11.5.2 Structure by Dendrites?

Verhoeven's Dendrite Model Step by Step

Let's start by looking closely at Verhoeven's "**nice wootz structure by dendrites**" hypothesis. A short version of the "structure by dendrites" hypothesis a given in this module; I will repeat it here for easier reading:
According to Verhoeven, what you need for making a wootz sword with a "nice" pattern that is based on a striated distribution of cementite as discussed before, are the following ingredients:

1. Proper starting material. If you want a "nice" pattern it is *not* sufficient (as Wadsworth claims) to have broken-up cementite particle in the starting UHSC that align themselves to a pattern upon rolling or forging.
2. You need traces of certain elements known as strong carbide formers (vanadium is best) in your starting material. These elements act as nucleation centers for metal carbide particles like VC or some combination of V-Fe-C and their formation competes and interacts with the "normal" Fe_3C cementite formation.
3. The distribution of the metal carbide particles in the final blade must have the same basic pattern as the cementite particles that actually form the visible pattern. This necessitates an inhomogeneous distribution of the crucial impurities in the starting material, and that comes about because:
4. Something that happens during the dendritic solidification of the original melt that produces a suitable inhomogeneous distribution of the metal carbides, which, upon drawing the ingot into a blade by forging (or rolling), produces a suitable *banding* i.e. the required layered structure of the cementite particles.
5. Points 1- 4 might already be sufficient for producing a pattern. For the formation of a well-visible *nice* pattern you need in addition several temperature cycles during (low temperature) forging,

Yes, this is quite complicated. And let me make clear right away that the " *banding*" mentioned above, while playing a key role in the whole process of wootz blade making, is a process that might also happen in modern steel making and that it is something that is not very well understood at present.

- Verhoeven and "his" master smith Al Pendray have succeeded in producing a very good kirk nardeban and rose pattern from scratch. So far nobody else seems to have been able to do that. That is certainly a strong point in the favor of Verhoeven's "dendrite" hypothesis, if not an outright proof? Well - not quite. Lots of ancient smiths have also produced "kirk nardeban" patterns from scratch, and their theories, if they had any, were certainly wrong.
  In what follows I'll discuss the "structure by dendrites" hypothesis of Verhoeven in some detail and put it into perspective. His 2007 paper, accessible by this link, provides the base.

First, let me point out that Verhoeven's hypothesis could easily work - provided a few "minor" points are met. It could easily work because most of it is based on sound and well-known scientific ingredients.
The first point to look at is the solidification of a liquid iron - carbon mix, that also contains traces of some key impurities, via formation of dendrites.. That is not an easy thing to do. I have given you an "easy" backbone module for the topic and you might want to refresh your memory now by looking at it.

- If you're not easily scared, you may also want to look at the following science modules dealing with solidification, segregation and dendritic growth:

  1. **Basics of Segregation**.
     Topics covered are: 1. Some basics about segregations. 2. Phase diagrams, "macroscopic" segregation and the segregation coefficient. 3. The flow of energy and particle currents through the solid-liquid interface during freezing - and what it implies.
     Mostly prose. Discussing why solidification is so unbelievably complex as soon as one looks at details.
  2. **Constitutional Supercooling and Interface Stability**
     Topics covered are: 1. Non-equilibrium and how systems try to get back to equilibrium. Exploiting the difference between currents and current densities. 2. What is constitutional supercooling and calculations for a simple model. 3. Supercooling, interface stability and dendritic growth plus some remarks to convection in the melt.
     Getting to the heart of dendrite formation. Some equations and a lot of illustrations.
  3. **Supercooling and Microstructure**.
     Topics covered are: 1 How supercooling plus segregation determines the microstructure of the forming solid. 2. A closer look at what happens when we cast an object. 3. Temperature gradient and interfaces velocity are the most important parameters for the microstructure.
     What solid structures look like depending on crystallization conditions. The relation between dendrites and grains.
  4. **4. Segregation at High and Ambient Temperatures**
     Topics covered are: 1 What could happen during cooling. 2. A simple model for macrosegregation at high temperatures 3. Microsegregation at high temperatures. 4. What is left at room temperature and a simple way to look at the effects of diffusion. The importance of microsegregation for the nucleation of precipitates.
     How the room temperature structure evolves and what all the impurities are doing till the end
  5. **Striations**.
     Striations, an universal expression of microsegregation, are necessary for wootz steel patterns but not contained in the preceding modules. Examples are given and discussed.

Forming striations right during solidification. This might happen in steel and certainly does happen in some materials. It might have some bearing on wootz pattern formation.

Now let's look at Verhoeven's "nice wootz structure by dendrites" hypothesis step by step. Before I start I need to point out two things:

1. Verhoeven does not always explicitly list the necessary spheroidization of the cementite. It thus must happen "on the side"; something entirely possible. Nevertheless, it is important.
2. In some of his papers Verhoeven seems to imply that the necessary layered structure of the cementites, also called "banding", comes directly from a banded structure of the carbide formers in the originally wootz cake. This is not correct. Verhoeven does not mean to imply that. Here is a quote with the correct statement (from this link): "*...the large mechanical deformation at the hot rolling temperatures has caused the planes of dendrites ... to rotate parallel to the surface of the steel plate during hot rolling...*".
   What this means is that he forging (or rolling) is instrumental for obtaining a good layered cementite structure.

First step: Have Strong Carbide Formers

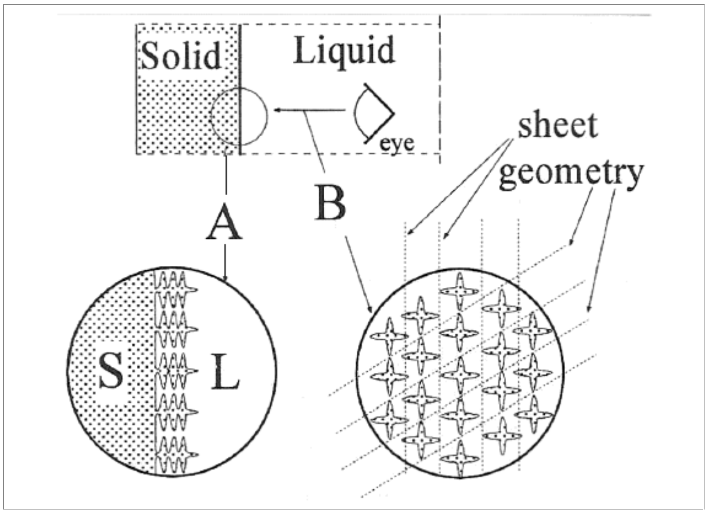
For starters, the high-carbon crucible steel material must contain some impurities that are strong carbide formers like (Nb), titanium (Ti) or vanadium. In the "science of alloying" module I have written:
" ***Very strong*** **carbide forming elements**, such as niobium (Nb), titanium (Ti) and vanadium (V), always form alloy carbides, preferentially at alloying concentrations less than 0.1 %. The microstructures of steels containing these elements will be radically altered."
Note that these elements form niobium, titanium or vanadium carbides and *not* iron carbide or cementite in the first step.

- Verhoeven claims a vanadium (V) level as low as 0.004 % is sufficient to cause nice wootz patterns later. Other just "strong" carbide formers like molybdenum (Mo), chromium (Cr) and tungsten (W) might also be good.
  A concentration of 0.004 % or 40 ppm is extremely low for iron / steel. Plenty of ancient crucible steels might have contained these impurities at such low levels. There is no particular problem yet with Verhoeven's hypothesis. However, it does sort UHCS samples in two camps: those with the proper impurities and those without. Only the first group is suitable for making blades with nice wootz pattern.
  Wadsworth would disagree

Second step: Have large dendrites during solidification

Solidify in such a way that *large dendrites* are produced at the solid-liquid interface. Note that it is not good enough to have dendrites. They must be rather large because in Verhoeven's model their average distance determines the distance between the cementite bands that form the pattern in the blade. Since forging reduces this distance (akin to what is shown here), it needs to be in the 0.5 mm region.

- To achieve that is quite possible. I have provided already several pictures that show large dendrites in steel. You need a slowly moving solid-liquid interface and a suitable temperature gradient or just the "right" slow cooling conditions *during* the solidification.
  Note that it doesn't matter for this how fast or slow you cool *after* everything has solidified.
  It is certainly possible to achieve this. Chances for getting large dendrites / grain structures tend to be better if the steel was liquid well above its melting temperature or well **superheated** and not just barely so; look at this picture.
  Verhoeven illustrates this (and a bit) more with the following picture:



Verhoeven's illustration of dendrite structure during solidification

- There is nothing wrong with that picture, except perhaps that it insinuates, just like this picture shown in the famous "Scientific American" article, that all dendrites, everywhere and at all times, are the same size are growing parallel to each other all over the place. That is *not* the case!

Third step: Realize that an inhomogeneous distribution of the carbide formers results

During solidification the carbide forming impurity atoms (and the carbon) strongly "segregate " into the region between the dendrites. This means that the iron between the dendrites, the iron that solidifies after the dendrites have formed, is *enriched* with carbide formers (and carbon), i.e. the concentration there us much higher than the nominal concentration. Inside the dendrites themselves the concentration is much lower, they are denuded of carbide formers (and carbon).
It is thus far more likely that carbides like vanadium-carbide forms between the dendrites than in the dendrites when the steel cools down. Since these metal carbides act as nucleation centers for the cementite that also needs to form during cooling but somewhat later, the primary cementite forming in hypereutectoid steels a high temperatures will also predominantly be found in the interdendritic areas, especially if you don't cool down very fast. This may also help to spheroidize the carbide.

- All of this is absolutely correct; it just makes ingenious use of basic segregation theory. One only needs to add that other defects like grain boundaries might also nucleate some primary cementite in competition with the metal carbides.

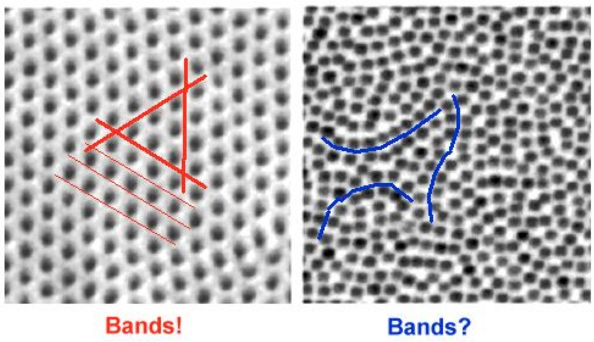
The big question: Does Step 3 produce sheets or bands of cementite in the blade?

Now it gets interesting. In the figure above there are dotted lines labeled "sheet geometry". The text going with it reads: "As shown in view B of Fig. 4 (*the figure above*), the interdendritic arrays possess a geometry that displays sets of *discrete sheets or bands*".

This is supposed to get you to believe that the carbide formers and thus also the cementite is arranged in *regular bands* inside your wootz ingot as soon as it has cooled down a bit after solidification.

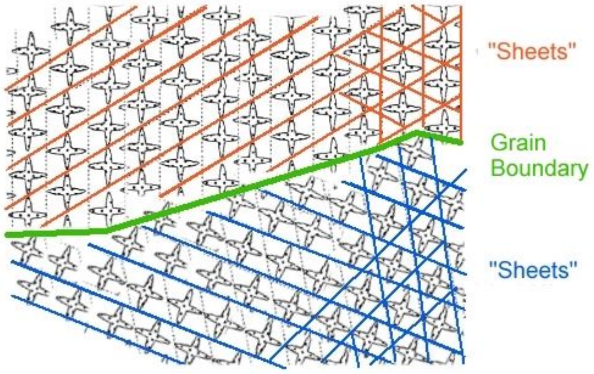
It is not! Or only up to a point. There are several reasons for this:

- *First* of all, there simply aren't *planes* of high vanadium or whatever concentration. There are lines! This pictures makes that clear.
- *Second*, even if one accepts the "sheet geometry" in Verhoeven's picture shown above for the sake of the argument, it does *not exist* like this in real materials, even within just one grain. Just look a the following pictures and imagine the black dots to be the top of the dendrites:



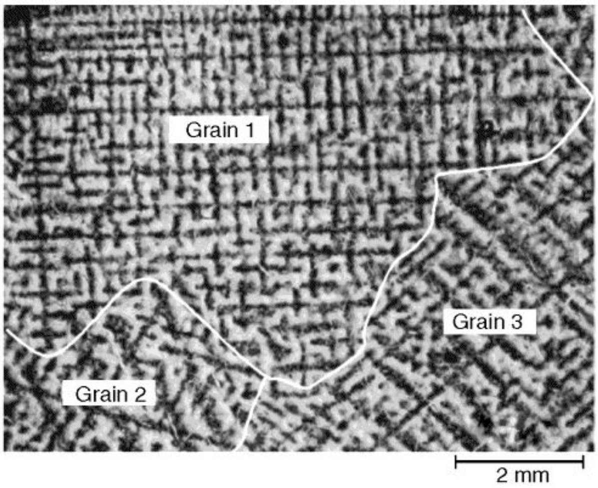
Areas denuded of something (black) and enriched in something (white)
Does the "something" form bands?

- You are looking at pores in indium phosphide (InP; left) and silicon (right); a bit more to that is here. But it doesn't matter what exactly is shown in the picture above. Think of the dark spots as tips of dendrites coming straight up at you. What you see is that the area between the dendrites can be described as three overlapping bands, indeed, but *only* as long as the dendrites are arranged in a rather perfect repetitive pattern (forming a "crystal", in other words). Real dendrites won't do that; the pictures in this link show that. So arrange them a bit disorderly like in the right-hand picture - and where are your bands?
- *Third*, the steel is poly-crystalline. The dendrite orientation changes from one grain to the next one, and so do the "sheets" or "planes". Modifying Verhoeven's picture to take this into account yields this:



There are no aligned sheets in poly crystals (schematic view)

- The drawing shows a schematic structure with perfectly aligned dendrites. An actual structure can be seen in this link or below



Real dendritic structure in 1.6 % C as-cast steel

Source: Verhoeven's book: Steel Metallurgy for the Non-Metallurgist; Fig. 15.4

- Ironically, this picture is from Verhoeven's book: "Steel Metallurgy for the Non-Metallurgist". It just makes clear that there no sheets aligned for long distances in poly crystals.

Enough! It is absolutely clear by now that there are no parallel sheets or bands of high impurity concentration *because of dendrites* that run nicely parallel to each other through the whole wootz ingot right after it solidified or after it cooled down to room temperature. This is not to say that there isn't an inhomogeneous distribution of impurities - it is just not banded in an orderly fashion because of dendrites!
To make that very clear:

No!
Verhoeven's "structure by dendrites" mechanism has not produced a wootz cake with a banded or striated distribution of carbides / cementite as shown in this picture.

- Verhoeven knows this, of course. In this article he writes: "The ingots (of wootz crucible steel made by him) are flat across the top displaying large radially directed surface dendrites. Their microstructure displays a combination of grain boundary and Widmanstätten cementite with *no apparent relationship to the prior dendrite arrays*." .
So let's look at the *crucial* next step:

Fourth step: Mechanically deform the ingot / wootz cake into a blade shape

That is the step where the necessary banded structure of the metal carbides and thus the banded structure of the cementite originates. Interestingly, this step is not prominently mentioned in Verhoeven's papers. Verhoeven, however, is quite aware of the importance of the mechanical deformation discussed here as a necessary ingredient for making wootz swords with a nice pattern. Here are some relevant quotes:

- A systematic study of longitudinal microstructures versus the extent of forging revealed that the alignment of the cementite particles occurred *gradually* during the *forging process.*
- The interdendritic arrays possess a geometry that displays sets of *discrete bands*. The metal flow during the *hot deformation* of the ingot into a plate form *causes some of these band sets to rotate into alignment parallel to the surface of the deformation*.

In plain words: Whatever distribution of carbide formers / cementite particles you have in the UHCS that you use for forging a blade, it is the massive mechanical deformation (by hammer in the old times, by a roller mill today, by whatever) that *might* align cementite particles in bands.
That is - in a small way - what I have shown to happen for purely geometric reasons before.
That's what Wadsworth more or less claimed all along. However, he did not invoke carbide formers, and they will make a difference as we shall see.
It is important to note:

- You cannot align just the carbide former *atoms*. They are just impurity atoms, sitting preferable in that part of a crystal that has solidified last, i.e. in the interdentritic space. Since they don't move much by diffusion during the whole process, their relative position doesn't change much. They go to wherever the iron atoms around them go.
- You cannot align carbon *atoms*. Since they move around like crazy by diffusion, their originally inhomogeneous distribution homogenizes quickly during normal solidification.
- But you don't have carbide formers and carbon atoms around for very long. First the carbide formers form carbides like vanadium carbide right where they are, removing some of the carbon atoms. Then the remaining carbon forms cementite precipitates wherever nucleation is easy - at the metal carbides and grain boundaries. And (relatively large) cementite particles you can align

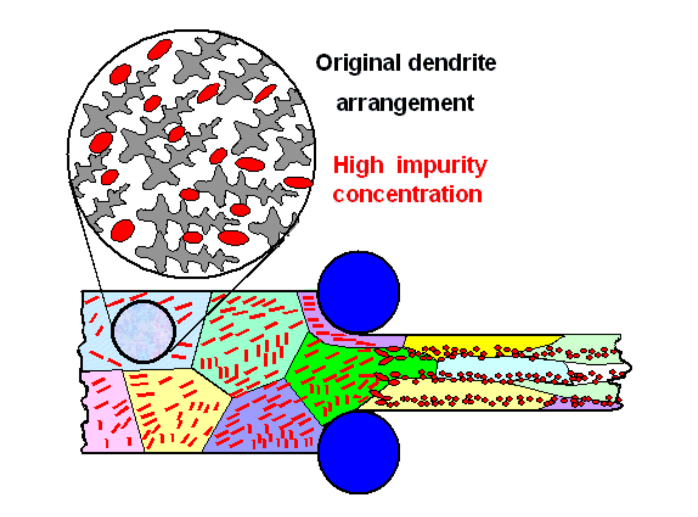
Also note that *after* solidification is complete, the dendrites do not exist any more. All that exists is a crystal like austenite that contains some dirt and possibly already some primary cementite. Only the distribution of those things in the crystal supplies a kind of vague memory of the former dendritic structure. In addition, there might be a few small-angle grain boundaries in places where the dendrite alignment was a bit off.

Now comes a surprise: Running a (hot) piece of *any* steel through a roller mill, reducing its thickness, often produces banded structures with a nicely staggered sequence of carbon-lean, carbon-rich, carbon-lean, ... , layers. Consult the advanced module for details. Verhoeven has actually written a big review paper[1)] about **banding** as that phenomena is called, full of complex stuff. It is entitled: "A Review of Microsegregation Induced Banding Phenomena in Steels".
However, Verhoeven (and everybody else) is rather vague about exactly how this *mechanical* alignment process works. He goes through great lengths to elucidate the various (and rather complex) mechanisms of cementite formation in various kinds of hypo- and hypereutectoid steel, and how it depends on cooling rates and God knows what else. Here is what he has to say about the **mechanisms** that are responsible for forming the bands during the heavy plastic deformation occurring during milling (or hammering):

Advanced Module **Banding**

- An *interesting question* that has not been studied in the literature is how the dendritically produced segregation arrays become so well lined up into the two-dimensional planar bands during rolling or forging of sheet materials.
- When observing strongly banded structures, it is *amazing* how well the bands line up with the deformation plane in sheet materials.
- The morphology of the ferrite and pearlite bands depends on the type of deformation employed. It has been found that deformation to rod shapes produces cylindrical morphologies, while deformation to plate (sheet) shapes produces planar morphologies.
- The presence of the planar bands in the deformed ingots indicates that during deformation some set of IR (interdentritic region) lattice planes *probably* becomes aligned in the deformation plane during the hot deformation. If this suggestion is correct, it seems likely that it is one of the high density planes of the IR lattice, {100} or {110}, that lines up in the rolling plane, perhaps by some type of lattice rotation.
- In this case, carbide banding is inevitable in the wrought product as the carbides often cannot be made to dissolve into the austenite on forging and will simply remain in the steel and *align during the hot working process.*

In other words: Verhoeven (and everybody else) does not know exactly how this **mechanical alignment** process happens. Nobody knows. I have studied a lot of papers and books and found no convincing explanation. Pretty much all authors weasel a lot because this is acutely embarrassing. Banding is a major (and mostly very unwanted) effect that occurs in much of steel processing - and we don't know exactly what happens!
However, Verhoeven concludes that pronounced banding is easier to obtain if the material already has "pre-banded" regions. He might well be right about this because banding does not always occur in structures containing mixes of hard and soft regions. The "grain boundary wootz" of Wadsworth or Harnecker's wootz is observed in steel that seems not to have produced banding upon deformation. I'm not sure if I subscribe wholesale to Verhoeven's point of view but Verhoeven knows a lot more than I do about banding and making wootz structures so let's go with it for the present.
Let's just look at a simple picture to illustrate what happens:



Schematics of banding during rolling / mechanical deformation

it is a very simple picture but shows the essentials (and I am repeating myself to some extent on purpose here):

- At any temperature after solidification (including room temperature) the slow-diffusing impurities, including all strong carbide formers, are still more or less where they were right after solidification at temperatures close to the melting point. They simply can't go very far if the cooling rates are not excessively slow.
- That is not true for atomically dissolved carbon. While it was also enriched between the dendrites during solidification, it can diffuse rapidly and covers large distances already at high temperatures. The distribution thus might be rather uniform at high temperatures.
- If strong carbide formers like vanadium (V) are present, the respective carbides may form already at high temperatures; they would tend to be found in the interdendritic regions.
- For UHCS steels, primary cementite forms as soon as the $\mathbf{A_{CM}}$ temperature is reached (look at the phase diagram!). This cementite may be found at the austenite grain boundaries, forming Widmanstätten type needles, or nucleate at metal carbides and form more or less spherical precipitates. Nobody has seen that structure because it transforms completely at the $\mathbf{A_1}$ temperature.
- As soon as austenite transforms to ferrite at the $\mathbf{A_1}$ temperature, the 0.76 % carbon still in solution needs to form cementite. In hypoeutectoid steel this is the first time cementite is is formed, in hypereutectoid crucible steel this secondary cementite comes on top of the primary cementite. In the most simple case the primary cementite just grows. If carbide formers dominated the cementite nucleation, the cementite and thus carbon-rich regions mirror the distribution of these slow diffusing impurities, a least up to a point. That would *not*, however, result in well-defined bands for all the reasons given above
- Rolling at high temperatures or equivalent hammer-forging, is the *decisive* process that causes the bands.

Banding due to rolling occurs in hypo- and hypereutectoid steel, including steel with no known addition of strong carbide formers. This might be seen as implying that carbide formers are not all that important for the formation of a nice pattern, in contrast to what Verhoeven claims. That is not quite true, however. The difference shows in three situations; two of which are (related) :

- Without strong carbide formers the primary cementite forms at grain boundaries, making spheroidization difficult if not impossible.
- Anneal the stuff at high temperatures for a long time. The cementite will dissolve and the released carbon atoms diffuse all over the place, homogenizing their concentrations in both case. The carbide forming elements, however, stay pretty much in place since they diffuse much more slowly than carbon. They also do not dissolve that easily. Now cool down again and cementite formation occurs once more at the places where the carbide formers are concentrated and thus in a banded distribution. Without carbide formers it would precipitate more uniformly all over the place.
  In other words: Without the carbide formers you loose an originally present banded structure during heating, with

carbide formers you reconstitute it.

- A banded cementite structure caused by banded carbides from carbide formers is more forgiving and easier to manipulate for the reasons given above. Exceed the transformation temperature once during forging and the structure will soften. But you can not only easily reconstitute it but even sharpen it by proper thermal cycling and Ostwald ripening. And that leads us to the:

Fifth step: Thermal cycling / Ostwald ripening

We now have a banded distribution of at least the carbide formers if not the cementite. It might be sufficient for producing a pattern but not yet for producing a *nice* pattern on wootz blades. Verhoeven lists as one of his 7 conditions for nice patterns: "There are no significant differences in particle size or shape on transverse versus longitudinal sections".
In other words; the cementite particles should all have about the same (and not too small) size.

- Well, we already know how to achieve that. Either straight Ostwald ripening at high temperatures but still below $\mathbf{A_1}$ or thermal cycling between just a bit above and below $\mathbf{A_1}$. I have described that that in detail before; here I will let Verhoeven describe what happens:

  These results show that during the thermal cycling the microsegregated impurities are causing the cementite particles to gradually increase in size and density along the remnant IRs (interdentritic regions) of the forged ingot as the number of thermal cycles increases.
  ...
  During the heat-up part of each thermal cycle the smaller cementite particles will be removed by dissolution while the larger particles will remain at a reduced size. During the cool-down portion of the cycles the larger particles will grow. It is not likely, however, that the smaller particles will reform at adequate rates to replace themselves during cool-down because this requires nucleation, and the presence of the nearby larger particles provides sites for cementite growth without need of nucleation. Hence if bands of larger particles once form, the cycling process will cause them to grow at the expense of the smaller particles.
  ...
  Hence it seems most likely that the cementite is simply nucleating on austenite/ austenite grain boundaries during the thermal cycling and then forming into aligned bands of c!ustered particles by the coarsening processes such as that discussed above along with some coarsening due the classical *Ostwald ripening mechanism*.

Now we are almost done - as far as "Structure by Dendrites" is concerned. I only need to mention that in some of what I have written you might replace the $\mathbf{A_1}$ temperature (where secondary cementite forms) by the **A_{CM}** temperature (where primary cementite forms) and look at the austenite formation instead of ferrite formation for getting some important inhomogeneities. But things are already complicated enough, so let's stop here.
Whatever happens in detail, the steps described above, if done right, make sure that the blade now contains sheets or bands of proper cementite particles that are roughly parallel to the blade surface. We can now produce nice patterns by using some forging tricks.
That will be covered in the next sub-chapter. Here it only remains to state two things. *First:*

Producing nice wootz patterns requires to do a lot of things "just right". There is, however, nothing mysterious about those "things".

- *Second:* I still need to announce the winner of the Great Verhoeven - Wadsworth Jousting Tournament. So:

The Winner is...

Me, of course, for figuring out what this was all about. But seriously now: **Verhoeven does come out ahead!**. He and his co-workers did shed a lot of light on the specifics needed to progress from a pattern to a nice pattern. Moreover, they actually made nice wootz structures, including kirk nardaban with roses, somebody nobody else so far has achieved as far as I know.
My only criticism is that some crucial issues are a bit underdeveloped in some publications (on both sides) and that it is not always stated outright that there are still some open questions.
It should also be clear by now that Verhoeven's work leads right into some topics of modern iron an steel research that are not yet fully understood. And that allows me to make a suggestion of my own:

All the problems around producing parallel bands of first carbide formers and later cementite precipitates disappear if that happens right during solidification. It is clear by now that this does not happen by a simple "dendrite mechanism". What about some other mechanism?
The wanted structure is actually known from the solidification of many other liquid-solid systems and called **striations**. I have already written a lot about that so I just give you the links:

- **What are Striations?**
  The 5th module in the "Segregation Science" Superlink. All about what striations are, where they have been observed, what causes them, and how they might relate to wootz patterns
- **Segregation and Striations in CZ Silicon**
  In his module you learn all about striations always found in the huge single crystals of silicon. They are quite well understood - and the mechanism behind their formation is not the same as the suspected one in crucible steel.
- **Microsegregation and "Current Burst" theory**
  A highly speculative hypothesis of striation formation in normally solidifying melts including dendrites
- **Science of Alloying**
  Some hints to striations in steel. An Application to "Wootz" Steel?

Enjoy!

---

[1] John D. Verhoeven: "A Review of Microsegregation Induced Banding Phenomena in Steels", Journal of Materials Engineering and Performance (JMEPEG), Vol. 9/3 (2000) p. 286 - 296