An Overview On Refining Technologies for Stainless Steel

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Stainless steel belongs to a class of chromium iron alloys possessing a minimum of 10.5% chromium as the major ingredient responsible for the corrosion resistance. It was in the beginning of 1913 that Harry Brearley noticed that a material with 13% chromium did not rust which led to the initial development of stainless steels. These steels are well known for their aesthetic appeal, excellent luster, high strength to weight ratio, usage in hygienic conditions and high durability. Through change in the chromium content and addition of other alloying elements like Ni, Mo, Mn, Cu, Ti, Nb etc., these steels are classified as austenitic, ferritic, martensitic, duplex & precipitation hardening type offering varied micro-structures, physical, mechanical and chemical properties for specific application requirements.

Earlier, stainless steel was considered as an elite material with proprietary production limited to rich nations. Prior to 1930, stainless steel grades like AISI 302, 409,410, 420,430 & 446 used to be produced and marketed. Later on, various stainless steel grades were developed. The annual production of stainless steel did not exceed one million tons till the mid 1950s.

Until 1950s, stainless steel was produced through Electric Arc furnace in a single stage process involving melt down, decarburization of the chromium bearing melt by oxygen blowing followed by de-oxidation and alloying. The problems faced through this process include long heat cycle affecting productivity, limitations of charge mix requiring costly low carbon ferrochrome, high refractory wear due to high temperature operation and low chromium recovery. Stainless steel making using BOF also started during this period and was later converted into an intermediate stage after EAF process followed by ladle treatment.

During 1960s, the concept of preferential oxidation of carbon over chromium materialized by raise in temperature and reduction in CO partial pressures with improved chromium recovery. This led to development of a host of refining processes for economic production of stainless steels with Electric Arc furnace as the primary stage of melting.

Refining Processes Classification

The selection of a particular refining process depends on the capital costs, operational costs, raw materials, logistics of the individual plant, down stream facilities available and the type of stainless steel to be made. Increased costs of scrap led towards usage of high carbon ferrochrome with increased decarburization rates in converters, carbon steel scrap use as coolant, ferroalloys or stainless steel scrap if found expensive are substituted by chrome ore with hot metal in converters followed by vacuum treatment for economic production of stainless steel, shift towards vacuum processes for high argon costs and installation of ladle furnace units for increased sequencing of heats through continuous casting with improved productivity are some of the steps initiated for economic production of stainless steels based on the refining process selected.

There are various secondary steel making processes available today to meet the specific needs of the individual stainless steel steel melt shops of a plant. These processes are broadly categorized into :

A. Vessel Stirring Systems
B. Vacuum Degassing Systems
C. Ladle Heating Systems

Today, 68.7% of the stainless steel produced is through AOD (Argon Oxygen Decarburization) units followed by 19.5% in converter/VOD (Vacuum Oxygen Decarburization), 6.8% VOD and 5% by converter units only. The processes can be combi-type such as duplex or triplex ones.

A. VESSEL STIRRING SYSTEMS

There are various vessel stirring methods for making stainless steels aiming at usage of least cost charge materials, significant alloy recoveries, reduced operating costs, productivity increases, quality improvements and specialized equipment operation.

Argon Oxygen De-Carburization (Aod)

It is a low cost stainless steel production method that can absorb large amounts of scrap and high carbon ferrochrome and is schematically illustrated in Fig.1. In this vessel, lime and dolomite are added just before charging de-slagged metal with typical start carbon levels of 3% & silicon contents of 0.4% received from Electric Arc Furnace followed by blowing at oxygen/inert ratios of 5:1 through tuyeres located at the lower side wall of the converter.

During the initial steps, alloys are added for weight, chemistry adjustment and to control temperature to a maximum of 1700C. Silicon is oxidized in the initial stage of blow. The oxygen/inert gas ratio is progressively decreased step wise as carbon content decreases i.e. 1:1 at 0.3% C, 1:3 at 0.15%C, 1:5 at 0.04%C and

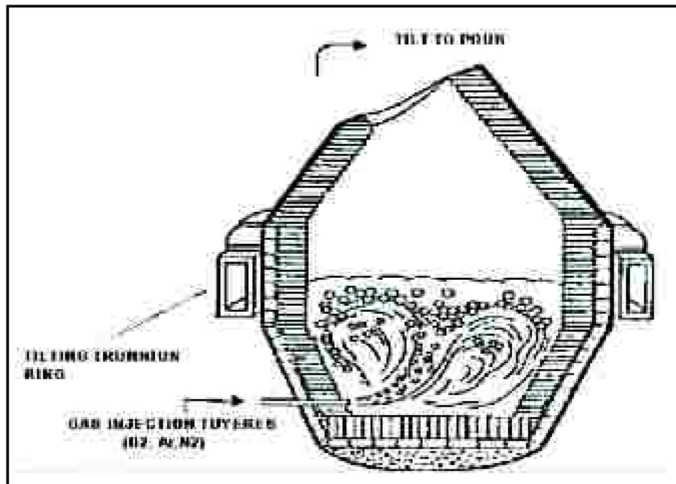

FIG.1. THE AOD PROCESS DIAGRAM

pure argon at 0.015%C in order to minimize chromium oxidation and controlling temperature. The length of de-carburization period is determined by the start carbon, silicon contentl, blowing rates, the amount & efficiency of additives and the aim carbon content. After de-carburization, a reduction mix consisting of silicon and/or aluminium is added along with fluxing agent (lime and spar) and stirred with inert gas for 5 to 8 minutes. Using 3 kg/ton of aluminium, 3 kg/ton of spar, slag basicity of 1.5-1.7 and temperature of 1700C, sulphur levels of 0.005% can be achieved. Basic slag is produced through addition of sufficient amount of lime for decreasing the activity of silica and followed by vigorous stirring that enables to offset the detrimental effect of chromium on bath oxygen content for production of low oxide inclusions coupled with high degree of de-sulphurization of the stainless steel. For low nitrogen steels (0.010%N), argon is used and for high nitrogen steels (0.24%N), nitrogen is the automatic choice for inert gas. Samples can be taken after stopping blow and final sample & temperature taken after reduction. If further trim additions necessary, it is preferential to add in the converter after making second slag followed by stir for 2 minutes or in tap ladle. Further developments took place through application of top and bottom blowing such as AOD-L process leading to improved production rates where in top lancing with oxygen coupled with oxygen/inert ratio of 3:1 to 5:1 through tuyeres can be blown for shortening the decarburization time.

Kawasaki Bop & Kawasaki Obm-S Converter

Kawasaki BOP converter looks similar to BOF with provision for oxygen lancing from the top and is shown in Fig.2. It possess seven bottom tuyeres that could blow oxygen with propane for tuyere cooling. Powdered lime injection provision from tuyeres is also available in this converter.

Kawasaki OBM-S converter process was developed by VAI, Austria and evolved from the BOP process with tuyeres installed either at side or converter bottom with top blown lance.

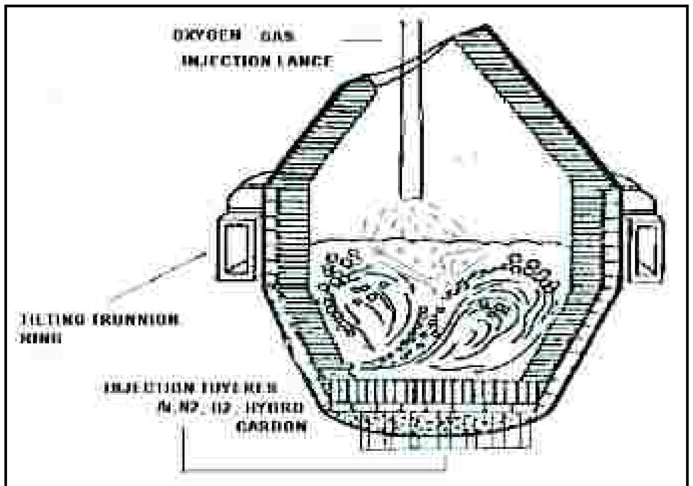

FIG. 2. KAWASAKI-BOP PROCESS

The top gases used are oxygen, nitrogen and argon and the bottom gases applied are oxygen, nitrogen, argon and hydrocarbons. Natural gas or propane is used for tuyere protection and improvement in refractory life. For AISI 304 refining through this vessel, oxygen to the tune of 29 Nm3/ton, nitrogen about 13 Nm3/ton, argon 16.5 Nm3/ton, silicon for reduction about 11 kg/ton, lime about 50 kg/ton, dolomite 20 kg/ton and fluorspar to the tune of 8 kg/ton are consumed.

Creusot Loire Uddeholm (Clu) Converter

The process uses steam as the diluting gas rather than generally used argon.

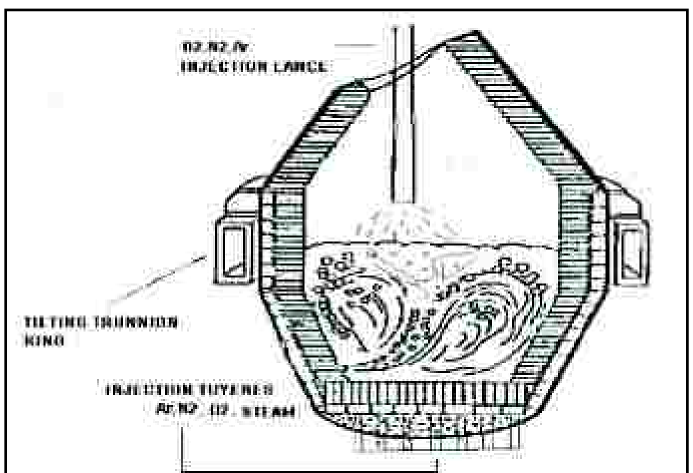

FIG. 3. CLU PROCESS

It was developed by Uddeholm of Belgium and Creusot Loire of France which is shown in Fig.3. The converter is bottom blown with provision for blowing oxygen, steam, nitrogen and argon while the top gases applied are oxygen, nitrogen and argon. Decarburization period starts with injection of oxygen-steam mixture. The process is inefficient due to endothermic reaction of steam with molten metal with chromium losses much higher than AOD process. Though argon consumption is reduced through this converter, the silicon consumption is very high and the usage of steam leads to high hydrogen pick up in stainless steels.

Presently, there has been a trend to use more of argon in place of steam for improving the process efficiency of this converter. When making AISI 304, oxygen to the tune of 27 Nm3/ton, nitrogen about 13.5 Nm3/ton, steam of 10.4 Nm3/ton, argon 7Nm3/ton, silicon for reduction about 15.5 kg/ton with hydrogen levels of 5.9 ppm are achievable in this converter.

Metal Refining Process (Mrp) Converter

This process was developed by Mannesmann Demag. The process involves charging of molten metal containing chromium and nickel in this converter with decarburization carried out using oxygen and inert gases & the process is schematically shown in Fig.4.

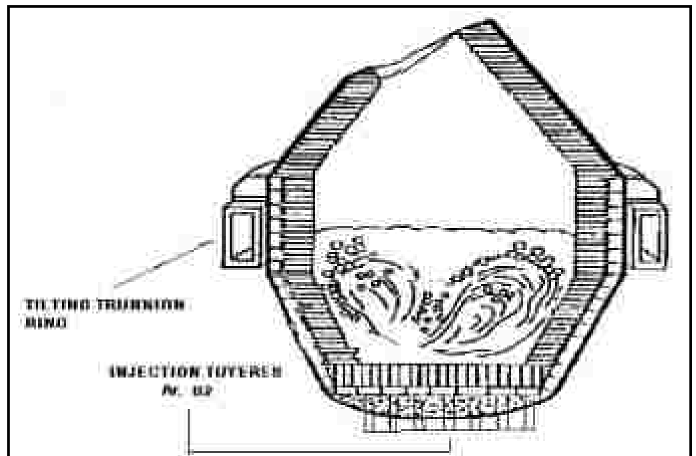

FIG. 4. METAL REFINING PROCESS

Initially, gases were alternately blown through tuyeres situated along the bottom of the converter and oxygen is blown into the melt without dilution with any inert gases. The desired oxygen blow is followed by blowing with inert gas only. The cycle of oxygen blow followed by inert gas lead to achieving low CO partial pressures, faster decarburization rates and increased chromium recovery leading to lower consumption of silicon for reducing chromium oxide from the slag. MRP L converter is a modification to this converter wherein oxygen is blown from the top and inert gases from porous elements present in bottom with replaceable bottom tuyeres and the process is capable for use of higher blowing rates than AOD and the tuyere erosion is minimal. After reaching intermediate carbon level, the molten metal from this converter is transferred to a ladle for carrying out decarburization.

Krupp Combined BlowingStainless(KcbS) Converter

This was developed by Krupp Stahl with modified BOF converter for combined blowing through the lance and tuyeres. The process is illustrated in Fig.5. The simultaneous introduction of process gas helps in increased decarburization rates resulting in reduction of refining time compared to AOD.

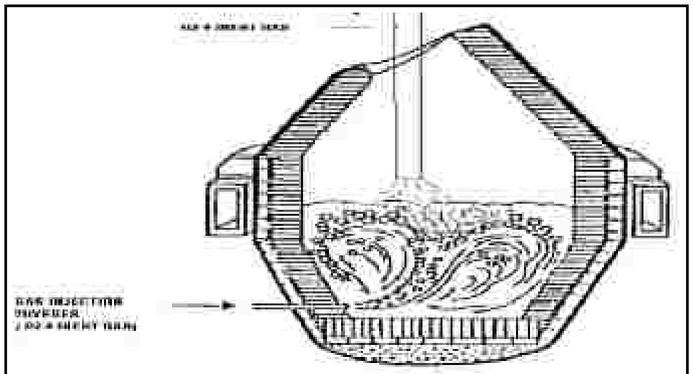

FIG. 5. KCB-S PROCESS

At the start of the blow, pure oxygen is blown simultaneously from top lance and side wall tuyeres. After reaching the desired temperature, ferroalloys and scrap addition are made during oxygen blow. After reaching a critical carbon content, oxygen content of the process gas is reduced by using inert gas like nitrogen or argon with oxygen to inert gas ratios of 4:1, 2:1, 1:1, 1:2 & 1:4 applied for getting lower levels of decarburization. When carbon of 0.15% reached, lancing is discontinued and process gas introduced through tuyeres when the aim carbon level is reached, silicon added for reducing chromium oxide in slag followed by lime and flux addition for achieving lower levels of dissolved oxygen content and excellent desulphurization of the stainless steel melts.

Argon Secondary Melting (Asm) Converter

This method was developed by MAN GHH in Germany and is shown in Fig.6. The tuyeres are placed along the bottom of the vessel with provision for injection of oxygen, nitrogen and argon.

A slight modification to this converter is ASM-L converter with top blown oxygen lance.

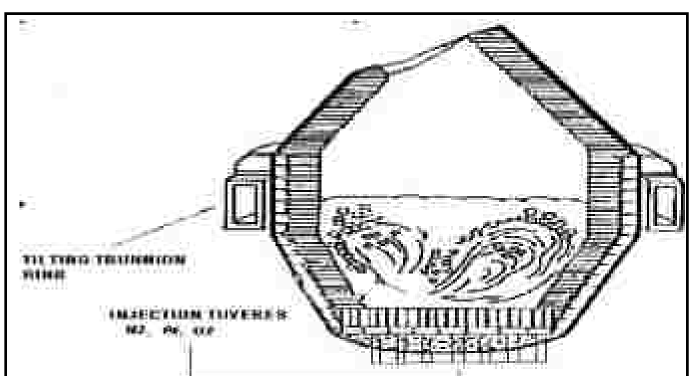

FIG. 6. ARGON SECONDARY MELTING CONVERTER

Sumitomo Top & Bottom Blowing (Stb) Converter

The process was conceptualized by Sumitomo Metal Industries and is illustrated in Fig.7.

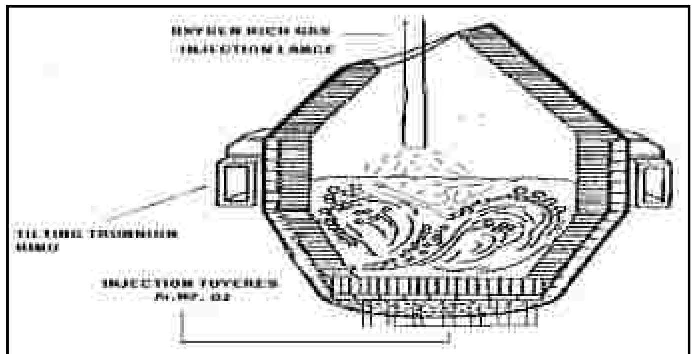

FIG. 7. STB CONVERTER

The method was developed to overcome difficulties in use of pure top or pure bottom blowing by combining both helping in reduced tuyere erosion and application of additional supply of oxygen rich gases from top lance with increased decarburization rates resulting in shortening decarburization time.

Top Mixed Bottom Inert (Tmbi) Converter

The method was adopted by Allegheny Ludlum Corporation as shown in Fig.8 with the converter looking like a BOF converter equipped with bottom tuyeres for injecting inert gases like argon or nitrogen. Desired mixture of gases are introduced primarily from the top lance and hence the name TMBI.

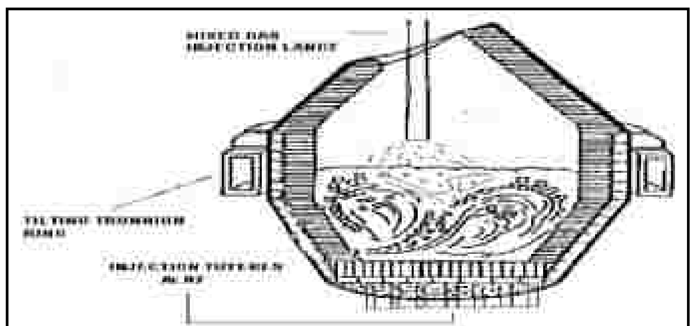

FIG. 8. TMBI CONVERTER

B. VACUUM DEGASSING SYSTEMS

Ruhrstahl Heraeus Ob (Rh-Ob) Process

The process was developed by Nippon Steel Corporation shown in Fig.9 which incorporates an oxygen injection facility near to the bottom of the vacuum chamber to enable production of stainless steel and low carbon steels.

Also, temperature recovery is achieved through use of aluminium in combination with oxygen and normal degassing practice is carried out for production of clean steels. The hot metal from blast furnace is fed to BOF where metal is alloyed with chromium and blown to carbon levels of 0.5% - 0.6% with final decarburization carried out in this process unit for making stainless steels.

Considering suppression of slag-metal mixing in circulation

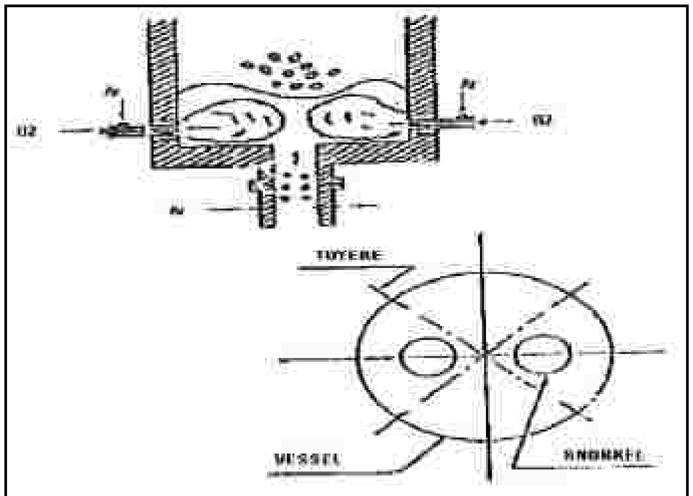

FIG. 9. RH-OB PROCESS

degassers with no de-sulphurisation, new techniques have been developed which involve injecting refining slag into the up leg of RH vessel and is reported to achieve de-sulphurisation to the tune of 80%.

Vacuum Oxygen De-Carburization (Vod) Unit

This is considered to be an important vacuum process for production of stainless steels and is shown in Fig.10. It is particularly suitable for special stainless steels that require the lowest carbon, nitrogen and hydrogen levels. In this process, the ladle is placed in vacuum chamber and there is a provision for oxygen lancing through vacuum tight gland and alloying additions. Basically, the method involves preferential oxidation of carbon over chromium leading to minimum chromium losses. Due to reduced freeboard available in the ladle, the initial carbon content of the melt should be as low as 1%. Here, oxygen injection is carried out at 100 torr 250 torr. Silicon is oxidized followed by carbon. De-carburisation occurs through start of co bubbling determined by initial temperature and silicon content of the liquid bath.

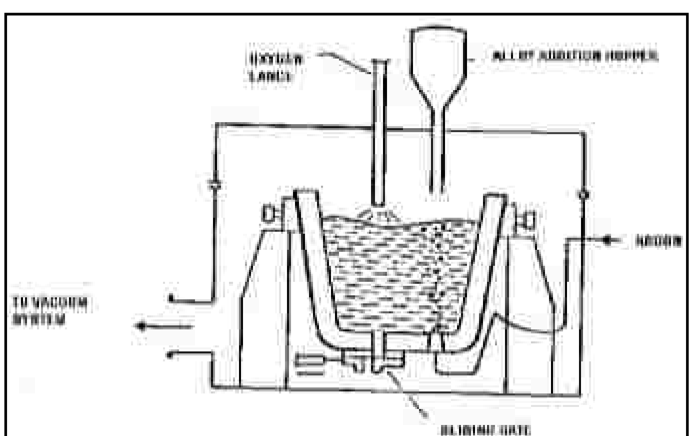

FIG. 10. VACUUM OXYGEN DECARBURIZATION UNIT

Constant rate of de-carburization occurs depending on the oxygen flow rate. The co:co2 ratio is monitored and at a bath carbon content of 0.08%, it increases rapidly. So, beyond this limiting carbon percentage, de-carburization rate falls independent of oxygen flow rate with simultaneous chromium oxidation. Oxygen lancing is ceased and the vessel pressure is reduced and argon stirring carried out to further the reaction between the dissolved oxygen and the remaining carbon. It has been reported that through vigorous stirring carbon can be reduced to levels of 0.005% and total (Carbon + Nitrogen) less than 0.015% are achieved. The refining sequence in general is controlled by combination of variation in oxygen flow rate, the lance tip to bath surface distance, control of vacuum pressure and the argon flow rate. Addition of sufficient amount of lime and aluminum helps in excellent de-sulphurisation of the melt.

C. LADLE HEATING SYSTEMS

Ladle Furnace has evolved as a process to facilitate increased sequencing of stainless steel through continuous casting. This furnace thus, acts as an excellent buffer between the primary melting unit and the continuous caster giving precise temperature and compositional control. It provides an option to the primary melting unit to tap at low temperatures leading to saving in time and energy. The unit is shown in Fig.11. Here, a refractory or a water cooled lid sits on a seal along the rim of the ladle. Three phase electric power is introduced through the graphite electrodes for heating the molten steel as a means to increase temperature with heating rate of about 3ºC 4ºC/min.

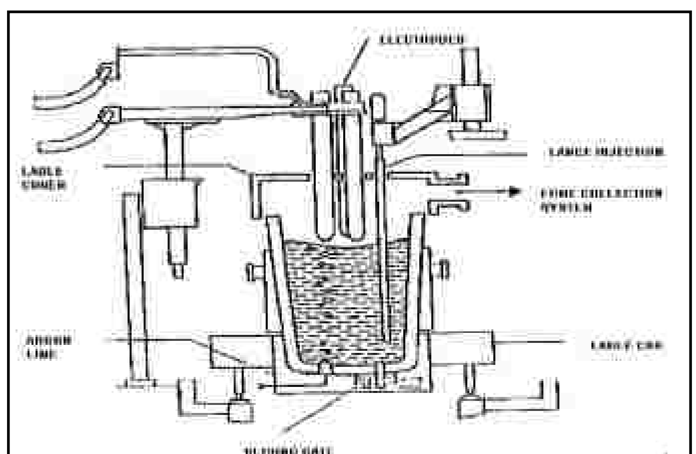

FIG. 11. SCHEMATIC DIAGRAM OF LADLE FURNACE

With the hoppers provided for alloying addition, chemistry adjustment can be carried out effectively.

Continuous developments in the refining of stainless steels paved way towards improvement in productivity, quality of the products and of course, improving the overall economics of stainless steel production in the world.

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