

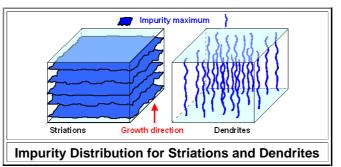
Segregation Science



5. Striations

What are Striations ?

The "water" pattern on wootz blades results from relatively large Fe₃ C cementite precipitates that are distributed in a "striated" manner. What does the mean? A picture is better than many words:



I define a *striated distribution of impurities* (or alloying atoms) as a quasi-periodic sequence of (possibly somewhat warped) planes *parallel* to the solid-liquid interface that are the loci of the highest impurity concentrations.

This is schematically shown on the left-hand site of the drawing above.

In contrast, the loci of high impurity concentrations that we get by dendritic growth occurs in (possibly somewhat warped) *lines* that are *perpendicular* to the solid-liquid interface.

This is schematically shown on the right-hand site of the drawing above.

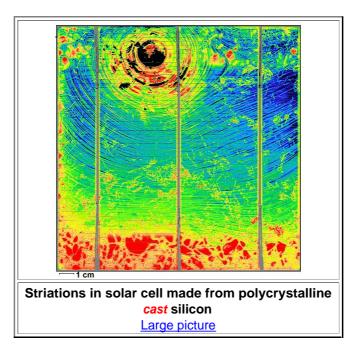
The distribution of carbides may follow these geometries. It is thus not uniform and may produce some pattern on the surface of a blade. However, only a *striated* pattern of cementite particles will give a *genuine* or "nice" wootz pattern, as we <u>shall see later</u>. We thus need striations of something suitable for nucleating cementite in our wootz starting material. Just having dendrites is not good enough! So how do we get striations?

The time has come to point out one of the little dirty secrets of segregation science:

Striations are very common. There is, to the best of my knowledge, no general theory of striations.

I'll give you *my* general theory on striations in <u>this module</u>. Here I first give you an example, and then discuss some pertinent features of striations.

The example comes from the research of my group and concerns silicon (Si) used for solar cells



Colors encode an electrical parameter of the solar cell. The three grey vertical lines and the faint horizontal lines show the "grid", the metallic contact to the surface of the cell. The striations are the diffuse lines circling around the "black sun" on top.

The picture is obtained by scanning a light beam across the solar cell and measuring some "electrical" response of the cell to the local illumination. The technique is rather complex (involving heavy complex-number math, for example) but doesn't need to worry us here. In essence, the method measures the local impurity concentration on a ppm level.

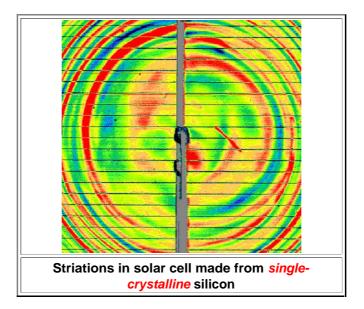
The striations clearly follow the contours of the former solid-liquid interface. They are not at all related to the grain structure, which is clearly visible in the red bottom part, and faintly in the greenish sector. They are also not related to dendrites except that dendrites also follow the contours of the liquid-solid interface up to a point: they are perpendicular to it. The distance between prominent striations is about 1 mm or somewhat less.

From this and other pictures it is clear that we have a striated distribution of impurities, following the contours of the solid-liquid interface throughout the whole block.

How the slice of silicon from which the solar cell was made was cut out of the big cast silicon block is shown below.

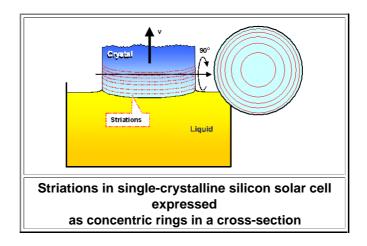
Solid-liquid interface Cross-section cast block	Cross-section through the middle of a cast silicon (Si) block. Since silicon expands upon freezing (like water, big exception!), it produces a "bump" that solidifies last instead of a <u>depression like all metals</u> . The last part to solidify also contains a high impurity concentration.
Geometry of silicon block and cut-out Si slice	

Now let's look with the same method at a solar cell made from *single crystalline* silicon:



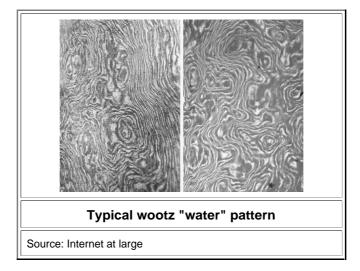
Colors encode an electrical parameter of the solar cell. The solar cell is about (4×4) cm² in this case and was cut from the center of a single crystalline Si wafer.

The concentric rings are supposed to be striations indicating the solid-liquid interface??? Yes, indeed! Why the concentric rings are traces of the solid-liquid interfaces becomes clear from this drawing:



Cutting a slice of the growing crystal will show concentric rings (actually a spiral) as the loci of highest impurity concentration.

This schematic figure, by the way, also goes a long way in explaining the "water pattern" on wootz blades; just look at the picture below.

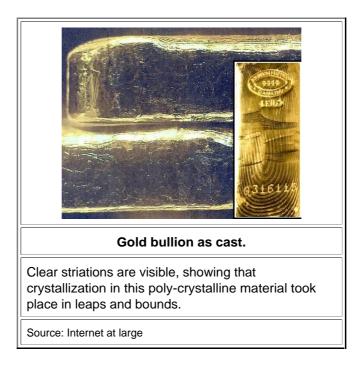


It is clear that the pattern results from cutting through a "warped" sequence of striations and not by cutting through dendrite "lines", cf. the <u>picture above</u>. How a striated variation of some impurity can cause the formation of large defects in an arrangement mirroring the striations can be seen in <u>this link</u>.

If you wonder what striations in silicon are going to tell us about wootz blades, I need to advice you now about the following points:

- You *do* find similar striations in nearly all single crystals. This is a truth backed by mountains of literature, for example the 1.800 pages monograph: "Springer Handbuch of Crystal growth" <u>1</u>) from 2010.
 - You would find similar striations in nearly all cast solids if you would look for them.

Here is a picture illustrating the second point. I found it some time after I wrote this module:



It's quite simple. Single crystal growth is a complex art, less than 40 years old, and the results are investigated thoroughly and in all directions. It's not so difficult to do because single crystals tend to be small. That's why there are many reports of striations.

Pouring liquid steel (or copper alloy, or any other metal alloy) into a mould is a well-established and highly optimized process for as long as 4000 years in some cases. You know what you get, no detailed structural investigations are needed any more. Nobody in her right mind would start investigations to search for something that is clearly irrelevant for the product. Not to mention that cast objects are often rather large and not easily put under a microscope.

I would be inclined to bet the fortune of my wife that one would find striations in most materials that resulted from a liquid-solid phase transformation under certain (rather common) conditions. In a <u>special module</u> I tell you why.

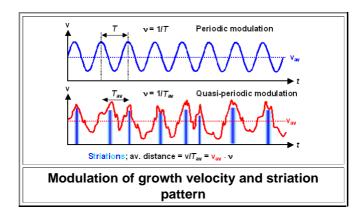
Here, I will give you just an idea of what causes striation.

The Origin of Striations

In the ponderous volume <u>mentioned above</u>, we read: "*Striations .. arise from fluctuations of the growth conditions, such as changes of the temperature, cooling rate, pressure, or convections in the solution or melt. These fluctuations lead to temporary changes in the growth rate and thus to changes in the impurity incorporation*". Yes, indeed! The only question is: what causes those fluctuations of the growth conditions?

There is more than one answer. Ken Jackson, in <u>his recollection</u> of the heroic days of "<u>inventing</u>" constitutional supercooling, shows a picture of striations (he calls it "banding") that was caused by convection in the melt. Vibrations due to some motors, rotating the crucible (not uncommon), and God knows what other kinds of external disturbances of a *periodic kind* are known to cause striations. But that cannot possibly be the one and only general answer!

Whatever, what obviously must happen is that the solid-liquid interface proceeds by switching from periods of relatively fast velocity to periods of relatively slow velocities in a quasi-periodic fashion like this:



The quasi-periodic modulation of the growth velocity could be more unordered or more like the sinus curve above, looking like a saw-tooth pattern, whatever. You get the drift: as long as we have a clearly recognizable average frequency v_{av} , leading to a quasi-periodic spacing of impurity concentration maxima (and minima) with an average spacing $d_{St} = v_{av} \cdot v_{av}$, we have quasi-periodic behavior. I spare you the bit about the Fourier transforms and so on.

It is important to realize that "good" striations do not quite fit the typical scales of micro or macrosegregation; they tend to be in between on a scale of typically several 10 µm to mm.

So why do we find striations ever so often? I'll give you the gist of my answer here, details can be found in this module.

First: Solid-liquid interfaces are always chaotic on some scale. There is just no way that exactly the same thing happens at any "pixel" in an area typically many cm² large *and* at any instant in time. There are always fluctuations, at least on a small scale.

In other words: there is no such thing as *steady state* on small time and distance scales. If we look at some small part of an advancing solid-liquid interface (a "pixel") at some point \underline{r} and at time t, we "see" what is happening. What is happening *next* at $t + \Delta t$ or at neighboring pixels at $r + \Delta \underline{r}$ is about, but not quite, the same thing. There is a stochastic component, a probability that describes unavoidable fluctuations.

Second: When the interface becomes unstable due to supercooling, the stochastic components get larger, fluctuations increase, and differences between here and there and now and then get larger. Almost miraculously, however, order or pattern may emerge as the fluctuations increase.

Let's look at dendrite formation as an example for order emerging from fluctuations. At a first glance, there seems to be nothing new; it correspond to what I covered <u>here</u>. But actually at this point we encounter a "bifurcation point", to (ab)use a chaos theory expression, where theory can go two ways:

1. Conventional theory for dendrites: Steady-state is assumed. In other words: Everything looks the same at all times. All dendrites grow a certain length per time unit, and the space between the dendrite solidifies with the same speed some distance behind the dendrite tips.

That's what all theories that are expressed in differential equations or just analytical expression always predict. Well - it's wrong. At best it is only correct as an average over time.

2. Stochastic pattern-formation theory: Steady state, while possible in principle, is extremely unlikely to obtain. On the scale of dendrites we have a stop-and-go situation. Dendrites grow quickly some distance, stop or slow down, speed up again, and so on. One period takes, on average the time t_{av}.

Alternatively, dendrites grow quickly some distance, stop, slow down and die because they were overtaken by other dendrites or because a new dendrite nucleates in the neighborhood, or.... Whatever. The situation is dynamic, things happen, and what you see here and now, is different from there an then. There is a time-dependence (not yet quasi-periodic) of what is going on. Since *on average* we will get exactly what steady-state models predict, the time dependence of any parameter must go through ups and downs, it must fluctuate or oscillate around some average value. That's also a way to describe chaos.

However, order may yet emerge from chaos. That will happen if the local up-down or on-off events *synchronize* to some extent. For example, dendrites may grow quickly some distance, stop, grow again, and so on. If they do that independently of each other, you have "chaos" on small distance and time scales but well defined averages on somewhat larger scale. It those dendrite *synchronize*, meaning that they do what they do in a kind of (messy) lock step, things are entirely different. Most dendrites then start growing or speeding up around the same time, and they stop growing or slow down around the same time. The whole interface then moves in a stop-and-go fashion, and that is exactly what we need for striations.

Synchronization (or "phase coupling") is the key word. Why should that occur?

Dendrite dynamics (or anything else) can synchronize for two major reasons:

- 1. Some *outside disturbance* just happens to have about the right frequency $v \approx 1/t_{av}$. This could easily do the trick and get the whole bunch to perform rhythmically. It's not unlike what would happen if a lot of people swerve around to some music in their heads, all with different speeds. The someone turns on a soft rhythmical noise. Almost everybody will then dance to the external rhythm but still to the music in the head.
- 2. There is some interaction between neighbors. It doesn't need to be very specific. Many different ways of relating to thy neighbor will bring about some synchronization.

In case you didn't notice: I'm talking pattern formation, or self-organization here; creating order out of chaos. Keywords that describe a pretty large part of theoretical physics. A part, unfortunately, that is not given to easy explanations and simple equations.

Nevertheless, self-organized pattern formation happens quite a lot in very different systems. I investigated that myself (by telling the really smart members of my group what to do) for a long time in systems that are, up to a point, the reverse of crystallization: dissolution of (semiconductor) crystals with some currents flowing through them in electrolytes (typically acids). For this we developed a theory that deals with the quasi-periodic pattern formation often observed in these systems. In this <u>advanced module</u> I will go into the details. Here we only note:

Striations, mirroring the liquid-solid interface geometry, are expressions of rhythmically advancing interfaces obtained by selforganization

Back to Segregation Science

On to

- 1. Basics of Segregation
- 2. Constitutional Supercooling and Interface Stability
- <u>3. Supercooling and Microstructure</u>
- <u>4. Segregation at High and Ambient Temperatures</u>
- 5. Striations This module
- Segregation and Striations in CZ Silicon
- Microsegregation and "Current Burst" theory