Influence of chemical composition on stainless steels mechanical properties

BOGDAN MOISĂ,
Departament of Materials Science, Mechatronics and Robotics
University Valahia Târgoviște
Adress B-dul Unirii, no. 18 - 24, 130082 Targoviste
ROMÂNIA
bogdarkk@yahoo.com

Abstract: Stainless Steel is a generic term for a large family of corrosion resistant alloys containing at least 10.50% chromium (according to the European standard EN10088) and may contain other alloying elements. Stainless steels can be divided into five categories: martensitic, ferritic, austenitic, ferritic so-called duplex, and precipitation hardening (PH). The importance of chemical composition and microstructure of stainless steels is still uncertain and contradictory results can be found in the literature. The chemical composition and the microstructure are not independent variables; the same microstructure can be obtained with different chemical compositions. The purpose of the present article is to review and discuss the available information about the effect of chemical composition (alloying elements) in stainless steels mechanical properties.

Key-Words: Stainless steels, alloying elements, chemical composition, mechanical properties.

1 Introduction
The strength of metals is that their atoms are held together by strong bonding forces. Such bonds are formed between metal atoms allowing their outermost electrons to be shared by all the surrounding atoms, resulting in positive ions i.e. cations being surrounded by a cloud of electrons (valence electrons). Because these valence electrons are shared by all the atoms, they are not considered to be associated with any atom in particular. This is very different from ionic or covalent bonds, where multicomponent systems, alloying elements can be found in the free state; as intermetallic compound with iron or with each other; as oxides, sulfides, and other nonmetal inclusions; in the form of carbides; or as a solution in iron. As to the character of their distribution in steel, alloying elements may be divided into two groups:

1) Elements that do not form carbides in steel (e.g. Ni, Si, Co, Al, Cu and N)

2) Elements that form stable carbides in steel (e.g. Cr, Mn, Mo, W, V, Ti, Zr, and Nb).

The first group elements do not form chemical compounds with iron and carbon, and consequently the only possible form in which they can be present in steel is in solid solutions with iron. The only exceptions are Cu and N. Copper dissolves in α-iron at normal temperatures in amounts of up to 1.0%. If the Cu content exceeds 7%, iron will contain copper in the free state as metal inclusions. Nitrogen also has a limited solubility in ferrite. When the N content is higher than 0.015%, nitrogen is found in steel in the form of chemical compounds with iron or some alloying elements (V, Al, Ti, and Cr). These chemical compounds are called nitrides. Alloying elements whose affinity for oxygen is greater than that of iron are capable of forming oxides and other nonmetal compounds. When added at the very end of the steel melting process, such elements (e.g., Al, Si, V, Ti) deoxidize steel by taking oxygen from iron. The deoxidizing reaction yields Al2O3, TiO2, V2O5 and other oxides. Owing to the fact that deoxidizers are introduced at the final stages of the steel melting process, the majority of oxides have no time to coagulate or to pass to slag, and as a result they are retained in the solid steel as fine nonmetal inclusions. In addition to a great affinity for oxygen, some alloying elements have a greater affinity for sulfur than iron does, and upon being introduced into steel, they form sulfides. Alloying elements that form stable carbides in steel can be found in the form of chemical compounds with carbon and iron or be present in the solid solution. The distribution of these elements depends on the carbon contents of steel and the concurrent presence of other carbide-forming elements. If a
steel contains a relatively small amount of carbon and a great quantity of an alloying element, then, carbon will be bound to carbides before the carbide-forming elements are completely used. For this reason excess carbide-forming elements will be found in the solid solution. If a steel has a large amount of carbon and little of the alloying elements, the latter will be present in the steel mainly as carbides.

Most alloying elements, except C, N, O, B and metalloids standing far from iron in the periodic table, dissolve in great amount in iron. The elements standing to the right of iron (Co, Ni, Cu, etc.) form solutions in iron only and do not enter into carbides. Thus one can state that alloying elements dissolve predominantly into basic phases (ferrite, austenite, cementite) of iron-carbon alloys or form special carbides.

2 Alloying elements in stainless steel

1) CARBON Carbon is a non-metallic element, which is an important alloying element in all-ferrous metal based materials. Carbon is always present in metallic alloys, i.e. in all grades of stainless steel and heat resistant alloys. Carbon is a very strong austenitizer and increases the strength of steel. In austenitic, ferritic, and duplex stainless steels, it is kept to low levels (typically 0.005% C to 0.03% C in low carbon grades) to retain the desired properties and mechanical characteristics. In martensitic stainless steels, carbon is deliberately added to obtain both high strength and high hardness, thanks to the formation of a martensitic structure. In martensitic grades, carbon is added as an alloying element, in amounts varying from 0.15% to 1.2% to make these alloys heat treatable by quenching and tempering to develop this martensite phase. The principal effect of carbon on corrosion resistance is determined by the way in which it exists in the alloy. If it is combined with chromium as a separate constituent (chromium carbide), it may have a detrimental effect on corrosion resistance by removing some of the chromium from solid solution in the alloy and, as a consequence, reducing the amount of chromium available to ensure corrosion resistance. This adverse effect of carbon can be caused if the alloy is cooled too slowly after hot working or annealing or subsequently reheated (as in welding operations). The consequence is an unwanted precipitation of carbide-containing chromium. This precipitation of carbon takes place at grain boundaries and is referred to as sensitisation. It has been demonstrated that the loss of chromium associated with the carbide precipitation lowers corrosion resistance and brings about susceptibility to localized corrosion, i.e. intergranular corrosion, at the grain boundaries following the network of chromium carbides.

2) CHROMIUM About 85% of the chromites mined is used in metallurgy, namely stainless steels, low-alloy steels, high-strength alloy steels, tool steels and high-performance alloys such as chromium-cobalt tungsten (or molybdenum) alloys, nickel-chromium-manganese-niobiumtantalum (or titanium) alloys, nickel-chromium-molybdenum alloys, cobalt-chromium alloys and some Maraging steels (high-strength alloy irons of the precipitation hardening type). Due to its strength and its high resistance to corrosion, chromium is often used in plating and metal finishing. The properties that distinguish stainless steels i.e. Fe-Cr-(Mo) alloys and Fe-Cr-Ni-(Mo) alloys from other corrosion-resistant materials depend essentially on chromium. The high degree of reactivity of chromium is the basis for the effectiveness of chromium as an alloying element in stainless steels. The resistance of these metallic alloys to the chemical effects of corrosive agents is determined by their ability to protect themselves through the formation of an adherent, insoluble film of reaction products that shields the metal substrate from uniform and localized attack. The protective film called passive layer or passive film. It is a very fine layer on the surface, of the order of 1.0 to 2.0 nm, which reduces the corrosion rate to negligible levels and has a structure similar to chromite. For passivation to occur and remain stable, the Fe-Cr alloy must have a minimum chromium content of about 11% by weight, above which passivity can occur and below which it is impossible. The corrosion resistance of Fe-Cr alloys tends to improve as the chromium content is increased, and definite changes happen at about 11% Cr, and again around 17% Cr.

3) NICKEL In stainless steels, nickel has no direct influence on the passive layer but exerts a beneficial effect, particularly in sulphuric acid environments. Thanks to nickel austenitic stainless steels, i.e. Fe-Cr-Ni(Mo) alloys, exhibit a wide range of mechanical properties that are unparalleled by any other alloy system.
today. For instance, these alloys exhibit excellent ductility and toughness, even at high strength levels and these properties are retained up to cryogenic temperatures. Nickel promotes the resistance to corrosion of the nickel-based alloys as compared with the iron-based alloys under conditions where the passive layers may be absent, or may be destroyed locally or uniformly. For example, pitting corrosion tends to progress less rapidly in high-nickel alloys. In Fe-Ni alloys, their original features can be explained by two major phenomena. A one is the abnormally low expansion in compositions close to INVAR (36% Ni) due to a large spontaneous volume magnetostriction and exceptionally high electrical permeabilities resulting from the disappearance of various anisotropies in the vicinity of 80% Ni. Nickel forms the base of high temperature superalloys because of its ability to develop an adherent oxide and precipitation hardening phases based on Ni3Al. Nickel is a moderate strengthener, and consequently large amounts can be added to low-alloy steel before strength increases to an undesirable level. In low-alloy steel, nickel appears to have a greater overall, beneficial effect on toughness transition temperature than any other substitutional alloying element.

4) **MOLYBDENUM** is used in stainless steels in amounts up to 8% and most commonly in the range from 2 to 4%. Even such relatively small percentages of molybdenum have powerful effects in improving the resistance to pitting in chloride environments and to crevice in both Fe-Cr alloys and Fe-Cr-Ni alloys. Molybdenum reduces the intensity of the oxidizing effect required to insure passivity and decrease the tendency of previously formed passive films to break down.

An increase in the chromium and molybdenum content mainly increases resistance to localized corrosion (pitting and crevice) and is particularly effective in the ferritic grades. In austenitic and duplex alloys, nitrogen also has a beneficial influence on the pitting corrosion resistance. In order to quantify these composition effects, empirical indices have been derived to describe the resistance to pitting corrosion in the form of Pitting Resistance Equivalent (PRE). For ferritic steels, the formula employed is:

\[
\text{PRE} = \% \text{Cr} + 3.3 \% \text{Mo}
\]

where the concentrations are in weight %, while for austenitic and duplex grades it is:

\[
\text{PRE} (N) = \% \text{Cr} + 3.3 \% \text{Mo} + K*\% \text{N}
\]

Where \( K = 16 \) for duplex stainless steels \( K = 30 \) for austenitic stainless steels Experience shows that there is a good correlation between the PRE value and the resistance to pitting corrosion. Stabilising additions, such as titanium and niobium and certain impurities (e.g. sulphur) can also have a marked influence on pitting.

5) **NIOBIUM** In micro-alloyed steels, the strengthening mechanisms are based on the precipitation of fine dispersed carbide (NbC). In stainless steels, as far as corrosion resistance is concerned, it is well known that stabilising the grade by Nb additions prevents the risk of intergranular corrosion in heat affected zones. To prevent this the niobium is added in sufficient amounts, depending on the carbon and nitrogen (ferritic types) levels. The theoretical amount of niobium required for full stabilization based on stoichiometric calculation is described by the equation:

\[
\% \text{Nb} \geq 0.2 + 5 \% \text{C} + \% \text{N}
\]

In ferritic stainless steels, the addition of niobium is one of the most effective methods for improving thermal fatigue resistance.

6) **TITANIUM** is a highly reactive element which forms stable TiN precipitate in the liquid phase, in the presence of nitrogen (N). In the presence of both C and N, titanium nitrides TiN (in the liquid phase) and titanium carbides TiC (in the solid phase) form, the latter surrounding the former. The most commonly used stabilizing element for stainless steel is titanium. The stoichiometric amount of Ti required for full stabilization is described by the following equation:

\[
\text{Ti} \geq 4 \% \text{C} + 3.4 \% \text{N}
\]

However, greater levels of Ti are required for full stabilization because Ti reacts with sulphur to form stable Ti sulphides, Ti2S. In practice, the generally accepted level of Ti required to fully stabilize a stainless steel, must therefore satisfy the following criteria:

\[
\text{Ti} \geq 0.15 + 4 \% \text{C} + \% \text{N}
\]

Titanium also improves resistance to pitting corrosion since stable Ti2S have been shown to form in preference to manganese sulphides (MnS) which are known to act as pit initiation sites. In low alloy steels, titanium has a strong desire to unite with carbon, nitrogen and oxygen. When dissolved in steel, titanium is believed to increase hardenability; however, the carbide-forming tendency of this element is so strong that it is frequently in the steel structure as undissolved carbides and in this way decreases hardenability.

7) **MANGANESE** The properties of manganese enable it to act as an alloying element and a
deoxidiser in steel. When added to molten steel, manganese will react with oxygen to form manganese oxide (MnO). Manganese will also combine preferentially with sulphur to form manganese sulphide, (Mn S). Besides entering into combination with oxygen and sulphur, manganese also influences the behavior of steel. The presence of manganese increases the hardenability of the steel. Very large additions of manganese, about 12 to 15%, make the steel (Hadfield’s steel) austenitic at room temperature. Manganese is usually found as an alloying element in all types of steel (carbon steels and stainless steels) to assist the deoxidation of the steel and to prevent the formation of iron sulphide inclusions which may cause hot cracking problems.

8) SILICON In small amounts, silicon confers mild hardenability on steels. Small amounts of silicon and copper are usually added to the austenitic stainless steels containing molybdenum to improve corrosion resistance in sulphuric acid. Silicon is commonly added to stainless steels to improve their oxidation resistance and is a ferrite stabiliser. In austenitic stainless steels, high-silicon content not only improves resistance to oxidation but also prevents carburising at elevated temperatures.

9) NITROGEN In austenitic and duplex stainless steels, nitrogen content increases the resistance to localized corrosion like pitting or intergranular. This is due to the precipitation of Cr2N nitride instead of Cr23 C6 carbide. Low-carbon austenitic stainless steel contains 0.03% maximum carbon in order to minimize the risk of sensitization during welding or heat treatments. The yield strength of low carbon grades is lower than that of standard grades. To overcome this problem, the low carbon grades with nitrogen addition (up to 0.2% nitrogen), have been developed. Nitrogen in solid solution raises the yield strength to at least the same level as in the standard austenitic grades.

3 Research and results

The study has been made on 24 stainless steel coils, grade 304 ASTM, thickness 0.5 mm. Samples were cut from the top and bottom of each coil after bright annealing treatment. The mechanical properties of interest for the study were tensile strength and elongation. Regression diagrams were calculated for the chemical composition. The elements from chemical composition of the stainless steel with most relevant results (Mo, P, Cr, Ni and Cu) are presented in the following diagrams.
Regression Analysis: T/S versus Cr

The regression equation is:
\[ T/S = -838.6 + 82.47 \text{ Cr} \]
\[ S = 12.9297 \quad R^2 = 35.1\% \quad R^2(\text{adj}) = 33.7\% \]

Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regress.</td>
<td>1</td>
<td>4155.3</td>
<td>4155.27</td>
<td>24.86</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>46</td>
<td>7690.2</td>
<td>167.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>47</td>
<td>11845.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Regression Analysis: T.S versus Ni

The regression equation is:
\[ T/S = 2054 - 173.2 \text{ Ni} \]
\[ S = 14.6560 \quad R^2 = 16.6\% \quad R^2(\text{adj}) = 14.8\% \]

Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regress.</td>
<td>1</td>
<td>1964.7</td>
<td>1964.71</td>
<td>9.15</td>
<td>0.004</td>
</tr>
<tr>
<td>Error</td>
<td>46</td>
<td>9880.8</td>
<td>214.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>47</td>
<td>11845.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Regression Analysis: T.S versus Cu

The regression equation is:
\[ T/S = 679.6 - 80.89 \text{ Cu} \]
\[ S = 10.5231 \quad R^2 = 57.0\% \quad R^2(\text{adj}) = 53.1\% \]

Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regress.</td>
<td>1</td>
<td>6751.6</td>
<td>6751.62</td>
<td>60.97</td>
<td>0.00</td>
</tr>
<tr>
<td>Error</td>
<td>46</td>
<td>5093.9</td>
<td>110.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>47</td>
<td>11845.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4 Conclusions

A comparison between two chemical compositions from different stainless steel suppliers (Arcelor and Columbus) has been made.
We can conclude based on the previous analysis and from the differences mentioned above that the content of Mo and Cu has a strong influence over tensile strength after the bright annealing process.

REFERENCES