Lecture 18: Stainless steel making

Contents:

Key words: Stainless steel, AOD process, EAF

Introduction

Stainless steels contain typically 10-30 % chromium besides other elements like C, Mn, Si, S etc. Chromium imparts corrosion resistance to steel. Varying amounts of other alloying elements like Ni, Mo, V, Ti, Ni, etc may be added to obtain certain specific property. There are different types of stainless steels like

Austenitic stainless steels: which contain 18% Cr, 8% Ni, and C is in between 0.03-0.15%

Ferritic stainless steels: which contain 12% to 30% Cr and 0.08% to 0.12%C.

Martensitic stainless steels: which contain around 13% Cr and C varying in between 0.15% to 0.25%. Certain grades contain C 0.6% to 0.95%.

Duplex stainless steels: in which Cr is around 25%.

Precipitation hardenable stainless steel: contain 18-20% Cr, 8 to 10 % Ni and copper, Titanium, Aluminum.

It may be noted that all stainless steels contain chromium and carbon besides other elements. Production of stainless steels requires controlling chromium and carbon.

Thermodynamics of decarburization of chromium melt

In stainless steel making both chromium and carbon oxidizes when decarburization of melt is done. The Ellingham diagram for oxide formation indicates that carbon oxidation in preference to chromium oxidation can occur at temperatures greater than 1220^{o}C, when both elements are in pure state. Under all practical conditions carbon oxidation can occur at temperatures above 1800^{o}C in presence of chromium.

Chromium oxidizes to Cr_2O_3 or Cr_3O_4 and C oxidizes to CO.

$2C + O_2 = 2CO$

$2Cr + 1.5\ O_2 = Cr_2O_3$ or

$3Cr + 2O_2 = Cr_3O_4$

Equilibrium distribution between Cr and C is represented by considering Cr_3O_4

$Cr_3O_4 + 4C = 3Cr + 4\ \{CO\}$ 1)

Assuming pure $Cr_3O_4$and Cr and using henry's law for carbon, it follows

$$K = \frac{[f_{cr}\ w_{cr}]^3\ p_{co}^4}{[f_C\ w_c]^4} \qquad 2)$$

$$\frac{[W_{cr}]^3}{[W_c]^4} = \frac{K \times (f_c)^4}{f_{cr}{}^3\ p_{co}^4} \qquad 3)$$

f_c and f_{cr} are activity coefficient of carbon and chromium in liquid iron at 1wt % standard state. Hilly and Kaveney proposed the following equation for distribution of chromium and carbon:

$$\log\left[\frac{w_{cr}}{w_c}\right] = -\frac{13800}{T} + 8.76 - 0.925 \log p_{CO} \qquad 4)$$

The effect of Ni

$$\log\left[\frac{w_{cr}}{w_c}\right] = -\frac{13800}{T + 4.21 Wt\%Ni} + 8.76 - 0.925 \log p_{CO} \qquad 5)$$

Equations 4and 5 describes distribution ratio of Cr and c in Fe-Ni –Cr-C melt. Table shows the influence of temperature and p_{CO} on the distribution ratio $(R) = \left[\frac{w_{cr}}{w_c}\right]$ without Ni and $R^1 = \left[\frac{w_{cr}}{w_c}\right]$ in the presence of 10Wt % Ni

Table: chromium /carbon distribution ratio

T(k)	$p_{co} = at1m.$		$p_{co} = 0.25atm$		$p_{co} = 0.1atm$	
	R	R^1	R	R^1	R	R^1
1873	25	36	89	129	207	301
1973	55	82	209	295	488	690
2073	128	173	460	619	1077	1477
2173	240	339	863	1220	2019	2852

We can infer the following form the table:

I. Increase in temperature increases R and R^1 at all p_{co} values. High temperature is required to suppress chromium oxidation in favor of carbon oxidation.
II. Decrease in p_{co} increases both R and R^1 at all temperatures.
III. Nickel increases R and R^1

The above observations suggest that high temperature is needed to remove carbon in presence of chromium, if stainless steel is produced at atmospheric pressure. If reduced pressures are used; lower temperature can cause oxidation of carbon.

Technology of stainless steel making

Electric arc furnace was used to produce stainless steel by melting scrap of the desired composition. EAF was used only as a melting unit.

Typically, charge consists of carbon steel scrap + stainless steel scrap +lime. The charge is melted in EAF and after melt- down period, the melt contains around 10% Cr, all Nickel and carbon. Melt consists of Fe- Cr –Ni –C alloy

Oxygen is blown onto Fe- Cr- Ni –C melt and basic $Cr_2\,O_3$ slag forms. Initially chromium oxidizes until bath temperature rises to $1800°C$. Carbon oxidation occurs once the bath temperature rises to $1800°C$ In the finishing stage, low carbon ferrochrome is added to make the chromium content of steel to a desired value. The disadvantages with this technology are

- High temperature is required which cause damage to the refectory lining.
- Low carbon ferrochrome is required which in expensive.

Basis of development of new technology

Thus a technology which can use high carbon ferro- chrome and to decarburize the bath at selectively lower temperatures would be required. If carbon is to be oxidized in preference to Cr at low temperatures, a reduction in pressure of CO from 1 atmosphere to lower value would be required. Reduction in pressure of CO can be achieved either by vacuum or by using a mixture of $Ar + O_2$. The former one is vacuum oxygen decarburization (VOD) and the later is (AOD)

AOD Process

The process in carried out in a converter type of vessel. Vessel is lined with magnesite brick. A mixture of argon +oxygen is injected through the tuyeres located on the side of the converter shell.

Fe-Cr- Ni-C alloy melt is prepared in EAF. Melt is charged in AOD vessel. High carbon-ferrochrome is charged. In the initial stage a mixture of O_2: Ar in 3:1 ratio is blown through the side tuyeres. When carbon reduces to 30% of the original value the ratio of O_2: Ar is changed to 2: 1 and blow is continued to attain 0.09 to 0.12% C. First stage of blow generates sufficient amount of heat due to oxidation of Cr and hence coolants are added (5% of the change). Stainless steel scrap is used.

In the final stage, the ratio of O_2: Ar is changed 1:3 to bring C to the desired value. Fe- Si is added to recover Cr from slag and slag basicity is maintained at 1.5 to 2 by adding lime.

$$Cr_3O_4 + \ 2Si = 3\ Cr + 2SiO_2,$$

Slag formation and slag metal reactions are facilitated by argon stirring of the bath. The bath is desulphurized to levels well below 0.015%.

References:

A. Chakrabarti: steel making
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