) at the mould wall.

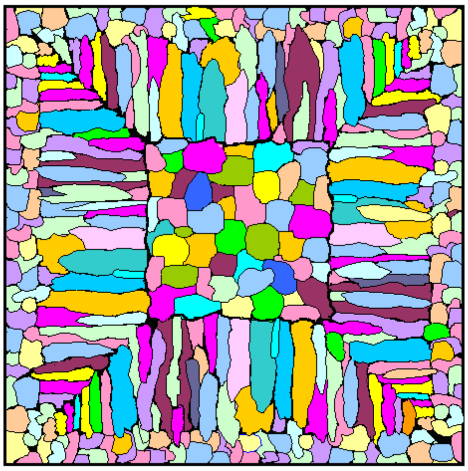
Shortly after "impact".
Another chill layer is added, already with some dendritic growth and the transition to directional dendritic growth occurs.
Dendrites are indicated in one grain.

- When two growth fronts meet - in the example above this will happen along the diagonals - it can happen that some liquid is trapped in "pouches" between already solidified parts. When these parts finally solidify, holes can develop since the solid typically occupies less volume than the liquid (the big exceptions being water and silicon (Si) that expand upon freezing). Along the "seams" we thus might expect more heavily distorted material.

- If we change the mold temperature or the cooling rate, the structure will look quite different in detail but roughly the same in general. Crystallization proceeds from the outside to the inside, and there will always be a tendency that the geometry of the solid-liquid interface is expressed in the microstructure, for example because grain boundaries tend to be perpendicular to it.
    - The microstructure will be **textured** , meaning that not all directions are the same on average. For example, some grain orientations are more prominent then others, or grains tend to be longer in some directions than in others. As a consequence, the properties of our cast material will not be *isotropic* or the same in all directions, and this is generally not so good.
    - Now to the question from above. *Why don't we see dendrites in the copper example?* Because after the liquid in between the dendrites has solidified, it is just pure copper, oriented in the same way as the dendrites in the grain and in no way different from the pure copper in the original dendrites. There is just nothing left to see.
      In contrast, the dendrites in the steel picture are visible because they reflect *segregation*, different concentrations of of impurities. The liquid in between the dendrite solidifies later and thus has different concentration of alloying elements and impurities compared to the alloy in the original dendrite. That's what is make visible after some kind of surface treatment and reveals the structure that was present during solidification.
- So far, we have looked a a hypothetical absolutely pure material that we cast into a cold mould. In a next step we could deviate from that just a *little bit*. We could, for example, introduce a tiny amount of some impurity and keep casting. We could also keep the pure material but crystallize very slowly with an almost planar solid-liquid interface. We can also do both things at the same time. The procedure then is called "*growing a silicon single crystal*" - and that is covered in a module of its own. You won't believe what tiny amounts of impurities can do to the final micro structure of a crystal!
    - In this module, however, we will now make a casting with a *binary alloy* or a ternary alloy or just about any mixture.

Microstructure of a Cast Binary Alloy

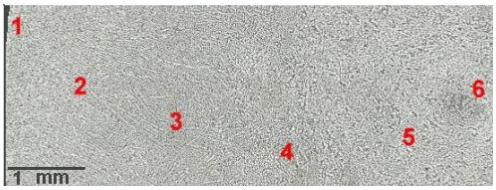
- Now let's look at a binary alloy, for example pure iron with 0.7 % or so carbon. Or just about any binary system with a low concentration of one component.
    - All other things being comparable to the example above, what we get now might *schematically* look like this:



Very schematic figure of grain structure after casting
a *binary* alloy

- The part that solidifies first looks not much different from that of the pure metal. The center, however, is very different - it consists now of "equi-axed", randomly oriented small grains. What has happened?
    - *Constitutional* supercooling has happened! Possibly on top of "normal" supercooling. Assuming that the minor constituent has a segregation coefficient smaller than one (rather common), it will prefer to remain in the melt. After a major part of the cast has solidified, the melt in the center is then rather enriched with the minor constituent, and thus has a *far lower melting point* than the original composition. That means we have *constitutional* supercooling on top of whatever else is going on and thus simply "heavier" supercooling in comparison to a pure substance. At some point in time this will now allow direct *homogeneous nucleation* of crystallites in the melt; check the nucleation module for details.
      Alternatively, small parts of the dendrites growing inwards might break off, floating around in the liquid, and supplying heterogeneous nuclei for crystals growing in the liquid. While the "breaking off" part could also happen with a pure substance, growth after heterogeneous nucleation is much faster if there is supercooling. Whatever, chances are that small solid particles will start to grow all over the supercooled liquid in the center of a cast of a

binary alloy. Convection in the melt might swirl them around, while gravity tends to sink them to the bottom. Whatever the detailed processes will be - in the center we will find the leftovers of equi-axed crystallites that generated in the melt, and that tends to be equi-axed small grains.
Of course, the figure above is schematic and idealized. Reality tends to be far messier. Here is an example:

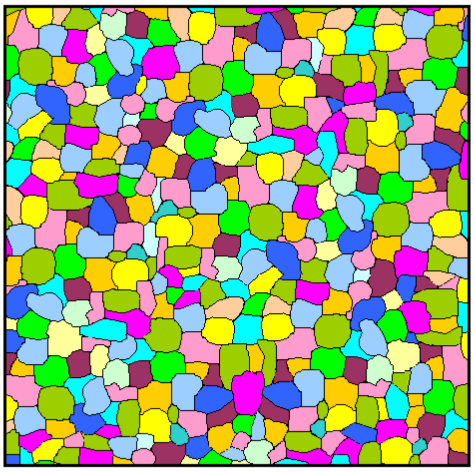


Structure of a cast steel
Large version

Source: http://www.metallograf.de/begriffe/gef-erstarrung.htm; with permission

- At "1" is the surface, around "6" the center of the cross-section through a round wire with 13 mm diameter.
  It is "1.5535 - 22MnB4" steel (or rather normal steel) with about (0,20 - 0,25) % C, 0,30 % Si, (0,90 - 1,20) % Mn and not much else. It was produced by continuous casting with magnetically stirred melt.
  You don't see much at this magnification. You can look a bit closer at the structure by using the large version or by switching to this illustration module. And don't complain! I did say that reality is far messier than what we like to show in nice schematic figures!

Now we get an idea. What do we have to do to produce the uniform small-grained structure shown below? That structure must be far better for most applications than the non-uniform structures obtained so far, so we want it.



Very schematic figure of ideal grain structure after casting.
Typically you also want small grains.

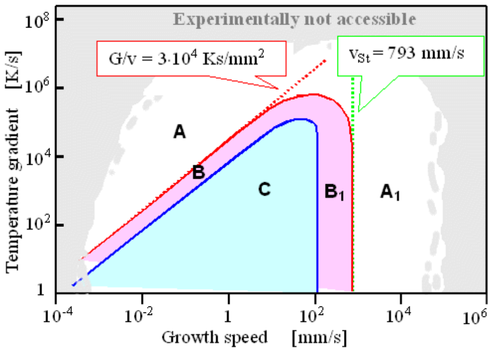
It's obvious: Supply easy nucleation in the melt! Have some very small solid particles floating around when you pour the liquid stuff into a mould. That will enlarge the central part of the microstructure shown farther above, and that's what we want.

- Is that true? Well, yes - up to a point. In reality, it is far more complicated.

Summing Up

In the preceding "Constitutional Supercooling and Interface Stability" module I have made clear that supercooling provides for interface instabilities and that a lot might happen then. The decisive quantity from the simple theory was the relation ***G*/v**, the quotient of the thermal gradient ***G*** at the interface and the velocity **v** of the interface. As soon as this number became smaller than some critical value, the interface becomes unstable.

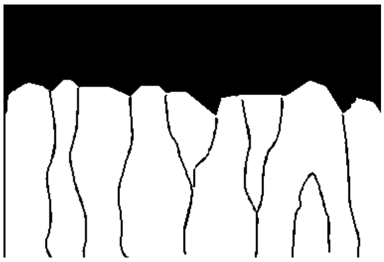
- More sophisticated theories show that this is indeed a good condition for "normal" casting or solid-liquid interface velocities. However, it fails at very large growth rates **v**. Taking this into account, a kind of "master" curve can be derived that looks, for example, like this:

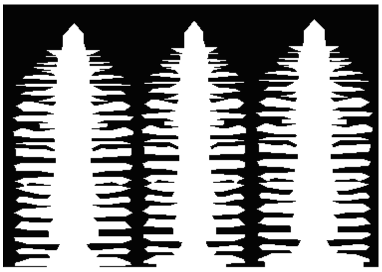


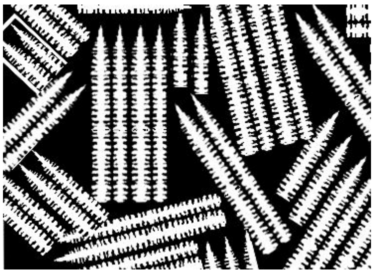
Relation between temperature gradient, growth speed, and growth modes for the nickel super alloy IN

Source: Redrawn after lecture notes form R: Völkl, Uni Bayreuth

- Note that this is a *quantitative* diagram with logarithmic axes. Nickel super alloys are used for jet turbines and the microstructure of these parts is of supreme importance and thus has caused a lot of research. The diagram is remarkable because it covers a huge parameter space - growth speeds and temperature gradients run over 10 or 8 orders of magnitudes, respectively!
  While it is easy to draw curves with very small or very large parameters; it is not so easy to do experiments at extreme condition. In reality not all combinations of parameters can be realized; this is indicated by the grey shadowing (my guess).
  Note also that interface velocities around a few mm/s are already very fast!
  - Inside the colored areas the interface is unstable while in the "**A**" and "**A_1**" areas but planar growth nonetheless occurs. I imagine that you can imagine that and therefore do not give a schematic figure. More interesting is what happens at **B** and **C**:

	**Region B:** Cellular growth takes place

	**Region C** Large dendrites grow perpendicular to the solid-liquid interface

	**Region C carrying over to B_1** Transition from fine dendrites growing in all directions in C to small equi-axed grains in B_1

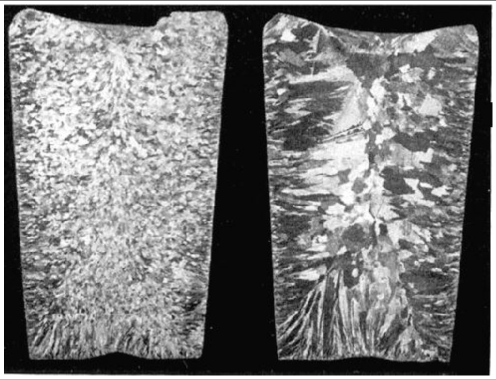
We can make that a bit more quantitative. There are some basic relations between the size of dendrites and the interface speed **v**:

Average distance between dendrites $\propto \frac{1}{v^4}$

Average distance between dendrite secondary arms $\propto \frac{1}{v^3}$

Average radius of dendrite tip $\propto \frac{1}{v^2}$

- What that tells us is that the structure gets rapidly finer with increasing interface velocity. This gives us an idea. If we pour a *superheated* melt into the mould, i.e. a liquid that is much hotter then the melting point, we have to remove far more thermal energy compared to pouring a melt just a little bit above the melting point. For the "cold" melt crystallization can occur faster and that means that the solid-liquid interface can move faster and the microstructure thus should be finer.
  In other words: I'm introducing another variable for casting, the **superheating of the melt.** It works quite well, as one can see from this example:



Melt temperature: 1100 K | Melt temperature: 1170

Microstructure of cast aluminum (+ 0.02 % titanium)
for different superheating of the melt

Source: From lecture notes of R: Völkl, Uni Bayreuth

- The melting point of aluminum is 934 K. Note the depression on top due to the volume contraction upon solidification

In this module I focussed on the microstructure of a cast object, or just about any object that results from a liquid-solid phase transformation. There is an obvious simple conclusion:

Casting is an exceedingly difficult part of Materials Science!

- And I haven't even covered what remains of segregation at room temperature! I will look into that in the next module.

- Back to Segregation Science
- On to
  - 1. Basics of Segregation
  - 2. Constitutional Supercooling and Interface Stability
  - **3. Supercooling and Microstructure** This module
  - 4. Segregation at High and Ambient Temperatures
  - 5. Striations

  - Segregation and Striations in CZ Silicon
  - Microsegregation and "Current Burst" theory