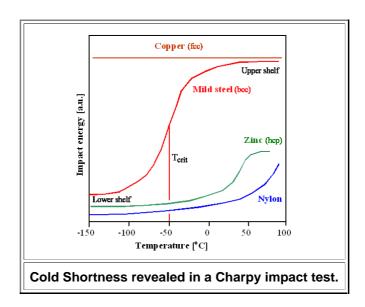
Ductile to Brittle Transition or Cold Shortness

Some Observations

Cold shortness was a big problem for a long time in sword making. It means that things get brittle when it's cold. The word "**short**" is old English, meaning "having a tendency to break or crumble" as in shortcake or shortening. It doesn't mean that things get smaller when it's cold.

Nowadays we call the more general effect that properties change from ductile to brittle with decreasing temperature "ductile to brittle transition" or *DBT*.

- Contrariwise, if we look at *increasing* temperatures, brittle materials may become ductile. DBT transitions are not restricted to iron and its alloys, however, they are rather common. They occur in more or less *all* bcc metals, to some extent in hexagonal (hcp) metals, in many non-metallic crystals and in polymers. There is, however, no cold shortness for fcc metals. They stay more or less ductile down to very low temperatures. The decisive question is what value we will find for the critical temperature *T*_{DBT} where the transition takes place. For pure iron and some steels *T*_{DBT} is well below "normal" temperatures but for some other steels it might be close to room temperatures. If we take silicon (Si), for example, we find it to be quite brittle at room temperature but ductile above a critical temperature of about 700 °C (1290 °F).
- Here is an example of what cold shortness looks like when you measure the fracture behavior in a <u>Charpy impact</u> <u>test</u>.



A *small* impact energy means that it is easy to fracture the material. In other words: it is brittle. A *high* impact energy means the material is ductile. In the picture above the critical temperature *T*_{DBT} for mild steel is -50 °C (-58 °F).

The impact energy is given in "a.u." = arbitrary units, meaning that numbers might be different for the different curves but that is not important here. **Upper shelf**" and "**lower shelf**" is steel engineering slang for the high and low fracture energy associated with ductile or brittle behavior, respectively. Their difference is a measure for the magnitude of the effect.

Hot shortness or red shortness, also a bane in early sword making, is completely different. Here we look at a ductile to brittle transition when the temperature goes up. Things that are ductile at low temperatures get brittle at high temperatures. That happens, for example, whenever some small amount of sulfur (S) is in the steel and precipitates at grain boundaries.

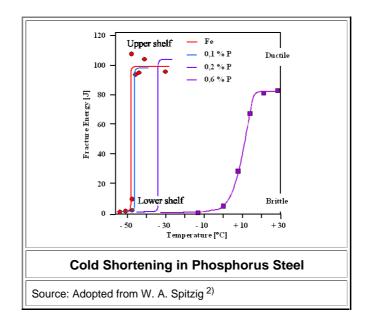
I could not find any pictures for red shortness in steel that is tied to sulfur. It doesn't seem to exist anymore because sulfur is under control. In contrast to cold shortness, the mechanism is rather clear and I won't go into it here.

Ductile to brittle transitions do not only happen as an effect of temperature. They may also be caused at a temperature that is initially well above the critical temperature *T*_{DBT} by, e.g., radiation (a major problem for steel in nuclear power plants), or exposure to hydrogen produced by some corrosion ("<u>stress corrosion cracking</u>"). Things like "<u>creep</u>" and "fatigue" might also be considered to fall under this heading.

If a ductile-to-brittle transition occurs in your material, you have a serious problem. If your material is under some mechanical load, it might simply break, often suddenly and without any warning. Major disasters we know about were caused by this. Most certainly there were also a lot of minor disaster we don't know about, for example when some warrior's sword suddenly broke because it became too cold for its TDBT.

For iron and steel, as I have stated <u>rather early</u>, red shortness is supposed to be caused by sulfur (and phosphorous, and ...), and cold shortness is supposed to be caused by phosphorous. That's all true but perfectly clean iron shows cold shortness, too; just at lower critical temperatures than iron with some phosphorus in it. So phosphorous only <u>raises</u> the critical temperature **T**_{DBT} of the DBT transition to noticeable levels. It doesn't really cause it. Below is a figure that illustrates this.

Care was taken to have an "ideal" iron - phosphorus system, with nothing else in there. <u>Charpy impact tests</u> provided the **fracture energy** (given in <u>Joule</u> [J]). Some (not all) experimental points are shown to give you an idea about experimental scatter.



- Several things become clear:
 - The critical temperature for pure iron is about T_{DBT} (pure Fe) = -50 °C (-58 °F). Your iron sword will never break because you simply don't use it when it's that cold.
 - The critical temperature increases with phosphorous concentration; at 0.6 % P it is T_{DBT}(Fe/0.6 P) ≈ +10 °C (50°F). Now you notice the effect.
 - The transition can be rather sharp. At 20 °C (68 °F) you may have a ductile phosphorous steel sword that
 is hard to break. But around freezing (0 °C (38 °F)) it will snap at the slightest impact since the fracture
 energy is now roughly 100 times smaller.

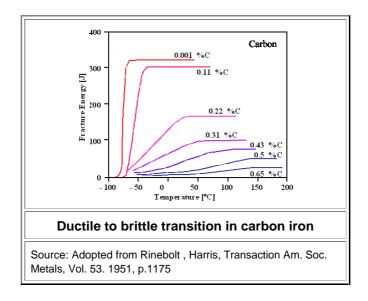
Looking at the two figures above, a few big "why" questions suggest themselves. I will state right away that they will not be easy to answer:

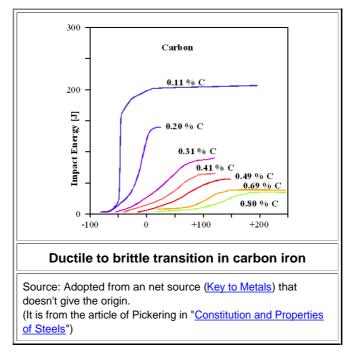
- Why is cold shortness somehow tied to the crystal lattice type? Why are <u>bcc</u> metals susceptible to cold shortness while <u>fcc</u> metals are not?
- Why is the DBT transition for pure iron so exceedingly sharp?
- Why and how does phosphorus influence cold shortness by raising TDBT?
- How about the rest of the periodic table? How do small amounts of whatever in iron influence the DBT transition?
- The answer, in the words of **Jianming Huang**, who wrote a PhD thesis entitled: "Ductile-to-Brittle Transition in Body Centered Cubic Metals..." in 2004 1, is:

"The (..) mechanism of this (ductile to brittle) transition still remains unclear despite of large efforts made in experimental and theoretical investigation.

I hate to admit it but I must agree with Jianming Huango. I can't give you a quick and easy explanation. I, or better Jianming Huango and his ilk, do know a few things, however, about brittle-to-ductile transitions. I can give you a general idea of what is at the root of "cold shortening" in iron even so some details are not yet clear. Before I do this, let's look at a few facts.

Here are two figures that shows basic cold shortness in iron and plain carbon steel:



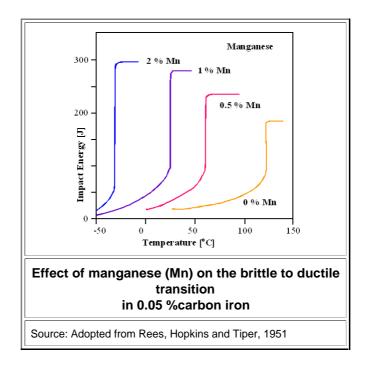


- While the curves look rather similar on a first glance, they give distinctly different T_{DBT} values for pure iron: -75 °C or -50°C (as before), respectively. On the absolute temperature scale (the only relevant one) that would be about -200 K or -225 K; a 12% difference. That's not too bad but tells us that things like grain size, possible unrecognized traces of other impurities, the way the Charpy impact test was done, and God knows what else, also influences T_{DBT} . In this case it might have been the difference between a "notched" and an "un-notched" specimen in the Charpy impact test..
- Here are a few rules for the dependence of the DBT transition temperature on test procedure and composition.
 The transition temperature at which brittle fracture occurs is lowered by:
 - 1. a decrease in carbon content,
 - 2. a decrease in velocity of deformation;
 - 3. a decrease in depth of the "notch";
 - 4. an increase in the radius of the "notch",
 - 5. a decrease in grain size.

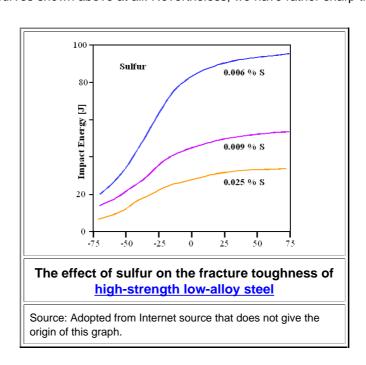
The second point is rather interesting. It tells us that the always very rapid **velocity of deformation** your sword experiences when hit by the cutting edge of your opponent, leads to a higher transition temperatures. In other words: In a sword fight your sword blade may behave like a brittle material even so it is perfectly ductile under normal conditions.

The last point, for example, tells you that "it is desirable, therefore, to use steel deoxidized or "killed" with aluminium and normalized to give fine pearlitic structure and to avoid the presence of bainite even if tempered subsequently and increasing the manganese content". Aha. For normal people that means: steel is a complex material, indeed!

Here are two more measured DBT transition curves dealing with manganese (Mn) and sulfur (S).

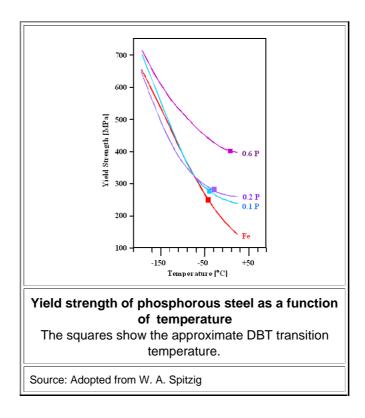


Obviously, manganese (Mn) is good for decreasing the critical temperature T_{DBT} to values that can be tolerated for most intended uses. But how come that $T_{DBT} \approx 120$ °C (248 °F) for manganese-free mild carbon steel? That does not agree with the curves shown above at all. Nevertheless, we have rather sharp transitions once more.



What we see is that sulfur is really bad for you—even in very low concentrations. It does not raise the DBT transition temperature very much like phosphorous, but tends to make the steel more brittle at all temperatures.

One last curve just to make clear that the large changes in fracture impact strength seen around the BTD transition temperature have nothing to do with tensile strength or hardness. You can be brittle and hard or brittle and soft, the same goes for ductility. What we see in the picture below is the yield strength (or hardness if you change the scale properly) of various phosphorous (P) steels as a function of temperature.

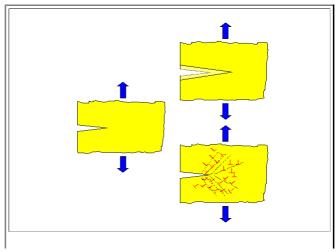


Shown is the yield strength of the same phosphorus steels as in the <u>figure above</u> as a function of the temperature. It is quite clear that phosphorous hardens iron at <u>higher</u> temperatures since the yield stress with 0.6 % phosphorus is 3 to 4 times large than that of pure iron. We <u>know that</u> already but what we didn't know is that the hardening effect more or less disappears at lower temperatures because the yield stress of the pure iron increases substantially with decreasing temperatures. It also becomes brittle at the temperature indicated. Note that the DBT transition temperature is <u>not</u> recognizable in the yield strength behavior.

The Explanation (Sort of)

- By now you must be thoroughly confused. That's fine, the experts in this area are also somewhat confused (they just don't admit it). What became quite clear, however, is that DBT transitions are always there and that exactly what will happen depends on many parameters, including some that the experimenter might not be aware of.

 As I have <u>stated above</u>, the exact mechanism of DBT transitions are still unclear. It is quite clear, however, that DBT transition behavior in bcc metals results form a competition between nanocrack growth and dislocation generation and movement.
 - Imagine a piece of steel under some tensile stress with a nanocrack at the surface or wherever. The specimen "wants" to get longer and has two options to do this as schematically shown in the figure below:
 - 1. The nanocrack opens up and grows into the interior. The separated pieces can move apart under the applied stress. The work piece elongates and fractures quickly as soon as the crack has grown through the whole of it.
 - 2. Dislocations are generated in areas where the stress is highest. That will be at the tip of the nanocrack. The dislocations move off into the interior of the crystal in such a ways that the stresses are reduced. The nanocrack will not grow. The plastic deformation always tied to dislocation movement makes the crystal somewhat longer but it does not fracture



Iron, Steel and Swords script - Page 5

What happens at DTB transitions

Left: A piece of material with a nanocrack under tensile stress.

Right top: The response is growth of the nanocrack. The material is brittle.

Right bottom: The response is generation and movement of dislocations. The material is ductile.

Both mechanisms compete against each other in a "winner takes all" kind of contest. Either the crack growth process wins, then almost no dislocations are generated and move, or the dislocation process wins, then the crack will not grow at all.

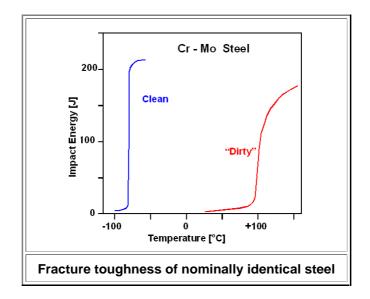
From the experiments it is clear that the temperature and impurity / alloy elements influence the fitness of the contestants in different and tricky ways.

- If, for starters, we look at an hypothetical ideal crystal, the major parameters are only
 - 1. Temperature as a measure of the thermal energy contained in the vibrations of the crystal atoms. Generating and moving dislocations always takes some energy and thermal energy thus always helps to generate and move dislocations. As it happens, in fcc metal crystals this help is welcome but not really needed. Dislocation movement is so easy anyway that the help of temperature is hardly noticed. In bcc crystals (or ceramics) the situation is fundamentally different. Without some help from temperature things become difficult at lower temperatures.
 - Crack growth doesn't care much about temperature. If there is sufficient stress, the bonds between the atoms break apart and it doesn't matter much if the crystal is hot or cold.
 - Surface and interface energy. A surface or interface always has a higher energy than a fictitious plane
 inside a perfect crystal since the atoms there do not have the best possible surroundings. A growing crack
 generates new surface and that takes a defined amount of energy.
 Refer to the fracture modules for details
- In many articles to DBT it is stated that dislocation movement in bcc crystals is more difficult in comparison to fcc crystals because the latter have more <u>glide systems</u> or different ways to move dislocations around. That is not really true. It's not how many ways you have to move dislocations around but how it depends on temperature. That dislocation movement in bcc crystals needs more thermal activation than in fcc crystals is, of course, tied to the same lattice geometry that defines the glide systems, but let's not confuse the issue here.
- DBT behavior is thus simply a result of which process needs less energy for its functioning. Energy is supplied by the applied stress and by the temperature. The dislocation process uses both contributions, the crack growth only the stress part. When the temperature goes down, the thermal energy available for the dislocation process goes down too, which means you need more stress to move them.
 - At the critical temperature T_{DBT} the stress is sufficiently large to promote crack growth and at smaller temperatures than T_{DBT} the crack growth mechanism takes over completely.
- Alloy elements, as we know by now, can do a lot of different things with respect to the microstructure. Let's enumerate the options to know what we are talking about next:
 - 1. They can be uniformly distributed as single dissolved atoms or small precipitates.
 - 2. They can form phases of their own, uniformly distributed in all kind of ways, e.g. as lamellae of cementite in ferrite.
 - 3. They may segregate in grain boundaries as atoms or as a sheaf of some phase they form with iron
 - 4. They may influence what the iron does, e.g. carbon enabling martensite formation.
 - 5. A mixture of all of the above.
- With respect to DBT transitions, we must consider how the impurities in one of those structures will influence crack growth and dislocation generation / movement.
 - As far as the dislocation mechanism is concerned, it is very likely that impurities make dislocation movement more difficult. That is the essence of hardening, after all. There might be just a small probability that in some special cases the generation of dislocations is made a bit easier with some suitable nuclei around, but the movement will still be more difficult. That would tend to raise T_{DBT} and that is what we see in most of the diagrams above.
- As far as crack growth is concerned, it might go easier or might be more difficult with impurities around. The first option will win if phases / precipitates formed by impurities are easier to crack than the regular crystal, meaning that their surface energy is smaller than that of iron. Since sulfur or phosphorous is not a particular strong material it stands to reason that a layer of sulfur or phosphorous in a grain boundary will give a crack a great opportunity to run along the grain boundary with little effort. That certainyl happens; freshy fractured phosphorous iron does fracture along the grain boundaries, which look silvery-white due to the phosphorous collected there. On the other hand, a tough-to-crack particle might stop a crack that hits it; at least it will slow it down.
- So about everything imaginable might happen, and as you have seen in the small collection of figures above, taken from the large world of DBT transitions in steels, a lot does happen. The DBT transition temperature might go up or down with some impurity concentration, the transition might become less sharp, and so on.
- You might be inclined to believe now that we do, after all, have a fairly good idea of what is going on. What is it we don't know?

Here is one of the major points, hotly disputed and not yet clear: Is it the *generation* of dislocations at the crack tip or their *movement* away from the crack tip that gets too sluggish low temperatures? Only fairly involved calculations with powerful computers, that are just now coming into the game, will answer that question in the near future

So just wait a while longer and DBT transitions will be fully understood.

Meanwhile - here is a puzzle for you. Shown is very different DTB behavior for nominally identical chromium-molybdenum steel:



The compositions of the two steels, if looked at closely, were:

	Cr	Мо	Ni	С	N	Si	Mn	S	Р
"Dirty"	21.22	2.020	0.020	0.019	0.038	0.490	0.840	0.008	0.010
Clean	20.32	2.100	0.010	0.004	0.004	0.010	0.010	0.006	0.007
Source: Constitution and Properties of Steels, p.538									

While there is a noticeable difference in the concentration of typically "good" alloy elements like <u>manganese</u> (Mn) or <u>silicon</u> (Si), it is not likely that those elements are responsible for the huge different in the DTB transition temperature observed for this particularly corrosion-resistant <u>ferritic high-alloy steel</u>. It can only be the little bit of carbon and nitrogen still present in the "dirty" variant.

One might speculate that we have a "Cotrell-Bilby cloud" at work once more (look it up!) but I don't know that for sure. What I do know is that here is one of the reasons why "clean steel" and "interstitial-free steel" gain more and more attention.

¹⁾ Huang, Jianming: "Microstructural Effect on the Ductile-to-Brittle Transition in Body Centered Cubic Metals Investigation by Three Dimensional Dislocation Dynamics Simulations", Thesis for Doctor of Philosophy in Mechanical and Aerospace Engineering; University of California, Los Angeles, 2004.

²⁾ W. A. Spitzig: "The Effects of Phosphorus on the Mechanical Properties of Low-Carbon Iron", Metallurgical Trans., Volume 3, May 1972, p. 1183 - 11 88.