METALLURGY OF CHROMIUM

Metallurgy:

Metallurgy is a domain of materials science and engineering that studies the physical and chemical behavior of metallic elements, their inter-metallic compounds, and their mixtures, which are called alloys.

Chromium:

Introduction:

Chromium (Cr) is an element of the 6th Group of the Periodic Table. Mean chromium content in the Earth's crust comes to 0.02%. The element chromium was first isolated in 1797 by Vauquelin from the mineral crocoites, which was discovered in 1765 in Russia by Pallas. Its name was derived from the Greek word chromos, meaning colour, because of the varied colours of its compounds. Pure chromium was obtained for the first time in 1854 by the electrolysis of aqueous solutions of chrome chloride. In 1908 a metal containing 99.9% Cr was obtained by the reduction of chrome oxide by hydrogen gas.

Chrome ore deposits are mined by both underground and surface techniques. Most chrome ore must be processed by the chrome ore processing plants. The mainly chrome ore beneficiation method is gravity separation. So the mainly used chrome ore concentrating equipments are ore wash box (sometimes it is called jigger), concentrating table, spiral classifiers, etc.

Sources:

Chromium occurs in nature as chromite ($FeO.Cr_2O_3$). The natural mineral is rarely pure, Cr_2O_3 being replaced by Al_2O_3, Fe_2O_3; the higher grade of ore contains about 55% Cr. Many ores are sufficiently up to the grade to market without any concentration processes. Chrome ores consist of chromospinelides: (Mg, Fe) Cr_2O_4 (magnesiochromite), Fe $(CrAl)_2O_4$ (aluminochromite), etc. Chromospinelides may contain up to 62% Cr_2O_3, the balance usually being iron, aluminum and magnesium oxides.

Chromium use through history:

- Chromium's most common use throughout history has been the production of various ferrous alloys (alloys containing iron) with the most common by far being the alloy ferrochromium.
- Chromium is also used to make:

a) Paint up to the 1980's

b) Lift

c) Escalators

d) Barbeques

e) Aeroplane frames

f) And many other things…

Activity & Ease of refinement:

☆ In relation to chromium's uses:

I. Chromium does not react easily; it possesses passivation, which makes it highly unreactive.

II. It does not corrode or oxidise easily;

☆ Therefore it is used to build & plate things to protect them from corrosion and oxidation.

III. Chromium ore (chromite) has a high abundance, and chromium is easy to extract;

☆ The relative ease of refinement allows chromium to be widely used.

Extraction process of chromium:

❖ Chromium is extracted commercially from chromite (chromium oxide), which is found naturally.

❖ Chromite has the formula Cr_2O_3.

❖ Chromium is extracted using the Thermite Process in which a reduction/oxidation reaction takes place with aluminunium.

- Chromite (chromium oxide) reacts with aluminum. The chromite is reduced to form pure chromium, and the aluminum is oxidized to form aluminum oxide.
- $Cr_2O_3 + 2Al_2O_3 = Al_2O_3 + 2Cr$

Energy input involved:

- The Thermite Process requires heat energy.
- This energy ‘drives’ the reaction.
- In turn the reaction produces a substantial amount of heat.
- Therefore energy input is necessary to successfully extract chromium from its ore

Processing:

- Large raw chrome ore for primary crushing are fed into the jaw crusher by Plate feeder and are reduced to 8 inches or smaller. After first crushing, the material will transferred to cone crusher by belt conveyor for secondary crushing; the crushed chrome ore stone will then transferred to vibrating screen for classifying. After classifying, the parts whose size below the mesh size will be transferred away as final products, while the other parts will return to cone crusher, thus forming a closed circuit. Size of final products can be combined and graded according to your specific requirement.
- The smaller crushed chrome ore is fed to ball mill for grinding. Inside the ball mill, the crushed chrome ore will grind the ore to about 0.2 mm with 3-inch steel balls.
- Screened products are transported to the jig for rough separation and to three concentrating tables for fine separation. Then, tailings are delivered into the jig in the next stage for screening for 4 times like this. All tailings in the concentrating table are sent to tailings reservoir after tailings dry stacking.

CASE:

- In crushing, it adopts traditional two-stage and a closed circuit system for ideal fineness. Besides, jaw crushers have large crushing capacity.

- In grinding and classification, with characteristics of large processing capacity and small floor area, superfine lamination autogenous mill can save energy by more than 85%.

- In classification, hydrocyclone and vibrating screen can enhance the classifying effects.

- It adopts the third generation tailings dry stacking technology, which can save energy by 60-80%. Furthermore, it can also protect the environment and build a base for green mine.

Metallic Chromium:

1. The high grade chromium ore is grounded and then roasted with soda ash (Na_2CO_3) at 800–1000°C in rotary kilns.

$$2Na_2CO_3 + Cr_2O_3 + 1.5O_2 = 2Na_2CrO_4 + 2CO_2$$

Limestone is added during roasting to avoid sintering. The roasted product is leached with water and filtered to separate the soluble Na_2CrO_4 from the iron oxide and gangue present in the ore. This Na_2CrO_4 is converted to $Na_2Cr_2O_7$ by sulphuric acid treatment.

$$2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

$Na_2Cr_2O_7$ in the aquous solution, is selectively crystallized by evaporation, and the crystals are separated by filtration. The dried $Na_2Cr_2O_7$ crystals are then converted to Cr_2O_3 by reduction with the help of Sulphur.

$$Na_2Cr_2O_7 + S = Cr_2O_3 + Na_2SO_4$$

Cr_2O_3 is finally reduced by Al (i.e. aluminothermic reduction) to yield metallic chromium.

$$Cr_2O_3 = 2Al = 2Cr + Al_2O_3$$

2. The carbothermic reduction of chromium seems to be of great technical interest.

The following reduction reactions occur as:

$$3Cr_2O_3(s) + 13C(s) = 2Cr_3C_2(s) + 9CO(g)$$

$$5Cr_2O_3(s) + 27Cr_3C_2(s) = 13Cr_7C_3(s) + 15CO(g)$$

$$Cr_2O_3(s) + 3Cr_7C_3(s) = Cr_{23}C_6(s) + 3CO(g)$$

$$2Cr_2O_3(s) + Cr_{23}C_6(s) = 27Cr(s) + 6CO(g)$$

Alloys of Chromium:

Ferro-Chromium:

Ferro-chromium (with 60% Cr and 6% C) was produced for the first time in 1893 by electric furnace. All grades of the ferro-chrome can be produced in the electric furnace. Many grades of the ferro-alloy are available with carbon content ranging from 0.06% to as high as 8%. The decisive factors for estimation of the quality of chrome ores are as follows:

- The content of chromic oxide; in order to produce ferro-chrome, the content of chromic oxide in ore should be at least 45%.
- The ratio of concentration of chromic oxide to that of ferrous oxide; it should be not less than 2.5 to ensure that the alloy will contain 60% Cr.
- The proportion and composition of the gangue, which determines the amount of slag to be formed in smelting, should be under controlled; a large bulk of slag will involve much energy spent on its melting and overheating, also a greater loss of chromium to slag.

High Carbon Ferro-Chrome:

While there is some reduction of iron in the solid state (with CO as the reductant), the reduction rate apparently only increases strongly once the chromite starts dissolving in the slag above 1500°C; the reduction reaction then occurs through reaction of dissolved chromium oxide in the slag with solid carbon, or with carbon and silicon dissolved in the metal. The relevant reactions of the reductant can be summarized as follows:

- Dissolution of carbon in the metal product.
- Reduction of silicon (presumably by production of SiO gas in the higher-temperature region, with reduction of SiO to silicon or silicon carbide higher in the furnace).
- Reaction of dissolved carbon with Cr_2O_3 in the slag as the metal descends to the hearth.
- Gasification by the Boudouard reaction: $CO_2 + C = 2CO$ (during direct reduction).

For the high carbon ferro-chrome production, finely ground ore is mixed with carbon (coke breeze) in the proportion of 1:3 at 1230°C:

$$FeO.Cr_2O_3 + 4C = 2Cr + Fe + 4CO$$

Stable carbides are also formed in the reduction of chromium oxide by carbon at 1100°C:

$$Cr_2O_3 + 27/7C = 2/7Cr_7C_3 + 3CO$$

FeO, present in ore, is also reduced by carbon:

$$FeO + C = Fe + CO$$

Iron reduced from ore promotes the reduction of chromium oxide, since chromium carbides, which appear in the later reaction, dissolve in iron with the formation of double carbides [(Cr, Fe)7C_3]

$$Cr_2O_3 + 2Fe + 27/7C = 2/7(Cr,Fe)_7C_3] + 3CO$$

At a sufficiently high temperature, the melt being formed can be decarbonized by the reaction:

$$1/3\ (Cr,Fe)_7C_3 + 1/3Cr_2O_3 = 3Cr + 7/3Fe + CO$$

Sulphur can be brought into the melt mainly by coke breeze. In operation with acid slag the main portion of sulphur passes to the melt and part of it is volatilized. The content of sulphur in high carbon ferro-chrome must not exceed 0.06%, and therefore the tolerable content in coke breeze is not more than 0.5% S.

Low Carbon Ferro-Chrome:

- Ferro-chrome with less than 2% C is produced by the silico-thermic process. For the production of the low carbon ferro-chrome, silicon is used as a reducer.
- First ferro-silico-chrome is made and then its silicon reduces chromium and iron oxides from chrome ore, the reaction is exothermic, i.e. can proceed at lower temperature.

$$FeO.Cr_2O_3 + 2Si = 2Cr + Fe + 2SiO_2$$

Extra-Low Carbon Ferro-Chrome:

- In the manufacture of extra-low carbon ferro-chrome (0.05–0.06% C), chrome ore is reduced with the silicon of ferro-silico-chrome.
- The reaction is exothermic, i.e. can proceed at lower temperature. At lower temperature the thick high chromium slag is made, which retards the diffusion processes and reduces the reaction rates sharply because ferro-chrome is smelted at a high temperature. Since iron lowers the melting point of the alloy and simultaneously lowers the concentration of chromium in it.
- Most of the silicon in ferro-silico-chrome is present as chromium and iron silicides; a certain amount of energy must therefore be spent to decompose them.
- By addition of lime, silica is bonded by lime to form $2CaO.SiO_2$, i.e. the activity of silica will be lowered. A higher basicity of slag (i.e. a lower content of free silica in it) results in less silicon remains in the metal and less chromic oxide in the slag.
- The optimum CaO/SiO_2 ratio is 1.7 to 1.8. An excessive high basicity results in higher losses of chromium into the slag.

Stellite:

- Formed from a variety of cobalt-chromium alloys designed to wear resistance.
- Completely non-corrosive and non-magnetic.
- Cuts things at high temperature.
- Expensive to Produce due to extreme durability ,done by grinding rather than cutting
- Used in saw teeth, hand facing, acid resistant machine parts, improved quality of poppet valves, valves seats and internal combustion engines greatly.
- Also used in M60 machine guns, starting from the chamber as well as jet turbines engine blades.

Stainless steel:

- Most common alloys which chromium is present in.
- Resistance to heat, malleable, resistance to corrosion, cost effective and resistance to water and oxidation.
- Many different types due to the ease amounts of each metal can be varied.
- Core metals are chromium, iron, aluminum, and titanium
- Stainless steel is used to make cutlery, cooking utensils, pots and pans, furniture, shelters , subway trains, fuel and chemical containers , piping and much more.

Properties:

- Pure chromium is a grey lustre metal.
- Chromium has an atomic mass of 51.996, specific gravity 7.19, melting point 1857°C, and boiling point 2672°C.
- Metallic chromium is bluish-white in colour, hard, brittle, and possesses a high lustre. It is highly resistant to corrosion by atmosphere, sea water and sulphur compounds.
- Chromium reacts with the anhydrous halogens, hydrogen chloride, and hydrogen fluoride. Aqueous hydrofluoric acid, hydrochloric acid, hydrogen bromide, and hydrogen iodide will dissolve chromium, as will dilute sulphuric acid. Hydrogen gas is evolved during the dissolution of chromium in dilute sulphuric acid, whereas in boiling concentrated sulphuric acid, sulphur dioxide is liberated.
- Iron and chromium can form a series of solid solutions. Chromium and carbon canformcarbides:Cr_4C(5.46%C),Cr_7C_3 (9.01%C)andCr_3C_2 (13.34%C), having meltingpointsat1520°,1780°and1895°Crespectively.Chromiumandsiliconform silicides Cr_3Si (melting point of 1710°C), CrSi (melting point of 1545°C), $CrSi_2$ (melting point of 1550°C), etc.; and the most stable silicide CrSi; these are more stable compounds than chromium carbides. Chromium can form CrN and Cr_2N nitrideswithnitrogen.Chromiumandoxygenformoxides:CrO_3 (acid oxide), Cr_2O_3 (amphoteric oxide), and CrO (basic oxide); among them Cr_2O_3 being the most important for metallurgy. Chromic oxide is a bright green powder, and is the stablest of the oxides with a specific gravity of 5.21 and melting point 2275°C.

Applications:

A. Metallic chromium is chiefly used for alloying purposes. Chromium is used as an alloying element, in the form of ferro-alloy, in steel; it contributes hardness and toughness, and resistance to wear, heat and corrosion.

B. Chromium is used up to 2% in medium and high carbon steels, usually for the hardening and toughening effects and for increased fatigue and wear resistance. Chromium steels containing 1% C and 1% Cr are very hard and are widely used in the manufacture of ball and roller bearings.

C. Chromium is used extensively as an alloying element in many grades of steels and alloys. Addition of chromium makes steel more liable to self-hardening and increases hardening depth. Chromium can also increase the strength and hardness of steel and lower the ductility.

D. In combination with silicon, chromium imparts heat-resisting properties to steel. High chromium steels (over 12% Cr) with a low carbon content become rust-resistant after hardening. With high content of carbon in steel, chromium can increase the wear resistance; it also increasing the ultimate strength at high temperatures.

E. The combination of chromium with nickel extends into the field of the non-ferrous alloys, to high resistance to oxidation at elevated temperatures. Ni-Cr alloys exhibit a remarkable resistance to both high temperature oxidation and corrosion, for use as heating elements in industrial and household electrical appliances.

F. The property of red-hardness gives to the Cr–Co–W-alloys a prominent position in the list of high-speed cutting tools. High carbon ferro-chrome is used as alloying element for the manufacture of alloy steel and chromium steel.

G. Low carbon ferro-chrome is used as a chromium addition for the manufacture of stainless steel, refractory steel and steels for cryogenic application.

H. Ferro-silicon-chrome has also found application for slag deoxidizing in the manufacture of stainless steel. Ferro-silicon-chrome (containing 48–51% Si, 30% Cr, 0.04% C) is used for making medium, low and extra-low carbon ferro-chrome.

The Recycling of chromium:

☆ Chromium is not currently recycled due to:

- The abundance of chromium ores and their ability to satisfy human needs for many hundreds of years.
- The relative ease associated with extracting chromium.

☆ However in the future a need may arise to recycle chromium :

- As chromium ores become depleted.
- As energy conservation becomes more of an issue.

☆ But in the short term and at present there is no need to recycle chromium.