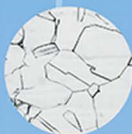
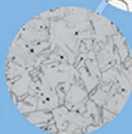


Stainless Steels

FOR DESIGN ENGINEERS

Michael F. McGuire




ASM
INTERNATIONAL

STAINLESS STEELS FOR DESIGN ENGINEERS

MICHAEL F. MCGUIRE



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Preface

The rate of growth of stainless steel has outpaced that of other metals and alloys, and by 2010 may surpass aluminum as the second most widely used metal after carbon steel. The 2007 world production of stainless steel was approximately 30,000,000 tons and has nearly doubled in the last ten years. This growth is occurring at the same time that the production of stainless steel continues to become more consolidated. One result of this is a more widespread need to understand stainless steel with fewer resources to provide that information. The concurrent technical evolution in stainless steel and increasing volatility of raw material prices has made it more important for the engineers and designers who use stainless steel to make sound technical judgments about which stainless steels to use and how to use them.

This book provides design engineers with an up-to-date source of information at a level useful for both metallurgists and other engineers and technicians. It seeks to bridge the gap between the internet where much current, but raw information is available and scholarly books and journals that provide theory that is difficult to put into practice. The content of the book is selected for utility for the user of stainless steel. The first section gives elementary metallurgy and identification of constituents of stainless, the effects of alloying elements and a significant section on corrosion. A second section is oriented toward processes important to users of stainless steel. The third section is about each family of stainless alloys and includes the most recent additions that have come to the market. The fourth section deals in some depth with the major applications for stainless steel. This last part is presented without the promotional bias which is found in many steel producers', alloy producers', and trade associations' literature. While a number of steel producers have provided assistance to the author, there has been no attempt to unfairly bias information in their favor. To the contrary, those producers responsible for generating factual, useful data for the user community are those who should benefit the most by books such as this. The author is particularly indebted to Allegheny Ludlum and John Grubb, and his many colleagues who assisted him, for technical assistance throughout the writing and to Carnegie Mellon University for their support. The author also wishes to thank Professor Sridhar Seetharaman at Carnegie Mellon University for his help in writing the corrosion chapter and others who helped: Roy Matway of CMU, Vittorio Boneschi of Centro-Inox; Paul Mason of Thermo-Calc; Bob Drab of Schmolz Bichenbach; Elisabeth Torsner and Chuck Turack Outokumpu, USA; Scott Balliett of Latrobe Steel; Jim Halliday and Fred Deuschle of Contrarian Metals Resources; Professors Tony DeArdo of Pitt and Gerhard Welsch of CWRU; the staffs of Centro-Inox, Euro-Inox, SSNA, The Nickel Institute; and the editorial staff at ASM International, Scott Henry, Eileen DeGuire, Charlie Moosbrugger and Steve Lampman. I would also like to thank the many members of my forum at Eng-tips.com who have contributed much collective knowledge and perspective to this book.

Michael F. McGuire, July 2008

CHAPTER 1

Metallurgy

Summary

COMPARED TO ALLOY STEELS, stainless steels are chemically complex. The large number of alloying elements makes possible a larger range of possible phases or basic crystal structures. The large amount of the alloying elements makes the deviation from the behavior of pure iron greater; consequently, the calculations that predict which phases will exist are more difficult. The three basic phases of stainless steels are ferrite, austenite, and martensite. The wide variety of alloys that exist is based on:

- Combinations of these phases
- Altering the composition of these phases
- Adding secondary phases for particular purposes

Metallurgy, as discussed in this chapter, focuses on phases normally encountered in stainless steels and their characteristics. In subsequent chapters on types of stainless steel, there are more detailed treatments of the alloys made of these phases and their properties.

Introduction

Most widely used alloy systems, such as carbon steels, alloy steels, and aluminum alloys, are relatively dilute solutions of several elements in the parent matrix. Carbon and alloy steels, with very few exceptions, are principally of the magnetic body-centered cubic (bcc) phase or a slightly distorted version of it. Aluminum alloys share the face-centered cubic (fcc) structure of pure aluminum. A given structure, which can have a certain range of compositions, is what is meant by a *phase*, just as a gas or liquid is a phase. In solid metals, there can be a number of

phases coexisting simultaneously. Stainless steel is an exceptional alloy system in that it is not a dilute solution. Alloy steels may contain several percent of alloying elements, such as carbon, manganese, nickel, molybdenum, chromium, and silicon, in addition to the impurities sulfur, oxygen, and phosphorus. Alloy steels typically contain very small amounts of titanium, niobium, and aluminum. The total amount* of these alloying elements seldom exceeds 5%. The same is true for most aluminum alloys. In contrast, stainless steels contain no less than about 11% chromium alone. Most stainless alloys have manganese, silicon, carbon, and nickel in thermodynamically meaningful amounts as well as large concentrations of nickel and/or molybdenum.

The result of the large number of alloying elements in relatively high concentrations is that stainless steel can have many stable phases concurrently. In almost every case, having phases other than the principal one or two phases for which the alloy was designed is undesirable because of the possibility of undesirable variations in mechanical or corrosion performance. The producer of stainless steel controls the chemical composition and thermomechanical processing, so that when the processor or end user receives the product it is usually in the correct condition. However, subsequent processing or service conditions may alter the carefully established phase structure. Therefore, it is necessary to discuss the phases that can exist in stainless steel and the conditions under which they form so that the enlightened user will know which phases to avoid and how to avoid them.

It is possible to use thermodynamics to calculate which phases may exist at a given tempera-

* All compositions are given in weight percent unless stated otherwise.

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ture for a given composition. It is not remotely feasible, however, to give an adequate treatment of the thermodynamics required to do this. The topic alone requires a book. The necessary knowledge has been embedded in proprietary computer programs that will be used instead.

Thermodynamics of Stainless Steel

Pure metals, from a practical viewpoint, are either liquid or solid depending on temperature, with the possibility of some trivial small gas vapor pressure. A law of thermodynamics is that the number of possible condensed (i.e., solid) phases equals the number of elemental constituents plus one. The solid has a crystallographic structure that may vary with temperature. Many metals have a less-dense bcc structure at high temperature and transform to a denser fcc structure at lower temperatures. Iron does this. Iron has the curious characteristic of transforming from fcc back to the low-density bcc at still lower temperatures. This is a result of the unpaired 3d orbital electrons (those that give rise to ferromagnetism) that are not given up as valence electrons, causing repulsive forces between atoms and requiring a more widely spaced structure.

All thermodynamic properties are based on interatomic attractions. In metals, the metal atoms give up valence electrons to the entire mass. These electrons are of varying energy states and highly mobile. They are responsible for the ability of metals to conduct heat and electricity well. The *attraction*, the strength of the bond, is proportional to the charge difference and distance. The attraction determines such macroscopic properties as melting temperature, density, and elastic modulus.

In this book, the main concern with thermodynamics is predicting which phases are present both at equilibrium and in the quite frequent metastable state. The prediction involves calculating the free energy of the various possible phases. The phase with the lowest energy is most favored, but others may have free energies that permit them to exist. The difference between these two is that the equilibrium state, that of the lowest free energy, may require atomic rearrangements to occur for equilibrium compositions to be reached on an atomic scale. If diffusion is too sluggish for these rearrangements to take place, the structure may retain the prior metastable structure indefinitely. This is

not a small, pedantic point. Most stainless steels are used in the metastable condition. For example, the common alloy 304 (also called 18-8) is normally used in the fully austenitic condition. It would “rather” be partly ferritic, but the substitutional diffusion of chromium in austenite that is required to form a ferrite phase of a separate composition is so slow that it cannot occur in terrestrial time frames. However, if energy is applied by mechanical shear, the austenite can transform without diffusion to the lower free-energy martensite phase, a quasi-bcc structure of lower free energy.

The calculation of which phases exist under equilibrium conditions proves to be extraordinarily difficult in complicated alloy systems. This is because thermodynamic values can be measured accurately only in the liquid state, so the values for the solid state are extrapolations. Also, the interaction between elements is very important in nondilute alloys such as stainless steel. Consequently, most published phase diagrams are experimentally derived. To determine which phases exist at a given composition and temperature, a sample is made, equilibrated at the appropriate temperature, and quenched to room temperature. It is assumed that the characteristic equilibrium phases have been frozen and are then identified by various techniques for structure, composition, and the like. This important work is obviously tedious and susceptible to experimental error and applies only to specific compositions. Any “what if” extrapolation to a different alloy composition carries the risk of error.

A practical tool has been developed that permits phase diagrams to be calculated for arbitrary compositions. These are computer simulated, mathematical models that can perform the complex thermodynamic calculations. To do this with accuracy requires databases of thermodynamic values. These values must be derived from computer analysis of experimental phase equilibrium diagrams. They are expensive to derive and validate, and only a few exist. Hence, they are proprietary. In Appendix 3, a license to one such program, Thermo-Calc, can be found. The version has a reduced three-element capability but uses the same proprietary thermodynamic database of the full version. The program allows determination of which phases can exist for any composition and temperature. Whether the phases will form depends also on kinetic factors. First, however, it is good to become familiar with the principal phases found in stainless steel.

Phases

Ferrite

The basis of stainless alloys is, of course, iron. Iron, as stated, solidifies as a bcc alloy before transforming to the denser fcc austenite at lower temperatures. At still lower temperatures, it reverts to the bcc structure. It is accurate to surmise from this that the free energy of both structures is close. Alloying elements that promote one structure over the other can therefore change which one predominates. The element that produces the ability to form the passive film that makes stainless corrosion resistant, chromium, has the characteristic of stabilizing the bcc structure. As chromium is added to iron, the temperature range over which austenite is stable grows smaller until, at about 12% chromium, ferrite is stable at all temperatures. This is, coincidentally, the approximate level of chromium needed to keep alloys from rusting under ambient conditions, but this effect is not related to whether the structure is bcc or fcc. The iron-chromium phase diagram (Fig. 1) shows the composition and temperature regions where ferrite (α), martensite (α'), austenite (γ), and sigma phase (σ) are stable.

While chromium is the principal ferrite-promoting alloying element, other elements have similar effects, but none produces the quality of stainlessness. Silicon, aluminum, molybdenum, tungsten, niobium, and titanium all favor ferrite. Carbon, nitrogen, manganese, nickel, and copper do not and expand the temperature range over which austenite exists. Elements that are insoluble in iron at austenite-forming temperatures, such as the impurities phosphorus, sulfur,

and oxygen, have no influence on which phase is favored. Again, it must be emphasized that the influence of an alloying element on structure has zero bearing on its influence on corrosion resistance.

The elements that promote ferrite over austenite also have the effect, at still lower temperatures, of promoting intermetallic compounds generally composed of iron, chromium, and some of those alloying elements. These are discussed separately.

Metals are effective solvents in both the liquid and solid states. An important part of steel-making is refining the molten metal to remove the undesired impurities dissolved in it. The normal technique is to add elements that react selectively with the targeted impurities to form an immiscible reactant that can become part of the slag and physically separated from the refined alloy. This is done for the primary impurities oxygen and sulfur. A third common impurity, phosphorus, is not so easily removed and must be excluded from raw materials to be kept under control.

In stainless steel, carbon and nitrogen can be detrimental impurities. Both are quite soluble in molten iron-chromium alloys and are fairly soluble in ferrite at high temperatures. This solubility decreases exponentially with temperature so that it is essentially zero at room temperature. These elements have small atomic sizes compared to iron and chromium and, when dissolved, squeeze into interstitial sites within the bcc matrix. Such interstitial solute atoms profoundly distort the structure. They are much more soluble in the fcc structure, which, while denser, has roomier interstitial spaces, so they stabilize that structure. To preserve the ferrite structure, carbon and nitrogen must be eliminated.

There are additional reasons to eliminate carbon and nitrogen. During cooling as these elements become less and less soluble, they must precipitate. The most thermodynamically favorable form in which they can precipitate is as a compound of chromium, with which they are very reactive. This occurs at the grain boundaries, where nucleation is favored, and depletes those regions of chromium, rendering them less corrosion resistant. A second effect is a loss of toughness due to these precipitates. The diffusion rates of carbon and nitrogen in ferrite are too high to prevent this precipitation by quenching.

Modern refining methods can reduce carbon plus nitrogen to under 0.020%, but even this is

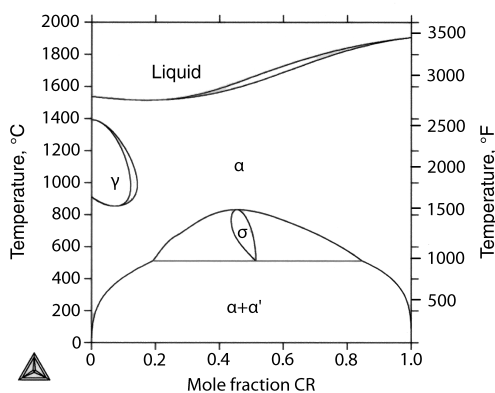


Fig. 1 The iron chromium phase diagram. Courtesy of Thermo-Calc Software

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too high. So, to avoid the detrimental effects of chromium carbide and nitride formation in ferrite, other benign carbides and nitrides such as those of titanium or niobium are allowed to form preferentially. This approach is called *stabilization* and is used for most ferritic alloys today. The older approach, as characterized by alloy 430, is to permit chromium carbides and nitrides to form but then to perform a subcritical anneal to rehomogenize the chromium and coarsen the precipitates so that they have only a small negative effect on mechanical properties.

Hydrogen and boron are other elements that can be interstitially dissolved in ferrite. Boron is normally found at levels of around 5 to 10 ppm. At higher levels, boron substitutes for carbon in carbides. Hydrogen is soluble to several parts per million by weight. It does not cause hydrogen embrittlement in annealed ferrite. If the ferrite is cold worked, the solubility of hydrogen increases as the defect structure accommodates hydrogen atoms. In this condition, ferrite may be embrittled by hydrogen, especially if it enters the metal through corrosion processes like pitting. This is one explanation of, and the most likely explanation for, stress corrosion cracking. While hydrogen is easily removed by argon oxygen decarburization (AOD), assuming absolutely dry blowing gases and additions are used, it can be picked up during pickling, welding, or annealing as well as by corrosion.

All stainless alloys rely on having a uniform level of chromium and the other element, molybdenum, which assists in corrosion resistance, distributed throughout the matrix. If there are locally low levels of these elements, localized resistance to corrosion is reduced, and localized corrosion can occur. This can occur by the precipitation of any phase that is richer in chromium or other corrosion-resisting elements. Because chromium is a reactive element, its success depends to a great degree on maintaining the homogeneity required for proper corrosion-resistant performance. Incorrect thermal processing is the main way homogeneity can be lost. Stabilizing makes it much easier to keep chromium from segregating in ferritic alloys.

A by-product of stabilization with titanium is that oxygen and sulfur are also eliminated as compounds of titanium along with carbon and nitrogen. These impurity elements would otherwise also precipitate as compounds containing some chromium, potentially depleting chromium in the vicinity of their precipitation.

The bcc structure of ferrite allows more rapid diffusion than does the fcc structure of austenite. This is true for both the interstitial diffusion of the elements helium, boron, carbon, nitrogen, and oxygen and the substitutional diffusion of all other elements. The rate of diffusion of all elements, both interstitial and substitutional, in ferrite is about two or three orders of magnitude higher than in austenite. The practical implication of this is that precipitation reactions generally cannot be suppressed by quenching in ferrite if they involve interstitial elements, whereas they can be in austenite. Intermetallic phases can form more rapidly in ferrite. This becomes an issue only when total chromium plus molybdenum exceeds about 20%, above which the sigma phase appears. This is thus only an issue for superferritic (high chromium content) alloys or for the ferrite phase of duplex (ferrite-austenite) alloys.

The mechanical properties of the ferrite phase are discussed extensively in Chapter 8, "Ferritic Stainless Steels." Here, it is only necessary to note that ferrite in stainless steel closely resembles low-carbon steel in mechanical behavior. It shares the following characteristics:

- A toughness transition that occurs around room temperature
- Notch sensitivity
- A yield point phenomenon
- Pronounced crystallographic anisotropy of mechanical properties
- High stacking fault energies and low work-hardening rates

These issues are dealt with in the same way as in carbon steel when these characteristics become an issue. The first two are controlled by reduction of interstitial levels and refining of grain size. The yield point is eliminated by slight elongation by temper rolling or elimination of interstitial carbon and nitrogen, whose interaction with dislocations causes the yield point. The anisotropy is either utilized to advantage by maximizing it, as in the case of deep-drawing alloys, or minimized by refining grain size and randomizing grain orientation by special thermomechanical processing.

Ferrite has a greater thermal conductivity and lower thermal expansion than austenite. Its strength decreases with temperature more than that of austenite, but the good match in thermal expansion between the ferrite and its oxide still makes it an excellent high-temperature

material. Ferrite has very nearly the same corrosion resistance as austenite, but since ferrite can hold no nitrogen in solution, it cannot benefit from this element. In duplex alloys, the ferrite is generally the more corrosion resistant phase because it is richer in chromium and molybdenum.

Austenite

The second major constituent phase of the stainless steel alloy system is austenite. Austenite has an fcc atomic structure. The fcc structure is common in many transition metals to the right of iron in the periodic table. As stated, the fcc structure should be considered normal for metals well below their melting temperature as it is a denser structure. The presence of the bcc structure relates to the unpaired 3d electrons, which provide ferromagnetism. Adding elements to iron that causes pairing of the 3d electrons diminishes ferromagnetism and promotes the fcc structure. Nickel and manganese are the most prominent alloying elements that do this, but the interstitials carbon and nitrogen are the most powerful austenite stabilizers on a percentage

basis. Their use is limited by their solubility and their tendency to form precipitating compounds with chromium. Manganese acts largely through its ability to promote nitrogen solubility. Super-austenitic stainless steels, such as S34565, use 4 to 6 % manganese to permit nitrogen levels of 0.4 to 0.6% to be achieved, resulting in higher pitting corrosion resistance.

Since all stainless steels contain principally iron and chromium, the addition of a substantial amount of austenitizing elements is necessary to transform the structure to austenite. As a rule of thumb, iron alloys require about 17% chromium and 11% nickel (or its equivalents) to remain austenitic at room temperature. One percent nickel can be replaced by about 2% manganese as long as nitrogen is present to maintain the same phase stability. The omnipresent carbon and nitrogen have an effect 30 times that of nickel, so even in the small amounts in which they are normally present, they have a significant effect. These stabilizing factors are mapped in the Schaeffler diagram of Fig. 2 (Ref 1), whose purpose is to predict the phase makeup of weld metal. Since welds solidify relatively rapidly, no carbides or intermetallic phases

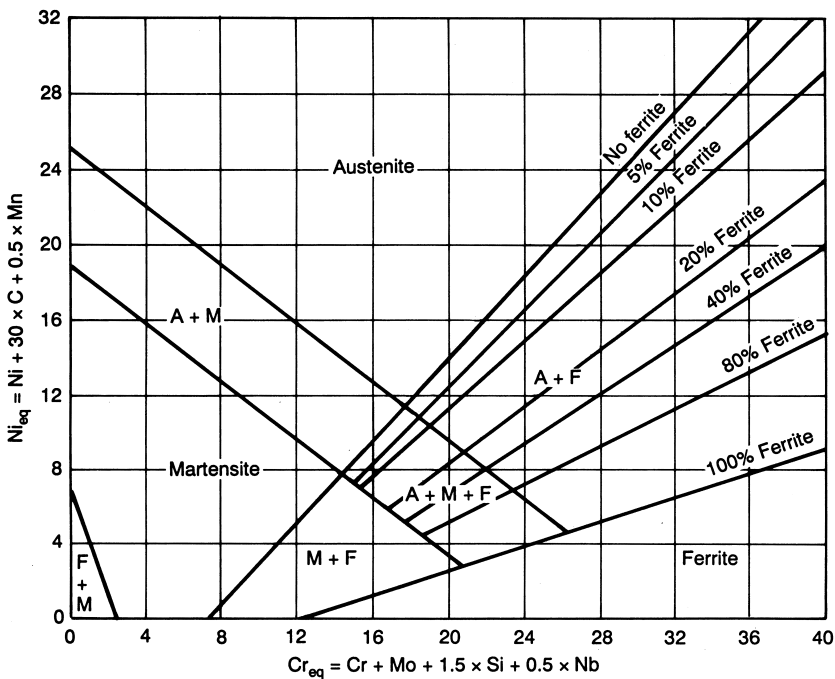


Fig. 2 Schaeffler-Delong constitution diagram showing phases present in as-solidified stainless steels at room temperature as a function of composition demonstrating carbon and nitrogen contributions to nickel effects. Adapted from A.L. Schaeffler, Constitution Diagram for Stainless Steel Weld Metal, *Met. Prog.*, Vol 56, Nov 1949, p 680-688; and W.T. Delong, A Modified Phases Diagram for Stainless Steel Weld Metals, *Met. Prog.*, Vol 77, Feb 1960, p 98

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form, and only ferrite, austenite, and martensite will be present. Thus, they provide useful information about the compositional effects on phase development in nonequilibrium situations. The nickel equivalent (vertical axis) summarizes how nitrogen, carbon, and other elements combine to create a nickel-like effect. The horizontal axis does the same for chromium and those elements that have a similar effect.

In most common stainless steels, austenite is normally present in the metastable state, for example, the retained austenite in alloy steels. Those with carbon above 0.02% would eventually break down into austenite plus carbides, and those with less than about 30% chromium plus nickel will form martensite if deformed sufficiently. But in the annealed state, the austenite in standard austenitic stainless steels will remain indefinitely as fully austenitic without precipitates unless heated above 400 °C (750 °C) for protracted periods of time or deformed extensively.

Interstitial elements are much more soluble in austenite than in ferrite. Of these, only nitrogen is considered a beneficial alloying element. It both strengthens and improves the pitting corrosion resistance of austenite. Carbon has a parallel effect, but its tendency to form chromium carbides limits its use and in fact leads to its minimization in most alloys. Before the AOD was developed and carbon levels in stainless steels were higher, austenitic stainless steels were sometimes stabilized by titanium or niobium to counter the effects of carbon. Both carbon and nitrogen stabilize the austenite phase, permitting lower levels of nickel to be used in austenitic alloys.

Interstitial atoms of carbon and nitrogen distort the fcc lattice, causing it to expand about 1% linearly per 1 wt% of solute (Fig. 3) (Ref 2). This produces solid solution hardening of the austenite. The work hardening of austenite is increased by nitrogen. A third interstitial solute, hydrogen, produces the same effect but to a lesser degree. Austenite is not embrittled by hydrogen to the extent ferrite or martensite is, but hydrogen does raise its flow stress and hardness while lowering its work-hardening rate.

Sulfur and oxygen are considered impurities because they form inclusions, usually chrome/manganese silicates and sulfides. If present in sufficient amounts, sulfur and oxygen precipitate as primary inclusions before or during solidification. In most austenitic stainless alloys, the remainder of these elements are near saturation in the as-solidified ferrite at very high temperatures

and then frozen in a state of supersaturation in the austenite when it forms on cooling. The sulfur and oxygen then precipitate during cooling or subsequent hot working as isolated inclusions. The interface between these inclusions and the matrix is the locus of corrosion pit initiation, quite probably because of chromium depletion occurring during and as a result of inclusion growth. When an alloy solidifies as austenite, sulfur immediately segregates to the grain boundaries because of its low solubility in austenite, and it forms a low-strength film with a low melting temperature. This causes poor hot workability and hot cracking of welds.

The diffusion rates in austenite are quite low compared to ferrite, so even interstitial elements cannot move quickly enough to precipitate below about 400 °C (750 °F). This permits carbon and nitrogen to exist in very high degrees of supersaturation if introduced below this temperature, as is done by various proprietary processes. The low diffusion rates restrict such colossally supersaturated zones to thin surface layers, but they can reach phenomenal hardness of over $R_c 70$. The austenite structure does not discourage the formation of intermetallic compounds such as sigma, but it does, fortunately, make their formation very sluggish, as seen in Fig. 4. The difference of three orders of magnitude for carbide formation reflects the difference between the diffusion of carbon and that of substitutional elements. The formation of sigma in ferrite is about 100 times faster than in austenite. Sigma is almost never seen in commercial 316 alloys.

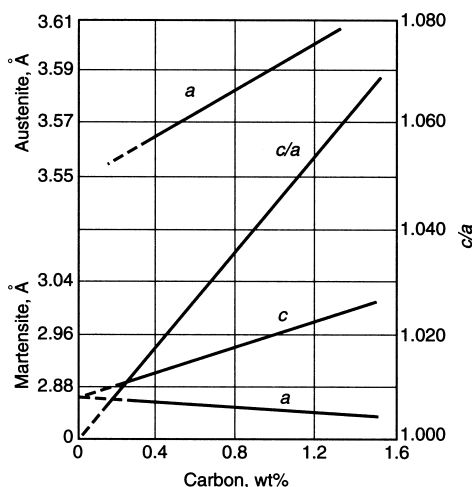


Fig. 3 Lattice expansions due to carbon. Source: Ref 2

The mechanical properties of austenite are quite different from those of ferrite. Austenite is characterized by:

- Low stacking fault energies leading to high work-hardening rates
- Good toughness even at very low temperatures
- Low notch sensitivity
- Lack of a sharp elastic limit
- Good high-temperature strength
- Fairly isotropic mechanical properties

While there is not a great deal of difference in the yield strengths of austenitic and ferritic alloys of similar alloy levels, austenitic alloys are more ductile, have high work-hardening rates, and therefore have higher tensile strengths. Austenite can be cold worked to extremely high strengths, around a maximum of 2000 MPa (290 ksi). Chapter 3, “Austenitic Stainless Steels,” gives a more thorough and quantitative treatment of the mechanical properties of austenite.

In duplex stainless steels, a secondary austenite, γ_2 , can form from ferrite below 650 °C (1200 °F). At this temperature, it has the same composition as the ferrite from which it forms and is called type 1. In the 650 to 800 °C (1200 to 1470 °F) range, a range that can be encountered in the heat-affected zone (HAZ) at γ/δ boundaries during welding, another type forms. This so-called secondary austenite, γ_2 , type 2, is somewhat enriched in nickel over the ferrite from which it forms but poorer in nitrogen than the primary austenite, giving it poorer corrosion resistance. Secondary austenite can also coform with sigma as γ/δ grain boundaries are depleted of chromium. This secondary austenite is called type 3 and is also poor in chromium.

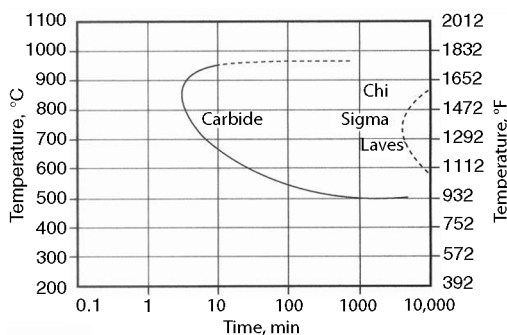


Fig. 4 Precipitation kinetics in 316 stainless steel. Source: Ref 3

The physical properties of austenite compared to ferrite include lower thermal and electrical conductivity and greater thermal expansion. It is also, of course, nonmagnetic.

Martensite

Martensite is a phase that forms from the diffusionless shear of austenite to a distorted cubic or hexagonal structure. This transformation can occur spontaneously on cooling or isothermally with externally applied deformation. It is essentially ferrite that has been formed with a supersaturation of carbon. The resulting structure is very fine and highly faulted, making it quite hard. As in carbon steel, the hardness of the martensite increases dramatically with interstitial content because of the huge strain interstitial elements impose on the bcc lattice, distorting it into tetragonality.

Martensite in stainless steels is restricted to alloy levels at which austenite can form at higher temperatures but at which the austenite is unstable at ambient temperatures. This gives martensite a fairly narrow composition range. The lowest alloy level is that of the basic 12% chromium steels with 0.1 to 0.2% carbon. The most highly alloyed martensites are found in the precipitation-hardening grades. Thus, martensitic stainless steels are inherently limited in corrosion resistance to a level no better than a 17 or 18% chromium alloy and often barely qualify as stainless after the chromium tied up as chromium carbide is recognized as not contributing to the corrosion resistance.

The as-formed martensite to the degree it has significant carbon content is hard and requires tempering to give it adequate toughness. The tempering reaction is the precipitation of carbon in the form of carbides with the concurrent loss of internal strain in the martensite lattice. The complexities of tempering require its discussion in detail to be found in Chapter 3, “Martensitic Stainless Steels.” It is worth noting, however, that all tempering involves carbide formation, thus losing some corrosion-fighting chromium.

There are two forms of martensite, the ϵ , epsilon, and the α' , alpha prime. Epsilon is formed in steels with low stacking fault energy, which are primarily the leaner austenitic alloys. Thus, it forms at cryogenic temperatures or by cold working. It appears in martensitic alloys of the precipitation-hardening type. It is nonmagnetic, has a hexagonal close-packed (hcp) structure,

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and is very difficult to identify microscopically. The α' martensite is the familiar magnetic variety known in alloy steels that forms both by quenching and by deformation.

The mechanical properties of stainless martensite are parallel to those of alloy steels. The high quantity of alloying elements in stainless give an extreme depth of hardening, so there is no concern with ancillary phases such as bainite. The physical properties are very close to those of ferrite of the same composition.

Intermetallic Phases

The number of phases that can coexist in an alloy is proportional to the number of alloying elements in the alloy. Table 1 lists data on the more common precipitates found in stainless steel. It is not surprising that stainless steel with iron, chromium, nickel, manganese, silicon, and often molybdenum, titanium, and niobium should have numerous ancillary phases. Intermetallic phases are normally hard and brittle. They can render the bulk alloy brittle when they form along grain boundaries. The other concern arising from intermetallic phase formation is the depletion from the surrounding matrix of

chromium or molybdenum, causing localized lower corrosion resistance. Intermetallic phases form by diffusion of substitutional alloying elements, which makes their precipitation slower than that of carbides, but they can form in a matter of minutes in alloy-rich grades. Deformation, which enhances substitutional diffusion, accelerates their formation. The principal intermetallic phases are described next.

Alpha Prime. Not to be confused with martensite, alpha prime is an ordered iron-chromium phase (i.e., iron and chromium atoms occupy specific, rather than random, sites on two intersecting superlattices). This structure is quite brittle. It forms at relatively low temperatures, between 300 and 525 °C (570 and 980 °F). Before its true nature was understood, its presence was known through its causing the phenomenon called *475 embrittlement*, originally called *885 °F embrittlement*. This is sometimes confused with temper embrittlement, which occurs in the same temperature range but is caused by phosphide precipitation on prior austenite grain boundaries of martensite. Alpha prime precipitation can cause 475 embrittlement in ferritic or duplex stainless steels and limits their use in this temperature range but not at higher temperatures, at which the phase dissolves. This phase forms at chromium contents as low as 15%, but fortunately it takes a relatively long time to form, on the order of hours, so it will not occur inadvertently during thermal processing such as welding or annealing.

Sigma. Sigma is a brittle tetragonal phase richer in chromium and molybdenum than either the ferrite or austenite matrix around it. It forms preferentially at ferrite-austenite boundaries in the temperature range 600 to 1000 °C (1110 to 1470 °F) in alloys with more than about 18% chromium plus molybdenum. Its composition is sometimes given as $(\text{CrMo})_{35}(\text{FeNi})_{65}$, but examination of the iron-chromium phase diagram shows that it is archetypically an equiatomic iron chromium compound. It is strongly promoted by silicon and suppressed by nitrogen. Stabilized alloy grades show more rapid sigma formation than unstabilized alloy grades (e.g., 347 versus 304). In unstabilized alloys the prior precipitation of carbides destabilizes austenite, leading to subsequent sigma formation. This makes alloys like 310H, essentially 25Cr-20Ni, especially prone to sigma formation.

Sigma forms much more rapidly from ferrite than from austenite because of the 100-fold

Table 1 Precipitated phases found in stainless steels

Precipitate	Structure	Parameter, Å	Composition
NbC	fcc(a)	$a = 4.47$	NbC
NbN	fcc	$a = 4.40$	NbN
TiC	fcc	$a = 4.33$	TiC
TiN	fcc	$a = 4.24$	TiN
Z-phase	Tetragonal	$a = 3.037 \text{ c} = 7.391$	CrNbN
$M_{23}C_6$	fcc	$a = 10.57\text{--}10.68$	$\text{Cr}_{16}\text{Fe}_3\text{Mo}_2\text{C}$ (e.g.)
$M_{23}(\text{C,B})_6$	fcc	$a = 10.57\text{--}10.68$	$\text{Cr}_{23}(\text{C,B})_6$
$M_6\text{C}$	Diamond cubic	$a = 10.62\text{--}11.28$	$(\text{FeCr})_{21}\text{Mo}_3\text{C}$; $\text{Fe}_3\text{Nb}_3\text{C}$; $M_3\text{SiC}$
$M_2\text{N}$	Hexagonal	$a = 2.8 \text{ c} = 4.4$	Cr_2N
MN	Cubic	$a = 4.13\text{--}4.18$	CrN
Gamma prime	fcc	$a = 3.59$	$\text{Ni}_3(\text{Al,Ti})$
Sigma	Tetragonal	$a = 8.80 \text{ c} = 4.54$	Fe, Ni, Cr, Mo
Laves phase	Hexagonal	$a = 4.73 \text{ c} = 7.72$	Fe_2Mo , Fe_2Nb
Chi phase	bcc(b)	$a = 8.807\text{--}8.878$	$\text{Fe}_{36}\text{Cr}_{12}\text{Mo}_{10}$
G-phase	fcc	$a = 11.2$	$\text{Ni}_{16}\text{Nb}_6\text{Si}_7$, $\text{Ni}_{16}\text{Ti}_6\text{Si}_7$

(a) fcc, face-centered cubic. (b) bcc, body-centered cubic.

higher diffusion rate of alloy elements in ferrite. This makes it a much larger issue in superferritic and duplex alloys, which have high chromium and/or molybdenum levels. Chapter 7, "Duplex Stainless Steels," contains an in-depth discussion of sigma.

Chi. Chi, χ , is similar to sigma except it contains more molybdenum and less chromium and has a cubic structure. It can coexist with sigma and forms in the same temperature range. It also precipitates at ferrite-austenite boundaries and has the same deleterious effects.

Laves Phase. The laves phase has the structure A_2B where A is iron or chromium and B is molybdenum, niobium, titanium, or silicon. It forms at 550 to 650 °C (1020 to 1200 °F) over the course of hours. Thus, although its effect would be deleterious, it seldom becomes a practical problem. It is possible for it to form at temperatures below sigma and above alpha prime, but the long times for formation make it rare.

Carbides, Nitrides, Precipitation Hardening, and Inclusions

Carbon and nitrogen are very important in all steels, but they take on a special significance in stainless steel because chromium, the essential alloying element of stainless steel, reacts more vigorously with carbon and nitrogen than iron does. Except for its role in hardening martensite and strengthening austenite at high temperatures, carbon is almost universally a detrimental impurity from a corrosion point of view and is minimized. Its beneficial effect on corrosion resistance when it is in solution is negligible because so little of it can be held in solution. Nitrogen has a lesser tendency to form compounds with chromium, so it is considered a beneficial alloying element in austenite but not in ferrite, in which it has essentially zero solubility. Common carbide and nitride precipitating phases are also listed in Table 1.

Carbides. $M_{23}C_6$ is the main carbide found in stainless steel. Its structure is orthorhombic, and it contains both iron and chromium. It can form at any temperature at which the host austenite or ferrite becomes saturated with carbon. It is mainly chromium carbide, but iron can substitute for chromium up to about 50%. Other elements, such as tungsten, vanadium, and molybdenum, can also dissolve in this carbide. The ratio of chromium to iron in the carbide increases with time and temperature, as chromium diffusion permits, up to a maximum of 4 or 5 to 1.

The precipitation of the carbide from ferrite occurs at grain boundaries, is extremely rapid, and cannot be suppressed by quenching. Less than 20 ppm carbon content is required to prevent its precipitation from ferrite, although up to 50 ppm can be effectively kept in solution by very vigorous quenching. From austenite, carbide precipitation occurs below about 900 °C (1650 °F) for carbon levels under 0.10% and at 650 °C (1200 °F) for carbon levels below 0.03%. For practical purposes, precipitation ceases below 500 °C (930 °F) due to the slowing diffusion of carbon. While carbon is essentially insoluble in austenite at room temperature, quenching can easily preserve up to 0.10% in supersaturation, as is commonly seen in type 301 stainless.

The carbide precipitation occurs first at grain boundaries. The chromium that combines with the carbon comes from the matrix in the immediate vicinity and therefore decreases the chromium content of that region, giving rise to the phenomenon of sensitization, which comes from the original phrase "sensitization to intergranular corrosion." Nickel and molybdenum decrease the solubility of carbon and thus accelerate the precipitation. Nitrogen retards precipitation. Cold work accelerates precipitation. The carbide has a hardness of about R_c 72. This makes the phase a useful constituent in wear resistance in martensitic alloys.

In higher carbon grades such as the martensitic stainless alloys, additional, more carbon-rich, carbides may form. These include M_7C_3 and M_3C . The latter carbide forms during the low-temperature tempering of martensite, while the former precipitates at higher temperatures.

Stabilizing carbides are those that are formed by the intentional addition of elements such as titanium and niobium. These elements form carbides of the type MC (metal carbide). The carbon in these compounds may be replaced by nitrogen or, in the case of titanium, sulfur. These carbides form preferentially over chromium carbides and thus prevent sensitization. They precipitate in both the liquid and solid states. In the solid state, the precipitate normally forms within grains. The Ti(CN) appears as a cube of gold TiN surrounded by gray TiC. The Nb(C,N) is less regularly shaped. They affect mechanical properties in ferrite both by their influence on recrystallization and by their ability to act as nucleation sites for brittle fracture

Nitrides. At low levels, nitrogen can substitute for carbon in $M_{23}C_6$. At higher nitrogen

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levels, Cr_2N can form. This can occur in duplex alloys if they are heated to a solution annealing temperature at which the alloy has high solubility for nitrogen. Cooling from these temperatures can cause the excess nitrogen to precipitate as needles of Cr_2N . Another nitride CrN can form in HAZs of welds.

Precipitation-Hardening Phases. Phases that have a very similar lattice match to the parent phase can precipitate coherently, that is, without changing the continuity of the crystal lattice. In these cases, the slight mismatch causes a strain that can significantly restrict dislocation movement and thereby strengthen the matrix. One such precipitate is gamma prime, an intermetallic, ordered, fcc phase with the composition $\text{Ni}_3(\text{AlTi})$. Copper forms the epsilon phase, essentially pure copper, which causes precipitation hardening. The secondary hardening of martensite due to the precipitation of molybdenum nitride or carbide is also a precipitation-hardening reaction.

Inclusions. Inclusions are principally oxides and sulfides that form in the melt (type I), at the end of solidification (type II), or in the solid (type III). Type I inclusions are the largest and are globular. Except when they are deliberately kept to improve machinability, they are physically removed by various steelmaking practices. Type II inclusions form in interdendritic spaces as the solubility of oxygen and sulfur drop on solidification. Type III inclusions precipitate the remaining oxygen and sulfur, up to 100 ppm for normal manganese-silicon killed stainless steels, in the solid state either on preexisting inclusions or as micron-size particles. Inclusions are mainly oxides and sulfides of silicon and manganese. If more reactive elements, such as aluminum or titanium, are present, their oxides and sulfides can also be present.

Sulfides and oxysulfides can be beneficial for machining as solid-state lubricants and chip breakers. Otherwise, their presence is detrimen-

tal as inclusions have been shown to be the initiation sites for corrosion pits, which have been linked to both their sulfur ions disrupting the passive layer and their chromium content causing slight local chromium depletion.

Properties of Stainless Steels

Physical and mechanical properties of representative stainless steel alloys are summarized in Appendix 2. Properties are also discussed in chapters specific to each alloy family. The reader is referred to primary sources, such as company web sites, such as Ref 4 and 5.

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