Period #5 Notes: Making Steel and Its Chemical Composition

A. MAKING STEEL

1.Iron Ore

Iron is a moderately reactive metal which joins readily with non-metals such as oxygen. This is why we do not find pure iron in the Earth's crust. Instead it is found as an ore, in which iron is chemically combined with oxygen or other non-metals.

Iron ore is a mineral substance which, when heated in the presence of a reductant, will yield metallic iron (Fe). It almost always consists of iron oxides, the primary forms of which are magnetite (Fe_3O_4), hematite (Fe_2O_3), limonite ($Fe_2O_3 + H_2O$), and siderite ($FeCO_3$). Usually, these minerals are mixed into rocks containing **silica**. Iron ore is the source of primary iron for the world's iron and steel industries.

Almost all (98%) iron ore is used in steelmaking. Iron ore is mined in about 50 countries.   The seven largest of these producing countries account for about three-quarters of total world production.   Australia and Brazil together dominate the world's iron ore exports.


Fig. 5.1 Hematite, a common iron ore.

2. Two-stage refinement of iron:

A two-staged process is typically used to make steel from iron-ore. First pig-iron is created from iron ore, and then steel is made from further refinement of pig-iron.

a. *Making Pig-Iron*:

The common industrial method to smelt (refine) iron ore is using a **blast furnace**. A blast furnace is charged with iron ore, charcoal or coke (coke is charcoal made from coal) and limestone ($CaCO_3$). Huge quantities of air blast in at the bottom of the furnace. The **calcium** in the limestone combines with the silicates in the ore to form **slag**. At the bottom of the blast furnace, liquid iron collects along with a layer of slag on top. Periodically, the liquid iron flows out the bottom of the furnace and cools. The liquid iron typically flows into a channel and indentations in a bed of sand. Once it cools, this metal is known as **pig iron**. See http://www.bbc.co.uk/history/british/victorians/launch_ani_blast_furnace.shtml for a nice demonstration of the basic ideas behind blast furnaces.

Removing oxygen chemically from a substance is called **reduction**. The blast furnace production of pig-iron involves reducing iron oxide. Most of the iron (III) oxide is reduced using carbon monoxide gas. This gas is a reducing agent which takes the oxygen away from iron (III) oxide.

iron (III) oxide + carbon monoxide → iron + carbon dioxide

$$Fe_2O_3 \ + \ \ 3\ CO \ \ \rightarrow \ 2\ Fe \ + \ 3\ CO_2$$
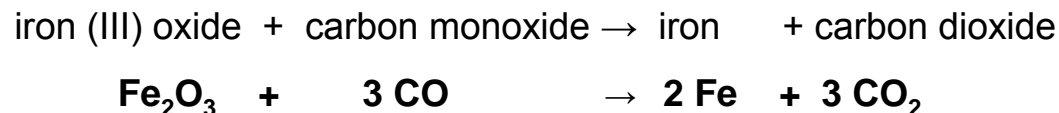
The carbon monoxide gas in this reaction is oxidized, changing into carbon dioxide. The overall process is a **redox** reaction, in which iron (III) oxide is reduced and carbon monoxide is oxidized.

Not all the iron (III) oxide is reduced by carbon monoxide in this way. Between 20% and 30%of the iron is produced by **direct reduction**, when the ore is directly reduced by carbon.

iron (III) oxide + carbon → iron + carbon monoxide

$$Fe_2O_3 \quad + \quad 3C \quad \rightarrow 2\,Fe + 3\,CO$$

In this reaction unburned carbon, not carbon monoxide, is the reducing agent. This carbon is oxidized to form carbon monoxide.

There are several reactions in the iron and steel making processes which involve acids and bases. One of the raw materials fed into the blast furnace is **limestone**, an almost pure form of calcium carbonate. Limestone decomposes in the hot furnace to give calcium oxide, which is a base.

calcium carbonate → calcium oxide + carbon dioxide

$$CaCO_3 \quad \rightarrow \quad CaO \quad + \quad CO_2$$

Calcium oxide joins with silica, one of the most abundant impurities in iron ores, to make calcium silicate, a salt which is formed as a molten **slag**.

calcium oxide + silica → calcium silicate

$$CaO \quad + SiO_2 \quad \rightarrow CaSiO_3$$

As a side point here, blast furnace slag which is a waste product from steel-making can actually be used as a cement replacement material to achieve stronger and more durable portland cement concrete mixes.

Pig iron contains 4 percent to 5 percent carbon by weight and a number of other impurities, and is so hard and brittle that it is cannot be used as a structural material. Three things are generally done with pig iron:

1. It is melted and oxidized to eliminate most of the carbon (down to 0.3 percent) and mixed with slag to create **wrought iron**. Wrought iron is the relatively soft, malleable iron that blacksmith works with to create tools, horseshoes, furniture and so on. When heated wrought iron, it is malleable, bendable, and easy to work with. As a result of this process, many strands of slag are mixed into the metal. These stringy slag inclusions give it a "grain" like wood that appears fibrous look when broken.

2. **Cast iron** is made by remelting pig iron, often along with substantial quantities of scrap iron, and taking various steps to remove undesirable contaminants and adjust the carbon content to between 2-4%. This is still a relatively high carbon content, making cast iron relatively brittle. Generally, cast-iron is used in civil engineering only where the loading on the material system is predominantly or exclusively compressive. Two common examples are as arch-like tunnel reinforcing segments, and as underground, low-pressure pipes.

3. It is further processed to create steel.

b. Making Steel

In refining pig-iron to make steel, much of the carbon content is removed as are other impurities. The Basic Oxygen Steelmaking (BOS) furnace is commonly used for this process. Recycled steel is often combined with pig-iron in the BOS to make steel.

Structural steels are often classified at least in part due to their relative carbon content as low, medium, and high carbon steels.

- Low carbon steels are frequently called *mild* steels and have carbon content ≤ 0.25%.

- Medium carbon steels typically have 0.3% ≤ carbon content ≤ 0.6%

- High carbon steels typically have 0.6% ≤ carbon content ≤ 1.5%

Calcium oxide (CaO) which played an important role in making pig iron also plays an important part in the BOS furnace. In particular, it helps to remove weakening impurities such as phosphorus and sulfur from the steel. In the BOS furnace, phosphate P_2O_5 combines with the basic calcium oxide to make tri-calcium phosphate $Ca_3(PO_4)_2$. Sulfate SO_4 in the melt also combines with calcium oxide to form calcium sulfate Ca_2SO_4. These compound forms part of a molten slag which collects on the surface of the molten metal.

B. IRON AND CARBON

Steel is many senses, an iron-carbon alloy. To better understand the important nature of the iron-carbon composition, it is helpful to consider the iron-carbon phase diagram. Before doing so, we'll consider the basics phase diagrams in general, and then consider the specific iron-carbon phase diagram.

1. Alloying and Phase Diagrams

Before beginning, it will be pointed out that two helpful references on phase diagrams for two-phase allows, beyond the information provided in the text, are:

1. The online Non-Destructive Testing (NDT) Resource Center available at:

   http://www.ndt-ed.org/EducationResources/CommunityCollege/Materials/Structure/phase.htm

2. Chapter 8 of <u>Foundations of Materials Science and Engineering, 2nd Ed</u>., by W.F. Smith (2004).

The starting point for an alloy of material A and material B is a temperature versus percent composition of the mixture by mass as shown in Fig. 5.2. When the material A fully comprises the mixture, the melting temperature is well defined at $(T_m)_A$. Similarly when material B fully comprises the mixture, the melting temperature is $(T_m)_B$.

For most intermediate states of the mixture, the melting point will not be well defined. Starting from very high temperatures in which the mixture is in a fully liquid state, the temperature at which solid material first begins to occur in the mixture is called the *liquidus* temperature. The locus of the liquidus temperature for varying mixture compositions gives the *liquidus* curve.
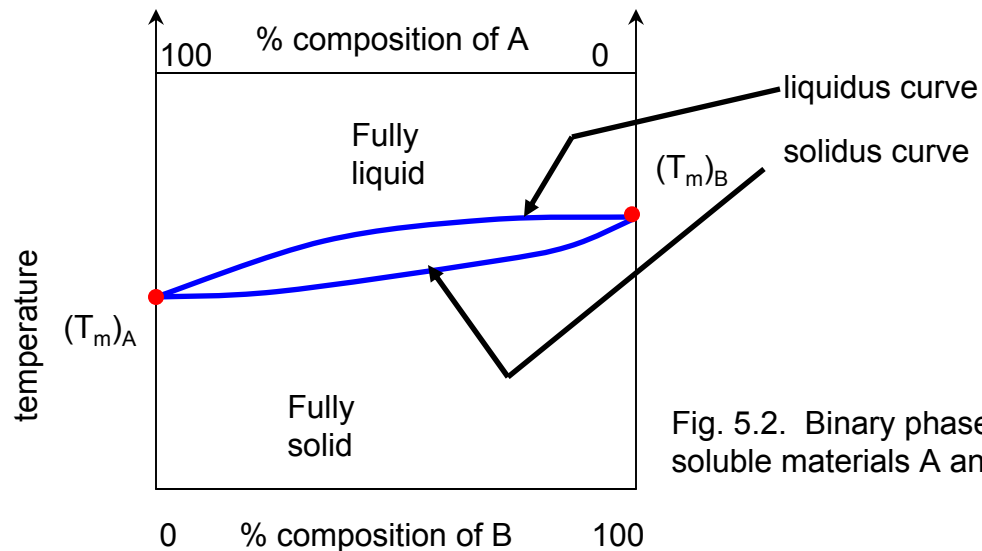

Fig. 5.2. Binary phase diagram for two soluble materials A and B.

Starting from very low temperatures in which the mixture is in a fully solid state, the temperature at which liquid material first begins to occur in the mixture is called the *solidus* temperature. The locus of the solidus temperature for varying mixture compositions gives the *solidus* curve.

Clearly, all points below the *solidus* represent fully solid compositions, and all points above the *liquidus* fully liquid states.

In the intermediate zone, the mixture will be partially solid and partially liquid. The exact composition can be determined from the phase diagram and the Lever Rule.

At some state point O which specifies the mass fraction m_A of material A and B (m_B) shown in the phase diagram of Fig. 5.3, the mixture is both liquid and solid. Obviously, $m_A + m_B = 1$.

Through the state point O is drawn a line of constant temperature that intersects the *liquidus* at L and the *solidus* at S. The fractions of the mix that are liquid and solid are denoted m^S and m^L, respectively, and clearly, $m^S + m^L = 1$.
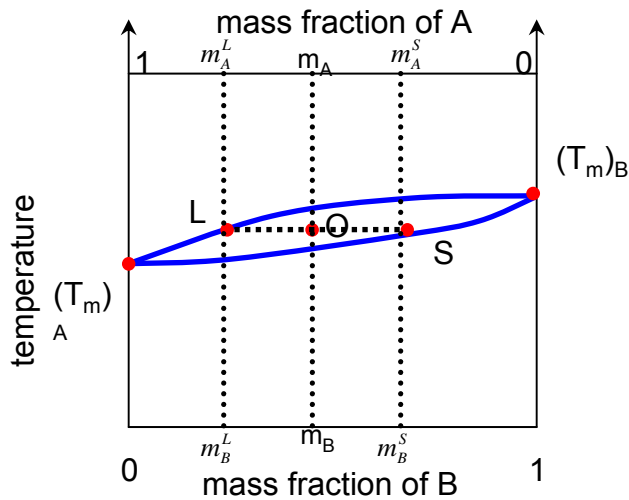

Fig. 5.3.

The mass fraction of A can be decomposed into its liquid and solid parts as follows:

$$m_A = m^L m_A^L + m^S m_A^S = m^L m_A^L + \left(1 - m^L\right)m_A^S$$

Thus we can solve for the mass fraction of the mixture that is liquid and solid:

$$m^L = \frac{m_A - m_A^S}{m_A^L - m_A^S}; \qquad m^S = 1 - m^L$$

There sometimes exists a mixture of the constituents that produces definite melting at a single temperature like a pure element. This is called the eutectic point. The phase diagram for a mixture that has a eutectic point is shown in Fig. 5.4. This typically occurs when the two materials have limited solubility in each other.

At compositions other than at the pure A, pure B and the eutectic point, when the alloy is cooled from a high temperature it will begin to solidify at a certain temperature but will remain in a mushy (liquid plus solid) condition over a range of temperatures. If experiments are conducted over a range of compositions to determine the temperature at which the alloys start to solidify, this data can be plotted on the phase diagram to produce a curve. This "start of solidification curve" will join the three single solidification points and is called the liquidus line.
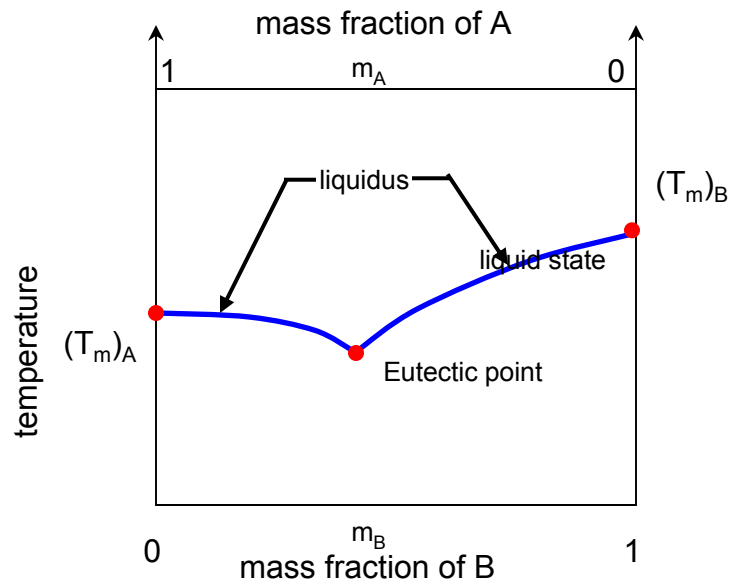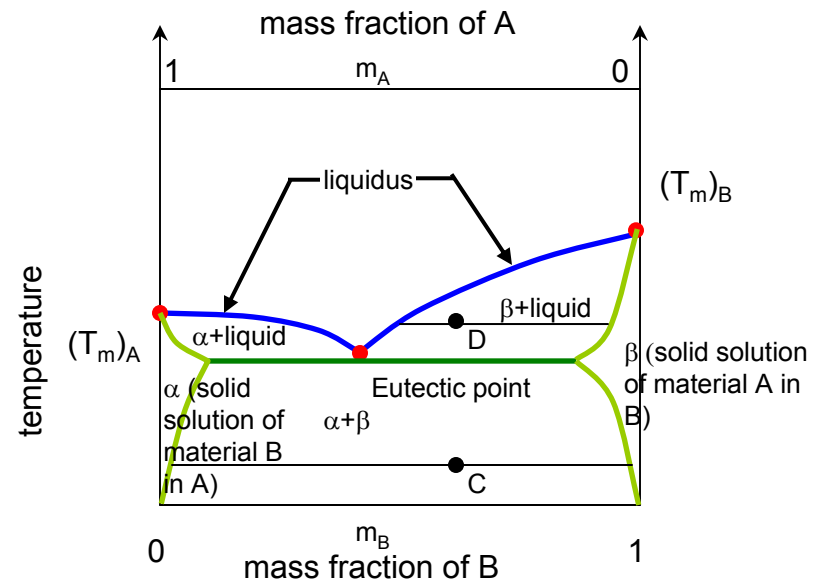
Fig. 5.4a.

Fig. 5.4b.

Up to a few percent of composition, it is possible for one element to remain dissolve in another while both are in the solid state. This is called solid solubility and the solubility limit normally changes with temperature. The extent of the solid solubility region can be plotted onto the phase diagram (Fig. 5.4b). In this example, the alpha phase is the region of solid solution where some of B atoms have dissolved in a matrix of A atoms. The beta phase is the region where a small percentage of A atoms have dissolved in a matrix of B atoms. It is important to note that some elements have zero solid solubility in other elements. An example is aluminum/silicon alloys, where aluminum has zero solid solubility in silicon.

If an alloy's composition does not place it within the alpha or beta solid solution regions, the alloy will become fully solid at the **eutectic temperature**. The eutectic line on the phase diagram indicates where this transformation will occur over the range of compositions. At alloy compositions and temperatures between the liquidus temperature and the eutectic temperature, a mushy mix of either alpha or beta phase will exist as solid masses within a liquid mixture of A and B. These are the alpha plus liquid and the beta plus liquid areas on the phase diagram. The region below the eutectic line, and outside the solid solution region, will be a solid mixture of alpha and beta.

EXAMPLES SOLVED IN CLASS:

Example 5.1: Consider a point C on the phase diagram of Fig. 5.4b having m_B=0.65. Estimate the mass composition of the mixture in terms of the solid alloys α and β.

Example 5.2: Consider point D on the phase diagram of Fig. 5.4b also having m_B=0.65. Estimate the mass composition of the mixture at point D.

2. The Fe-Fe$_3$C Phase Diagram

A fairly detailed iron-(iron-carbide) phase diagram is shown in Fig. 5.5. The range of the abscissa is from 0% carbon to only 6.7% carbon, beyond which the iron phase is entirely in the form of iron-carbide.

Pure iron at temperatures below 912°C (1670°F) exists in the α-ferrite form which has the BCC arrangement of atoms.

At temperatures between 912°C-1394°C (1670°F-2552°F) iron changes crystalline form to an FCC arrangement called γ-austenite.

From 1394°C-1539°C (2552°F-2802°F) iron returns to a BCC crystalline form called δ-ferrite.
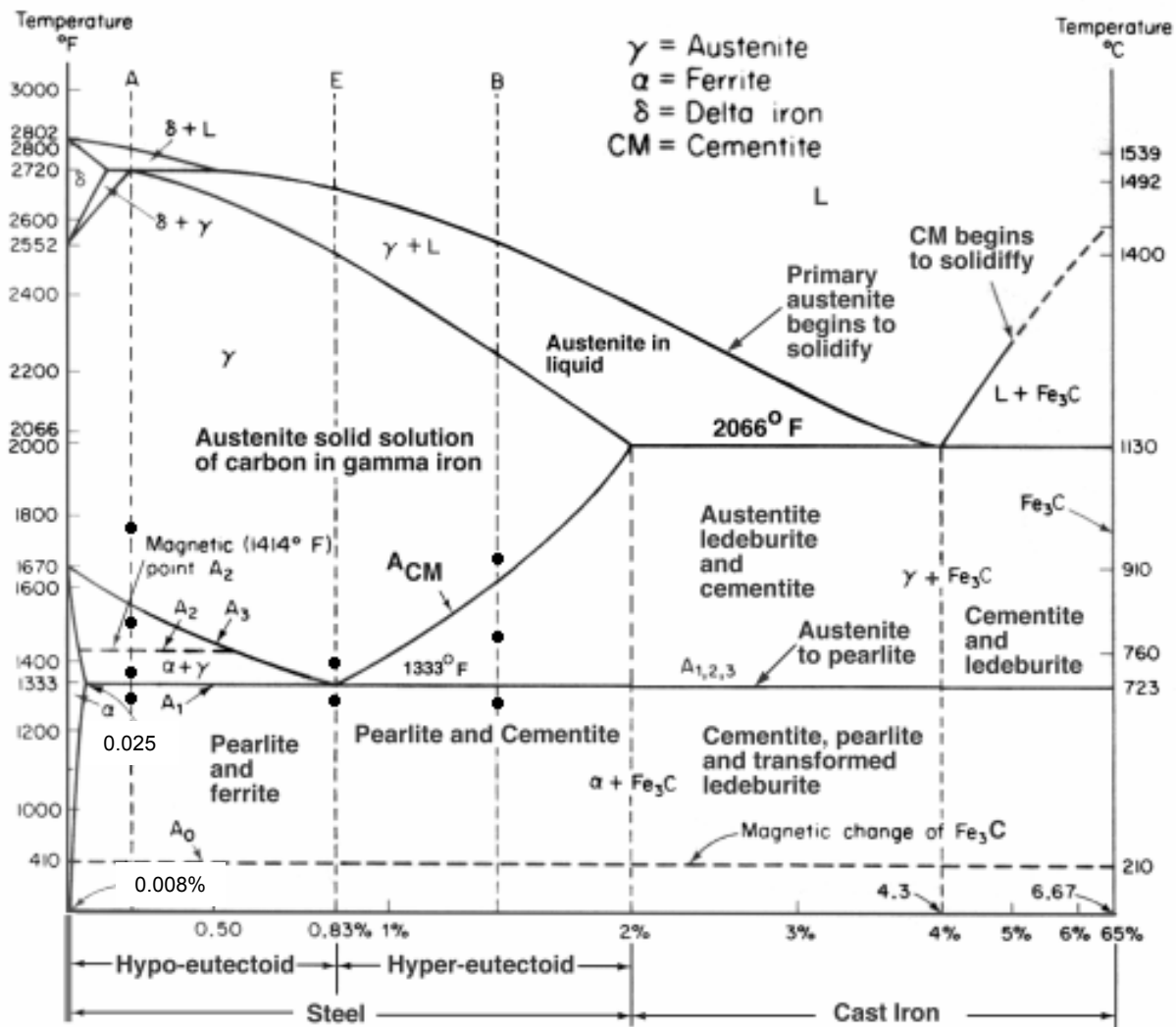
Fig 5.5: Fe-Fe$_3$C Phase Diagram, *Materials Science and Metallurgy*, 4th ed., Pollack, Prentice-Hall, 1988

Along the left axis of the diagram, it can be observed that carbon is mildly soluble in α-ferrite up to a peak of 0.77% carbon at 727°C.

Any additional carbon content in the steel results in the formation of the Fe_3C compound iron-carbide, which is also known as cementite. This compound while very strong, makes steel very brittle. Most structural steels have a very low carbon content, less than 0.3%, to avoid problems with brittleness.
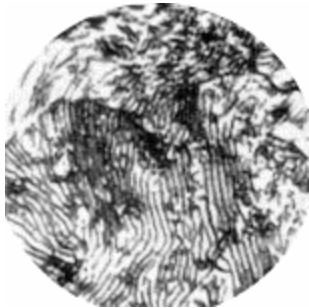

Fig. 5.6. Lamellar pearlite microstructure of a slowly cooled eutectoid steel. The light regions are ferrite, and the dark regions cementite.
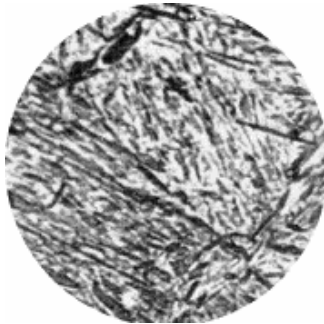
For steel having a carbon content less than 0.83%, the steel exists in the form of a ferrite-pearlite hypo-eutectoid shown in Fig. 5.6. Pearlite is mixture of alternate strips of ferrite and cementite in a single grain. The name for this structure is derived from its mother of pearl appearance under a microscope. A fully pearlitic structure occurs at 0.83% carbon. Further increases in carbon will create cementite at the grain boundaries, which will start to weaken the steel. Decreases in carbon content below 0.83% create pearlite rich in ferrite.

It should be emphasized that the relatively ductile pearlite microstructure is obtained only upon relatively slow cooling of steel from above 723°C.

Fig. 5.7. Martensite microstructure of a plain-carbon steel.

If austenite steel is cooled quickly from temperatures above 723°C the lamellar microstructure does not have a chance to form, and instead, a **martensite** microstructure is formed. (Fig. 5.7). In **martensite**, the carbon remains in solution in the BCC iron ferrite unit cell. Martensite is metastable in that if reheated back above 723°C and allowed to cool more slowly, it would not re-form.

Martensitic steel is generally very strong and hard, in direct proportion with the carbon content. The ductility and toughness of martensite decrease in direct proportion with carbon content.

Martensitic steel is usually formed by **quenching**. Usually, only the skin layers of steel plates can undergo cooling rapid enough to form martensite. Thus it is not unusual to have a hard, strong, brittle layer of martensite steel on the skin of a specimen, and to have a more ductile pearlitic interior structure that has cooled more slowly.

Since quenched steel can have residual thermal stresses due to the fact that the different regions cooled at different rates, it is usually **tempered**. Tempering involves heating a martensitic steel to a temperature below the eutectoid temperature of 723°C, holding the steel at that temperature for a few hours, and then cooling it quickly from the tempering temperature. During tempering, some of the metastable carbon that remained in solution with ferrite, precipitates out in varying forms and amounts, improving the ductility of the steel. Residual thermal stresses are also reduced in tempering.

C. GRADES OF STRUCTURAL STEEL

Most grades of structural steel have carbon contents ≤ 0.3%, since ductility is usually a concern in civil structures.

In the U.S. there are two primary systems for designating different types of steel:

- The American Society of Testing and Materials (ASTM) system; and

- The American Iron and Steel Institute (AISI) system.

Worldwide, there are numerous other designation systems. The European Union and Japan have their own systems.

Table 5.1. Properties of ASTM Low Carbon and HSLA Steel Alloy Designations

Steel type	ASTM Designations		F_y MPa [ksi]	F_{ult} MPa [ksi]	El. %	Chemical Composition (max percent)								
						C	Cu	Mn	P	S	Ni	Cr	Si	Mo
Carbon	A36		251 [36]	404-558 [58-80]	23	.26	.2	.75	.04	.05				
	A53 Gr. B		244 [35]	418 [60]	23	.25	.4	.95	.05	.05	.4	.4		.15
	A 500	Gr. B	293 [42]	404 [58]	21	.30	.18		.05	.06				
		Gr. C	321 [46]	432 [62]	21	.27	.18	1.4	.05	.06				
	A501		251 [36]	404 [58]	23	.30	.18		.15	.06				
	A 529	Gr. 50	349 [50]	453-700 [65-100]	19	.27	.2	1.35	.04	.05				
		Gr. 55	384 [55]	483-700 [70-100]	19	.27	.2	1.35	.04	.05				
High-Strength, Low Alloy (HSLA)	A 572	Gr. 42	293 [42]	418 [60]	24	.21		1.35	.04	.05				
		Gr 50	349 [50]	453 [65]	21	.23		1.35	.04	.05				
		Gr. 55	384 [55]	488 [70]	19	.25		1.35	.04	.05				
		Gr. 60	418 [60]	523 [75]	18	.26		1.35	.04	.05				
		Gr. 65	453 [65]	558 [80]	17	.26		1.35	.04	.05				
	A 618	I&II	349 [50]	488 [70]	22	.20	.2	1.35	.04	.03				
		III	349 [50]	453 [65]	22	.23		1.35	.04	.03			.3	
	A 913	Gr. 50	349 [50]	418 [60]	21	.12	.45	1.60	.04	.05	.25	.25	.4	.07
		Gr. 65	453 [65]	558 [80]	17	.35	.35	1.60	.04	.05	.25	.25	.4	.07
	A992		349-453 [50-65]	453 [65]	18	.23	.60	0.5	.35	.05	.45			.15
Corros. resistant (HSLA)	A242		349 [50]	488 [70]	18	.15	.2	1.0	.15	.05				
	A588		349 [50]	488 [70]	21	.19	.4	1.35	.04	.05	.04	.7		

Table 5.2. High-Strength Quenched and Tempered Weathering Steels

Steel type	ASTM and Other Designations		F_y MPa [ksi]	F_{ult} MPa [ksi]	El. %	Chemical Composition (percent)								
						C	Cu	Mn	P	S	Ni	Cr	Si	Mo
Quenched and Tempered Low Alloy Steel	A852 also HPS 70W		488 [70]	592-767 [85-110]	19	0.11 max	.25-.4	1.1-1.4	.02 max	.006 max	.25-.40	.45-.70	.30-.50	.02-.08
Quenched and Tempered Alloy Steel	A514 also HPS 100W	Gr. P	620 [90]	793 [115]	16	0.12-0.21		.45-.7	.035 Max	.04 Max	1.2-1.5	.85-1.2	.2-.35	.45-.6

A few noteworthy points:

• A242, A588, A852, and A514 steels are known for having good weathering properties. That is to say, they resist dry corrosion much better than the carbon and other HSLA types.

• The highest strength steels presented in Tables 5.1 and 5.2 are processed through quenching and tempering. Quenched and tempered steels are usually available only in plate and bar shapes.

• Since the high-strength weathering steels will be more costly than other types of steel, they should be used only when the superior properties are truly needed.