Alloying Elements in Stainless Steel and Other Chromium-Containing Alloys

by Pierre-Jean Cunat

Metals account for about two thirds of all the elements and about 25% of the mass of the Earth. These are mainly around us in the form of metallic alloys which are used because of their various properties and characteristics, such as strength, ductility, toughness, corrosion resistance, heat resistance, thermal expansion, thermal and electrical conductivity.

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 electrons are shared by one or two atoms. The metallic bond is therefore strong and uniform. Even if the added elements are non-metals, alloys still have metallic properties.

Most metals are not used in their pure form but have alloying elements added to modify their properties and this can be used for specific applications. The presence of a proportion of a second element associated with a metal to form an alloy, e.g. chromium with iron to form Fe-Cr alloys, can drastically alter some of its properties.

Pure iron is too soft to be used for the purpose of structure, but the addition of small quantities of other elements (carbon, manganese or silicon for instance) greatly increases its mechanical strength. This is because the different atom sizes of other elements interrupts the orderly arrangement of atoms in the lattice and prevents them from sliding over each other as easily.

Alloying elements have the capability to block slip planes. In the case of chromium added to iron (Fe-Cr alloys), there is another advantage, which consists of a tremendous increase in the corrosion resistance of the new metallic alloy compared to pure iron. There are more than a hundred chromium-containing metallic alloys. Each one was developed for a particular need, and each has its own set of properties and characteristics.

The most important characteristics common to all chromium-containing alloys, among them stainless steels, is that they contain sufficient chromium to make them corrosion resistant, oxidation resistant and/ or heat resistant.

All of these alloys contain chromium (Cr), manganese (Mn), silicon (Si), carbon (C), nitrogen (Ni), sulphur (S), and phosphorus (P), and may contain: nickel (Ni), molybdenum (Mo), titanium (Ti), niobium (Nb), zirconium (Zr), copper (Cu), tungsten (W), vanadium (V), selenium (Se), and some other minor elements.

Published in cooperation with the International
Chromium Development Association.
The publication is available in print from
ICDA, 45 Rue de Lisbonne, F-75008 Paris,
Fax +33 1 40 76 06 89, e-mail mailbox@chromium-asoc.com

Stainless Steels

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, austenitic-ferritic so-called duplex, and precipitation hardening (PH).

Martensitic Stainless Steels: Fe-Cr-C-(Ni-Mo) alloys

These alloys have a chromium content that ranges from 11.50 to 18.00%. They have relatively high carbon content from 0.15 to 1.20% compared to other stainless steels and molybdenum can also be used. These grades can be hardened through heat treatment to offer strength and hardness. They are magnetic. The common uses are knife blades, surgical instruments, shafts, etc.

Ferritic Stainless Steel: Fe-Cr-(Mo) alloys

In ferritic grades, carbon is kept to low levels (C‹0.08%) and the chromium content can range from10.50 to 30.00%. While some ferritic grades contain molybdenum (up to 4.00%), only chromium is present as the main metallic alloying element. These grades cannot be hardened through heat treatment. Ferritic grades are magnetic and chosen when toughness is not a primary need but corrosion resistance, particularly to chloride stress corrosion cracking (SCC), is important. Common uses are automotive exhaust systems (11.00%Cr), automotive trim (17.00%Cr-1.50%Mo), hot water tanks (18.00%Cr-2.00%Mo-Ti).

Austenitic Stainless Steels: Fe-Cr-Ni-(Mo) alloys

In austenitic grades, carbon is usually kept to low levels (C ‹ 0.08%). Chromium content ranges from 16.00 to 28.00% and nickel content ranges from 3.50 to 32.00%. This chemical composition allows them to maintain an austenitic structure from cryogenic temperatures up to the melting point of the alloy. These alloys cannot be hardened through heat treatment. The key properties of these types of stainless steel are excellent corrosion resistance, ductility and toughness. Common uses are: Food processing equipment, equipment for the chemical industry, domestic appliances, and architectural applications.

Duplex-Austenitic-Ferritic Stainless Steels: Fe-Cr-Ni-(Mo)-N alloys

In duplex stainless steels, carbon is kept to very low levels (C ‹ 0.03%). Chromium content ranges from 21.00 to 26.00%, nickel content ranges from 3.50 to 8.00% and these alloys may contain molybdenum (up to 4.50%). These grades have a mixed structure of ferrite (50%) and austenite (50%) and offer physical properties which reflect this structure. These alloys are magnetic, and offer higher tensile and yield strengths than austenitic stainless steels. Common uses are in marine applications, petrochemical plant, desalination plant, heat exchangers and papermaking industry.

Precipitation Hardening (PH):
Fe-Cr-Ni-(Mo-Al-Cu-Nb)-N alloys

High strength, middling corrosion resistance and ease of fabrication are the primary benefits offered by this family of stainless steel grades. These grades develop very high strength after a low temperature (500-800°C) heat treatment. Since lower temperature can be used, concerns with part distortion are minimized, allowing them to be used for high precision parts. Precipitation-hardened stainless steels have an initial microstructure of austenite or martensite. Austenitic grades are converted to martensitic grades through heat treatment before precipitation hardening can be done. Precipitation hardening (PH) results when the heat aging treatment causes hard intermetallic compounds to precipitate from the crystal lattice as the martensite is tempered.

Common uses are in the aerospace and some other high-technology industries.

2. 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 localised corrosion, i.e. intergranular corrosion, at the grain boundaries following the network of chromium carbides.

Graphite – Lake Harbour (Canada) – Courtesy of Ecole des Mines de Paris

3. Chromium

3.1 Discovery, History and Sources

In 1797, the French professor of chemistry, Louis-Nicolas Vauquelin discovered chromium oxide, as a part of "red lead" (lead chromate $PbCrO_4$), a lead ore from Beresovsk (Ural). In 1798, he had isolated the metal chromium (chrome in French) by reducing the oxide. It is named after the Greek word chroma (χρωμα) meaning colour.

The principal ore is chromite, a spinel corresponding to the general formula $(Mg, Fe^{++}) (Cr, Al, Fe^{+++})_2O_4$ and the simplified formula Cr_2O_3, FeO.

Chromium is the 13th most abundant element in the Earth's crust, with an average concentration of the order of 400 ppm. 14 million tonnes of marketable chromite ore were produced in 2002. South Africa accounted for 46% of production whilst Kasakhstan and India represented 36%, Brasil, Finland, Turkey and Zimbabwe together provided 14% of the total production whilst 12 smaller producer countries added the balance of 4%. At the present consumption levels, demonstrated reserves will last for several centuries and less economical identified resources are sufficient to double that availability.

Louis-Nicolas Vauquelin (1763-1829) studied pharmacy in Rouen and Paris. He became professor at the "Ecole Polytechnique" (1794), the "Collège de France" (1801), the "Museum d'Histoire Naturelle" (1804) and at the "Ecole de Médecine de Paris" (1809). He also discovered beryllium (1789) and osmium (1804).

Chrome ore: Chromite – Mine Dyne (New Caledonia) – Courtesy of Ecole des Mines de Paris

3.2 Physical Properties

Chromium is a silver-grey transition metal with a relative atomic mass ($^{12}C=12$) of 51.996, an atomic number of 24, and a melting point of 1,875°C and a density of 7.190 kg/dm^3. It is in group VI of the periodic table. Chromium has a body-centred-cubic (b.c.c.) crystal structure.

3.3 Metallurgical Applications for Chromium

About 85% of the chromite mined is used in metallurgy, namely stainless steels, low-alloy steels, hig-strength alloy steels, tool steels and high-performance alloys such as chromium-cobalt- tungsten (or molybdenum) alloys, nickel-chromium-manganese-niobium-tantalum (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.

3.4 The Role of Chromium in Stainless Steels

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 localised 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.

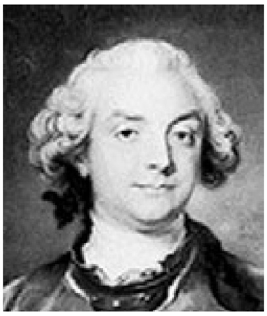
For further information, please go to the website of the International Chromium Development Association (ICDA), www.chromium-asoc.com

4. Nickel

4.1 Discovery, History and Sources

In 1751, the Swedish mineralogist and chemist Axel Fredrik Cronstedt discovered nickel as an impurity in an ore-containing niccolite (nickel arsenide). He reported it as a new element and proposed the name of nickel for it. This element is 24th in the order of abundance in the Earth's crust with an average concentration of 80 ppm. The two major sources of this metal are the nickel-bearing sulphide inside iron-copper pyrites deposits in Canada, Russia (Siberian mines), New-Caledonia and South-Africa and the nickel-bearing laterite deposits such as garnierite (South East-Asia, Australia and the Caribbean). World mine production of nickel totalled 1.26Mt in 2001, the highest output ever recorded. The principal producing countries were Russia (20%), Canada (15%), Australia (15%) and New Caledonia (10%).

Nickel ore: Garnierite (New Caledonia) – Courtesy of Ecole des Mines de Paris



Axel Fredrik Cronstedt (1722-1765), Swedish mineralogist and chemist, was one of the first to recognise the importance of the chemical constituents of minerals and rocks and is noted for his efforts to establish a new mineralogical system. He is also credited with developing an experimental procedure involving the systematic use of blowpipes for analysing the chemical composition of minerals. He wrote "An Essay towards a System of Mineralogy" (1758).

4.2 Physical Properties

Nickel is a silver-white transition metal with a relative atomic mass ($^{12}C=12$) of 58.69, an atomic number of 28, a melting point of 1,453°C and a density of 8.902 kg/dm^3. It is in group VIII on the periodic table. It has a face-centred-cubic (f.c.c.) crystal structure. Nickel is ferromagnetic up to 353°C, its Curie point.

4.3 Metallurgical Applications for Nickel

About 65% of nickel production is used in stainless steels, compared to 45% ten years ago. High-performance alloys (nickel-based), cobalt-based and iron-nickel-based high-performance alloys) represent another growing metallurgical end-use for nickel.

4.4 The Role of Nickel in Stainless Steels

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 magnetrostriction 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 Ni_3Al.

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.

For further information, please go to the website of the Nickel Development Institute (NiDI), www.nidi.org

5. Molybdenum

5.1 Discovery, History and Sources

Although the metal was known to ancient cultures, molybdenum was not formally identified until 1778, when the Swedish chemist and apothecary Carl Wilhelm Scheele produced molybdic oxide by attacking pulverized molybdenite (MoS_3) with concentrated nitric acid and then evaporating the residue to dryness.

Initially, this element was extracted from what was thought to be lead ore and it was mistakenly named for the Greek word molubdos (μολυβδοσ), which is the Greek word for lead.

Following Scheele's suggestion, another Swedish chemist and mineralogist, Peter Jacob Hjelm, isolated the first metallic molybdenum in 1782 by reducing molybdic oxide (MoO_3) but it was not until 1895 that the French chemist and Nobel Prize laureate, Henri Moissan, produced the first chemically pure molybdenum metal by reducing it with carbon in his electric furnace, thereby making it possible to conduct scientific and metallurgical research into the metal and its alloys.

Carl Wilhelm Scheele was apprenticed to an apothecary in Gothenburg when he was 14 years old. When he was 28 he moved to Uppsala to practice as an apothecary. He was elected to the Stockholm Royal Academy of Sciences in 1775. Also in 1775 he moved to Köping where he established his own pharmacy. In 1777, Scheele published his only book, Chemical Observations and Experiments on Air and Fire.

Molybdenum ore: Molybdenite – Noerkheia (Norway) – Courtesy of Ecole des Mines de Paris

Molybdenum remained mainly a laboratory issue throughout most of the 19th century until the technology for the extraction of commercial quantities became practicable.

In 1891, the French arms manufacturer, Schneider S.A., introduced molybdenum as an alloying element in the production of armour plate at its works in Le Creusot. In 1900, two American engineers, F.W. Taylor and P. White, presented the first molybdenum based high speed steels at the Exposition Universelle de

Paris. Simultaneously, Marie Curie in France and J.A. Mathews in the U.S.A. used molybdenum to prepare permanent magnets.

This element is in 38th position in the Earth's crust with an average concentration of 15 ppm. The major molybdenite deposits are in the U.S.A., Chile, China, Canada and in the former Soviet Union. The remainder is distributed between Mexico, Peru, Iran and Mongolia. The global mine production is around 140,000 tons per year with 27% in the U.S.A., 20% in China, 25% in Chile and 8% in Canada.

5.2 Physical Properties

Molybdenum is a silver-white transition metal with a relative atomic mass ($^{12}C=12$) of 95.94, an atomic number of 42, a melting point of 2,610°C and a density of 10.22 kg / dm^3. It is in group VI on the periodic table. Molybdenum has a body-centred-cubic (b.c.c.) crystal structure.

5.3 Metallurgical Applications for Molybdenum

The high melting point of molybdenum makes it important for giving strength to steel and other metallic alloys at high temperatures. It is also added to metallic alloys because of its resistance to corrosion.

Although low alloy steels, stainless steels and cast iron makes up the biggest market segment, molybdenum is also used in certain high performance alloys, such as the Hastelloys and Inconel. Molybdenum is also used as electrodes in electrically heated furnaces, as filament for electronic applications and as catalyst for the refining of petroleum.

5.4 Role of Molybdenum in Stainless Steels

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.

For further information, please go to the website of the International Molybdenum Association (IMOA), www.imoa.info

Chromium and Molybdenum

Stainless Steels

An increase in the chromium and molybdenum content mainly increases resistance to localised 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.

Alloy Steels for High-Temperature Service

To accommodate the effects of temperature and thermal cycling, a segment of technology has been developed to guide the design and the selection of materials. The usual corrosion threat is oxidation and it is well known that oxidising become more active with increasing temperature. The corrosion problem at high temperatures may be complicated by other phenomena, such as localised stress-oxidation cracking, chemical reaction with sulphurous gases and attack by hot hydrogen.

A survey of the alloys commonly employed in high temperature service shows that chromium and molybdenum are the two most frequently used alloying elements. Chromium is effective for increasing strength and improving oxidation resistance whereas molybdenum increases strength at higher temperatures. This improvement of the oxidation resistance is credited to the affinity of chromium for oxygen and as a consequence a protective film is formed on the surface of the chromium-containing steels.

The efficacy of chromium and molybdenum in improving strength and oxidation resistance is so outstanding that chromium-molybdenum-containing steels dominate the high-temperature field of construction materials. Table 1 lists representative alloy steels often used for high-temperature service.

Common designation	Maximum temperature in air (°C)
0.5% Cr - 0.5% Mo	570
1.25% Cr - 0.5% Mo	590
2.25% Cr - 1.0% Mo	630
3.0% Cr - 1.0% Mo	640
5.0% Cr - 0.5% Mo	650
7.0% Cr - 0.5% Mo	680
9.0% Cr - 1.0% Mo	820

Table 1: Typical chromium-molybdenum-containing steels for high temperature service.

This listing starts with a 0.5% chromium-0.5% molybdenum-containing-steel and progresses through steels of increasing chromium content up to 9.0%. Many high-temperature or heat-resisting steels have a higher chromium content, but they are considered as high-alloy-steels, such as stainless steels, and are not included in the present listing.

One of the most important points to bear in mind is that chromium and molybdenum, although added to increase strength and oxidation resistance at high temperatures, also promote hardenability.

An important application, in which steels are subjected to high temperature service, is the refining and reforming equipment of the petroleum industry. Many of the reactors in refining plants operate at high temperatures and strong demands are made for durability. Two main problems have been encountered in catalytic reformers. They are linked to the operative temperature and pressure. Catalytic reformers operate in the range of 450 to 570°C at pressures greater than 15 bar in contact with a flow of hydrogen-containing gas mixtures.

Tool Steels

Tool steels are used for making engineer's tools (punches, dies, molds, tools for cutting, blanking, forming, drawing, steering and slitting tools). They are generally grouped into two classes:

1) Plain carbon steels containing a high percentage of carbon, about 0.80-1.50%

2) Alloy tool steels, in which other elements (chromium, molybdenum, vanadium, tungsten and cobalt) are added to provide greater strength, toughness, corrosion and heat resistance of steel.

Chromium improves the corrosion and heat resistance, increases the depth of hardening during heat-treatment and the high temperature strength. In high-speed steels (containing up to 12.00 % Cr), chromium plays an important role in the hardening mechanism and is considered irreplaceable.

Molybdenum (about 0.50-8.00%) when added to a tool steel makes it more resistant to high temperature. Molybdenum increases hardenability and improves fatigue property and wear resistance.

6. Niobium

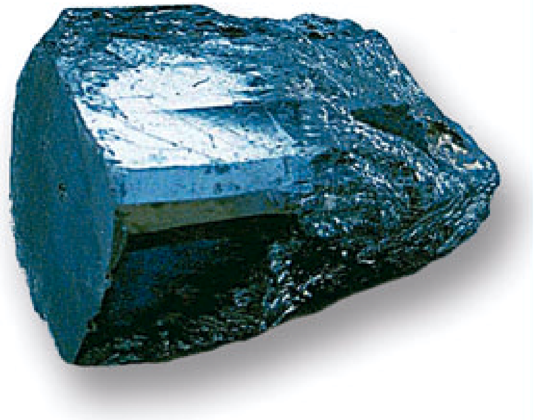
6.1 Discovery, History and Sources

Niobium was discovered in 1801 by Charles Hatchett in an ore called "columbite" sent to England in the 1750s by John Wintrop, the first governor of Connecticut – U.S.A. Hatchett named the new element columbium. The present name of the metal is due to Heinrich Rose, a German chemist who, when separating it in 1846 from tantalum, identified it as a new element and named it "Niobe" meaning "daughter of Tantalus" because tantalum is closely related to niobium in the periodic table.

Charles Hatchett Award instituted by Companhia Brasileira de Metalurgia e Mineraçao – CBMM – and confered by the institute of Materials – London

Charles Hatchett (1765 – 1847), English manufacturer and chemist, was an expert in analysis. He was elected to the Royal Society in 1794. Thanks to his expertise in analysis, Hatchett ran his own laboratory in Roehampton (close to London) and was frequently called upon as a consultant.

The earliest information about niobium usage is dated 1925, when it was utilised to replace tungsten in tool steel. However, until the beginning of the 1930s, niobium had no industrial importance. Niobium is efficient in preventing intergranular corrosion in some stainless steels and it found its first industrial application for this purpose.



Niobium ore: Niobite – Mina Gerais (Brazil) – Courtesy of Ecole des Mines de Paris

In the 1950s, with the start of the space race, there was a significant increase in the interest in niobium due to its properties as a light refractory metal. The discovery that a small amount of niobium added to a carbon steel significantly improved its properties led to the use of the micro alloy concept.

Pyrochlore is the most abundant mineral phase containing niobium. The most important pyrochlores are bariopyrochlore from residually enriched carbonatite at Araxa, Brazil (Nb_2O_5 / 66%, BaO/14% and H_2O / 8%) and pyrochlore from primary carbonatrite at St. Honoré, Quebec (Nb_2O_5 / 68%, CaO / 14% and Na_2O / 5.8%). Columbite corresponds to

$FeNb_2O_6$, it is derived by the weathering of granites. Of all the elements in the crust of the Earth, niobium is number 33 in order of abundance with an average concentration of the order of 25 ppm.

Reserves are about 460 million tons, sufficient to satisfy current world demand for about 500 years.

6.2 Physical Properties

Niobium is a shiny, white transition metal with a relative atomic mass ($^{12}C=12$) of 92.906, an atomic number of 41, a melting point of 2,468° C and a density of 8.57 kg / dm^3. It is in group V on the periodic table. Niobium has body centred cubic (b.c.c.) crystal structure.

6.3 Metallurgical Applications for Niobium

Nowadays, the most important application for niobium is an alloying element for micro-alloyed steels in which it is used to strengthen the metal structure. An important secondary application for niobium is in super alloys operating in the hot section of aircraft engines. Niobium is also utilised in stainless steels (austenitics and ferritics) as a stabilising element and to improve creep resistance (ferritics) and for purposes involving supraconductivity (niobium – titanium alloys), which permitted the development of modern magnets.

6.4 The Role of Niobium in Stainless Steels

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 stabilisation based on stoichiometric calculation is described by the equation:

$\%Nb \geq 0.2 + 5\ (\%C + \%N)$

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

7. Titanium

7.1 Discovery, History and Sources

Titanium was discovered by the Reverend William Gregor in 1791 and isolated in Creed, Cornwall, U.K. He recognised the presence of this new element in menachanite, a mineral named after MENACCAN.

Several years later, in 1795 in Berlin, the element was rediscovered in the ore rutile (TiO_2) by a German chemist, M.H. Klaproth. However, the pure metal was not made until 1910 by Matthew A. Hunter, who heated titanium tetrachloride ($TiCl_4$) with sodium in a steel reactor at 700 – 800° C. In the 1950s titanium came into use as a structural material. The element is named after the Titans, in Greek mythology, the sons of Uranus, the Sky god and Gaïa, the Earth goddess. Titanium occurs in combination as oxide or silicate in rutile and anatase (TiO_2), ilmanite ($FeTiO_3$), perovskite [(Ca, Fe) TiO_3]. Titanium is the 9th most abundant element in the Earth's crust, with an average concentration of the order of 6,000 ppm.

Titanium ore: Rutile - Parsksburg (USA) – Courtesy of Ecole des Mines de Paris

Mining of titanium minerals is usually performed using surface methods. In 2000, Australia, Canada, India, Norway and South Africa led the world production of the order of 2 million tonnes of concentrated titanium mineral. Titanium and zircon are contained in sand deposits that are estimated to total 540 million tonnes. Titanium sponge is the rudimentary form of titanium metal. In 2000, titanium sponge was produced in China, Japan, Kazakhstan, Russia, Ukraine and the U.S.A. Titanium metal is produced by melting titanium sponge.

7.2 Physical Properties

Titanium is a hard silver metal with a relative atomic mass ($^{12}C = 12$) of 47.867, an atomic number of 22, a melting point of 1,668° C and a density of 4.54 kg / dm^3. It is in group IV on the periodic table. Titanium has an hexagonal close-packed (h.c.p.) structure.

7.3 Metallurgical Applications for Titanium

Only about 5% of the annual world production of titanium ore goes into making titanium metal. Titanium metallic alloys are used in aerospace, marine, chemical engineering and other applications for their high strength-to-weight ratio and corrosion resistance in neutral and oxidising environments. Titanium is commonly utilised in stainless steels (austenitics and ferritics) as a stabilising element.

Titanium is also very effective as a micro alloy in steel, influencing the microstruture by the formation of nitrides (TiN) and carbides (TiC).

7.4 The Role of Titanium in Stainless Steels

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 stabilising element for stainless steel is titanium. The stochiometric amount of Ti required for full stabilisation is described by the following equation:

$$Ti \geq 4\ (\%C) + 3.4\ (\%N)$$

However, greater levels of Ti are required for full stabilisation because Ti reacts with sulphur to form stable Ti sulphides, Ti_2S. In practice, the generally accepted level of Ti required to fully stabilise a stainless steel, must therefore satisfy the following criteria:

$$Ti \geq 0.15 + 4\ (\%C + \%N)$$

Titanium also improves resistance to pitting corrosion since stable Ti_2S have been shown to form in preference to manganese sulphides (MnS) which are known to act as pit iniation 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.

Titanium and Niobium as Stabilising Elements: Dual Stabilisation

Stabilising elements are added to Fe-Cr-(Mo) alloys and Fe-Cr-Ni-(Mo) alloys to prevent sensitisation to intergranular corrosion following a sojourn of the alloy within the temperature range in which precipitation of chromium carbide might occur. The function of these stabilising elements is to combine preferentially with any carbon for Fe-Cr-Ni-(Mo) alloys and with any carbon and nitrogen for Fe-Cr-(Mo) alloys that might otherwise precipate as a chromium carbide and a chromium nitride (Fe-Cr-(Mo) alloys). This leaves the chromium in solid solution in the alloy where it belongs and the full corrosion resisting qualities of the alloy are therefore preserved. Dual stabilisation with titanium and niobium provides the best mechanical properties for weldments. This behaviour might be related to a better grain size control and probably to a modification of the nature and morphology of precipitates. The optimal dual stabilisation content is given by the equation:

$$\%\ Ti + 4/7\ (\%\ Nb) \geq 0.15 + 4\ (C + N)$$

The advantages of this dual stabilisation can be summed up as follows: The TiN precipitates formed in the liquid phase act as nucleation sites for crystal growth, resulting in a fine-grained equiaxed structure that improves the mechanical properties of weldments.

Less Nb is required for full stabilisation, thereby further reducing the amount of low melting phases that might form at the grain boundaries.

8. Manganese

8.1 Discovery, History and Sources

In 1771, the Swedish chemist Carl Wilhelm Scheele recognised manganese as a new element. It was isolated in 1774 by another Swedish chemist, Johann-Gottlieb Gahn (1745 – 1818) by reducing manganese dioxide MnO_2. At the beginning of the 19th century, both British and French metallurgists began considering the use of manganese in steelmaking.

Manganese ore –Manganite - Ilfeld (Germany) – Courtesy of Ecole des Mines de Paris

Manganese is the 12th most abundant element in the Earth's crust, with an average concentration of the order of 1,100 ppm. The major manganese deposits are essentially situated in South Africa, China, Australia, Gabon, Brazil, Ukraine, India, Kazakhstan and Mexico. The world production of manganese ore is in the order of 20 million tonnes per year and the world reserves are estimated to be 600 million tonnes of ore. There are also large manganese reserves on deep ocean floors in the form of polymetallic nodules. They are estimated at 2 – 300 million tonnes of manganese.

8.2 Physical Properties

Manganese is a grey-white metal with a relative mass ($^{12}C = 12$) of 54.938, an atomic number of 25, a melting point of 1,245° C and a density of 7.43 kg / dm^3. It is in group VII on the periodic table. Manganese has a complex cubic crystal structure.

8.3 Metallurgical Applications for Manganese

Manganese is essential to steel making because of two key properties: its ability to combine with sulphur and its powerful deoxidation capacity. Some 30% of the world production of manganese is used for its properties as a sulphide former and deoxidiser. The balance of 70% is used as an alloying element.

Relatively small quantities of manganese have been used for alloying with non-ferrous alloys, mainly in the aluminium industry.

Its ability to stabilise the austenite in steel is used in the "200 series” of austenitic stainless steels in which its content varies from 4 to 15.5%.

8.4 The Role of 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 behaviour 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.

9. Silicon

9.1 Discovery, History and Sources

In 1823, the Swedish professor of medicine, Jöns-Jacob Berzelius discovered amorphous silicon by heating potassium in an atmosphere of gaseous silicon tetrafluoride, SiF_4. In 1854, the French professor of chemistry, Henri-Etienne Sainte-Claire Deville prepared crystalline silicon, a second allotropic form of the element.

Silicon is not found free in nature, but occurs chiefly as oxide and as silicates. Silicon is the second most abundant element in the Earth's crust, with an average concentration of about 27%.

Jöns-Jacob Berzelius (1779 – 1848) studied medicine in Upsala (Sweden). He became professor of medicine and pharmacy in 1807 at the University of Stockholm. He was elected to the Stockholm Royal Academy of Sciences in 1806.

Henri-Etienne Sainte-Claire Deville (1817 – 1881) studied chemistry. He became professor at the University of Besançon in 1806 and at the " Ecole Normale Supérieure" in 1812. He was elected to the French Academy of Sciences in 1861.

Silica: Quartz – Guerrero (Mexico) – Courtesy of Ecole des Mines de Paris

The world production of industrial sand and sand gravel, often called “silica”, “silica sand” and “quartz sand” which includes sands and gravels with high dioxide (SiO_2) content is of the order of 110 million tonnes per year.

9.2 Physical Properties

Silicon is a dark-grey metalloid (silicon is not considered as a metal) with a relative mass ($^{12}C = 12$) of 28.085, an atomic number of 14, a melting point of 1,414° C, and a density of 2.33 kg / dm^3. It is in group IV on the periodic table. Silicon has a diamond (dia) structure.

9.3 Metallurgical Applications for Silicon

Silicon is a metalloid (non-metallic element) produced by the reduction of silica (SiO_2) at high temperatures.

Silicon is an important alloying element for both ferrous and non-ferrous metals. It is used extensively as a deoxidiser in steel making (carbon steel and stainless steel). In heat resisting stainless steels its presence improves oxidation at high temperatures. In cast irons silicon acts as graphitiser since it decomposes and so reduces the amount of combined carbon. It confers on electrical steels (up to 5% Si) some specific magnetic properties.

It is used in combination with copper to form what are known as silicon brass (copper-zinc alloys) and silicon bronzes. Silicon – aluminium alloys containing 5% or more silicon are used for castings.

9.4 The Role of Silicon in Stainless Steel

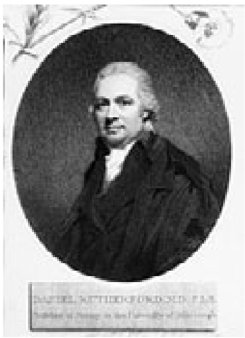
In small amounts, silicon confers mild hardenability on steels. Small amounts of silicon and copper are usually added to the austenitic stainless steels containing molybdenum to improve corrosion resistance in sulphuric acid.

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.

10. Nitrogen

10.1 Discovery, History and Sources

It seems that nitrogen was discovered in 1772 by Daniel Rutherford. The word nitrogen is made up from two Greek words: νιτρο (nitro) meaning saltpetre and γενεξ (genes) meaning producing. This is because the most important use of nitrogen was as saltpetre, a compound called potassium nitrate, well known as a fertiliser.



Daniel Rutherford (1749 – 1819), Scottish chemist and physicist. As a physicist, he was one of the first to recognise the importance of "specific heat". As a chemist, he was credited with discovering magnesia and carbon dioxide.

10.2 Physical Properties

Nitrogen is as a relatively inert gas, with a relative atomic mass ($^{12}C = 12$) of about 14, and an atomic number of 7. It constitutes about 78% of the Earth's atmosphere by volume and 76% by mass. Each molecule of nitrogen is made up of two nitrogen atoms linked together extremely strongly. In a nitrogen molecule, the three lines joining the two atoms represent a triple bond.

10.3 Metallurgical Applications for Nitrogen

Nitrogen (as carbon) is an interstitial element in steel because its atomic size is sufficiently small relative to that of iron, chromium or nickel, to allow this element to enter the α-alloys and the γ-alloy lattices as interstitial solute atoms. The solubility of nitrogen is greater in austenite (γ) than in ferrite (α), because of the larger interstices available. The solubility for nitrogen in austenite is as high as 2.4% while in ferrite it is only 0.1% at the temperature of 1,100° C. Nitrogen has a major influence on the precipitation kinetics of intermatlic compounds like carbides, nitrides and carbo-nitrides.

10.4 The Role of Nitrogen in Stainless Steels

In austenitic and duplex stainless steels, nitrogen content increases the resistance to localised corrosion like pitting or intergranular. This is due to the precipitation of Cr_2N nitride instead of $Cr_{23}C_6$ carbide.

Low-carbon austenitic stainless steel contains 0.03% maximum carbon in order to minimise the risk of sensitisation 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.

11. Cobalt

11.1 Discovery, History and Sources

Cobalt was discovered in 1735 by the Swedish chemist George Brandt. This element is 30th in order of abundance in the Earth's crust. With an average concentration of 20 ppm, the two major cobalt deposits are in Zaire and in Zambia. The remainder of mined cobalt comes from Canada, Australia and Morocco.

Georg Brandt (1694 – 1768), Swedish chemist, was the son of an iron worker and from an early age he helped his father with metallurgical experiments. He studied medicine and chemistry at Leiden. In 1727, he was appointed director of the Laboratory of the Council of Mines in Stockholm and three years later became warden of the Royal Mint and Professor of Chemistry at the University of Upsala.

11.2 Physical Properties

Cobalt is a silvery-white transition metal with a relative atomic mass ($^{12}C=12$) of 58.933, an atomic number of 27 and a melting point of 1,495° C and a density of 8.92 g/cm^3. It is in group VIII on the periodic table. Cobalt has an hexagonal close packed (h.c.p.) crystal structure.

Cobalt ore: Skutterudite – Irhtem (Morocco) – Courtesy of Ecole des Mines de Paris

11.3 Metallurgical Applications of Cobalt

Cobalt is alloyed with iron, nickel and other metals to make an alloy with special magnetic properties. Cobalt is a major constituent of the "Super Alloys", which are used principally in:

- High temperature applications, e.g. gas turbine components
- Wear resistant alloys
- Hard-facing alloy consumables (welding)
- Orthopaedic implants
- Tool steels.

11.4 The Role of Cobalt in Cobalt-Chromium Alloys

Cobalt-chromium alloys are used in demanding applications and have contributed significantly to both industrial and biomaterial products.

The chemical composition of representative cobalt-chromium alloys is shown in table 2. Co-Cr alloys are well suited to high-temperature creep and fatigue resistant applications. For this reason, they are good candidates for applications where thermal fatigue is a critical design issue.

Co-Cr-Mo alloys are considered as reference materials for artificial orthopaedic implants, most notably as artificial hips and knees. The addition of nitrogen, of the order of 0.15%, to achieve high strength with good ductility and without sacrificing corrosion resistance and bio-compatibility. These alloys combine the generally contradictory properties of very high mechanical strength and exceptional corrosion resistance.

For example, it is possible to obtain

- Adjustable tensile strength between 1,000 and 2,500 MPa both by cold working and ageing
- Hardness up to 60 HRC
- Fatigue resistance (as shown in Table 3)
- Corrosion resistance

Number of Cycles	Permissible Stress (Mpa)
10^4	1,800
10^5	1,200
10^6	900
10^7	700

Table 3: Fatigue resistance of Co-Cr-Mo alloys

The uniform corrosion (‹ 0.05 mm/yr) and pitting corrosion resistances are excellent at about 100° C in 10% solutions of acetic acid, ammonium chloride, ammonium sulphate, ferric chloride, formic acid, nitric acid, phosphoric acid or sodium chloride.

Alloy Name	C	Cr	Ni	Mo	W	Mn	Si	Fe	N	Co
X-40	0.50	25.0	10.	--	7.5	0.5	0.9	‹ 2	--	Bal
WI-52	0.45	21.0	--	--	11.0	0.4	0.4	2	--	Bal
HS-25	0.10	20.0	10.0	--	15.0	1.2	0.8	‹ 3	--	Bal
ASTMF-75	0.25	28.0	‹ 1	6.0	‹ 0.2	0.5	0.8	‹ 0.75	0.15	Bal
Co6	1.1	29.0	‹ 3	‹ 1.5	5.5	0.6	0.8	‹ 3	--	Bal
MP35N		20.0	35.0	10.0						Bal

Table 2: Nominal chemical composition of various Co-Cr Alloys (wt. %)

In spite of their high cost compared to steels and because of their remarkable resistance to mechanical loading and chemical aggression, these alloys are used whenever safety considerations are of prime importance, e.g. springs and fasteners for aerospace applications, medical engineering, surgical implants. Highly polished components include femoral stems for hip replacements and knee cordyles.

Cobalt alloys for wear resistant applications have served in extremely harsh conditions. Carbon is used in conjunction with chromium and more refractory elements to produce high hardness, carbide-rich material. Hardness values ranging from HRC 30 – 70 are obtainable. Co6 is the most common cobalt wear resistant alloy. Its ability to withstand sliding and abrasive wear comes from its volume fraction of carbide formed from the following elements:

- carbon (1.1% C)
- chromium (29% Cr) and
- tungsten (5.5% W)

The cobalt matrix has a high-work hardening sensitivity, which combines with the carbide fraction and allows to achieve excellent wear resistance associated with a high degree of corrosion resistance.

Cobalt is a valuable alloying element for high-speed tool steels. It has the effect of raising to softening temperature of ferrite so that tools made from cobalt-alloy steel can operate at high temperatures, maintaining their cutting capacity.

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