

The Role of Alloying Elements on the Fabricability of Austenitic Stainless Steel

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How many times have fabrication problems developed when a new coil or a new heat of steel is put in production? The problems can be tearing, cracking, scratching, poorer weld penetration, poor electropolished surface or a host of other problems. The usual procedure to determine the source of the problem is a hardness test, tensile test, and metallographic cross section and to review the mill test reports. Sometimes the source of the problem is spotted, but most often nothing out of the ordinary is found. In these cases the problem lies in the composition of the steel even when the alloy is within the specified composition of the steel.

Alloy Design

Austenitic stainless steels are designed to give corrosion resistance in many environments, resistance to hydrogen and 885° F (475° C) embrittlement, good strength, good ductility and low hardness. In its simplest form stainless steel is iron with 12% minimum chromium. This is what makes stainless steel rust resistant and allows the passive film to develop.

Stainless steel exists in three metallurgical conditions depending on composition and heat treatment: ferritic, martensitic and austenitic. These names refer to the crystallographic structure: ferrite is body-centered cubic, austenite is face-centered cubic and martensite is a distorted tetragonal which is the distorted face-centered cubic structure being changed into a body-centered structure. The characteristics of these structures are tabulated in Table I and are illustrated in Figure 1.

Table I: Metallurgical Types and Structures

Metallurgical Type	Crystal Type	No. Of Atoms	Phase Name
Ferritic	Body-Centered Cubic	9	Alpha or delta ferrite
Austenitic	Face-Centered Cubic	14	Gamma Iron
Martensitic	Distorted Tetragonal	10-13	Quenched or Tempered Martensite

Pure iron is body-centered cubic, existing from absolute zero to its melting point. As certain elements are added a “gamma loop” or austenite is created. These elements are carbon, chromium, nickel, manganese, tungsten, molybdenum, silicon, vanadium and

silicon. Of these elements nickel, manganese, chromium and carbon have the ability to extend the gamma loop the farthest. It is the combination of nickel and chromium that allows the austenitic stainless steel to be face-centered cubic from absolute zero to the melting point. It is this gamma loop that differentiates the ferritic alloys from the martensitic alloys. Martensitic stainless steels have a narrow chromium range, 14 – 18%, and must contain carbon, because only in this range can pure austenite be formed on heating, thus obtaining martensite on quenching. Ferritic alloys are either below 14% or above 18%. Varying the alloying elements can modify the range. The most common method is to keep the carbon content low.

The most common austenitic stainless steels are based on the 18-8 composition, 18% Cr + 8% Ni. If the steel has more than 8% nickel it is austenitic, if it has less nickel then it becomes duplex, that is austenite with ferrite islands. At 5% nickel the structure is about 50% austenite, 50% ferrite, and below 3% it becomes all ferrite. Therefore 8% nickel is the basis for the lowest cost austenitic stainless steel.

When alloying elements are added to the steel, they may take one of the positions in the basic crystal. These are called substitutional alloys and the alloy remains single phase. Other elements are small enough they can fit between the atoms and are called interstitial elements and the alloy remains single phase. Other elements will combine to form their own unique crystals and form certain phases. Still others act as dirt in the alloy and are called inclusions.

In this paper we will limit our discussion to the austenitic stainless steels, although many of the comments will apply to the other types as well. Table II lists the controlled elements in ASTM A240 compositions for the most common austenitic stainless steels. Many of the troublesome elements are not controlled, so it is essential that they be called out in either a customer specification or on the purchase order. Do not assume the alloy you buy is made to the mid range of each element. Since 1988 the steel mills have instituted a program called “alloy shaving” that uses the minimum alloying elements that will just prevent hot shortness and cold rolling cracking.

Closer control of the alloying elements is possible because of the development of the Argon-Oxygen-Decarburization (AOD) refining process that produces very low carbon and sulfur content in the steel. The use of AOD allows the extensive use of scrap metal. In fact, some heats are nearly all remelted scrap metal. The only disadvantage is a continual build-up of non-specified tramp elements like copper, boron and calcium. These elements may cause problems and their presence may explain why two different heats that have the “same” chemistry, at least according to the CMTR, act so differently.

Table II: ASTM Composition of Common Austenitic Stainless Steels

UNS	Alloy	C	Mn*	Si*	Cr	Ni	Mo	N*	Cu	Other
S30100	301	0.15	2.00	1.00	16.00-18.00	6.00-8.00	...	0.10
S30200	302	0.15	2.00	0.75	17.00-19.00	8.00-10.00	...	0.10
S30400	304	0.08	2.00	0.75	18.00-20.00	8.00-10.50	...	0.10
S30403	304L	0.030	2.00	0.75	18.00-20.00	8.00-12.00	...	0.10
S30409	304H	0.04-0.10	2.00	0.75	18.00-20.00	8.00-10.50
S30451	304N	0.08	2.00	0.75	18.00-20.00	8.00-10.50	...	0.10-0.16
S30453	304LN	0.030	2.00	0.75	18.00-20.00	8.00-12.00	...	0.10-1.16
S30500	305	0.12	2.00	0.75	17.00-19.00	10.50-13.00
S30908	309S	0.08	2.00	0.75	22.0-24.00	12.00-15.00
S31008	310S	0.08	2.00	1.50	24.00-26.00	19.00-22.00
S31600	316	0.08	2.00	0.75	16.00-18.00	10.00-14.00	2.00-3.00	0.10
S31603	316L	0.030	2.00	0.75	16.00-18.00	10.00-14.00	2.00-3.00	0.10
S31651	316N	0.08	2.00	0.75	16.00-18.00	10.00-14.00	2.00-3.00	0.10-0.16
S31653	316LN	0.030	2.00	0.75	16.00-18.00	10.00-14.00	2.00-3.00	0.10-0.16
S31700	317	0.08	2.00	0.75	18.00-20.00	11.00-15.00	3.00-4.00	0.10
S31703	317L	0.030	2.00	0.75	18.00-20.00	11.00-15.00	3.00-4.00	0.10
S31725	317LM	0.030	2.00	0.75	18.00-20.00	13.50-17.50	4.0-5.0	0.20
S32100	321	0.08	2.00	0.75	17.00-19.00	9.00-12.00	...	0.10	...	Ti5(C+N) min, 0.70 Max
S34700	347	0.08	2.00	0.75	17.00-19.00	9.00-13.00	Cb10Cmin 1.00Max

*Maximum

Note: Sulfur is limited to 0.030 max and Phosphorous to 0.045

The Role of Delta Ferrite

Delta ferrite usually is controlled to prevent microcracks in stainless steel welds during welding. The best chart to predict the delta ferrite is the Schaeffler-DeLong Diagram, Figures 2 and 3. The Welding Research Council (WRC) Diagram is the newest chart to predict delta ferrite, but does not appear to be as good as the Schaeffler-DeLong Diagram for the purpose of predicting fabrication difficulties since it does not take manganese into account. Figure 2 has the ASTM composition limits for Type 304L and Figure 3 the limits for Type 316L superimposed with actual ferrite numbers from 172 heats. The trend in the past several years has been to higher delta ferrite contents.

As described earlier, delta ferrite has a body-centered cubic structure. It during solidification and is retained in the structure at room temperature. Heat treatment, which involves holding at 1900 - 2000° F (1040 - 1100°C) for at least 10 minutes at temperature, will dissolve delta ferrite up to 7-8%. Above that level, some delta ferrite remains in the structure as a second phase. Additional heat treatment or longer time at temperature has little effect on reducing the ferrite effect when the content is this high.

To calculate the delta ferrite in an alloy heat, use the composition listed in the certified mill test report (CMTR) and plug the values into the chromium and nickel equivalent equations for the Schaeffler-DeLong. Delta ferrite is controlled by the chromium, molybdenum, niobium (columbium), silicon, nickel, carbon, nitrogen, manganese and copper. The higher the delta ferrite, the more transformation martensite is formed and the lower the ductility.

The presence of delta ferrite causes a number of problems with the austenitic stainless steels:

1. In the lower nickel austenitic alloys such as Types 301, 302, 304, and 316, cold working causes martensite to form. Higher delta ferrite means more martensite transformation. As the martensite increases, the ductility decreases and the potential for fracture increases.
2. If secondary operations like Electropolishing are performed, the delta ferrite will preferentially dissolve leaving a white or dull surface. This is especially true for welded parts. If the delta ferrite is too high, the part is unsuitable for service in this environment since it cannot be heat treated out.
3. In corrosive environments, especially if acid chlorides are present, the delta ferrite will preferentially dissolve. If the delta ferrite is present in welds, the weld will totally dissolve. If the delta ferrite is too high, the part is unsuitable for service in this environment since it cannot be heat treated out.
4. If the delta ferrite is below 2% the alloy is good for fabrication, but the alloy may develop microcracks during welding.

The optimum delta ferrite content for welding is 2 – 5% as determined by the Welding Research Council. This should be the aim-for range for all of the low nickel austenitic stainless steels.

The Role of Carbon

Since the advent of AOD refining, carbon control in stainless steel is almost a non-issue except for those who specify the “straight” grades either through ignorance or for the higher ASME allowable stress values from the Boiler and Pressure Vessel Code. The “straight” grades are the original, pre-AOD refining era, high carbon varieties, usually with 0.08, 0.12 or 0.15% C. For most applications the “L” grades, with 0.030% C maximum, are preferred and should be used wherever possible.

Carbon is an interstitial alloying element. As a result it can diffuse rapidly through the structure and concentrate on the grain boundaries. The primary problem is precipitation of chromium carbide. Formation of chromium carbide depletes the grain boundaries of chromium, thus destroying the corrosion resistance. Fortunately, a short-time heat treatment at 1850° F (1010° C) will dissolve most chromium carbide, except when the carbon content is so high the part cannot be quenched fast enough. Figure 4 illustrates the effect of time-temperature and carbon content on the formation of chromium carbide on cooling from heat treatment temperatures. This chart shows that the typical carbon levels in today’s AOD refined “L” grade steels of 0.024% would require nearly 50 hours at 1000° F (540° C) to cause chromium carbide to precipitate. This chart also indicates that carbides will eventually form if the component is held at temperatures in the range of 1000° F (540° C). The solution is to use a stabilized stainless steel that contains either titanium or niobium (columbium). These elements preferentially form carbides, thus prevent chromium carbide from forming.

Carbon has a number of effects on the fabricability:

1. High carbon increases the tensile strength of the alloy and its hardness. With this increased strength comes decreased ductility, thus a greater tendency for fracture. It is not possible to anneal a high carbon stainless steel to a low hardness level. The only solution is to use “L” grade alloys.

2. High carbon means difficulty during quenching after heat treatment. To prevent carbide precipitation, the alloy must be quenched at or near the solution anneal temperature. Some high carbon grades are impossible to quench fast enough to prevent carbide precipitation, especially those with heavy cross sections.
3. Field welding the straight grades, where it is not possible to heat treat after welding, will corrode in even benign water.

Calcium

Calcium is a strong deoxidizer and is used by some steel mills to kill the melt. Most of the calcium comes from the slag, refractories and mold powders during melting and casting. It is associated with boron in some grain boundary precipitates as Figure 8 shows. These compounds form very slaggy welds. Most steels run in the range of 0.0010 – 0.0020%, but occasionally a very slaggy weld will have 0.0145 – 0.00175% calcium. The lower limits do not appear to be a problem, but the higher levels are.

Boron

Boron is one of those elements that some steel mills love and other mills avoid. Boron is added to the melt for sliver control during hot rolling. Boron is not an element that builds up as a residual. It is easy to tell which mills use boron because their heats are in the range of 0.0070 – 0.0185%. The solubility limit is reported to be in the range of 0.010%. Steel from the mills that avoid the use of boron is in the range of >0.0001 – 0.0006%. Boron is impossible to identify using microprobe analysis because of its low atomic number. The only reliable analytical method is inductively coupled plasma spectroscopy with the appropriate standards. Standard emission spectroscopy does not appear to detect boron with the same sensitivity as ICP spectroscopy.

Sulfur

Weld penetration difficulty can occur when the sulfur content is too low. During AOD refining the residual sulfur is reduced to 0.001% or less. This is desirable to produce low inclusion steel, but very bad for weld penetration. In recent years the BPE (Bio-Pharmaceutical Equipment) Committee of the ASME has specified the sulfur content of all steel components for the pharmaceutical industry to have a sulfur content of 0.005 – 0.017%. This means the steel must be resulfurized at the time of casting. Most of these steels have a mean sulfur range of 0.012 – 0.014%. No adverse problems have been identified with sulfur at these low concentrations except a tendency to have a higher inclusion count. Inclusions are insoluble non-metallic “dirt” in the steel. One school of thought says these inclusions may lead to a higher pitting corrosion rate.

Sulfur, together with controlled manganese and silicon, control the convection currents in the weld pool so the heat is carried deep into the weld. Elements that reverse the convection currents producing low penetration welds include calcium, titanium, aluminum, magnesium and the rare earths.

Manganese

Another element that aids weld penetration is manganese. The ideal range is between 1.5 and 1.75%. Manganese does three things to aid the stability of stainless steel:

- promotes the formation of austenite
- combines with the sulfur to form manganese sulfides
- increases the solubility of nitrogen.

The only negative aspect of manganese is its tendency to form inclusions in the steel, especially in the presence of sulfur. For this reason some semiconductor applications limit manganese to 0.5% maximum or in some cases to 0.05% maximum.

Silicon

Silicon is added to the steel to assist deoxidation following AOD refining and to improve fluidity of the molten metal. Several problems can arise from high silicon levels during welding:

- “sagging” of the weld;
- promote ferrite formation;
- and formation of weld slag spots, especially if the cover gas is contaminated with oxygen or if moisture is present.

Most of the common austenitic stainless steels limit silicon at 0.75%. If the silicon becomes too high it will promote ferrite formation, and during cold working form transformation martensite. The presently accepted silicon range is 0.4 – 0.5%.

Copper

The jury is still out on copper. In the range of 3 – 4% copper improves corrosion resistance to sulfuric acid. At low levels and in combination with other elements copper will produce age hardening. But the copper content is creeping upward because it is being introduced through the use of scrap metal during compounding the melt, and AOD refining does not eliminate it. Today, the copper content of most of the common stainless grades, 304, 304L, 316, 316L, is in the range of 0.4 – 0.5%. Ten years ago they were half that. Table II shows that copper is not controlled. Copper may not be all-bad, since it improves resistance to sulfuric acid corrosion. However, if the alloy is to be used for any type of human implant it may cause problems.

Titanium and Zirconium

Titanium and/or zirconium are popular elements for deoxidizing the melt after AOD refining. Deoxidation is necessary to prevent fracture of the ingot during hot rolling, so the steel mills want totally “killed” steels. Because oxygen promotes weld penetration, excess titanium and/or zirconium will reverse convection currents and cause variations in weld uniformity. Longitudinal welds will develop arrowheads, a slag spot will form, and then the weld becomes normal again. In addition, excess titanium and/or zirconium scavenge oxygen from the cover gas and forms slag spots on the weld. It appears that titanium/zirconium levels in the range of 0.001 – 0.004% have little effect on the weld quality, but when the concentration is in excess of 0.007% problems may develop.

Aluminum

Aluminum is another element that is used to deoxidize the steel. It acts much the same as titanium both as a slag former and its tendency to form arrowheads on the weld with an associated slag spot. Aluminum in the range of 0.006% appears to be safe, but residuals in excess of 0.010 may cause slag formation.

Magnesium

Like titanium and aluminum, magnesium is a strong deoxidizer. In the past it was used in some deoxidizer compounds, but today it is normally not added to the melt for deoxidization. It shows up in the steel from the slag and refractory lining of the AOD converter, ladle and caster. All steel mills have about the same amount of residual magnesium, in the order of 0.006 – 0.008%. This does not appear to be a problem.

Rare Earths

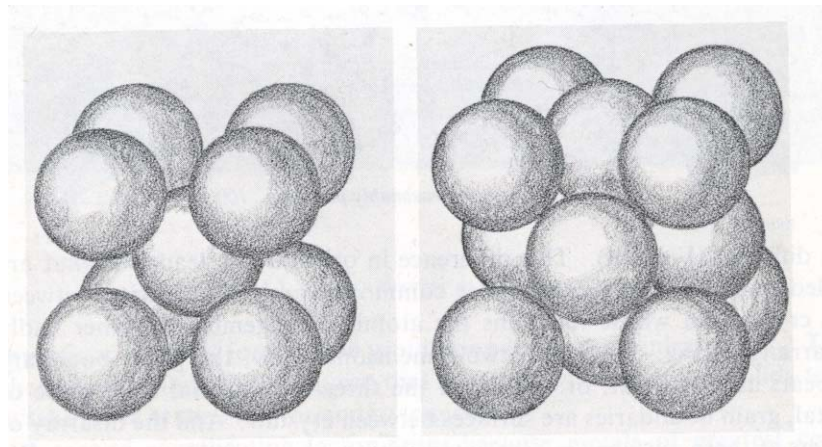
The common rare earths include cesium, yttrium and lanthanum. They are powerful deoxidizers and result in lack of weld adherence of the joint surfaces and weld cracks. Those alloys that have intentional additions are variable in weldability, exhibit weld cross cracks and may show balling of the weld metal on the surface. The levels where problems develop are in the range of 0.005% of any of the three elements. Thankfully, very few mills use rare earth additions. None of them should.

Summary

Variations within the composition limits of stainless steel alloys can affect both the mechanical working and welding characteristics of the alloy. These variations can cause different heats of steel to perform quite differently. Today's steel is melted to the lean side of the composition resulting in problems that were not encountered 15 or more years ago. In addition the tramp elements are increasing and changes in deoxidation practice are introducing other problems. Specifically, these are the factors that affect fabricability and weldability:

1. Delta ferrite content is increasing and with it reduced ductility because of martensite formation. Delta ferrite in welds cause corrosion problems and pitted welds following Electropolishing. The elements that control delta ferrite formation are chromium, molybdenum, niobium (columbium), silicon, nickel, carbon, nitrogen, manganese and copper.
2. Carbon increases the strength and hardness of the steel and decreases the ductility. In addition, carbon above 0.035% may precipitate along the grain boundaries during welding.
3. Sulfur is desirable for welding since it promotes deep penetration. However, it forms sulfide inclusions in the steel that may affect surface quality, perhaps pitting and act as stress risers.
4. Manganese promotes weld penetration but forms manganese sulfide inclusions. Manganese increases the solubility of nitrogen, so it is of help with high nitrogen steels.
5. Silicon, in moderation, is good. In excess, silicon increases the delta ferrite, causes welds to sag and become slaggy.

6. Copper is increasing in the steel because of remelting so much scrap. The jury is still out on its effect.
7. Titanium and zirconium are added as deoxidizers or carbide formers. It appears that a little is good, but too much is bad.
8. Aluminum is added as a deoxidizer, so a little is good. Too much aluminum causes ductility and welding problems. The same is true for magnesium.
9. Calcium is used as a deoxidizer and is picked up from the melting refractories. It is bad.
10. Boron is used as a means of sliver control during hot rolling. It is bad.
11. Some mills add rare earths a deoxidizer. They cause problems during welding. Except for use in certain high temperature superalloys they have few redeeming qualities.



Body-Centered Cubic

Face-Centered Cubic

Figure 1: Atomic arrangement for the unit cells of stainless steel. Ferrite is Body-Centered Cubic and Austenite is Face-Centered Cubic.

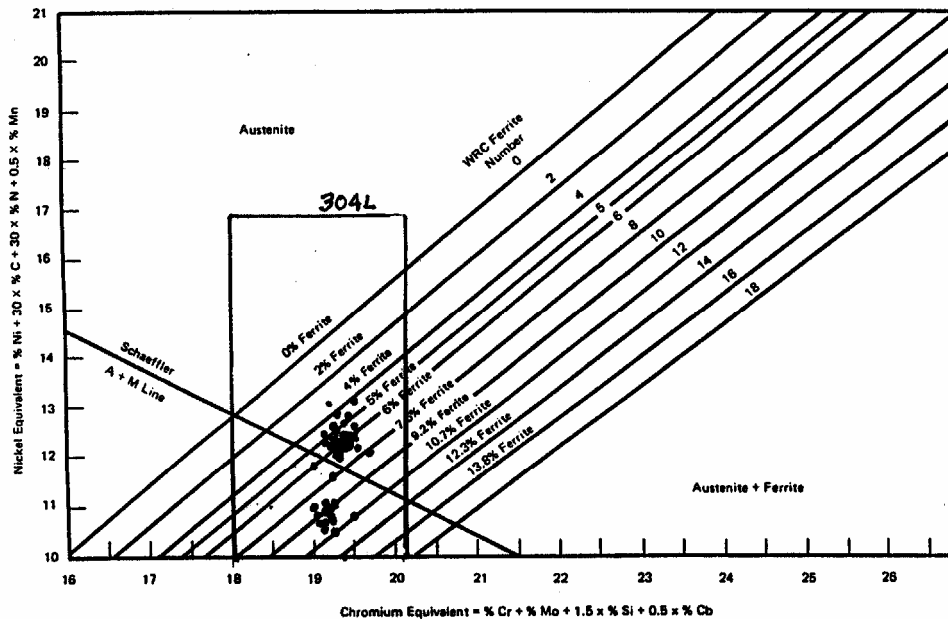


Figure 2: The Schaeffler-DeLong Diagram for determining the delta ferrite potential based on the alloy composition. This hart shows the composition limits for Type 304L. The black dots represent actual heats. The group clustered around 5 – 6% is older heats, the group around 10-12 FN represent the newer heats.

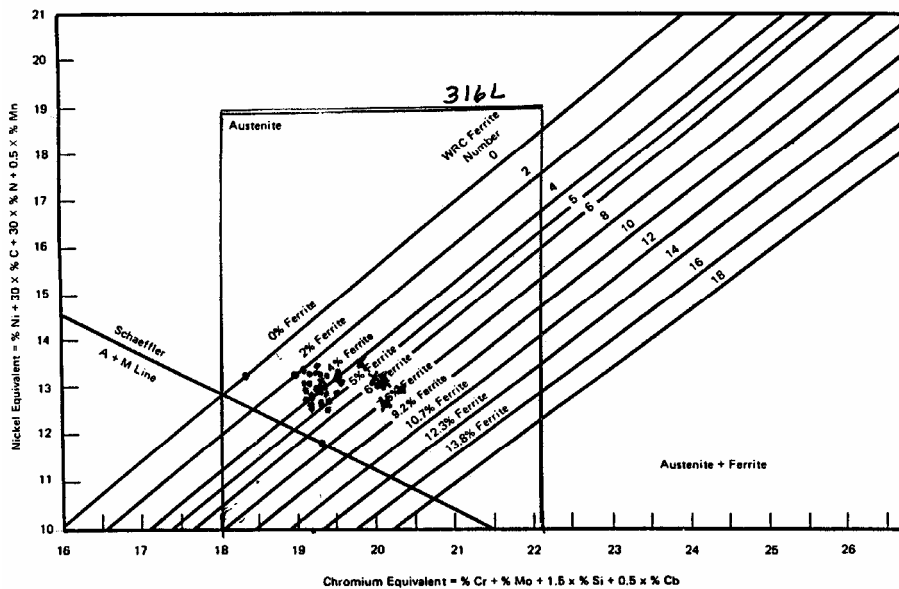


Figure 3: The Schaeffler-DeLong Diagram with the composition limits for 316L superimposed. Note that most of the 72 compositions are clustered around 4% FN and later heats around 6 FN. This delta ferrite range should not cause problems during fabrication.

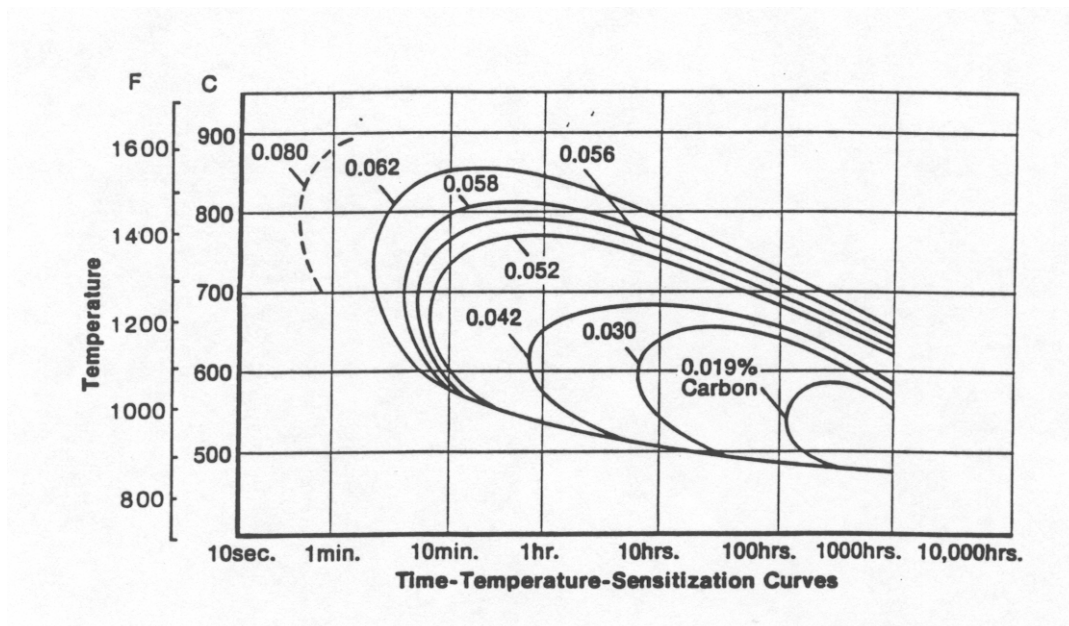


Figure 4: Effect of carbon on the time required to form chromium carbide. Carbide precipitation occurs inside the loop to the right of various carbon content curves.

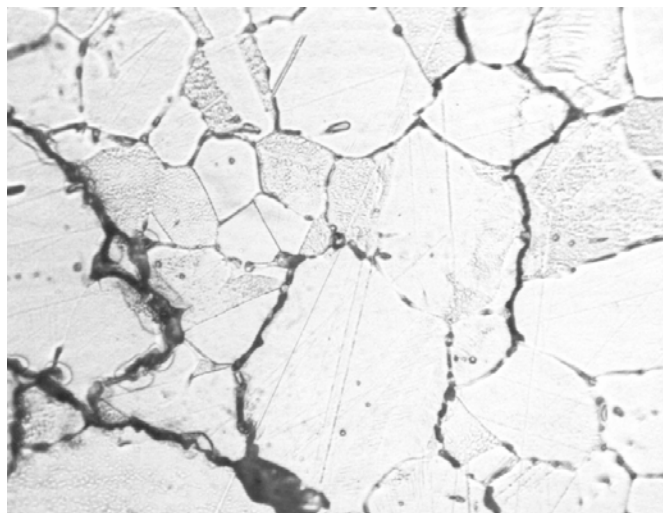


Figure 5 The effect of calcium boride on the ductility of Type 316L stainless steel. The black areas are cracks, and the small gray areas around the grain boundaries, especially in the lower right corner, are the calcium boride particles. They cannot be annealed out. 500X