Theoretical Graphite Growth in Ductile Iron

by David Sparkman May 10th 2010 all rights reserved

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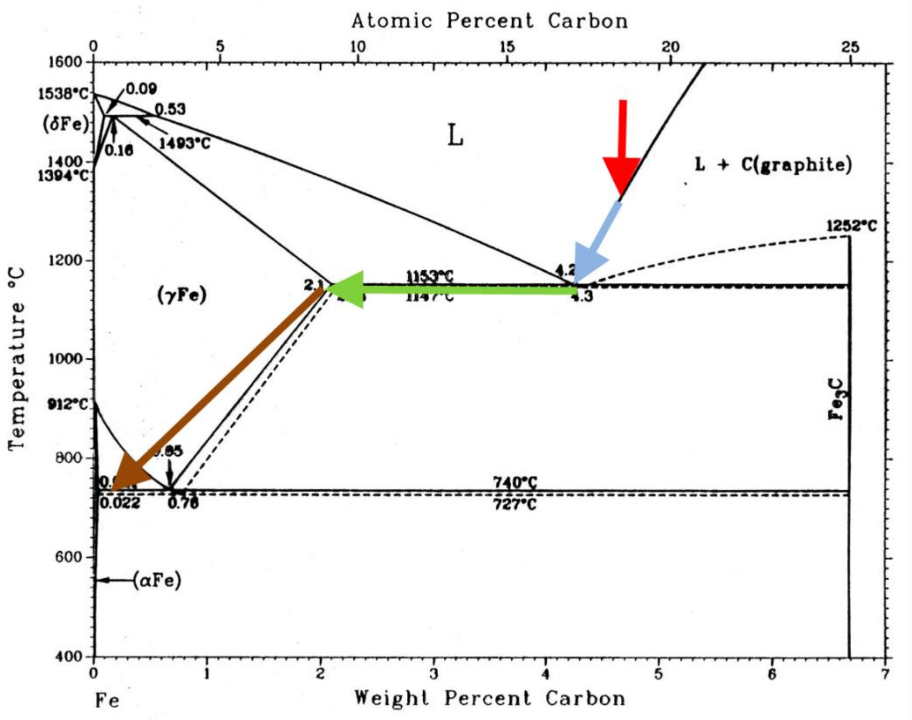
Follow with me the phase diagram below and I will explain some of the things that were taught in Materials Science 101. The red arrow represents the carbon content of some hyper-eutectic molten iron of about 4.6 C.E. Furthermore, let's assume a 3.8 carbon and a 2.4 silicon to make the 4.6 C.E. As the temperature drops, the molten iron contracts. The gates should still be open, so the loss in volume is made up from the risers and runner system.

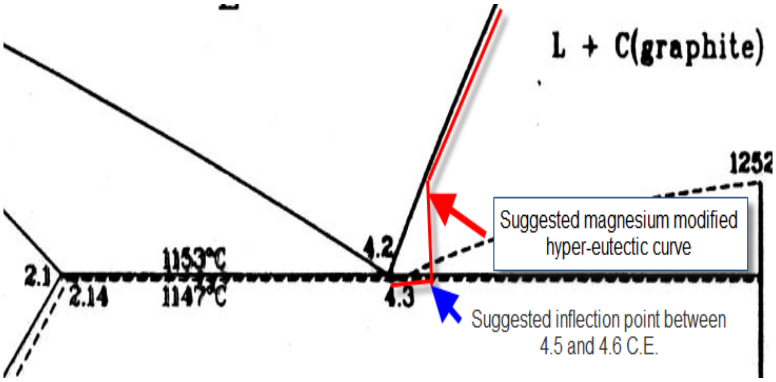


As it reaches the graphitic liquidus and follows the blue line downward, the carbon equalivant content of the iron changes to 4.3. This loss is entirely due to carbon changing into graphite so the amount of graphite will be 4.6-4.3 or about 0.3 % by weight. Graphite occupies about 3 times the volume of its percent concentration, so that means that 0.9% volume expansion of the iron occurred during the temperature loss represented by the blue arrow. The gates are still probably open so this volume expansion pushed iron back into the risers. Solid risers are generally a sign of hyper-eutectic iron and shrinkage.

Next the casting goes though the eutectic arrest and we follow the green arrow. This brings the C.E. down to 2.1%. With all of the silicon being solid, we might safely assume that the C.E. is now 100% carbon. That would mean that the graphite is the balance. So 3.8 C – 0.3 C (came out earlier) – 2.1% C = 1.7% graphite or a graphite volume of 5.1%. This does assume steady state graphite growth, and if this errors, I would expect a little more graphite. Meanwhile the iron has contracted considerably when it changed from liquid to solid. Not all of the contraction was offset by the graphite, so there are stresses in the soft metal. These stresses can be embedded in the grain boundaries as either thicker grain boundaries (less dense than the crystals) or be relieved by shrinkage or suck-ins.

As the casting continues to cool, it continues to contract, but the carbon continues to move to the graphite sites and grow the volume of graphite. If there is sufficient alloying in the metal, up to 1% of the carbon can be tied up as pearlite or martensite[1]. Furthermore about 0.3% of the carbon remains hidden in the iron even at room temperature. This can be shown by the growth in graphite volume of about 1% during heat-treating even when pearlite is not present. It may also explain the changes in iron during cold treatment.

The balance of the carbon that is not tied up in pearlite/martensite, or as hidden carbon, then goes to the graphite nodules and causes the graphite to occupy 9 to 10 % of the volume of the casting (10-11% if heat treated). The brown arrow represents the loss of carbon to the graphite as we pass though the eutectoid temperature. If the pearlite is not stabilized, the carbon content continues toward the estimated lower limit of 0.2 to 0.3% carbon. Again, this lower estimated limit does not show up as pearlite, but only reveals itself during heat treating as an increase in graphite volume and a reduction in the brittleness of the casting (minor decrease in tensile and yield with significant increase in elongation).



One trick that is possible in ductile iron that is not mentioned very much is to suppress the formation of graphite in the liquid with magnesium. Depending on a lot of variables we don't yet understand very well, irons with a C.E. of up to 4.55 to 4.60 can freeze with no graphitic liquidus! This exhibits itself as a thermal analysis curve without the graphitic liquids arrest and a micro that does not exhibit bimodal distribution. This of course means that the casting can benefit by retarding that volume increase until after the gates have frozen off giving almost 1% more total volume to the casting to offset shrinkage. Of course, if the graphite expansion occurs when the gates are frozen, but before the mold walls are thick enough to take the pressure, mold wall movement occurs, and massive shrinkage results. Though I have seen many hyper-eutectic chemistries result in a single eutectic arrest, research still remains to be done on what the rules of chemistry competition are that provide this plateau. This would be a great project for some college student to undertake.

So this trick is difficult to pull off.

1. Don't exceed some balance in chemistry that causes graphite to form in the liquid.
2. Be sure that the gates close off before the graphite starts to grow and create volume.
3. Be sure that the graphite grows as late as possible so that the casting walls are strong enough to not bulge out from this expansion and cause mold wall movement.

Because of item 3, this trick is generally limited to smaller size castings. In the real world, the gates don't always freeze off at the best time. Some of the expansion does get lost to the risers. It is probably better to err in that direction than to have the gates freeze early and not be able to feed the loss in volume due to the liquid metal contraction.

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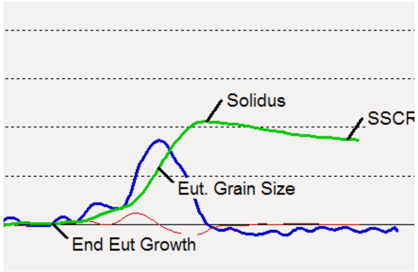
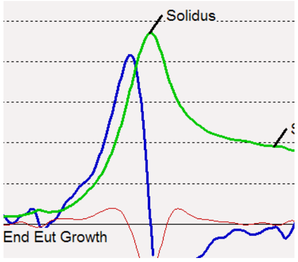
[1] Dr. Carl Bates demonstrated that machinability problems that we have seen with pearlitic ductile irons was due to pearlite exceeding the traditional 0.8% carbon content. He did this by comparing the thickness ratio of the cementite plate vs. the ferrite plate and showing that the carbon content of the cementite could exceed 0.8% and that it correlated with increased toughness of the iron as measured by machining.

Preventing Shrinkage

The issue of shrinkage is one of balancing graphite growth with the natural shrinkage of the matrix of metal. At the eutectic temperature, the matrix moves to a 2% carbon content with the balance being ejected as graphite. This is not enough graphite to replace the lost volume of the casting at this temperature and so a deficit of about 4% to 5% volume has to be made up at this point. The preferred method is to generate disorder in the grain boundaries which shows up as "stress" – an endothermic reaction of the thermal analysis curve. The unwanted method of replacing this volume deficit is to generate voids in the casting as either micro-shrinkage or micro-porosity. In this case the stress as seen by thermal analysis is greatly reduced or eliminated. One additional factor no one has considered is the final freezing temperature of the grain boundaries. The theory is that the longer the grains remain loose, the more stress can be taken up by the boundaries and the less likely the casting is to pull voids. This freezing temperature is highly dependent on the concentration of tramp elements in the grain boundaries. So while we are suspicious of the presence of too many tramps in our metal, they may be assisting us in preventing shrinkage.



No stress in the grain boundaries



High Stress in grain boundaries

Summary

To summarize, only about half of the graphite is produced in the casting by the time the grain boundaries freeze off at the solidus point. The rest of the final graphite grows as the casting cools down with almost all of it finished by the time the eutectoid temperature is reached: about 740 C. The percent contraction of the steel matrix of the casting does not occur on the same time frame as the percent graphite growth, and the result is stress which reveals itself as an endothermic peak at solidus. The stress energy is "stored" in the grain boundaries as a more open grain boundary, or is relieved by a shrinkage or suck-in defect. If the stress is still present when the remainder of the graphite grows, then, like a hipped (hot isostatic pressure) aluminum casting, the grain boundaries densify under the resulting hydrostatic pressure. If shrinkage released the stress and we start with dense grain boundaries, then we could speculate on if the resulting pressure would "grow" the casting in the thinker sections making one think we might have had mold wall movement. It would be difficult to tell the two causes apart.

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