Chapter 9:

High-Strength Low-Alloy Steel

Introduction

One notable limitation of mild steel is the temperature range in which it can be used. Its strength falls off rapidly above 350 °C (660 °F), and at sub-zero temperatures it loses ductility and fails by brittle fracture. Traditionally, the most convenient and inexpensive means of providing higher-strength steels has been to increase the carbon content. Structural steels containing up to 0.35% C have been used to provide girders, channels, beams, and plates of yield strengths on the order of 300 to 350 MPa (43 to 50 ksi). However, their use in the modern context has been limited because of hot forming, heat treatment, and welding difficulties. Moreover, increasing carbon content from 0.1 to 0.3% raises the ductile-to-brittle transition temperature from −50 to 50 °C (−60 to 120 °F). During World War II, costly failures of several oil tankers and equipment in chemical plants and oil refineries occurred because of brittle fracture.

The plain carbon steels have some other disadvantages, such as a decrease in ductility, toughness, and fabricability with increased carbon content; rapid deterioration of physical properties with increased temperature; and limitation of optimum heat treatment effects to thinner sections only. Moreover, the strength properties of plain carbon steels are too low to meet the demands of the modern trends for higher pressure, higher capacity, and/or large-size units.

These limitations of plain carbon steels are to a great extent overcome by the high-strength low-alloy (HSLA) steels, without appreciably higher cost, compared with special steels. The HSLA range of application extends from −100 to 650 °C (−150 to 1200 °F), their ductility is nearly the same, they have more strength and toughness, and their yield strength and proof stress are far superior to those of carbon steel. This ultimately results in a saving in the cost of construction, as will be demonstrated below. HSLA alloys with specific properties, such as high abrasion resistance, heat resistance, and impact strength at low temperatures are also produced.

As noted in Ref 1, there is no precise definition for the term HSLA steels. One definition mentions not more than 6% alloying additions, and two others define it in terms of minimum yield strength of 275 and 350 MPa (40 and 50 ksi). The American Iron and Steel Institute (AISI) defines it as “a specific group of steels with chemical composition especially developed to impart higher mechanical properties values, and, in certain of these steels, materially greater resistance to atmospheric corrosion than is obtainable from conventional carbon steels. HSLA steel is generally produced with emphasis on mechanical properties requirements rather than chemical composition limits ...” (Ref 2). In keeping with this, some of this discussion will include alloys containing more than 6% of alloying additions with specific properties.

Categories and Specifications

HSLA steels include many standard and proprietary grades designed to provide a desirable combination of properties, such as strength, toughness, resistance to creep, corrosion resistance, formability, and weldability, often to meet specific requirements of modern technology. Reference 3 lists nearly 600 such steels. A summary of the characteristics and applications of the HSLA steels described in ASTM specifications is available in Ref 4. This chapter will discuss HSLA steels under the following categories:

- Conventional HSLA steels, prized for high strength and creep resistance; mostly chromium-molybdenum steels, with nickel added in some compositions to enhance corrosion resistance.
- Weathering steels, which contain small amounts of alloying elements such as copper and phosphorous for enhanced corrosion resistance and solid-solution strengthening; some new compositions contain a
microalloying element for grain refinement and strengthening.

- Microalloyed steels, which contain minute quantities (generally 0.1% or less) of one or two of the strong carbide or carbonitride forming elements such as niobium, titanium, vanadium, etc., for precipitation strengthening, grain refinement, etc.; optimization of these properties by controlled thermomechanical processing is their essential feature.

- Dual-phase steels are those which have a fine dispersion (15 to 35%) of martensite or bainite in a ferrite matrix to provide a good combination of ductility and high tensile strength.

Keep in mind the fact that these categories are somewhat loose, as the modern HSLA steels in all of them contain microalloying constituents.

Conventional HSLA Steels

These are structural steels that have both high strength and good resistance to atmospheric corrosion. The structural steels may be categorized as (1) those with yield strength in the range of 300 to 350 MPa (43 to 50 ksi) that conform to ASTM specifications such as 242 and 588 and are not intended for heat treatment; and (2) those that are intended for heat treatment, quenching, and tempering or normalizing; they have naturally high yield strengths, on the order of 550 to 650 MPa (80 to 93 ksi), and they usually conform to ASTM 514 for welded bridges and structures, and to ASTM 517 for high-strength alloy steels for pressure vessels and plates. Welding these steels must not adversely affect the properties of the plate, particularly in the heat-affected zones. Normalized steels have lower yield strengths, on the order of 300 to 415 MPa (43 to 60 ksi), and they meet the requirements of ASTM 633.

Effect of Alloying Elements

One or more of the alloying elements, such as chromium, molybdenum, nickel, copper, silicon, and vanadium, are normally used as alloying additions. The first three of them are the most common. Almost all of these alloying elements increase strength, hardenability, and creep resistance. Usually manganese is also present as a constituent of unalloyed, primary steel. Nickel strengthens ferrite, refines grain, and improves low-temperature toughness and resistance to corrosion in general and fatigue fracture in particular. The addition of more than 3% Ni is required for any significant improvement in corrosion resistance. Nickel is more effective in combination with chromium and molybdenum. As much as 9% Ni depresses the ductile/brittle transition temperature to −196 °C (−320 °F). Chromium stabilizes ferric and chromic carbide and improves hardenability, corrosion resistance, abrasion resistance, and high-temperature performance. Molybdenum also increases hardenability, toughness, and strength at high temperatures. It enhances corrosion resistance in general and resistance to hydrogen attack and pitting in particular.

Copper improves resistance to atmospheric corrosion and mechanical properties. Vanadium improves grain size and mechanical properties. Manganese and silicon may be present in the composition of primary steel. Manganese is a mild, solid-solution strengthener in ferrites. It improves hot-working characteristics, and it combines with sulfur to form MnS, which improves machinability. Silicon is a powerful deoxidizer and strengthens ferrites as well. As already stated, fully-killed steels contain 0.15 to 0.35% Si. It has a strengthening effect in low-alloy structural steels. In larger amounts, it increases resistance to scaling at high temperature. For imparting corrosion resistance, particularly in an HCl environment, 5% Si is required. The addition of 0.2 to 1.5% Cu along with 5% Si further improves corrosion resistance. Among the constituents of primary steel, phosphorous is the best solid-solution strengthening element in ferrites, but because it is detrimental to weldability, its concentration is not usually allowed to exceed 0.1% by weight.

Corrosion Resistance and Applications

Low-alloy steels are intended primarily to improve the mechanical properties of steel. For example, a steel containing 1% Cr and 0.5% Cu has a very high tensile strength, over 1.6 times that of mild steel, and its rate of rust formation is one third that of mild steel. The addition of alloying elements in this range improves its corrosion resistance as well, but not to the extent of transforming them into a noncorrosive material. Thus, there is a marginal improvement in most cases, which does not enlarge their field of application over that of carbon steel on this account alone. For example, in natural water, the corrosion resistance of HSLA steel and plain carbon steel is the same. In sea water, the rate of attack is nearly the same but pitting is much less in HSLA steel. Nevertheless, life expectancy is improved or prolonged at a cost which may or may not be economically advantageous. But where high strength is required, as in a pressure vessel or a huge reactor operating at moderately high temperatures, their use is a must. This will be demonstrated below.

Thus a marginal improvement in the corrosion resistance of low-alloy steels and a marked improvement in their mechanical properties has recently enlarged their field of application in industry because of the employment of higher pressures, temperatures, and rates of flow in modern processes, to boost production. A number of HSLA steels may be available to meet the demands of mechanical properties in a particular situation or a process. The design engineer has to choose one or two among such steels that can withstand the rigors of aggressive process streams and fabrication techniques at reasonable cost. Thus, for a specific application, their corrosion characteristics are important on that account. And therefore the dependence of mechanical properties and corrosion behavior on composition (which determines cost as well) also becomes an important consideration.

Table 9.1 summarizes the applications of some HSLA steels in industry. Most of these steels are valued
### Table 9.1 Applications of conventional HSLA steels in industry

<table>
<thead>
<tr>
<th>Major Alloying Elements</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5Mo; 1Cr-0.5Mo; 2.5Cr-0.5Mo; 4-6Cr</td>
<td>High-strength and creep-resistant steels for: 1) Pressure vessels and boilers operating at elevated temperatures 2) Oil refinery heat exchangers, reactor vessels, crackers, tubes, and furnaces</td>
</tr>
<tr>
<td>1-2% Cr</td>
<td>Handling steam in BWR conditions (nuclear power generation) and for some turbine components</td>
</tr>
<tr>
<td>1.5-2% Cr, 2-4% Ni, and 0.2-0.7% Mo</td>
<td>Resistant to erosion corrosion and temper brittleness. Used for: 1) Reactors and vessels operating at high temperatures and pressures in oil refining, petrochemicals, and coal conversion, and also for hydrogen service at high temperature in these and other industries 2) High-temperature steam and wet-steam service</td>
</tr>
<tr>
<td>2.25Cr-1.0Mo</td>
<td>Under geothermal conditions</td>
</tr>
<tr>
<td>9Cr-1.0Mo</td>
<td>Use under aggressive conditions in oil-well service up to 100 °C (212 °F)</td>
</tr>
<tr>
<td>2% Cu, Cr and Ni</td>
<td>Boiler exhaust components and rustless steel structures in chemical and steel industries, petroleum refineries, and marine service</td>
</tr>
<tr>
<td>2-9% Ni</td>
<td>Cryogenic applications; 9% Ni grade for handling liquified NH₃, O₂, and N₂</td>
</tr>
<tr>
<td>5-9% Cr</td>
<td>Oil refinery applications, handling sulfur-bearing crucibles, heat exchangers, and furnace tubing</td>
</tr>
</tbody>
</table>

for their high strength and their resistance to creep and erosion-corrosion. Construction codes for process equipment and ASTM standard specifications for refinery steels are available in Ref 5.

These steels are often designated by their major alloying elements. It is worthwhile to recapitulate here the important characteristics of two such widely used groups: nickel steels and chromium-molybdenum steels.

### Nickel Steels

The addition of nickel to steel refines grain size; increases strength and toughness; improves resistance to attack by chemicals, particularly alkaline salts; and effects an appreciable improvement in resistance to alkaline media. When the amount of nickel exceeds 3%, the effect or improvement increases in proportion to nickel content. Nickel also improves resistance to corrosion fatigue in oil well brines containing hydrogen sulphide. However, even up to 5% Ni in 0.1% C steel has not been found superior to plain carbon steel in Panama Canal seawater. As stated above, the addition of nickel avoids brittle fracture at subzero temperatures, and in copper-bearing steels it minimizes hot shortness.

### Chromium-Molybdenum Steels

Low-alloy chromium steels find extensive use in oil refineries because of their resistance to crude oils containing sulfur. Alloys containing 4 to 6% Cr are often used. Figure 9.1 shows the rate of corrosion of these steels at different temperatures. As mentioned earlier, the addition of 2% Cr to steel reduces hydrogen embrittlement, but in actual practice Ni-Cr-Mo steels are used, as chromium and molybdenum together have a synergistic effect on corrosion resistance as shown in this figure.

Hydrogen attacks steel at elevated temperature and pressure, by combining with the carbon in steel to form methane bubbles (2H₂ + C → CH₄) along grain boundaries, and when these bubbles grow to a larger size they adversely affect the mechanical properties of steel. Methane under pressure tears open the grain boundaries. Such hydrogen damage can be prevented by alloying the steel with strong carbide formers, such as chromium, molybdenum, titanium, vanadium, etc., which bind the carbon firmly. Elimination of iron carbide from the microstructure ensures stability against hydrogen attack. But Cr-Mo alloy steel can suffer hydrogen damage if transition carbide is formed by fast cooling after welding.

The addition of molybdenum to chromium steel further improves its high-temperature strength, creep resistance, and resistance to temper brittleness and hydrogen attack at elevated temperature. Some degree of resistance to hydrogen sulphide, which is often present in hydrating gases, is also afforded. Low-alloy steels containing 0.5% Mo, 1.25% Cr and 0.5% Mo, or 2.25% Cr and 1.0% Mo, are used in power plants and process industries. Figure 9.2 shows the safe zones for various low alloy steels in a hydrogen atmosphere. Such high temperatures and pressures are encountered in oil refineries during cracking and regeneration of catalysts by hot hydrogen treatment, and in ammonia synthesis reactors and synthesis gas coolers.

According to Ref 6, experience in the oil and power industries has shown that steels containing molybdenum may graphitize above 850 °C (1560 °F) unless they contain, in addition, a minimum of 0.7% Cr. Therefore, when such high temperatures are encountered, particularly in welded construction, the use of Cr-Mo steel is a must. A typical composition of European low-molybdenum steel used for such purposes contains 0.2% C, 0.5 to 0.8% Mn, 0.15 to 0.35% Ni, and 0.25 to 0.35% Mo. Unlike chromium and molybdenum, nickel is not a carbide stabilizer and does not enhance resistance to hydrogen attack. It is added to improve the strength characteristics. Table 9.2 shows the composition and properties of different grades of Cr-Mo steel according to ASTM-387.

A 2.25Cr-1.0Mo steel is the preferred material of construction in oil refining, petrochemicals, and coal...
conversion equipment, where hydrogen is used at higher pressures and temperatures in pressure vessels. But where the pressures exceed 20 MPa at elevated temperatures, steel containing 3Cr, 1.5Mo is used. One such composition contains 1.4Mn-3Cr-1.5Mo-0.08V. According to Ref 7, this steel provides superior resistance to hydrogen-induced cracking (HIC) and decarburization of heavy sections exceeding 400 mm (15 in.), and is used for high-pressure vessels for hydrogen service.

Because of the increase in crude prices in recent years, deep hydrocarbon reservoirs have become commercially viable. Deep wells in excess of 4500 m (19,500 ft) encounter high temperatures, high pressures, and high concentrations of H$_2$S, CO$_2$, and brine (Ref 8). A151400 series steel with 11% Cr and 0.4 to 0.8 Mo resist stress-corrosion cracking of tubular material for casings, tubing, and couplings.

**Weathering Steels and Other Copper-Bearing HSLA Steels**

Weathering steel is primarily a low-alloy copper-bearing steel, which has assumed importance for the processing industries because of its corrosion resistance in atmospheres surcharged with acid pollutants such as SO$_2$, CO$_2$, H$_2$S, etc. Copper also imparts excellent strength and toughness to HSLA steels at relatively low cost. Moreover, when microalloying elements are added to copper-bearing steels, acicular bainite microstructure is produced, which imparts high fatigue strength and offers resistance to fatigue crack growth and HIC. One negative effect of adding copper is vulnerability to hot shortness during hot-working. However, process control during production or the addition of Ni and Si mitigate this shortcoming.

The maximum solubility of copper in ferrite at room temperature and up to 600 °C (1110 °F) is on the order of 0.35%. Reference 9 reports that an increase from 0.01 to 0.1% in copper content of carbon steel reduces corrosion.
penetration by over a third, from 0.660 to 0.20 mm (0.24 to 0.008 in.), as shown in Fig. 9.3. Further increase in copper content marginally improves corrosion resistance.

Copper is an optional addition for some structural steels. The use of steel tubes containing 0.2 to 0.5% Cu is recommended for locomotive boilers in Ref 10. This source suggests that more than 0.35% Cu is likely to create cathodic spots of precipitated copper, which can induce some corrosion. In fact, carbon steel tubes with 0.25% Cu have been used by railroads. There is evidence (Ref 11) that the copper content of steel has little effect on the corrosion rate in sea water. By contrast, Refs 12 and 13 show that, on the basis of tests with synthetic sea water, which becomes acidic under boiler conditions, copper in steel reduces the depth of pitting. It was found that 0.2% Cu in steel has the same effect in controlling pit depth as raising pH value to pH = 8. But again, the beneficial effect of copper disappears from the welded tubes, as seen in curve 4, Fig. 9.4, on dependence of pit depth on the copper content of steel (Ref 13).

When the composition of a low-alloy steel contains chromium, molybdenum, nickel, phosphorus, etc. in addition to copper, corrosion resistance is further enhanced, and in addition there is a marked improvement in mechanical properties. Chromium and nickel are added, up to 0.5 to 1.0% each. In fact, none of the alloying constituents of weathering steel exceed 1%, and it has also been found that raising the phosphorus content of copper-bearing steels from 0.01 to 0.1% enhances corrosion resistance and strength by 20 to 30%. Accordingly, the term weathering steel implies a class of low-alloy steels that contain small amounts, less than one percent each, of copper, chromium, molybdenum, nickel, phosphorus, and silicon, which promote the formation of a protective rust layer that acts as a self-healing barrier against further corrosion. Light structural grades of these steels are covered by ASTM A-242, and heavier grades by ASTM A-588. There are further variations under these main grade categories, per Table 9.3. In the course of time these steels develop fine-textured, tightly adhering protective films.

The low-alloy weathering steels are now being used extensively in the chemical and metallurgical industries and in thermal power plants, as structural materials of
Materials Selection for Corrosion Control

Table 9.3 Composition of steels used in atmospheric corrosion tests. Source Ref 15

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>Composition, % by Weight</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM Specification</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A242-75, Type 1</td>
<td>0.15 max</td>
<td>1.00 max</td>
<td>0.15 max</td>
<td>0.05 max</td>
<td>—</td>
<td>—</td>
<td></td>
<td>0.20 min</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>A242 Test Material</td>
<td>0.09</td>
<td>0.65</td>
<td>0.11</td>
<td>0.032</td>
<td>0.29</td>
<td>0.66</td>
<td>0.52</td>
<td>0.27</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>ASTM Specification</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A588-82, Grade B</td>
<td>0.20 max</td>
<td>0.75-1.35</td>
<td>0.04 max</td>
<td>0.05 max</td>
<td>0.15-0.50</td>
<td>0.50 max</td>
<td>0.40-0.70</td>
<td>0.20-0.40</td>
<td>0.01-0.10</td>
<td>—</td>
</tr>
<tr>
<td>ASTM Specification</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A588-77a, Grade B</td>
<td>0.20 max</td>
<td>0.75-1.25</td>
<td>0.04 max</td>
<td>0.05 max</td>
<td>0.15-0.30</td>
<td>0.50 max</td>
<td>0.40-0.70</td>
<td>0.20-0.40</td>
<td>0.01-0.10</td>
<td>—</td>
</tr>
<tr>
<td>A588 Test Material</td>
<td>0.13</td>
<td>1.02</td>
<td>0.008</td>
<td>0.018</td>
<td>0.22</td>
<td>0.27</td>
<td>0.64</td>
<td>0.21</td>
<td>0.062</td>
<td></td>
</tr>
<tr>
<td>0.21 Cu Test Material</td>
<td>0.02</td>
<td>0.35</td>
<td>0.005</td>
<td>0.013</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.21</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>0.021 Cu Test Material</td>
<td>0.07</td>
<td>0.35</td>
<td>0.009</td>
<td>0.020</td>
<td>&lt;0.001</td>
<td>0.01</td>
<td>0.02</td>
<td>0.021</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

Reference 16 has recent data on ASTM A588 steel, employed for bridge structures, to indicate that these steels are not immune to atmospheric corrosion as originally assumed. Under dry conditions and alternate wet and dry cycles of nearly equal periods, this steel forms a protective rust layer. However, under wetter conditions and in the presence of stagnant water, it forms a non-protective rust layer. The presence of chloride as well as other acid-forming pollutants in the atmosphere enhances corrosion. The presence of salt and high humidity, favorable for water condensation, promotes pitting.

Corrosion Characteristics

Corrosion characteristics of weathering steels depend in a complex manner on climatic parameters, including temperature and humidity, pollution levels, exposure conditions, and composition of weathering steel. The rate of corrosion stabilizes to a low value in two to four years under outdoor conditions. A dark brown to violet patina develops in polluted atmosphere in course of time. The patina develops in longer time in rural atmosphere. A compact rust is formed which cannot be easily wiped off the surface.

The optimal environment for the formation of a protective patina is alternate dry and wet periods, which is not uncommon in chemical plants. In roofed areas, the typical dark patina may not be obtained, but instead a layer of rust in lighter color, which, too, has somewhat protective properties except under marine conditions or in a high-chloride content atmosphere. In fact, weathering steels are only marginally superior under indoor conditions, in soils and under immersed conditions. Table 9.4 gives the variation of corrosion rates of weathering steel after stabilization, per Ref 17. In rural atmospheres, the patina takes more time to attain stability and the difference between the performance of mild steel and weathering steel is not so marked as in a polluted atmosphere, as is evident from the data in the table.

Reference 18 makes clear the importance of a time factor and the role of composition of weathering steel (called Atomofix) on its corrosion resistance. The results, summarized in Tables 9.5, 9.6, and 9.7 on composition properties and corrosion rate, confirm the already stipulated beneficial effect of phosphorous and marginally

Construction, and they will find more application in fast-growing industrially polluted atmospheres. Reference 14 reports on long-term exposure tests in ten different chemical plant environments, to compare the corrosion resistance of weathering steels with that of carbon steels. The results confirm that the low-alloy weathering steels have far superior corrosion resistance in all types of aggressive chemical environments, including organic vapors and chlorine and sulfur compounds. Copper-bearing steels also corrode at a lower rate in non-oxidizing atmospheres, compared with plain carbon steels. Figure 9.5 shows the relative corrosion resistance of carbon steel, copper-bearing steel, and weathering steel.

Reference 15 reports the results of recent outdoor corrosion tests conducted on weathering steels and other copper-bearing steels in rural, industrial, and marine environments after exposure for 16 years. The compositions of test specimens conforming to ASTM specifications A242 and A588 are given in Table 9.3. According to their data, weathering steel ASTM A242 is at least 16 times more corrosion resistant than 0.021% Cu steel and at least four times more corrosion resistant than 0.21% Cu-bearing steels, and weathering steel ASTM A588 is approximately eight times more durable than 0.021% Cu steel and approximately twice as durable as 0.21% Cu steel.
Table 9.4 Calculated steady-state corrosion rates of steel on free exposure in different types of atmospheres. Source: Ref 17

<table>
<thead>
<tr>
<th>SO₂ level µg/m³</th>
<th>Type of atmosphere</th>
<th>Corrosion rate in µm/yr (µin./yr)</th>
<th>Mild steel</th>
<th>Weathering steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Above 20</td>
<td>Rural</td>
<td>5-10 (197-394)</td>
<td>2-5 (79-197)</td>
<td></td>
</tr>
<tr>
<td>20 to 115</td>
<td>Urban</td>
<td>10-30 (394-1182)</td>
<td>2-6 (79-239)</td>
<td></td>
</tr>
<tr>
<td>Above 115 (generally up to 200)</td>
<td>Industrial</td>
<td>730 (28,762)</td>
<td>76 (2994)</td>
<td></td>
</tr>
</tbody>
</table>

Table 9.5 Compositions of selected weathering steels

<table>
<thead>
<tr>
<th>Designation</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Chemical Composition</th>
<th>P</th>
<th>Ni</th>
<th>Y</th>
<th>B</th>
<th>Al</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomofix 15217A</td>
<td>0.12</td>
<td>0.3</td>
<td>0.25</td>
<td>0.5</td>
<td>0.3</td>
<td>0.06</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Atomofix 15217B</td>
<td>0.12</td>
<td>0.9</td>
<td>0.25</td>
<td>0.4</td>
<td>0.3</td>
<td>0.04</td>
<td>0.30</td>
<td>0.02</td>
<td>-</td>
<td>0.01</td>
<td>0.02Nb</td>
</tr>
<tr>
<td>Atomofix 16224</td>
<td>0.17</td>
<td>1.2</td>
<td>0.45</td>
<td>0.8</td>
<td>0.55</td>
<td>max</td>
<td>0.6</td>
<td>0.06</td>
<td>min</td>
<td>0.06Nb</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.12</td>
<td>0.7</td>
<td>0.15</td>
<td>0.7</td>
<td>0.3</td>
<td>0.03</td>
<td>0.7</td>
<td>0.03</td>
<td>0.002</td>
<td>0.3Mo</td>
<td></td>
</tr>
</tbody>
</table>

Table 9.6 Mechanical properties of selected weathering steels

<table>
<thead>
<tr>
<th>Designation</th>
<th>50 mm (2 in.) thick plate</th>
<th>12 mm (15/32 in.) thick plate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield Strength MPa (ksi)</td>
<td>Tensile Strength MPa (ksi)</td>
</tr>
<tr>
<td>Atomofix</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15217A</td>
<td>-</td>
<td>345 (50)</td>
</tr>
<tr>
<td>15217B</td>
<td>335-345 (49-50)</td>
<td>355 (51)</td>
</tr>
<tr>
<td>16224</td>
<td>685 (99)</td>
<td>800-950 (116-138)</td>
</tr>
</tbody>
</table>

Table 9.7 Corrosion rates of weathering steel alloys Atomofix A and B

<table>
<thead>
<tr>
<th>Environment</th>
<th>Alloy</th>
<th>Corrosion Rate in µm/yr (µin./yr) in first 10 years</th>
<th>Stabilized rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rural atmosphere</td>
<td>Atomofix A</td>
<td>40-65 (1576-2561)</td>
<td>1-2</td>
</tr>
<tr>
<td></td>
<td>Atomofix B</td>
<td>65-90 (2561-3546)</td>
<td>2-3</td>
</tr>
<tr>
<td>Urban atmosphere</td>
<td>Atomofix A</td>
<td>60-95 (2364-3743)</td>
<td>1.5-2.5</td>
</tr>
<tr>
<td></td>
<td>Atomofix B</td>
<td>80-140 (3152-5516)</td>
<td>3-7</td>
</tr>
<tr>
<td>Industrial atmosphere (with SO₂ as main contaminant)</td>
<td>Atomofix A</td>
<td>150-260 (5039-10,244)</td>
<td>8-15</td>
</tr>
<tr>
<td></td>
<td>Atomofix B</td>
<td>170-360 (6698-14,184)</td>
<td>7-25</td>
</tr>
</tbody>
</table>

deleterious effect of microalloying on corrosion resistance.

The application of weathering steel under open-air conditions at optimally load-carrying structures, such as cranes in steel plants and bridges, represents a remarkable means for cutting down corrosion losses. As there is no need to apply protective coatings, maintenance also is minimized.

Even when a protective coating is required on such a steel for additional protection, for facade purposes or identification, it is easy to apply, as the patina on this steel is adhering and receptive, and there is no need to clean it except for removing superficial dust or moisture.

The weathering steels have also performed better in energy systems where materials of construction are exposed to fluctuating temperatures and the conditions are conducive to dew-point corrosion in flue gases containing sulfur. Refs 19 and 20 report that in an atmosphere of hot flue gases obtained from combustion of sulfur-bearing oil with 3 to 4% S, the performance of weathering steel was found to be better than that of cast iron, mild steel, 18-8 stainless steel (AISI 304 and 316), and aluminum up to 110 °C (230 °F). Above 120 °C (250 °F), stainless steel was found to be superior.

Microalloyed HSLA steels containing copper are finding increasing application where high strength and
Table 9.8  Application and composition of some Cu-bearing microalloyed steels

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition (%)</th>
<th>Yield Stress MPa (ksi)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryalism</td>
<td>0.08C, 0.35Si, 1.25Mn, 0.02Nb, 0.25Ni, 0.30Cu</td>
<td>355 (51)</td>
<td>Ship building, storage tanks (Ref 21)</td>
</tr>
<tr>
<td>Offshore Type I</td>
<td>0.10C, 0.45Si, 1.25Mn, 0.015Nb, 0.18Ni, 0.28Cu</td>
<td>355 (51)</td>
<td>Offshore structures and platforms (Ref 21)</td>
</tr>
<tr>
<td>Mn-Mo-Cu</td>
<td>0.14C, 0.31Si, 1.4Mn, 0.03Al, 0.17V, 0.03Nb, 0.22Mo, 0.48Cu</td>
<td>483 (70)</td>
<td>Pipeline fittings and sour gas applications (Ref 22)</td>
</tr>
<tr>
<td>Experimental Nippon Steel</td>
<td>0.024C, 0.19Si, 1.17Mn, 0.04Al, 0.041Nb, 0.19Ni, 0.29Cu, 0.0015B</td>
<td>483 (70)</td>
<td>Sour gas linepipe; resistance to HIC (Ref 23)</td>
</tr>
<tr>
<td>Ni-COP (A710)</td>
<td>0.04C, 0.28Si, 0.48Mn, 0.038Al, 0.038Nb, 0.90Ni, 0.70Cr, 0.19Mo, 1.16Cu</td>
<td>550 (80)</td>
<td>Ships, offshore platforms, sour gas handling (Ref 24)</td>
</tr>
<tr>
<td>Cu-B-Nb (Expl)</td>
<td>0.04C, 0.01Si, 1.3Mn, 0.01Al, 0.06Nb, 1.0Ni, 1.85Cu, 0.0009B, 0.035Ti</td>
<td>690-790 (100-114)</td>
<td>Linepipe, naval structure; applications at sub-zero temperatures (Ref 25)</td>
</tr>
<tr>
<td>WEL-TEN 80</td>
<td>0.14C, 0.27Si, 0.9Mn, 0.04V, 0.9Ni, 0.6Cr, 0.43Mo, 0.2-0.5Cu, 0.001B</td>
<td>800 (116)</td>
<td>Elevating racks for offshore platforms (Ref 26)</td>
</tr>
</tbody>
</table>

Corrosion resistance are valued. These alloys are resistant to HIC and find fairly wide application under severe marine conditions where strength, corrosion resistance, fabricability, and weldability in particular are equally important, as shown in Table 9.8.

Copper-bearing microalloyed HSLA steels maintain their inherent toughness even at high strengths. In addition, they are able to resist HIC in H2S environments (Refs 21 and 22), and in areas affected by welding heat (Ref 23), and therefore they are finding extensive application in sour-gas applications. The addition of 0.3% Cu is considered sufficient to form a stable protective film, for this purpose, as demonstrated by Nippon Steel for ultralow-carbon-boron steel (Table 9.8). An alloy designated ASTM A710 has been used extensively for ship bottoms and offshore oil drilling and exploration structures (Ref 24). For example, A710 has been extensively used in the construction of USS Ticonderoga (CG47) guided missile cruiser (Ref 25). This alloy has excellent strength and low-temperature impact resistance when quenched and aged. These properties can be attributed to its microstructure, which has a very fine-grained ferrite, acicular ferrite, and martensite-austenite. Other copper-bearing alloys used in marine service are also listed in this table (Refs 26 and 27).

**Mechanism of Corrosion Resistance**

The rust formed on weathering steels is more dense and compact, compared with that on mild steel, which effectively screens the steel surface from the moisture and aggressive constituents of the atmosphere. Initially, a film of FeOOH (Ref 28) is formed, as in the case of plain carbon steels. After some exposure to industrial and urban atmospheres, the alloying constituents play their role. Copper in weathering steel forms basic copper sulphate in the presence of SO2, which is invariably present as a pollutant. The basic sulfates have low solubility and they block the pores in rust layers, decreasing their porosity. Nickel, too, forms an insoluble basic sulphate. There is also evidence of the formation of insoluble phosphates and phosphides. All these sparingly soluble compounds fortify the rust layers. This is confirmed by the fact that in the course of time the weathering steel attains a nobler potential as compared to the unalloyed carbon steel.

Work reported in Ref 29 on the electrochemical and surface analytical investigation of weathering steel has shown that phosphides of copper and nickel are formed at the surface. These phosphides are more stable, with respect to anodic dissolution, than iron matrix. They also accelerate the cathodic reduction of oxygen and consequently restrict its inhibition by growing oxide layers in the active-passive transition region. The steels used in their investigation contained 0.08 to 0.12% C, 0.34 to 0.46% Cu, 0.062 to 0.066% P, 0.06 to 0.08% Ni, etc.

**Microalloyed Steels**

Microalloying has a relatively recent history. The positive role of grain refinement and precipitation on the mechanical properties of steel was clearly understood by the early 1960's. At a conference on Metallurgical Developments in Carbon Steel at Harrogate (U.K.), during 1963, metallurgists first took serious note of the fact that microalloying can simultaneously initiate precipitation and grain refinement. Rapid development started thereafter, as is evident from the spate of almost a dozen international conferences and seminars on the subject from 1980 to 1990, to elucidate this role and develop fine details for the optimization of microalloying phenomena. Thus it
was established that the addition of minute quantities (nearly 0.1% or less) of strong carbide-forming and nitride-forming elements, such as cobalt, niobium, titanium, vanadium, etc. have a profound influence on the properties of steel without raising the ductile-to-brittle transition temperature. The precise addition of one or more of these microalloying elements, coupled with careful processing, i.e., rolling and thermal treatment, have resulted in much stronger and tougher steels, with yield strengths of 375 to 700 MPa (55 to 101 ksi), and with almost tailor-made properties to withstand the rigors imposed by advances in other related mechanical fields and by the constraints of depleting resources.

The outstanding properties sought during microalloying are high strength and toughness, resistance to brittle fracture, cold formability, and weldability. These are achieved by judicious selection of microalloying additions for the purpose in view and precise control of thermomechanical processing. The structural parameters controlled by these means are:

1. Size and configuration of precipitates
2. Size and shape of grains
3. Phase transformations
4. Dislocation density
5. Non-metallic inclusions

Precipitation and Grain Refinement

The carbides and nitrides of microalloying constituents such as carbon niobium, titanium, vanadium, etc., and their carbonitrides are far more soluble in the austenite phase than in the ferrite phase, and their solubility in both phases decreases with temperature. Figure 9.6 shows the solubility product of the above compounds, per Ref 30 and 31. On cooling they precipitate out in a fine state in ferrite and contribute substantially to the strength of the alloy. According to Ref 31, carbide dispersions have two main roles. (1) In austenite, they refine the grain size during controlled rolling of microalloy steel, with a subsequent substantial influence on ferrite grain size resulting from austenite-ferrite transformation (2). During and subsequent to phase transformation, a fine carbide dispersion forms which has a substantial strengthening effect. The toughness of steel increases with the fineness of grain size. The manner and form in which the alloying elements and their compounds are further dispersed and conditioned by thermomechanical processing has a profound influence on the properties.

Often partial precipitation takes place in the austenite phase during cooling, pinning the grain boundaries. As a result of the improvement in strength effected by grain refinement, with grain size 5 to 20 μm, and the precipitation of carbides, nitrides and carbonitrides, it has been possible to reduce carbon content to approximately 0.1% for optimal toughness and also reduce free nitrogen to almost nil. Even a trace of nitrogen gas, as little as 25 ppm, raises the transition temperature by 35 °C (95 °F). Thus, in addition to enhanced strength, there is improvement in toughness, ductility, weldability, lowered transition temperature, and resistance to HIC. At the same time, sulfur, phosphorous, and oxygen are also reduced to the lowest levels, to minimize inclusions such as sulfides.

Microalloying can adversely affect toughness to a degree. The fine precipitates in ferrite, while contributing to strength, tend to reduce low-temperature toughness. During welding, the microalloying elements in austenite solid solution tend to form bainite in weld metal and the heat-affected zone, reducing somewhat the toughness of welded joints and seams.

The above is a simple explanation of the complex role of the many microalloying elements. In addition, there are many variations in thermomechanical treatment processes, and volumes have been written on the subject. For an in-depth study, Refs 32, 33, and 34 would make an excellent beginning.

Applications

A wide range of HSLA steels have been developed for many applications demanding high yield strength, toughness, formability, and weldability, through judicious use of molybdenum, niobium, titanium, and vanadium, either singly or in combination, in addition to a new generation of microalloying additions such as calcium, zirconium, and the rare earths. Consequently, designers are able to use higher payload figures, for a saving of 15 to 45%, in addition to allowing for higher safety factors. Along with the synergistic effect of combining two or more microalloying elements, each imparts its own special attributes. For example, adding titanium facilitates the precipitation of niobium carbonitrides and helps control sulfide morphology. Ferrite grain refinement required for the optimum development of the above properties is achieved by a combination of microalloying and thermomechanical treatment, controlled rolling in particular, during the production of HSLA steels.

Molybdenum enhances the strength and hardenability of microalloyed steel by retarding the precipitation of carbides in the austenite phase during cooling, which
increases the potential for precipitation hardening in ferrite, per Ref 35. Therefore, microalloying in molybdenum-bearing steels is common. Strengthening of carbon molybdenum steels with 0.085% V has been mentioned above, and Mn-Mo-Nb steels have been developed for high-temperature pipe, as reported in Ref 36, and 9Cr-1Mo steel microalloyed with niobium and vanadium has been developed for steam boilers in power plants.

Recently, Nippon Steel has introduced ultra-low-carbon bainite ULCB steels, which belong to X60 to X-80 grades and are used extensively for pipelines in sour-gas environments. Per Ref 37, the composition of X-70 grade is 0.03C-0.14Si-1.9Mn-0.018P-0.003S-0.05Nb-0.018Ti-0.001B. Adding boron and scrupulously controlling interstitials by further addition of titanium at 3.4 x 10^-6 to control nitrogen, have been key factors in their development. Niobium in ULCB steels refines austenite grain size, which improves strength and toughness.

Commercial grades of API X-60's (C-Mn-Nb) and X-70's (C-Mo-Nb-Cr) have also been used for line pipes, after subjecting them to accelerated cooling during their production. Many modifications of X-60's and X-70's, with or without copper, containing varying amounts of microalloying and other elements are being produced competitively and tried under marine conditions.

However, despite these metallurgical improvements, users and contractors must be adept in rigidly observing prescribed thermal treatment and welding instructions.

Reports in Ref 38 from trials of HSLA steel in the North Sea at temperatures of 0 to 18 °C (32 to 65 °F) suggest that the addition of 1.3 to 1.4Cr, 1.5Al, 0.5Mn, 0.5Mo, and 0.05Ni to steel with carbon content of 0.01 to 0.15% increases corrosion resistance two to four times vs unalloyed steel. There is no benefit in increasing the aluminum and molybdenum, because pitting resistance is detrimentally influenced.

**Dual-Phase HSLA Steels**

During the production of HSLA steels, their mechanical properties are enhanced by controlling their microstructure, through solution strengthening, precipitation hardening of microalloying constituents with simultaneous grain refinement, dislocation hardening, etc. But increased strength is always accompanied to some extent by decreased ductility and toughness. Modern manufacturing techniques employed for press-formed components for the automotive and allied industries and for pipe forming require high-strength steel to have sufficient ductility and toughness to resist crack propagation and yet have good formability and weldability for ease of fabrication. To meet such conflicting demands at reasonable cost, an approach was borrowed from composite materials technology, which is based on combinations of hard and soft components. For steels, a fine dispersion of 15 to 35% martensite or bainite in a ferrite matrix makes a good combination of high toughness and ductility. This constitutes a dual-phase HSLA steel, a composite of compatible phases of coherent interfaces, one of which is ductile, while the other has high strength and hardness. This has been achieved by controlling alloy chemistry, including microalloying elements, grain size, microstructure, and thermomechanical processing. The aim is to change the microstructure from ferrite-perlite to ferrite containing islands of martensite-austenite, the microalloy constituent, which can decrease the rate of strain-induced work hardening, increase uniform elongation and strain, and maximize uniform strain. Dual-phase steels offer high yield strength, in the range of 400 to 750 MPa (58 to 109 ksi). Reference 39 gives a detailed, yet concise account of dual phase formation which is useful for those interested in further detail.

In short, its high work-hardening rate after plastic deformation, combined with its high uniform elongation, gives dual-phase HSLA steel formability equivalent to much lower strength mild steel. This combination offers weight savings for press-formed and die-formed aircraft and automobile components, such as wheel hubs, chassis parts, bumpers, etc., which makes dual-phase HSLA steel a cost-effective substitute for such applications.

**Fabrication Characteristics**

The hardenability of HSLA steels increases with increasing alloy content, and this makes fabrication more difficult. Precautions must be taken at all stages of formation and fabrication, preheating is required, cutting speeds must be reduced, and tack welding is necessary. Reference 40 recommends the following measures during fabrication of low-alloy steels:

1. Preheat for cutting, removing hardened edges before cold-forming
2. Heat treat cold-formed components to reduce strain
3. Heat treat after hot forming to restore properties
4. Weld with low-hydrogen processes, with strict control of backing, holding, and issue of electrodes
5. Preheat at or below the Mf temperature, at which martensite formation is complete, delaying post-weld heat treat until transformation from austenite is complete, and taking special preheat care for fit-up welds
6. Use austenitic electrodes to attach external bridge pieces and stringers
7. Heat treat to simulate production conditions, to verify material and weld metal properties

Welding ultra cryogenic 9Ni steel is difficult because it is not possible to use a matching consumable electrode. A Ni-Cr-Mo alloy may be used, which should have a coefficient of thermal expansion as near as possible to the parent alloy. Reference 41 discusses at length problems involved in fabricating HSLA steels, along with their solutions, with original references that may be consulted for further details.
Table 9.9 Comparison of mild steel and low alloy quenched and tempered steel for spherical gas storage tanks to store 30,000 m³ (1,059,300 ft³) of gas at a pressure of 100 N/cm² (145 lb/in²).
Source: Ref 43.

<table>
<thead>
<tr>
<th>Items</th>
<th>Low alloy steel A</th>
<th>Low alloy steel B</th>
<th>Mild steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of vessels necessary</td>
<td>1</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>Related total weight of shell plate</td>
<td>1</td>
<td>1.35</td>
<td>3.2</td>
</tr>
<tr>
<td>Relative total weight of other steel required for supporting structure, etc.</td>
<td>1</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>Relative area needed at site</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diameter of vessels m (ft)</td>
<td>39 (128)</td>
<td>31 (102)</td>
<td>4.0</td>
</tr>
<tr>
<td>Capacity of each vessel m³ (ft³)</td>
<td>30,000 (1,059,000)</td>
<td>15,000 (529,500)</td>
<td>1500 (52,950)</td>
</tr>
<tr>
<td>Shell thickness mm (in.)</td>
<td>35 (1/4)</td>
<td>37 (1-15/32)</td>
<td>35 (1/4)</td>
</tr>
</tbody>
</table>

Steel A quenched and tempered to 830 MPa (120 ksi) tensile strength and 670 MPa (97 ksi) yield strength. Steel B to 620 MPa (90 ksi) tensile strength and 450 MPa (65 ksi) yield strength. Maximum metal weldable at the site: 38 mm (1 in.) Higher strength HSLA steels are now available.

Economics of HSLA Steel Construction

According to Ref 42, heat-treatable, weldable, high-strength, low-alloy construction steels are used in pressure vessels, such as tanks used for hauling liquefied gases at ambient temperature. These vessels meet the ASME pressure vessel code when fabricated from such steels, while permitting a reduction in tank wall thickness.

Use of HSLA steels offers advantages for purely mechanical reasons. In the design of pressure vessels, proof stress or yield strength must conform with ASME and other codes. To obtain maximum value in terms of these properties, proper heat treatment is essential. In calculating the cost of a thinner HSLA vs a thicker and less expensive mild steel, consideration should be given to the savings realized in fabrication, transportation, erection, and foundation construction as well. Table 9.9 compares the use of 1 or 2 high-pressure gas storage tanks fabricated of quenched and tempered alloy steel vs 20 smaller ones of mild steel, per Ref 43. Weight is also an important factor in pressure containers for transporting liquefied gases by road or rail. Of course, availability of expertise and raw materials, and of fabrication and heat treatment facilities are also important considerations in the final analysis of the application.

In summary, HSLA steels are employed in industry where operating temperatures are above 400 °C (750 °F) or below 0 °C (32 °F); where increased strength, ductility, and toughness are required; and where improved resistance to corrosion is a bonus quality. Differences in the behavior of the same alloy exposed to similar environments have occurred because of variations in heat treatment, minor differences in composition, and local variations in what appeared to be similar environments. To meet such situations, special grades, including proprietary grades, of these steels are available for specific processing plant applications.

Sometimes HSLA steels, which cost 3 to 7 times as much as plain mild carbon steel, are used to line or clad it. A similar analysis to that shown in Table 9.9 can be helpful in deciding if lining mild steel with HSLA steel is more economical than making the entire unit of it.

Suitable HSLA steels are also specified for extremely low temperatures, for corrosion resistance, for heat resistance, and for abrasion resistance. They are also employed for transportation, construction and material handling. IS:1570 (1961), Schedule IV, gives the chemical composition and mechanical properties of HSLA steels classified under wear resistant, creep resistant, hardened, tempered, and case-hardening steels.

The above is rudimentary treatment of the economic aspects of HSLA steels, which is discussed in detail in Ref 44. Notwithstanding the apparent merits of these steels, each specific application area requires careful assessment of the cost/performance trade-offs, with special emphasis on performance and design.

REFERENCES

3. E.E. Fletcher, High Strength Low-Alloy Steels, Battelle Press, 1979

115
Materials Selection for Corrosion Control

16. A. Raman, ibid., p 16
18. L. Rozlikova, Utilization of Weathering Steels in Czechoslovakia, Reprints of Tenth International Congress on Metallic Corrosion, Vol I, India, 1988, p 101-102
24. R.J. Jesseman and G.J. Murphy, ibid., Vol XXXIII (No. 4), p 8.1 to 8.10
34. HSLA Steels, Microalloying, ASM International, 1988
42. E. Chosey, Met. Prog., Vol 93 (No. 2), 1968, p 62-65
44. M. Isagki, “The Use of High Strength Steel for High Pressure Gas Storage Tanks,” paper presented at European Coal and Steel Community IV Congress, 1963
45. J. Lessells (p 15-30), and S.S. Hansen (p 31-42), in Microalloyed HSLA Steels, ASM International, 1988