Tramp Elements in Grey and Ductile Iron

by

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More and more low alloyed steels are being produced these days. These steels are finding their way into your charge yards. Some of the elements entering your process are not even being checked with your standard chemical analysis equipment. The concentrations of these elements causing adverse effects may be so low they may not be detectable with arc spark spectrometers.

A major effect of tramp elements is they change the temperature of the graphite and white iron eutectic. If everything else such as cooling rate and the level of inoculation stays the same, this can lead to serious problems. Figure 1 is an idealized equilibrium phase diagram. This diagram can be considered as a road map for structures that form during cooling from liquid to solid iron.

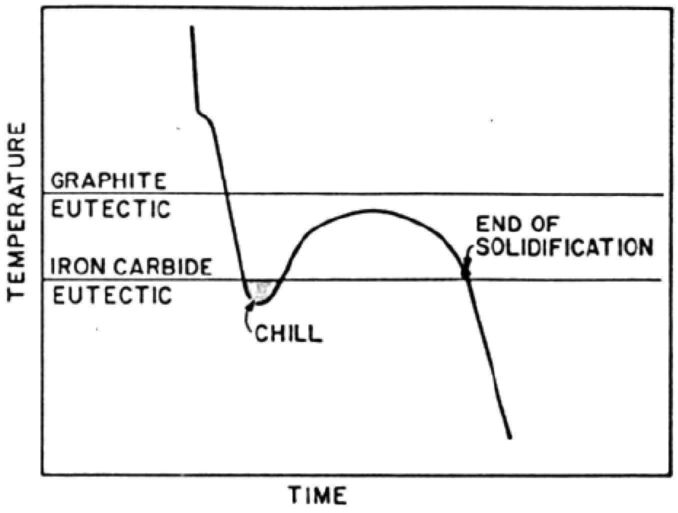


Figure 2

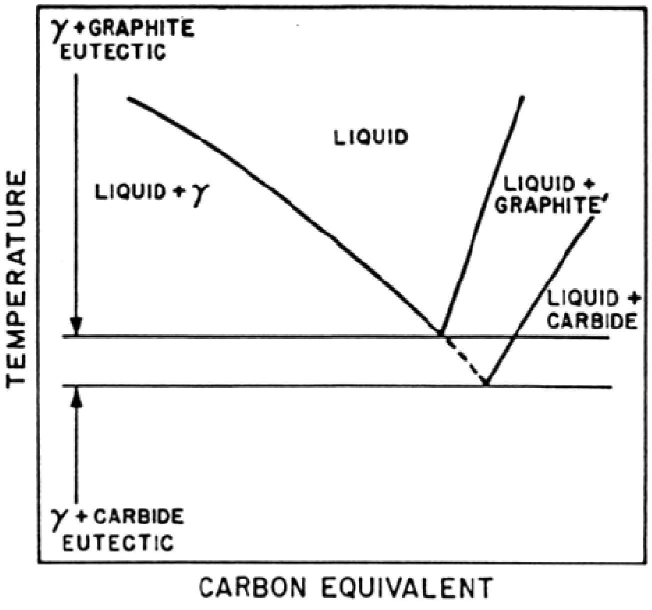


Figure 1

In the real world, the iron temperature falls below the equilibrium temperature before solidification begins. This is because something needs to initiate solidification. If the iron temperature drops below the carbide eutectic temperature before there is enough energy differential to cause solidification to begin then carbides form. This initial solidification releases enough energy to raise the temperature of the remaining liquid to above the carbide eutectic and the rest of the liquid solidifies as austenite and graphite eutectic. Inoculation is used to provide sites for solidification to begin at a higher temperature preventing carbides from forming.

If the situation shown in Figure 2 occurs then iron carbides will form in the super-cooled area of the castings. This is frequently corners and edges where the heat extraction rates are very high. If tramp elements affect these eutectic temperatures and cause them to be raised or brought closer together, iron carbides will form.

Eutectic carbides in the corner of a light-section nodular iron casting (etched 4% picral × 75).

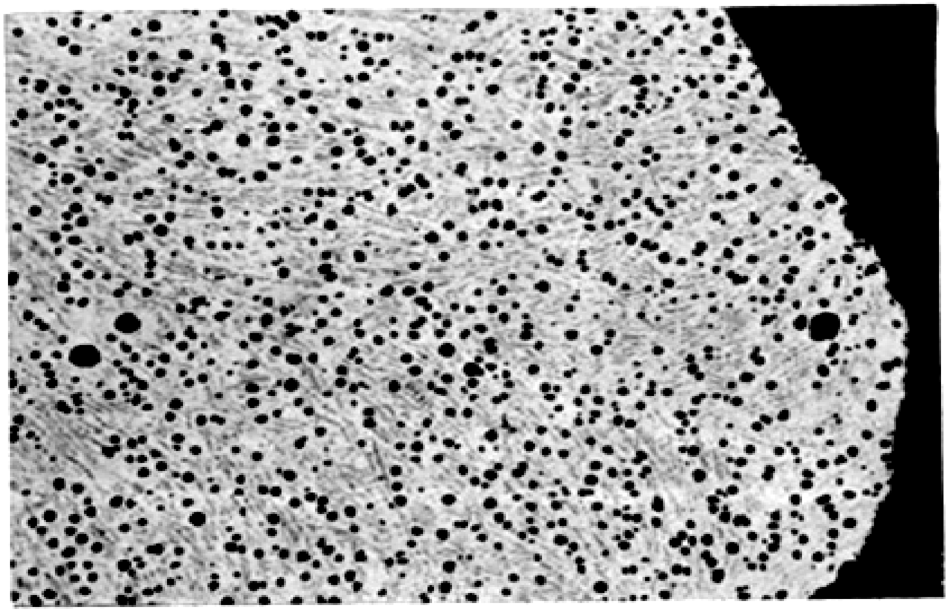


Figure 3

Figure 3 is an example of carbide formations in the corners which makes the machine shops very unhappy.

The phase diagram shown in Figure 4 shows the effect of various elements on the graphite and white iron eutectic temperatures. Some elements such as chromium, a carbide stabilizer, cause the two temperatures to be closer together. Elements considered graphitizers, such as silicon, widen the spread between these two temperatures.

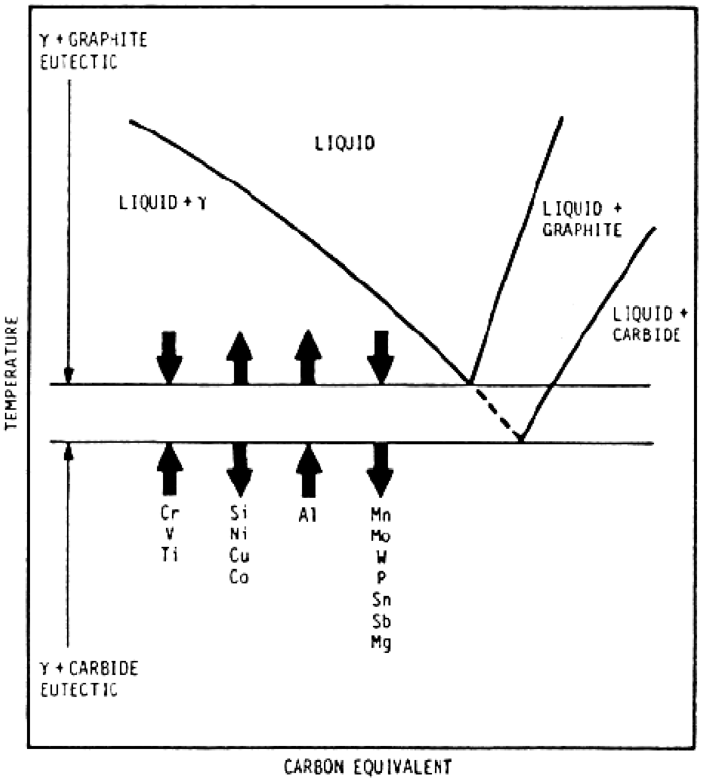
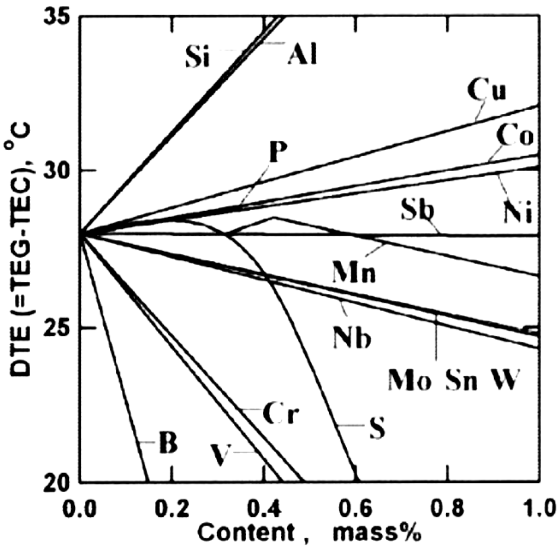


Figure 4

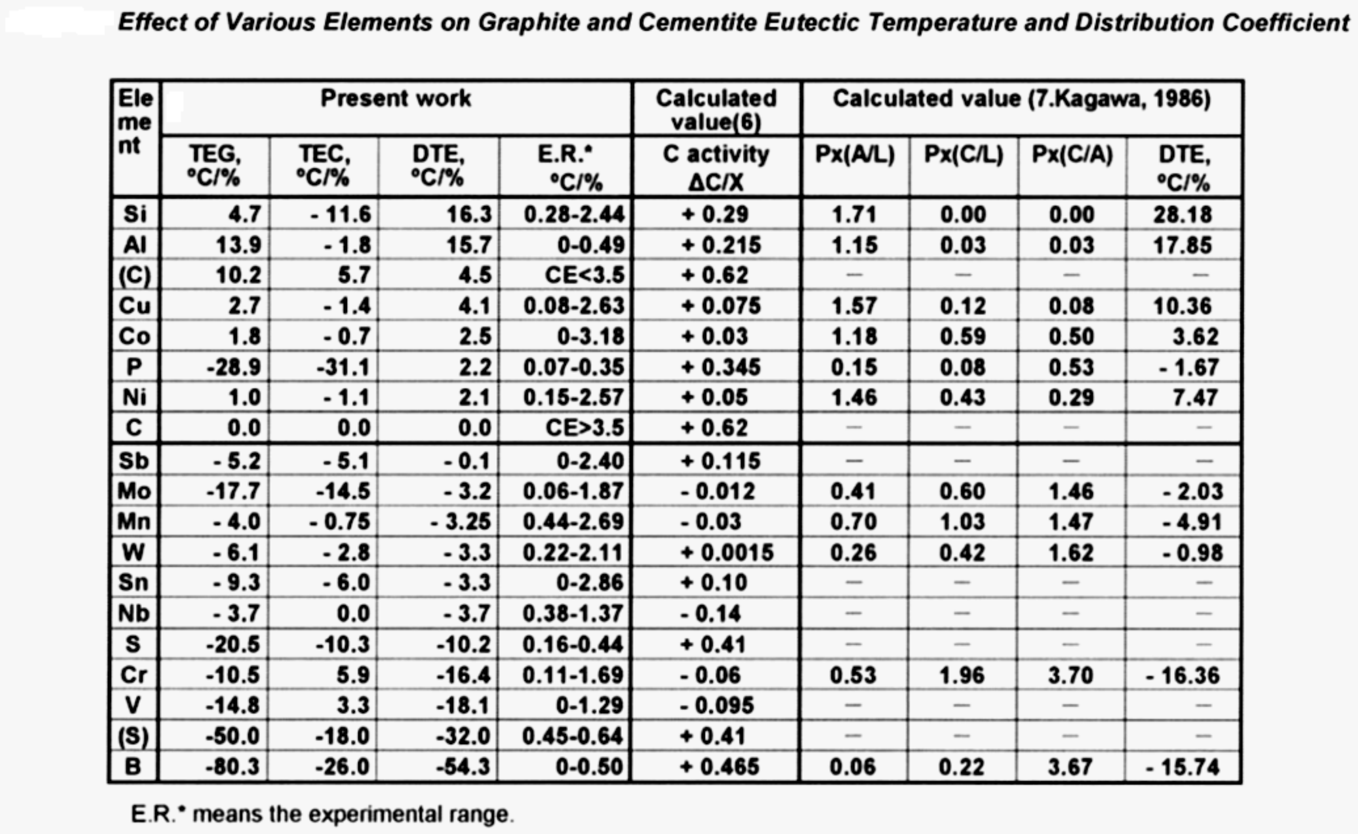
In 2005, Kanno and others presented a paper at the AFS Casting Congress in which they showed the effects of many elements on what they called the DTE. This is the temperature difference between the graphite and white iron eutectic temperature. In "normal" iron we typically see the difference to be 35-45 ˚C. Figure 5 shows that a small increase in some elements can make a very big difference. If segregation of these elements to the last liquid to solidify is taken into account, this effect can be quite dramatic.



Effects of alloying elements on DTE: DTE = TEG – TEC.

Figure 5

Figure 6 is a chart from the same paper and may be helpful in getting a feel for the effects of tramp elements on the graphite and white iron eutectic temperatures.



Effect of Various Elements on Graphite and Cementite Eutectic Temperature and Distribution Coefficient

Element	Present work				Calculated value(6)	Calculated value (7.Kagawa, 1986)			
	TEG, °C/%	TEC, °C/%	DTE, °C/%	E.R.* °C/%	C activity ΔC/X	Px(A/L)	Px(C/L)	Px(C/A)	DTE, °C/%
Si	4.7	- 11.6	16.3	0.28-2.44	+ 0.29	1.71	0.00	0.00	28.18
Al	13.9	- 1.8	15.7	0-0.49	+ 0.215	1.15	0.03	0.03	17.85
(C)	10.2	5.7	4.5	CE<3.5	+ 0.62	—	—	—	—
Cu	2.7	- 1.4	4.1	0.08-2.63	+ 0.075	1.57	0.12	0.08	10.36
Co	1.8	- 0.7	2.5	0-3.18	+ 0.03	1.18	0.59	0.50	3.62
P	-28.9	-31.1	2.2	0.07-0.35	+ 0.345	0.15	0.08	0.53	- 1.67
Ni	1.0	- 1.1	2.1	0.15-2.57	+ 0.05	1.46	0.43	0.29	7.47
C	0.0	0.0	0.0	CE>3.5	+ 0.62	—	—	—	—
Sb	- 5.2	- 5.1	- 0.1	0-2.40	+ 0.115	—	—	—	—
Mo	-17.7	-14.5	- 3.2	0.06-1.87	- 0.012	0.41	0.60	1.46	- 2.03
Mn	- 4.0	- 0.75	- 3.25	0.44-2.69	- 0.03	0.70	1.03	1.47	- 4.91
W	- 6.1	- 2.8	- 3.3	0.22-2.11	+ 0.0015	0.26	0.42	1.62	- 0.98
Sn	- 9.3	- 6.0	- 3.3	0-2.86	+ 0.10	—	—	—	—
Nb	- 3.7	0.0	- 3.7	0.38-1.37	- 0.14	—	—	—	—
S	-20.5	-10.3	-10.2	0.16-0.44	+ 0.41	—	—	—	—
Cr	-10.5	5.9	-16.4	0.11-1.69	- 0.06	0.53	1.96	3.70	- 16.36
V	-14.8	3.3	-18.1	0-1.29	- 0.095	—	—	—	—
(S)	-50.0	-18.0	-32.0	0.45-0.64	+ 0.41	—	—	—	—
B	-80.3	-26.0	-54.3	0-0.50	+ 0.465	0.06	0.22	3.67	- 15.74

E.R.* means the experimental range.

Figure 6

As solidification of the original liquid iron takes places, the solid iron may not be able to hold as much of some elements as the liquid does. These elements are forced out and into the remaining liquid. This raises their concentration in the liquid and can raise or lower the graphite and white iron eutectic temperature of the remaining liquid.

Figure 7 shows an idealized situation where the last liquid is not solidified before the temperature gets below the white iron eutectic temperature. This can be caused by the carbide eutectic being raised by elements forced into the remaining liquid. This situation will produce carbides in the last iron to solidify which are the cell boundary areas or the thermal centers of castings.

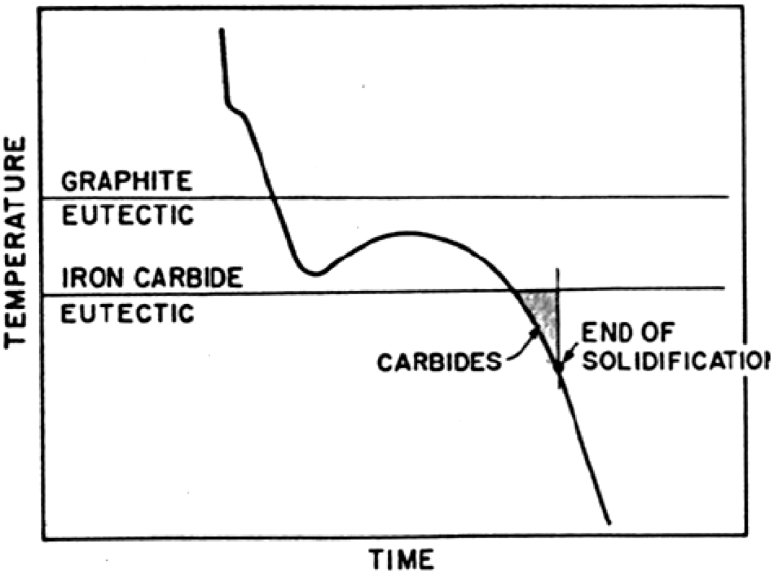
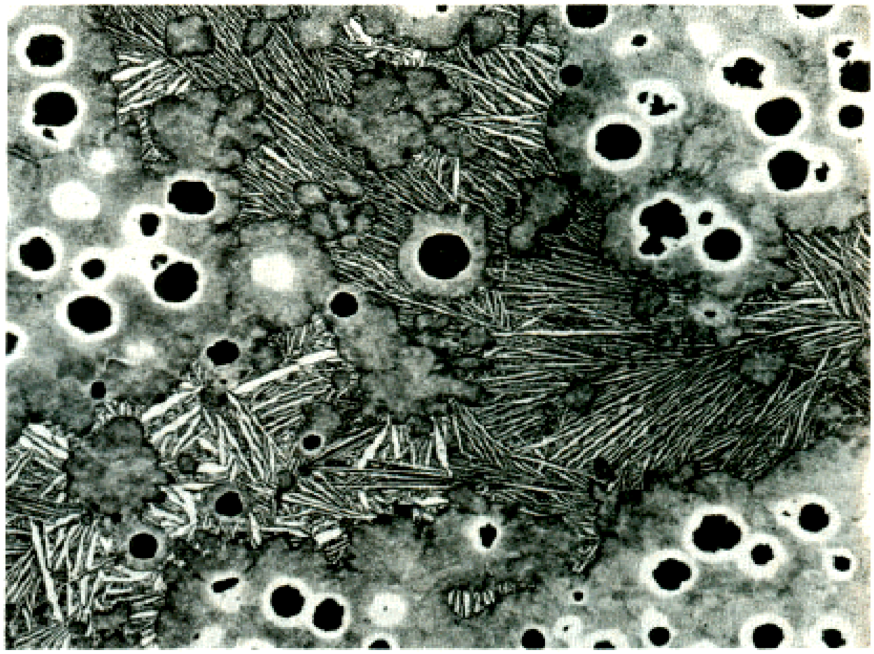


Figure 7

In this situation the increasing concentration of elements raises the carbide eutectic temperature in the liquid to the point that it is above the liquid temperature and this last liquid solidifies as carbides.



Inverse chill of acicular form present at the centre of a 30mm-diameter nodular iron bar. Etched in 4% picral. × 100

Figure 8

Figure 8 is an example of inverse chill. It occurs at the thermal center or the last place to solidify. If a drilling operation encounters this type of structure, a broken drill will very likely be the result. This may be extreme but this same type of tramp element enrichment of the liquid can lead to cell boundary carbides that can be very difficult to detect and can adversely affect machining.

I'd like to discuss several specific elements that we have seen in recent years. Some elements, such as lead, also affect the form of the graphite that solidifies. Lead is found in many places. Free machining steels are alloyed with lead, obsolete brass can contain high levels of lead, and some bearing races use Babbitt metal which may contain very high levels of lead.

Lead, in very small concentrations, affects the graphite shape. Figure 9 shows a form of flake graphite called Widmanstätten graphite. When small amounts of lead contaminate the melt and in the presence of some hydrogen, this type of graphite can form. It has detrimental effects on mechanical properties. Other elements such as tellurium and bismuth in very small amounts can also promote this form of graphite. These two elements are used extensively in the production of malleable iron to ensure a fully carbidic structure as- cast. Using significant amounts of obsolete railway cast scrap could contaminate the melt with these elements.

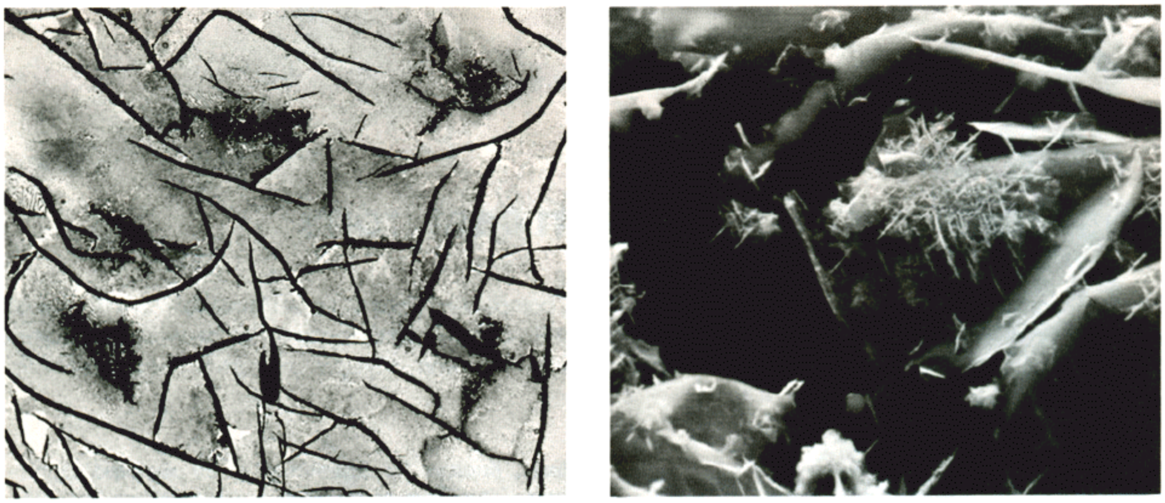


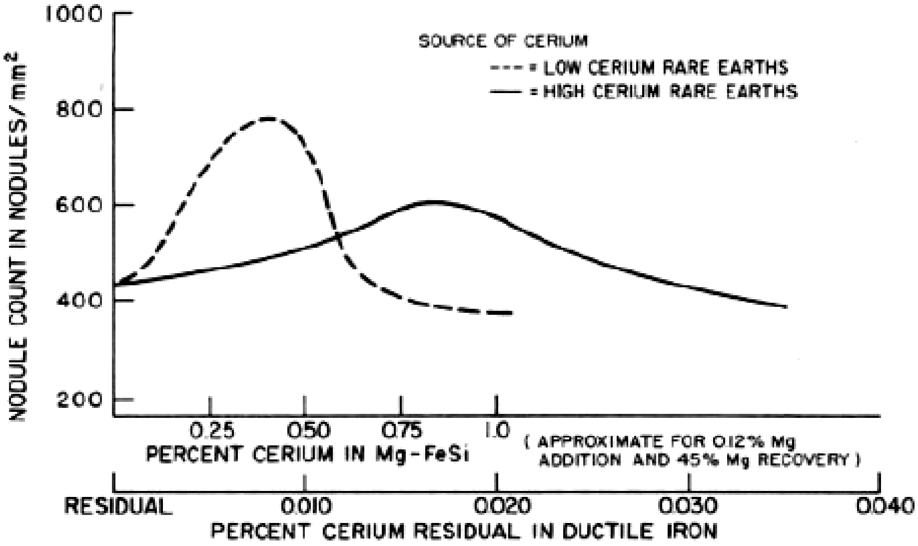
Fig. 1a 'Widmanstätten' graphite. Etched in 4 per cent picral. × 100.

Fig. 1b 'Widmanstätten' graphite. Stereoscan × 580.

Figure 9

Bismuth is sometimes added to ductile iron in small amounts and balanced with cerium. This is done to promote high nodule count in heavy section ductile iron.

Cerium and rare earth elements are frequently added to DI primarily to tie up elements like lead, tellurium, antimony and bismuth to name a few. When combined with the rare earth elements, they do not degrade the mechanical properties.

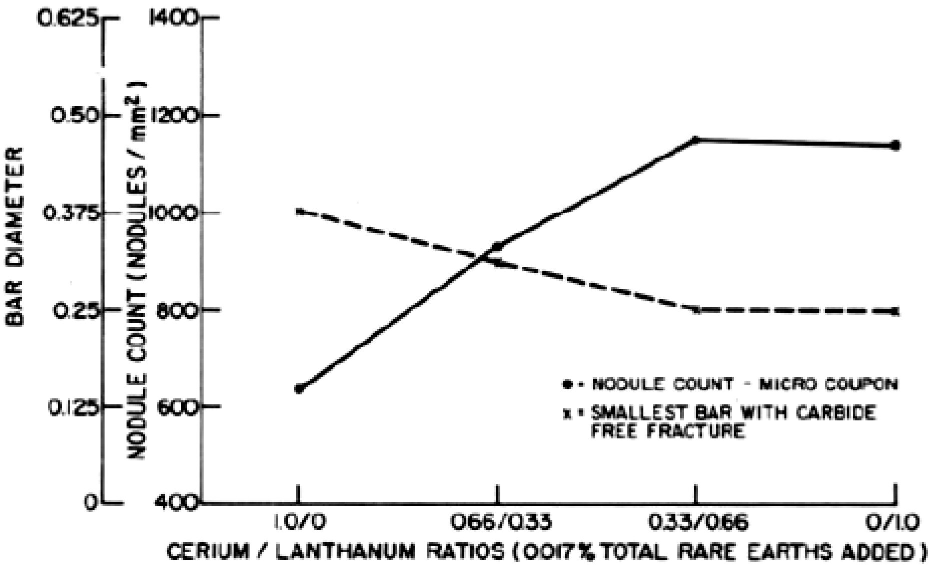


Composite diagram comparing effects of high and low cerium rare earth additions on graphite nodule count.

Figure 10a

Lalich, in a paper published in 1974, indicated that the type of rare earth addition used may determine the appropriate level of cerium. When using high cerium rare earth material, the cerium levels should be approximately 0.015%. If the rare earths were of a low cerium containing material such as mischmetal, the cerium levels should likely be about half that level. The other rare earth lanthanum adds about an equal amount when mischmetal is used.

In the graphs shown in Figures 10a and 10b, it appears that low cerium bearing rare earth addition may be a better material. At a constant total rare earth level, smaller sections were made carbide free when using low cerium content rare earth materials. Cerium is a potent carbide stabilizer and although a small amount can be beneficial, too much can lead to carbides particularly when the magnesium levels are high.

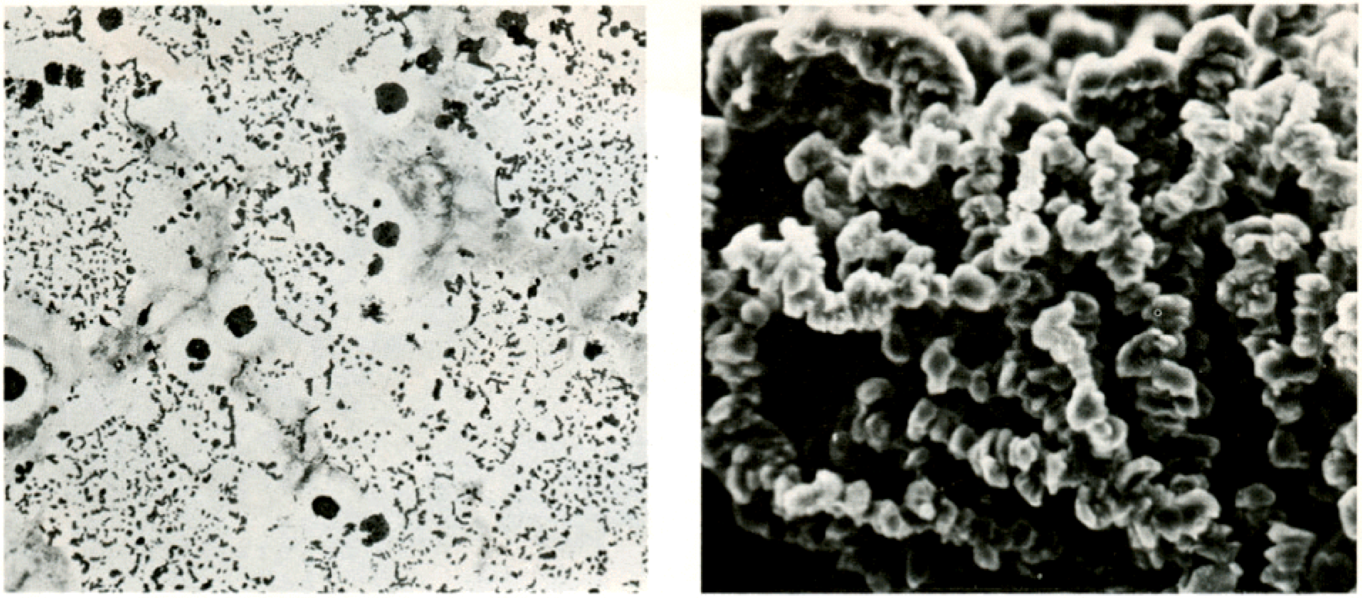


Graphite nodule count and carbide content as a function of cerium/lanthanum ratio.

Figure 10b

Frequently, in fact, almost all ductile iron contains a small amount of cerium or rare earth elements. This is typically added to tie up tramp elements that may be picked up from the steel and cast scrap. The old saying ***"A little bit is good but a lot is not necessarily better!"*** applies to this practice. If a very pure charge is being used with very low residual levels, too much cerium can cause "chunky" graphite to form.

As seen in the Figure 11 photograph on the right, "chunky" graphite is interconnected graphite and will reduce the mechanical properties very rapidly. Cerium is also a very potent carbide stabilizing element and if it gets too high, especially if the magnesium levels are high, it can lead to carbides.

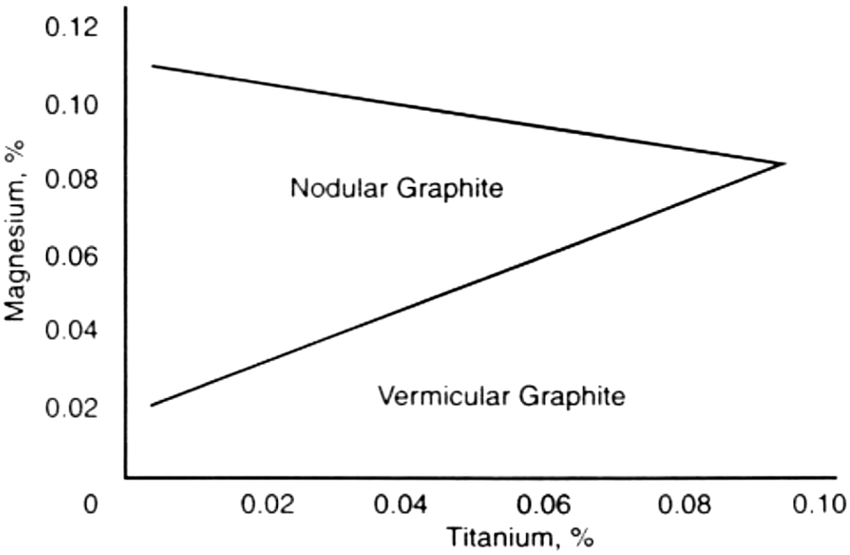


'Chunky' graphite. Etched in 4 per cent picral. ×100.

'Chunky' graphite. Stereoscan ×1840.

Figure 11

Titanium is sometimes added to iron intentionally. When used appropriately, this can be beneficial. Titanium has and still is used to produce CGI. When added to nodular iron it restricts the growth of nodules and causes the vermicular form of graphite to form. This is good for making CGI but bad for making DI. Figure 12 shows the effect of raising levels of titanium on the level of magnesium that is required to produce nodular iron. Above approximately 0.09-0.1% Ti, it is difficult, if not impossible, to produce acceptable DI microstructures.



Influence of Titanium on the Nodularizing Effect of Magnesium.

Figure 12

As mentioned above, titanium is used to produce CGI. The downside of using titanium to produce CGI is that titanium carbonitrides are formed. These are very hard and cause poor tool life when machining CGI produced with titanium additions. In some applications this may be good because these same titanium carbonitrides enhance sliding wear resistance.

In gray iron, titanium is added to control nitrogen pinhole defects. This is quite effective and requires approximately a 0.025-0.035 % titanium addition. When adding titanium for this purpose, it is not uncommon to have to reduce the CE of the iron because nitrogen is a pearlite stabilizer and when it is tied up with titanium, increased amounts of ferrite form that produces reduced hardness and strength. Titanium also promotes undercooled graphite that can promote higher levels of ferrite. Frequently a 0.1-0.2 % reduction in CE is required to compensate. It is likely possible that another pearlite stabilizing element could be added but that would be an additional cost. Remember that when titanium gets above the 0.035 % level, it can begin to affect graphite shape and will promote undercooled graphite structures.

One last element that has been causing recurring problems is boron. This has been an issue for DI producers trying to make pearlitic grades of DI. One suggested theory for why very low levels of boron make it difficult to produce pearlitic DI is that boron ties up nitrogen which is a potent pearlite stabilizer. These same boron nitrides can also act as nuclei on which graphite precipitates during solidification. This would increase nodule count potentially and higher nodule counts can lead to more ferrite and lower hardness.

One foundry reported data shown in Figure 13. They were trying to produce 80-55-06 DI. When the boron levels were above 0.001% there were issues with low Brinell hardness levels. Even when they raised their alloy additions of copper, they were not able to successfully maintain the castings in the required hardness range.

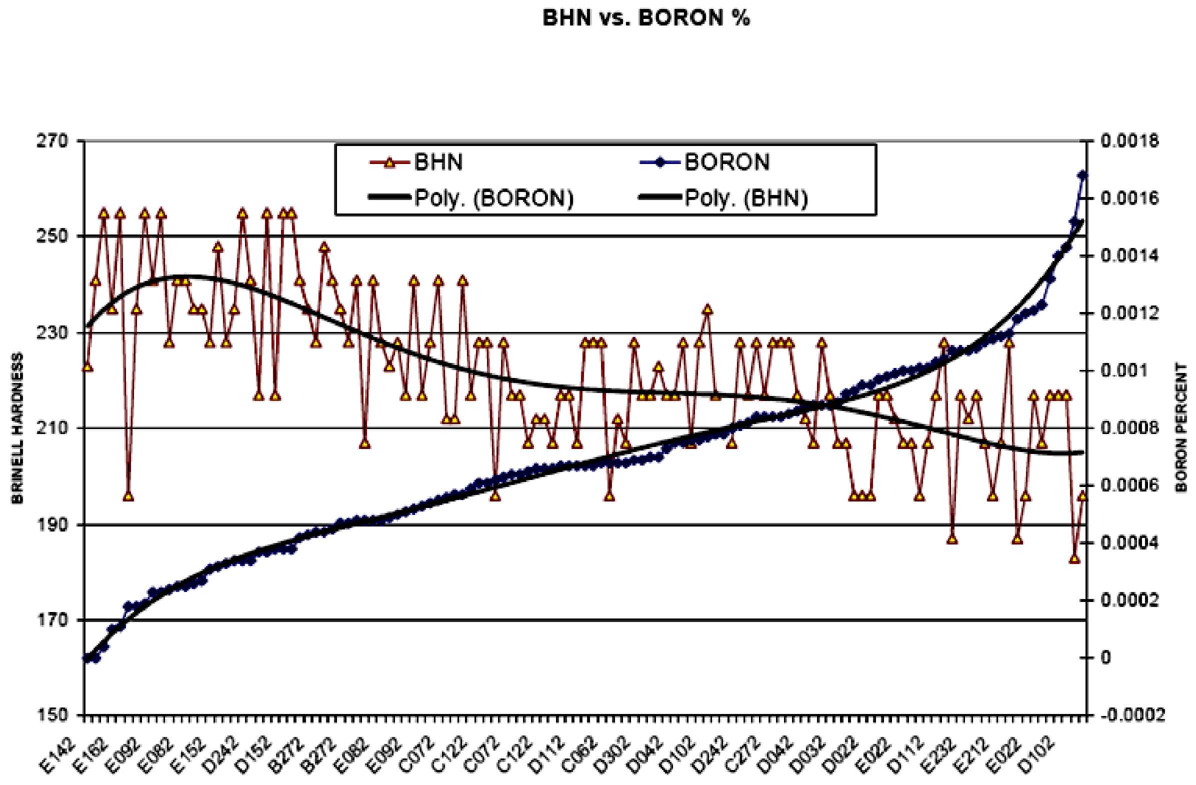


Figure 13

That foundry now monitors their boron levels and, based on their analysis, they adjust their alloy additions. Once they exceed 0.0009%, they pull pearlitic DI jobs and only run ferritic DI. We have seen this happen at numerous foundries over the last several years.

Measured Spectrographic B Level	% Cu	% Mn
≤0.0003% (3 ppm)	0.35 to 0.4	0.30 to 0.35
0.0003 to 0.0006%	0.4 to 0.45	0.30 to 0.35
0.0006 to 0.0009%	0.50 to 0.55	0.35 to 0.40
≥0.0009%	Go to 65/45/12	

Figure 14 is a CCT curve diagram that we use to determine microstructures that form when iron cools. This diagram describes what happens during continuous cooling of iron through the eutectoid region. The eutectoid region is the temperature range where austenite which is formed during solidification transforms to ferrite and pearlite. This temperature region is also affected by changes in alloys. Alloys move these curves up and down but more significantly to the right. Ferrite begins to form when the iron temperature falls below the upper critical temperature and if the iron temperature stays above the lower critical temperature long enough for the transformation to take place, a ferritic microstructure would occur. If the austenite is not completely transformed by the time the temperature drops below the lower critical temperature, the austenite will transform to pearlite.

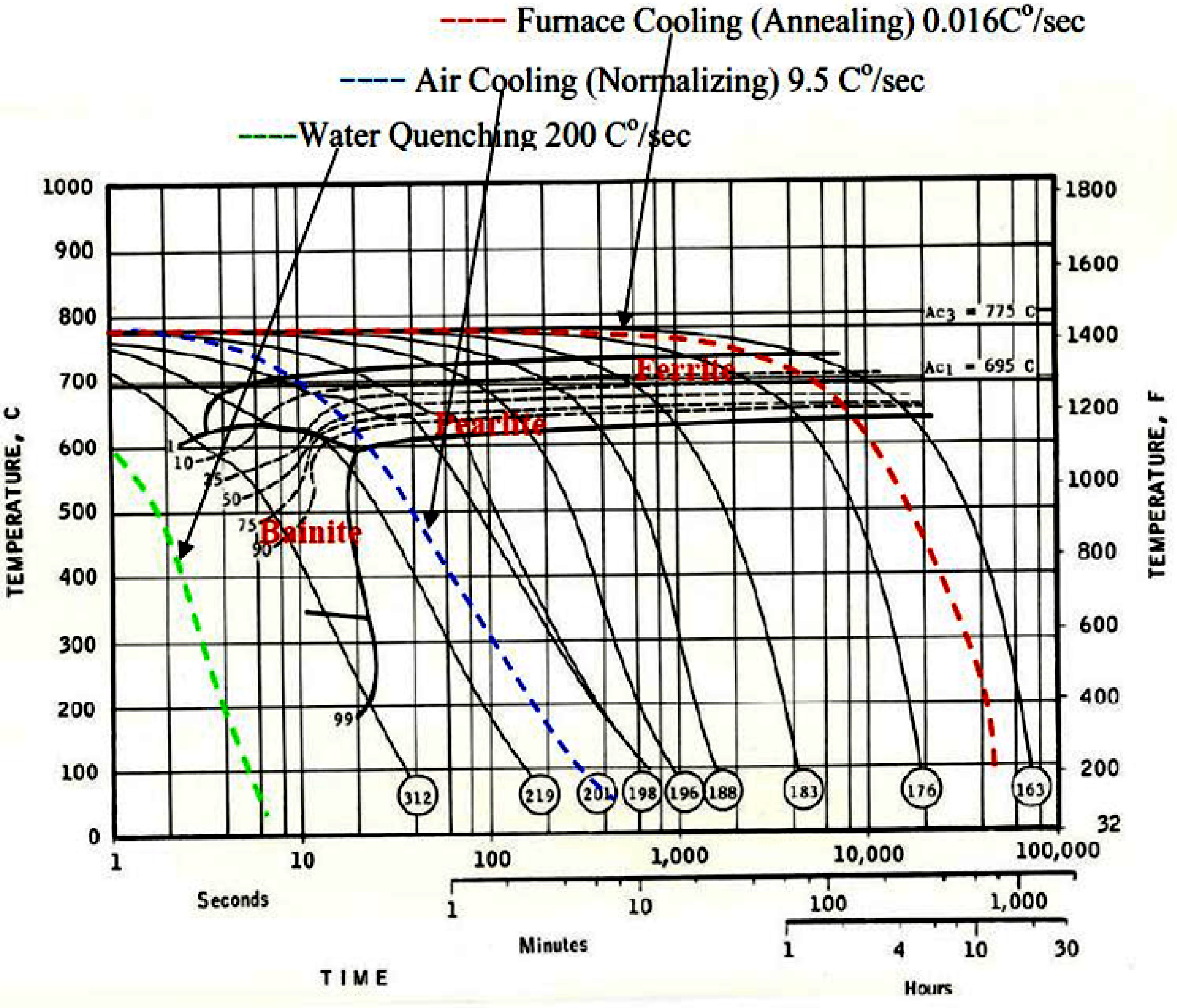


Figure 14

Alloys have different effects on the upper and lower critical temperature. These are the lines marked on Figure 14 as Ac1 for the lower critical temperature and Ac3 for the upper critical temperature. These formulas can be used to calculate these temperatures. These alloy effects can expand the region where ferrite begins to form. If this happens, then at the same cooling rate, potentially more ferrite would form before the lower critical temperature where the pearlite transformation begins.

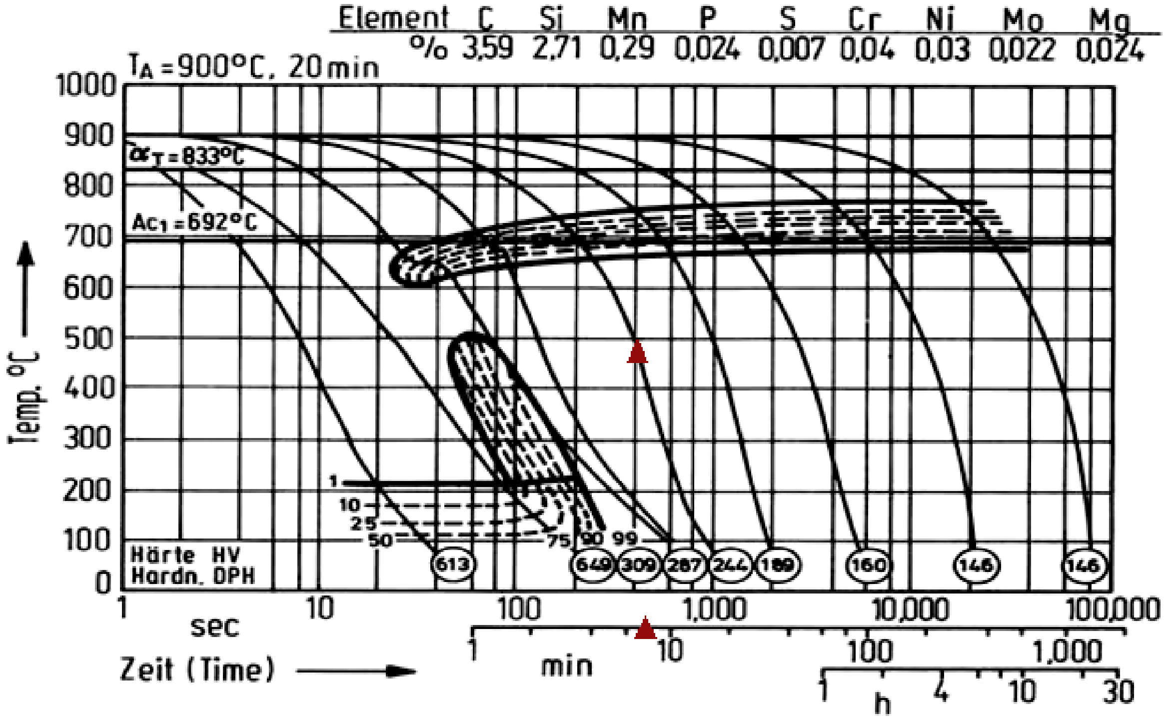


Figure 15a

The numbers in the ovals at the bottom of Figure 15a are expected matrix hardness values. If the normal cooling rate and chemistry produces a hardness of 244, then moving back up this curve to 463˚, the resulting time for the iron to cool was approximately 6-7 minutes. The expected matrix microstructure from the half cooling chart on the bottom is 45% ferrite and 55% pearlite.

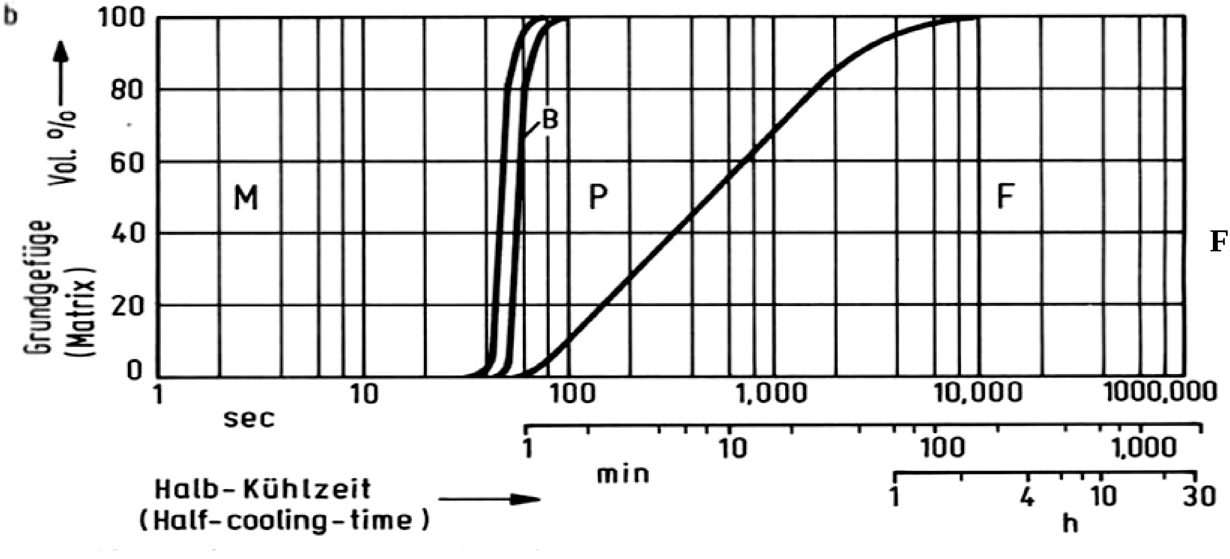


Figure 15b

Matrix structure (without consideration for non-transformed austenite) after continuous cooling

The x axis or the time axis for Figure 15b chart is called the half cooling time. This is the time it takes for the temperature of the iron to cool from the eutectoid temperature, on this chart 900˚C (1652˚F), to half way to room temperature. For a 900˚C eutectoid temperature that temperature would be 463˚ (865˚F). This chart is for a normal ductile iron.

Below is the CCT curve when Boron at 0.0023% or 23 ppm is in the iron. With the same half cooling time as in the previous curve at the same 6-7 minutes, the expected microstructure would be approximately 60% ferrite and 40% pearlite and the expected hardness is 212. This is very close to the effect reported at several foundries.

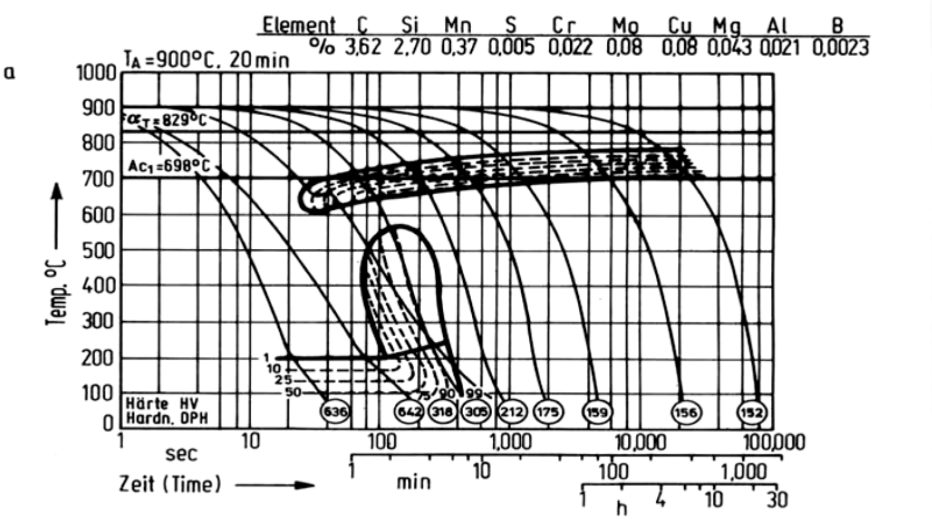


Bild 14 a. ZTU-Diagramm für kontinuierliche Abkühlung
Fig. 14 a. CCT-diagram

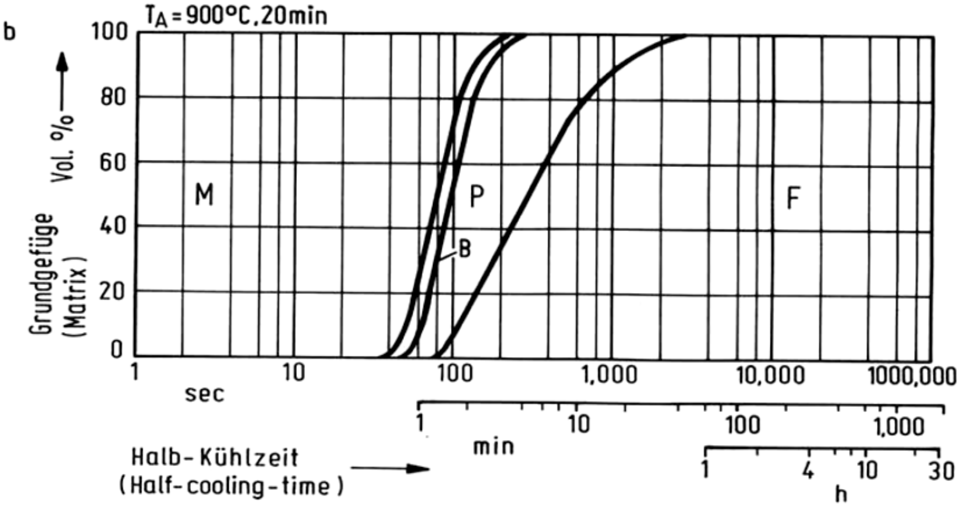


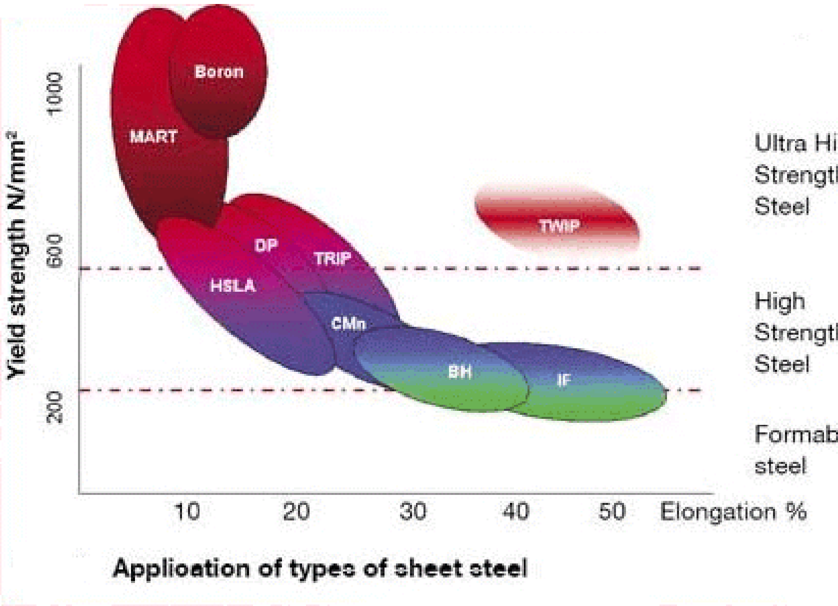
Bild 14 b. Gefügemengen-Schaubild für kontinuierliche Abkühlung (ohne Berücksichtigung von nicht umgewandeltem Austenit)
Fig. 14 b. Matrix structure (without consideration for non-transformed austenite) after continuous cooling

Figure 16

There has been a significant increase in micro-alloyed steels. One grade that has seen extensive use is Interstital Free Steel. This is a very low carbon steel that has very good formability. The use of this allows thinner steels to be formed into more intricate shapes. This type of steel is used on car body panels.

Boron is added to this type of steel to improve the formability. Another grade of steel used very extensively is bake hardening steel. This type of steel is also alloyed with boron to promote the transformation of the steel matrix when the paint gets baked. This transformation allows for improved dent resistance in the body panels and thus a thinner steel can be used which reduces weight.

High strength Boron steels are also used to form the structure around the passenger compartment. I would suspect that these grades of steel are finding their way into other products either by design or substitute of these very formable steels for other grades of low carbon steel. The level of boron in the IF Steel and the Bake Hardening steel is somewhere around 0.002-0.004 %. If 40% of this type of steel is used in furnace charges, levels of boron that foundries are experiencing could easily be reached. Figure 17 shows the types of sheet steel being produced.



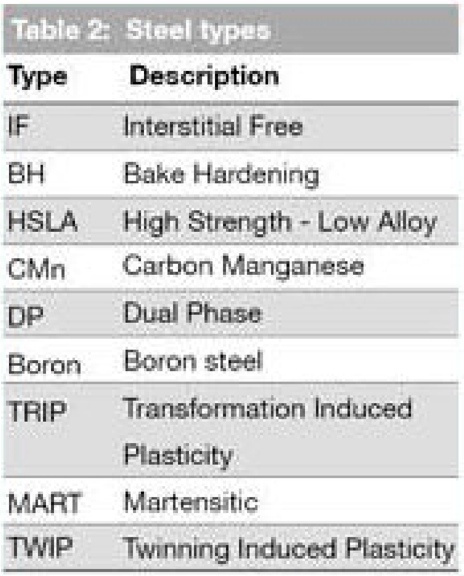


Table 2: Steel types

Type	Description
IF	Interstitial Free
BH	Bake Hardening
HSLA	High Strength - Low Alloy
CMn	Carbon Manganese
DP	Dual Phase
Boron	Boron steel
TRIP	Transformation Induced Plasticity
MART	Martensitic
TWIP	Twinning Induced Plasticity

Figure 18 shows some areas of an auto body where different types of steel are being used.

The Boron problem

- Very low levels of Boron have been increasingly found in ductile iron at several of our members recently.
- Boron is being used much more extensively in steel.
- This element is becoming a very serious problem.

Boron Solution?

- We could dilute it out with more virgin iron units from pig iron.
- There has been some research that suggests it can be fluxed out.
- We need research to find a solution to this problem. The steel producers are not going to stop producing it.

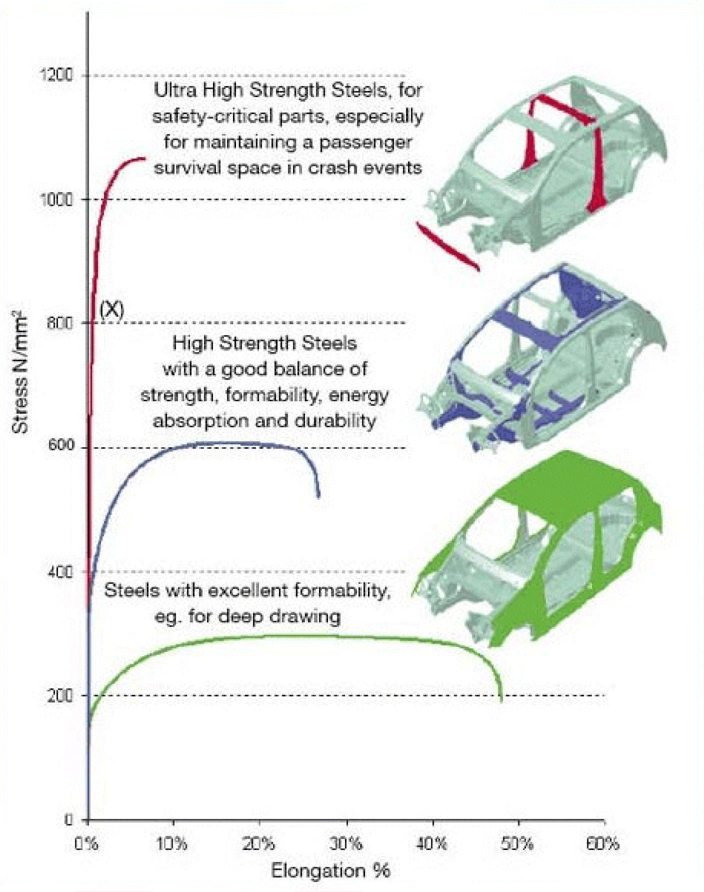


Figure 18

Conclusions

- Relatively small changes in the concentration of trace elements can have a profound effect on the quality of iron castings.
- More and more of these elements are being added to steels being produced which find their way into foundry charge yards.
- The concentration of some of these elements may be at or below the detection level of the spectrometers in use.
- There is a great deal of information published in the literature that can help solve a problem. Frequently a specific problem was solved and a solution published in the past.

In closing, I just want to point out some work done by Gary Ruff thirty years ago when he was a graduate student. The paper was published in the 1976 AFS Transactions and the title is ***"Control of Graphite Structure and Its Effect on Mechanical Properties of Gray Iron"***. The paper itself is very interesting but what I found most useful was a very extensive reference list and appendix attached to this paper. I would suggest everyone make a copy for their own reference. Obviously this is more directed toward gray cast iron and over the last 30 years even more work has been published that is not referenced in this paper. It is still a very useful reference to check the potential effects of different elements.

Gary listed chemical elements and the reported effects of each of these elements with the reference to the paper that reported the effect. This is a very useful document which allows for quick access to older information which can be evaluated to its applicability to current issues.

Figure References:

Figures 2,3,4,7 - "A Modern Approach to Alloying Gray Iron", J.F Janowak & R.B. Gundlach; AFS Transactions 1982

Figure 5,6 - "Effects of Alloying Elements on the Eutectic Temperature in Cast Iron", T. Kanno, et.al.; AFS Trans. 2005

Figure 8 - "Nodular (SG) iron - Possible Structural Defects and Their Prevention", BCIRA Journal; September 1981

Figure 9,11 - "Abnormal Graphite in Cast Iron", BCIRA Broadsheet 138-2

Figure 10 - "Effective Use of Rare Earths in Magnesium Treated Ductile Cast Irons", Lalich; AFS Trans. 1974

Figure 12 -"The Sorelmetal Book of Ductile Iron", QIT, First Printing 2004

Figure 13 - ICRI Member Foundry data, undated

Figure 14 - "Phase Transformation Kinetics and Hardenability of Medium-Carbon Steels" , Witold W. Cias, **undated.**

Figure 15, 16 - "Heat Treatment of Nodular Cast Iron-Transformation Diagrams", Rohrig & Fairhurst, 1979.

Figure 17, 18 - "Steel - The Basics", Corus Automotive Engineering, date unknown.