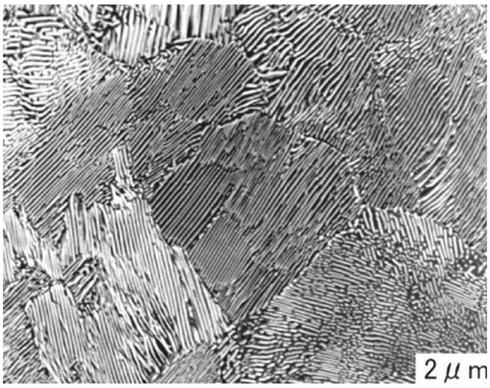
7.1.2 A Lustrous Surprise

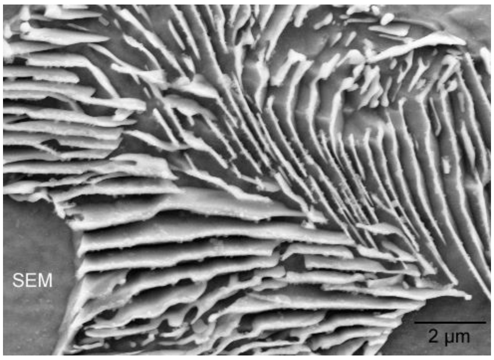
- Now let's look at the γ + cementite phase that we expect to be the stable (or "nirvana") phase at room temperature for our eutectoid composition.
  - If we cool the mix down very s l o w l y, giving the steel plenty of time to get close to nirvana, we see something as shown below in our microscope (after polishing and defect etching, of course).

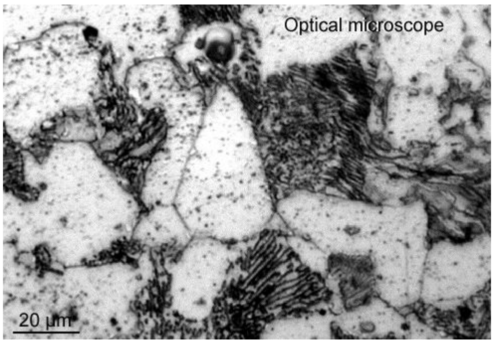


Structure of steel with the eutectoid composition
This is actually a picture from a scanning electron microscope (SEM). In an optical microscope this structure would not be clearly visible.
Here is another one

Source: Eyuep Duman, Diploma Thesis: "Druckabhaengigkeit der Invar-typischen Instabilitaeten von Fe_3C- (Zementit) Partikeln"; Physics department; University Duisburg-Essen / Germany 2006. By permisison; thanks for letting me use it.

- Very pretty but I bet this is not what you expected, if you expected anything. Here is another picture from an ancient sword showing exactly the same kind of "zebra" pattern.
  - What *you* see is a kind of *zebra pattern* of dark and bright stripes inside different grains. It should produce a "déjà vue" feeling, however. We have looked at similar pictures before.
    What *I* see is the classical ordered structure relating to eutectic or eutectoid points in a phase diagram. In the case of steel we get a highly ordered layered structure of *ferrite* (dark) and *cementite* (white).
    Next, let's look at a different sample at higher magnification in a scanning electron microscope or at the highest magnification (about 1000×) in a light microscope:



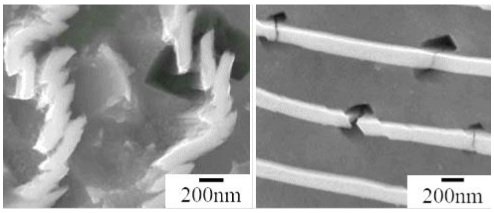


Structure of hypoeutectoid steel

- These pictures are from a commercial piece of medium carbon steel taken by a student of mine. There are some "normal" grains and some grains with the "zebra" structure.
  In the SEM picture, the cementite is white and sticks out of the ferrite matrix. In the light microscope picture the cementite is black. In neither case has this color anything to do with the true color of the stuff.
  Whatever else one could "see" in these pictures, one things is clear: What we do *not* have are large grains of ferrite interspersed with some grains of cementite, as you were entitled to expect from the phase diagram. What we do have is a structure that is not determined all that much by where the steel wanted to go ("nirvana", the ultimate goal) but by **kinetics**, the available path to the goal.
  Sometimes the path to paradise is meandering and stony. If you get stuck on the way, you may find yourself in very different conditions compared to what you were aiming for.

How do I know what these pictures show? How do you know that I'm not pulling your leg? Well, without some additional knowledge neither of us can tell. My additional knowledge comes from several sources. First, the theory behind phase diagrams, nirvana and so on simply predicts what one should get, and second, we have far more advanced analytical tools nowadays that allow me to check if I'm right.

- Scanning electron microscopes , for example, only show the surface (in contrast to transmission electron microscopes) but they may also reveal the chemical composition of what is there. Our colleagues 100 years ago did not have this, they had to find the proper interpretation of their pictures by other means and lots of work.
  The next pictures demonstrate that once more. You also see in the left-hand picture that "banging" the whole thing mechanically fractured the brittle cementite while the ferrite in between just deformed plastically by dislocations running through it. That is an interpretation once more because you cannot see the dislocations in a SEM picture.
- Cementite, as we ascertained before, is a crystal but does not support dislocation movement at room temperature. It thus must be brittle like most ceramics, the material class it belongs to.
  You can also see deep etch pits around cracks in the cementite. The cracks allows the etchant to penetrate deeper into the material and to etch the ferrite "from the side".



Cementite platelets embedded in ferrite as seen with a SEM	
Cold rolling (akin to banging it with a hammer at room temperature). The ferrite has deformed plastically, the cementite actually fractured.	After slow cooling, just like in the optical microscope picture above.
Source: M. Umemoto et al., Toyashi Uni. of Technology, "Mecanical Properties of Cementite and Fabrications of Artificial Pearlite", Materials Science Forum, Vol 426 - 432 (2003) pp 859 - 864 Here is the paper with more pictures	

Now comes an important point: The rather typical "zebra" structure for ferrite + cementite (or α + Fe_3C in more prosaic terms) found at the eutectoid composition and below the 727 ^{o}C (1341 ^{o}F) transition temperature has its own name; it is called **pearlite** because it shows a pearl-like luster.

Plenty of "*why questions*" come up:

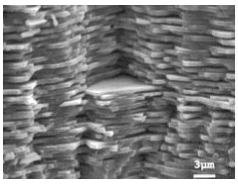
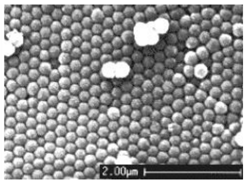
- *Why* do we find the pearlite structure and not some other structure?
- *Why* does it have a pearl-like luster?
- Come to think of it, *why* do **pearls** and **nacre** (=mother-of-pearl) show a "luster", while diamonds and toenails don't?

Let's start with the last question first:

- *Nacre*, the stuff pearls, mother-of-pearl, sea shells and some snail shells are made of, is a layered **composite material** - just as eutectoid steel. The distance between the layers of a soft protein and hard **calcium phosphate** is in the lower µm range, just like the distance between the soft ferrite and hard cementite platelets in steel.
  The wavelengths of visible light is also in this range, and that means we get *interference effects* . In simpler words: the reflection of light from such surfaces changes with viewing direction and the effect of that when we look at it we call **luster**. Nowadays we call structures like this "**photonic crystals**", and the most amazing natural photonic crystals are perhaps the wings of some butterflies and beetles, and in particular *opal*.

Advanced Link **Photonic crystals**

- **Opals** are crystals, yes, but not of atoms but of comparatively gigantic balls of amorphous glass in the form of silicon dioxide (known as quartz in its crystalline form, look at an old figure for the difference). The interference of light caused by a periodic structure that is "coarse" enough to be on the same scale as the wavelengths of light (say around 100 nm - 1 µm) causes the luster or other remarkable optical effects of opals, pearls and nacre, butterfly wings, and pearlite.
  Nacre, by the way, has another superficial relation to steel: it is composed of *hard* calcium phosphate platelets embedded in a *soft* protein matrix, reminiscent of what you might associate with a damascene blade.

	
Mother-of-pearl (nacre) and opal as seen with a SEM.	
Neatly packaged platelets of relatively hard calcium phosphate are "glued" together by (invisible) thin layers of soft protein.	"Huge" spheres of amorphous quartz (SiO_2) balls form an fcc crystal. "Huge" refers to the fact that these spheres are about 600 times larger than the atoms usually forming a crystal, containing about 300.000.000 atoms.
Source: With permission from the group of my late friends U. Gösele and J. Woltersdorf, MPI Halle, Germany	Source: Internet at large

But I'm digressing. Let's consider the first question now. *Why* does an eutectoid iron-carbon mixture produce the intricate pearlite structure when it must change from simple austenite to ferrite + cementite? It's certainly not the nirvana structure; that would be one large cementite precipitate in a ferrite matrix.
Well, the crystal invokes another well-known principle:

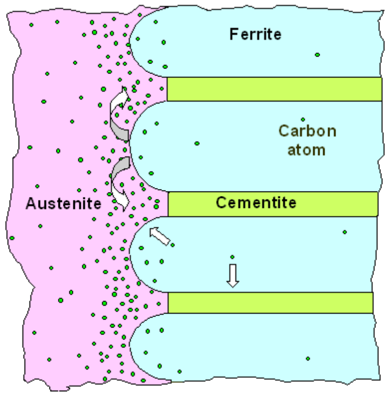
Principle of supreme laziness:

Don't spend a lot of energy for attaining the impossible.
Go for a compromise that needs the least effort.

Consider: The phase transformation in question involves *a lot of work*. The lattice type must change from fcc to bcc wherever ferrite is to be made, and the surplus carbon must be expelled from the ferrite and moved to wherever a cementite crystal is to be.

- All of this involves moving atoms around:
  - All iron atoms must move somewhat to adopt to the new lattice type. Some must move a lot to make room for the cementite.
  - The carbon atoms must move a lot to get away from the ferrite and into the cementite.

  Making large grains of ferrite with some large cementite precipitates or grains in between, while good for nirvana, simply involves too much work or moving around of atoms.
  The crystal goes for a compromise.The typical eutectic structure that constitutes pearlite is the structure that results when one optimizes the scale of the structure to be made to the distance the carbon atoms can move. We called that quantity diffusion length. We thus expect structures on a scale that is comparable to the diffusion length of carbon interstitials, making sure that most if not all carbon atoms can make it to some evolving cementite.
  The following figure shows how that leads to the layered structure:



Formation of the eutectic / eutectoid "zebra pattern"
by minimizing carbon diffusion

- What is going on is rather clear. If the spacing of the cementite lamellae is no larger than the total diffusion lengths of the carbon atoms, all of them can get there.
  This is something we can calculate; I actually did this in a science module.
  - Within reasonable cooling rates from about 1.000 ^{0}C (1832 ^{0}F), the master curve in the science module predicts lamellae spacings between roughly 0.1 µm if you cool rather rapidly (50 K/s) and about 10 µm if you cool slowly (1 K/s). That is just what you tend to find, look at the pictures above and elsewhere.
- The *principle of supreme laziness* is related to "**Occam's razor**" (look it up yourself). While it is not a basic law of nature, expressible in precise equations, it is a pretty good guideline with some philosophical implications.
  - Suppose, for example, you are *almighty* and about to make a universe, complete with galaxies, planets, living beings, pizza, beer and red wine. You could, of course, simply put all the required atoms (around 10^{80}) and photons (far more) in the proper place. That's certainly a thing an almighty being can do - but it is a lot of work.
  - So if you are an almighty being but *somewhat lazy*, you just make a few basic laws (like the first and second law) and some universal constants like the speed of light or the Boltzmann constant (plus, perhaps, some pizza and red wine).
    All you have to do after that is to relax, enjoy your food, and wait. After 15 billion years or so, your universe will have made itself, complete with galaxies, planets, iron (quite a lot, in fact), living beings, tele evangelists, bankers and slugs.
  - Now, if you are an almighty being and *extremely lazy*, you make nothing at all. You just wait a bit longer. A lot of universes of all kinds will form all the time and eventually there will be one with pizza, wine, the natural laws as we know them, lawyers and hemorrhoids.
  - Finally, if you are an almighty being and *almighty lazy*, you don't even bother to make yourself. The odds are that there will still be a universe with me in it eventually.
- No - don't throw lightning bolts at me, or whatever else you have, for these blasphemous thoughts. The culprit is actually **Peter Atkins** who goes on about that (and the first and second law) in his wonderful books at length.
- While I was taking you into the rather lofty realm of universe making, you probably wondered why I did not pose another question up there:
  What are the **mechanical properties of pearlite?**
  - I do not need to ask this question because we know the answer from theory! We have areas were dislocations can move freely, and areas where they can't move at all. The material will be rather hard. There is some ductility but far less than in soft ferrite.
  - That's a bit brusque for now but I will get back to it in due time.