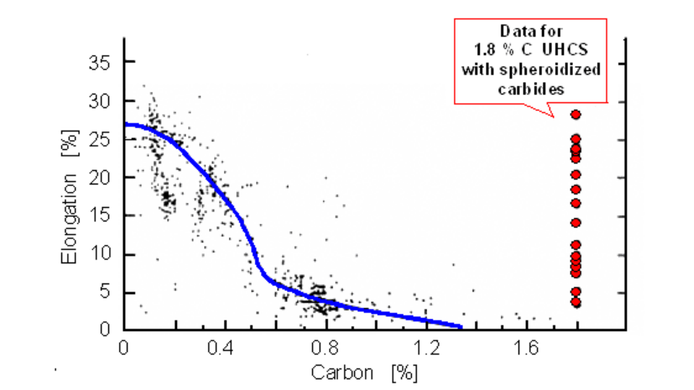
10.4.2 Making Old-Fashioned Crucible Steel in Modern Times

Old and New

After the advent of the blast furnace around - roughly - 1500, the cast iron produced was the raw material for making steel. Since it was liquid once, the steel produced from it was rather homogeneous and without slag inclusions, just like crucible steel. Producing steel from cast iron happens by taking some of the surplus carbon out. In theory you can stop taking carbon out as soon as you have reached the concentration you want. It is not an easy thing to do in practice but it has been done. Stopping the carbon reducing process early produces ultra-high carbon steel (UHCS) but nobody, it appears, made that kind of stuff during the middle ages. The fact that it wasn't done most likely means that nobody wanted it done.
Objects like swords made from cast-iron derived normal steel were still made by forging. **Casting steel** started wth Huntsman around 1750 on a small scale but only came into its own - roughly - around 1850. Cast steel is by definition crucible steel in the sense that it was liquid once, and that its carbon content was established while the steel was liquid. Once more it would have been no problem to make ultra-high carbon steel (UHCS) and thus a facsimile of ancient crucible steel, and once more, nobody made some. UHCS was not in large demand then, nor is it now.

- *Why*? Why did the "West" not appreciate UHCS, considering that is is a very hard steel? To answer in the words of J. Oleg D. Sherby, one of the researchers who worked most of his life on the topic: "Ultrahigh carbon steels (1.0 to 2.1%C), now designated as UHCS, have been viewed for most of this (20th) century as belonging in the “no man's land of carbon steels” being sandwiched between the extensively-utilized high carbon steels (0.6 to 1.0%C) and the mass-produced cast irons (2.1 to 4.3%C).
Ultrahigh carbon steels’ position in the “no man’s land of carbon steels” is because UHCS have been considered to be brittle at room temperature and thus have been generally ignored commercially. The origin of this belief can be traced to the classic work of Howe, published in 1891, in which the tensile ductility of steel was studied as a function of carbon content."
Here is the classical curve of Howe, augmented by the new data of Sherby and colleagues:



Elongation vs. carbon content for carbon steel;
(data collected by Henri Howe, 1891)
and modern data for 1.8 %C UHCS

Source

- Good old Howe, whoever he was, thus pronounced UHCS to be useless - but not lightly. He had a hell of a lot of data points as you can see. However, all his data points were from UHCS where the grains were completely enclosed in a brittle cementite shell and that cannot but render the composite brittle, too. I have dealt with that extensively before.
What you can do to alter that deplorable state of being is to break up the cementite. Disperse it in the form of small lumps in a continuous or contiguous matrix of ferrite, and you should have some ductility. You know by now, I take it, that for UHCS the phase diagram predicts a mixture of ferrite and cementite. It only remains to produce this mixture by having cementite particles in a ferrite matrix instead of having pearlite grains encased in additional cementite lining the grain boundaries.

How could one produce a "nice" ferrite / cementite mixture that is stable at room temperature? Sort of little spheres of cementite embedded in a continous matrix. A "**spheroidization of the cementite**", in other words, is what you want. There are three major ways to get this:

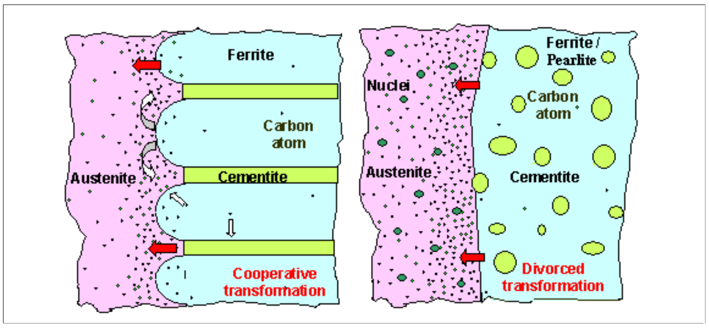
1. Anneal at very high temperature for a long time. Since cementite, like all precipitates, likes to minimize the interphase area, it tends to do this by balling up, forming spheres. Give the atoms enough opportunity to move around, meaning enough time and temperature, and this will always happen. Of course, above the A_1 temperature of 727 ^{o}C (1341 ^{o}F) you only work with the primary cementite but that is the "bad" one at the grain boundaries.
2. Break up the cementite with a hammer or by any other means of deformation You best do this *below* the A_1 temperature to get *all* the cementite. At higher temperatures (where smithing typically occurs) cementite also

ceases to be brittle and then won't break. What broken cementite looks like you can see here.

3. Forming spherical carbides by employing the "**divorced eutectoid transformation**" or ***DET***.

The *first* possibility is not very attractive - high temperatures and time equals money. Moreover, while making spherical particles or *spheroids* of cementite is advantageous for the crystal in terms of energy, making *plain carbon* (graphite) is even better. If you overdo it, you might end up with a structure akin to white cast iron; totally useless for making swords.
In fact, one of the first modern publications dealing analytically with wootz steel and swords, the remarkable 1962 paper "Damascus Steel in Legend and Reality" by **Carlo Panseri** [1)], does report that 0.3 % of the 1.42 % total carbon in a magnificent wootz blade was present in graphite form.
The *second* treatment will always happen if a sword is forged - provided the smith keeps the temperature low. It then is more or less mixed up with the
third way: inducing a *divorced eutectoid transformation*.
Combining all three treatments in a smart way will produce "Damascus steel, defined as a hypereutectoid ferrocarbon alloy, with partially ~~and heterogeneously~~ spheroidized cementites, having a carbon content normally running between 1.2 and 1.8 percent." [1)]. Panseri knew his stuff. I just needed to strike out the "heterogeneously" because that is not yet there.

"How do you divorce an eutectoid transformation?" you might now ask. "I wonder if I even want to know about it. My own divorce was messy enough, after all", would also be a perfectly normal reaction. Well - don't worry, or at least not too much. There was no divorce; the term only means that there wasn't any cooperation either between the cementite and the ferrite when both were formed from austenite.
A picture says more then thousand words:



Cooperative and divorced transformation from austenite to ferrite and cementite

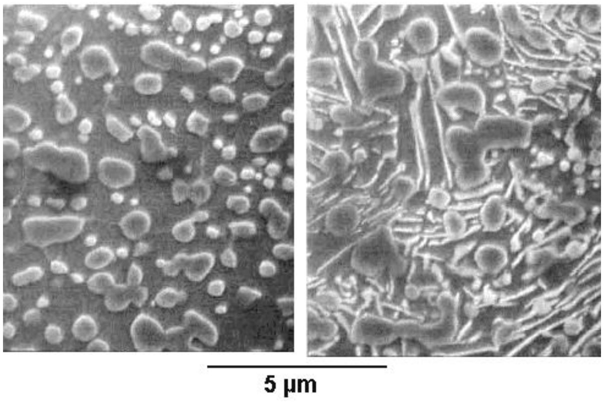
In the normal *cooperative*mode, ferrite and cementite form together as shown and discussed before. The result is the famous pearlite "zebra" structure as seen upon etching in pretty much all metals that underwent an eutectic / eutectoid transformation during cooling. With increasing cooling rates the distance between the lamellae gets smaller because the diffusion lengths decreases. If you cool too fast at "normal" carbon levels, you first start to produce bainite , no longer with a clearly defined zebra structure, and finally martensite. You would be justified in calling the formation of bainite a "DET", too; some people actually do this.
However, if we look at UHCS, a divorced transformation ideally produces spheroidized cementite particles in a ferrite matrix, just as shown above.

What does it take to produce a nice DET structure? Either a lot of luck and cunning or a very good understanding of what is going on. In essence it boils down to:

- Annealing at high temperatures for a sufficiently long time span. But not just *any* high temperature. You have to be pretty close to A_1 or it won't work. Complications may come from the fact that other elements in your steel may change A_1 somewhat.
- Cycling for long times (like 2 days) from just above to just below A_1 may work even better.
- And so on.
- But you need *nuclei* to act as starters for the large cementite spheres you want to have in the room temperature ferrite. These nuclei need to be present already in the austenite.

The only problem remaining is to supply those nuclei. They must be very small cementite particles because in our hypereutectoid steel we can only dissolve about 0.7 % carbon close to A_1, and the rest must exist as cementite. We can produce these nuclei by doing whatever is needed, essentially annealing at high temperatures. If these nuclei are *randomly* distributed, we will have a random distribution of the large cementite particles found later in the ferrite; if not, not.
We are inching towards pattern formation here!

That all this works is shown here:



SEM picture of fully and partially spheroidized UHCS

Source O. D. Sherby, J. Wadsworth, 1997

- On the left we have fully spheroidized cementite in a UHCS-1.8 %C sample. The treatment included tempering around A_1 and deformation by hot rolling. On the right hand side the sample has been annealed for a while at 840 ^oC, i.e. well in the austenite region, and the "zebra" pearlite now starts to form again during cooling. It goes without saying that spheroidized UHCS is no longer brittle but has some ductility; the red data points in the picture on top are from samples like the ones shown here.

Would there be a difference between a modern UHCS and an antique wootz cake or bulad egg? Both are very hard but with some ductility left.
Well, yes, of course. The modern "crucible" UHCS would contain some *defined* amounts of manganese, silicon, and some unspecified and possibly unknown traces of this and that - but no appreciable amount of phosphorous. It would also be rather uniform throughout.
The bulad egg would contain more or less *random* amounts of this and that, including possibly some (beneficial) manganese but quite possibly also some phosphorous. Moreover, it could be a "bad egg" if it was not completely molten but only partially. Then it was only a mix of a carbon rich liquid and some solid and relatively carbon-lean austenite, look at the phase diagram. It wasn't very uniform either in this case.
So what is better? It is not *impossible* that some UHSC containing some undefined impurities would be better with respect to basic *mechanical* properties in comparison to a well-defined modern UHSC that contains only what was put into it. It is not impossible - just *very unlikely*.
So is there anything that wootz can do that a modern UHSC cannot?

- Well - maybe the ability to arrange the spheroidized cementite particles in such a way that they form a nice pattern, the famous "water" or "damascus" pattern, is special? Good question, just a bit stupid. We know of course that *some* wootz cakes or bulad eggs do offer that possibility - there are swords with the "water" pattern, after all. The real question is

Can you make a water pattern from any *modern* UHSC?

- That is "the" question. The answer isn't in yet. Some people looking into the issue say "yes", some say "no". Searching for the answer proceeds like in the old days: the champions of the two factions fight it out in a jousting tournament:

The Great Verhoeven - Wadsworth Jousting Tournament

There is no shortage of people who have addressed the issue. Two guys, however, have not only addressed the issues but started a veritable jousting tournament, taking stabs at each other (with pens) in turn. I'm referring, of course, in alphabetical order to John. D. Verhoeven and Jeffrey Wadsworth and the men-at-arms who go along with them.

- **John D. Verhoeven** is a distinguished Emeritus Professor of Materials Science and Engineering, College of Engineering of Iowa State University. He worked in areas like electrotransport, thermotransport and convection in liquid metals, directional solidification, superconductivity, cast irons, steels and **Damascus Steel** in his capacity as Professor at Iowa State; publishing a lot of papers.
- **Jeffrey Wadsworth** we have met before. He is President and CEO of Battelle Memorial Institute since January 2009. Before that he was the deputy director for science and technology at Lawrence Livermore National Laboratory, the manager of the Metallurgy Department at the Lockheed Research and Development Division of Lockheed Missiles & Space Company Inc. and affiliated with Stanford University. He has authored or co-authored more than 260 papers on a wide range of materials science and metallurgical topics, too

Special Module **The Tournament**

These guys are heavyweights and their jousting is fun to watch from the sideline. They both are limping a bit after 26 years of stabbing at each other (with pens), but none has yielded yet and both seem to be still capable to mount a horse and charge. Here is (simplified) what the fight is all about

- Wadsworth champions the: **Yes** - you can make a **nice** water pattern from *any* old or modern ultra-high carbon steel (UHSC). The cementite forming the pattern is essentially the cementite you had in your steel before forging.
- Verhoeven goes for the **No** you can't" option. You need special UHCS with traces of special impurities like vanadium (V) to nucleate cementite in *new* structures that are quite different from the ones in the steel before forging.

- Mind you, the tousle is not about if you can or cannot make a pattern with any modern UHSC steel. It is about:

Can you make a *nice* water pattern from modern UHSC?

The emphasize is on "*nice*" because you can definitely get *some* pattern with any modern high-carbon steel. Verhoeven claims that you only get a "nice" pattern (he calls it, for example, "museum-quality" as opposed to "granular") if the original steel contained some carbide-forming trace impurities like vanadium (V) or molybdenum (Mo) that become distributed inhomogenously due to dendrite formation during solidification. More about pattern appreciation in this module.

- So who is right? I'll tell you if you send me some money in unmarked large bills. Or maybe in the next chapter. Until then use the link above and enjoy the tournament.

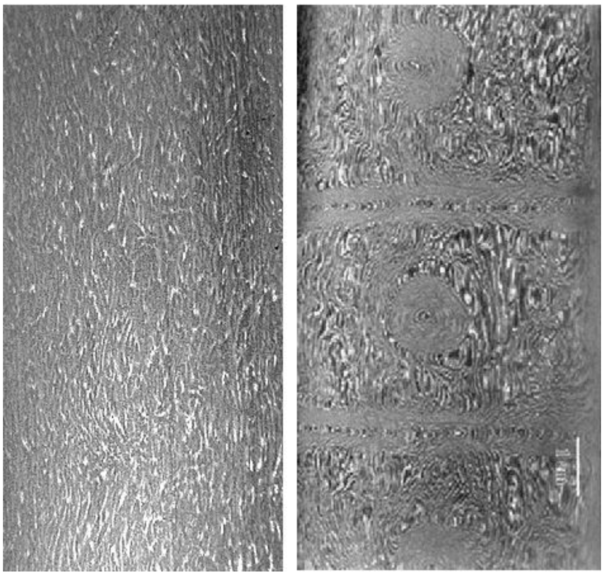
Making Crucible Steel the Old-Fashioned Way

There seem to be very few old wootz cakes / bulat eggs around, and whatever there is cannot be used for experimenting. So let's make some, following the old recipes as far as we can. Maybe with a few shortcuts in the beginning. You don't need to build a kiln and burn charcoal anymore to get the temperature up - we have electricity for that. But that doesn't matter. Whatever is in the crucible doesn't care *how* it is made hot. It might care if the atmosphere is oxidizing or reducing, though.

- Verhoeven began a unique collaboration with master blade-smith **Alfred H. Pendray** in 1988. The idea was to prove his point by recreating blades just as nice as the ones we admire in museum from crucible steel made for this purpose. Pendray was infected by the scientific spirit and charged his crucible with high purity stuff and deep thoughts about the rest.
  Richard (Ric) Furrer, however, did his crucible experiments under the influence of beer. Both guys produced crucible steel from which blades could be forged. Here are their recipes:

Smith	Alfed H. Pendray	Richard Furrer
Iron source	1. High-purity iron 2. Sorel iron (high-purity iron with a carbon concentration around 4 %; i.e. high purity cast iron).	1. Iron powder (presumably high purity) 2. Cast iron
Carbon source	1. Sorel iron 2. Charcoal 3. Special green leaves	1. Cast iron 2. Dandelions from the backyard
Slag former	1. Glass shards 2. Additional unspecified ingredients	Freshly crushed green glass (from beer bottles)
Process / Philosophy	Melt iron, liquid glass (=slag) is on top and protects steel. Leaves produce hydrogen (H) that helps carburization Without leaves and glass the finished ingot tends to be brittle	Seal crucible air-tight Heat for about 3 hours. Don't worry, have some beer with the guys, cool slowly
Result	In both cases the relative amounts of carbon source and pure iron determine the carbon concentration in the final product.	

- **Alfed H. Pendray** is a blacksmith and the former President of the American Knifemaker's Guild. Not only is he an expert on "wootz" steel but as a farrier has shoed some of the most famous (and valuable) thoroughbred race horses in the world. He has worked together for more than 20 years with John D. Verhoeven.
Richard Furrer started as a black smith and is now running the "Door County Forgeworks". He is an internationally renowned expert for ancient metallurgy who works with scientists from several universities and teaches classes there.
Both produce wootz cakes of quality, and both can make blades with a definite water pattern:

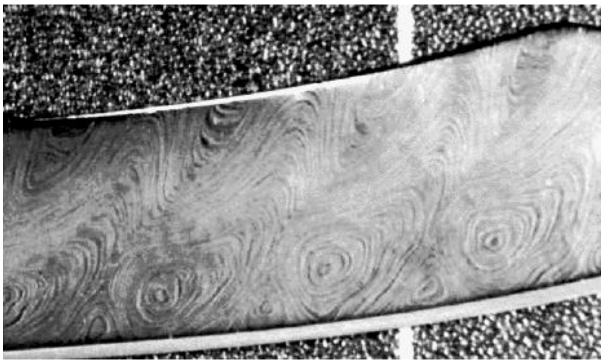


Water pattern on modern wootz blades
Left: Furrer school; Right: Pendray's work

Source: Left: From the Internet pages of the Furrer disciple Owen Bush; who made a wootz blade in Furrer's smithy. Right: Pendray's work as published here

- Pendray's piece show a "Mohammed's ladder with roses" pattern, the most complex pattern made in the old days.

Incidentally, Pendray confirms what I suspected some time ago: Organic matter as a source of carbon might be advantageous because it also supplies gases like hydrogen, helping the process.
Meanwhile several smiths produce modern wootz blades with a pattern. You find an example in Calabrés paper, by looking for the work of a Russian smith named Mr. Ivan Kirpichev, or by looking at the work of Eric M. Taleff [3], a researcher who coauthored several papers with Wadsworth and Sherby. Or just search the Net, you will find more.



A genuine wootz pattern (not pattern welded) according to Taleff [3])

Source

- But are those modern patterns "*nice* " patterns? The one above might qualify, I believe, even so it is not traditional. But that is a touchy topic since it is a matter of taste and it is hard to define where "nice" ends and "inferior" starts. From what I have seen, Pendray's blades take the price. So far he seems to be the only one who recreated the "ladder and rose" pattern as shown above. Verhoeven attributes this to traces of vanadium that are contained in the Sorel iron used (without knowing this) for the making of the wootz. This might well be true and the question now is:

Why are traces of vanadium (or molybdenum, or ....) necessary for making *nice* pattern?

- I'll look into this in the next chapter where I finally will get to swords

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1) Carlo Panseri: "Damascus Steel in Legend and Reality" reprinted in Gladius, IV (1965), pp. 5-66; originally published in ARMI ANTICHE, Bulletin of the Accademia di Marclano, Turin, sole number for **1962**, and translated to English by H. Bartlett Wells. Washington DC, in 1965

2) Rafael Calabrés et al.: "Traditional Forging of Swords and Knives with Legitimate Damascus Steel", Prakt. Metallogr. 38/6 2001 . p. 325 - 337
(Note the "*Legitimate*")

3) Eric M. Taleff: "Microstructural Characterization of a Knife with Damask Patterning", Technical Report, Internet
Taleff investigated a "blade created from a commercial tool steel using a combination of thermal and mechanical processing steps." His conclusion concerning the pattern shown above is: "The knife blade examined clearly falls into the category of a genuine damascus steel. The damask pattern it exhibits results from microstructural bands in the distribution of very fine carbide particles."