

Chapter 12

Refining of Stainless Steels

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12.1 Introduction

Stainless steels contain from 10 to 30% chromium. Varying amounts of nickel, molybdenum, copper, sulfur, titanium, niobium, etc. may be added to obtain desired mechanical properties and service life. Stainless steels are primarily classified as austenitic, ferritic, martensitic, duplex or precipitation hardening grades. The first stainless steel grades that were commercially produced in the United States were similar to 302, 410, 420, 430, and 446. These five alloys were produced and marketed prior to 1930. In subsequent years, the grades similar to 303, 304, 316, 321, 347, 416, and 440 were brought to market.

In the early stages of their production, stainless steels were melted using an electric arc furnace. Stainless steels were made to contain no more than 0.12% carbon. A large fraction of production of stainless steels was melted to a maximum carbon content of 0.07 or 0.08%.

In those early days, carbon steel scrap, iron ore, and burnt lime were charged into an electric arc furnace. After the scrap was molten, carbon was removed by adding ore until the carbon content reached 0.02%. The electrodes were then raised and the slag removed as completely as possible. Desired amounts of ferrosilicon, burnt lime, and fluorspar were added and the temperature of the bath was raised so that a large amount of low carbon ferrochromium could be added to achieve the aim chromium level. The desired amount of the low carbon ferrochromium was added in two or three separate batches. The bath had to be mixed thoroughly by rabbling or reladling and slag had to be kept fluid by continuous additions of ferrosilicon, lime and fluorspar. After all the desired chromium was in the alloy, a sample was taken for preliminary analysis. Final additions were made and the heat was brought to the desired tapping temperature and tapped.¹

Until about 1970, the majority of stainless steel was produced in the arc furnace. With the advent of tonnage oxygen production, the electric furnace stainless steel melting practice changed from the above. Gaseous oxygen could be used to improve the rate of decarburization. This could be achieved by injecting oxygen gas into the liquid steel using a water-cooled lance. The faster oxidation of carbon with high oxygen potential was accompanied by the adverse reaction of extensive oxidation of chromium to the slag. This necessitated a well-defined reduction period in which ferrosilicon was used to reduce the oxidized chromium from the furnace slags.

In the late 1960s, a number of laboratory studies were performed to understand the thermochemistry of the stainless steels.² One of these studies was by Krivsky, who studied the carbon-chromium-temperature relationships. His experiments involved blowing oxygen onto the surface

of the baths of molten chromium alloys. He was trying to perform the experiments under isothermal conditions but found it difficult because of the exothermic nature of the oxidation reactions. Krivsky added argon to oxygen in order to control the temperature. He found that with argon dilution he could decarburize the melt to even lower levels of carbon without excessive oxidation of chromium.³

Krivsky's observations led to initial experiments where argon-oxygen mixtures were injected through a lance into the bath in the arc furnace. It was found that argon injection in the wide and shallow bath of an arc furnace did not influence the decarburization reaction completely as predicted. Hence, after many experiments, the developers decided that a separate refining vessel was necessary to develop a commercial process. At Joslyn Steel (now Slater Steels), a 15-ton converter with three tuyeres was built. The first successful heat was made in October 1967. These successful trials led to patents for the argon-oxygen decarburization (AOD) process for the refining of stainless steels and other specialty alloys⁴ by the industrial gases division (now Praxair, Inc.) of the Union Carbide Corporation.

The AOD process revolutionized stainless steelmaking. It lowered the cost of production of stainless steels significantly. It allowed operators to use electric arc furnaces for melting down of

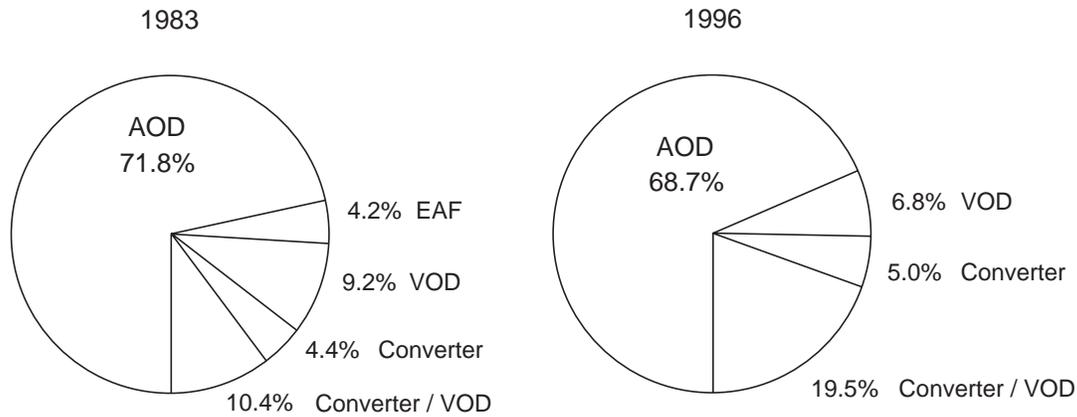


Fig. 12.1 Stainless steel production by process for two selected years.

stainless and carbon steel scraps with desired amounts of low cost high carbon ferrochromium. The decarburization operation was moved out of the electric furnace and into the newly designed converter. The oxidation-reduction operation could be conducted at very high productivity rates. Additionally, the quality of the alloys produced was improved. The process was adopted by major stainless producers at a very rapid rate. As shown in Fig. 12.1, the AOD process is the predominant method for making stainless steel in the world.⁵ A schematic of a modern AOD vessel is shown in Fig. 12.2.

Duplex processes are used for making stainless steels. There is an electric arc furnace or similar melting unit that melts down scrap, ferroalloys and other raw materials to produce the hot metal. The hot metal, which contains most

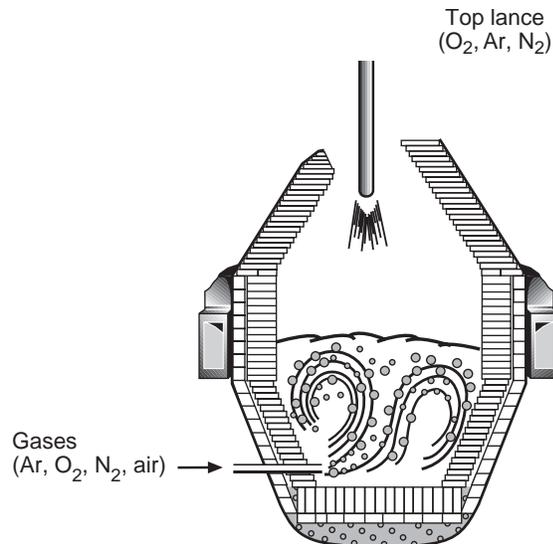


Fig. 12.2 AOD vessel.

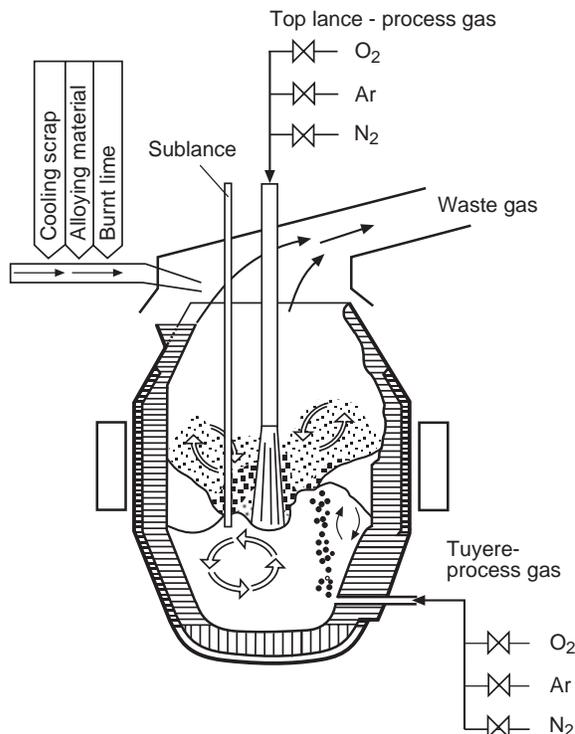


Fig. 12.3 Schematic of KCB-S process.

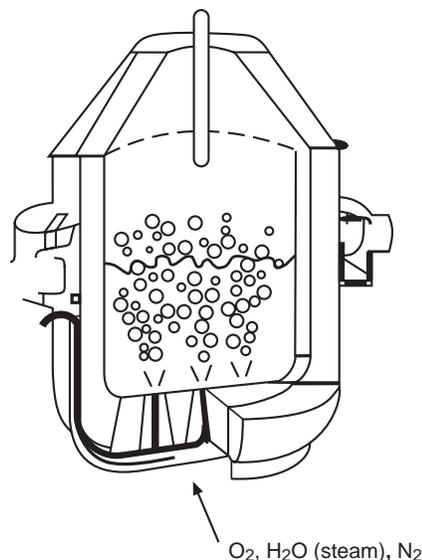


Fig. 12.4 CLU vessel.

of the chromium and nickel as well as some other alloying elements, is the charge to the converters. The converters are used to achieve low carbon stainless steels which may be tapped into a teeming ladle. The EAF-AOD process is one such duplex route. The versatility of the AOD process led steelmakers to re-examine the use of different converters for melting of stainless steels. This led to the development of several other converters for duplex processes. These include: KCB-S⁶ process developed by Krupp Stahl, shown in Fig. 12.3; K-BOP⁷ process used by Kawasaki Steel Corporation; K-OBM-S⁸ promoted by Voest Alpine; metal refining process (MRP)⁹ developed by Mannesmann Demag; Creusot-Loire-Uddeholm (CLU)¹⁰ process, shown in Fig. 12.4; Sumitomo top and bottom (STB)¹¹ blowing process by Sumitomo Metals; top mixed bottom inert (TMBI)¹² process used by Allegheny Ludlum Corporation; VODC¹³ process tried by Thyssen where vacuum is applied to the converter; and AOD/VCR¹⁴ process developed by Daido, shown in Fig. 12.5.

The development work to make stainless steels using conventional BOF converters had begun in the late 1950s and early 1960s. By the mid-1960s, some steelmakers were using existing BOF converters for a partial decarburization followed by decarburization in a ladle under vacuum to make the low carbon stainless steels. These processes are known as triplex processes because three process units, such as electric arc furnace, a converter for pre-blowing, and a vacuum decarburization unit for final refining, are involved. The steels undergo

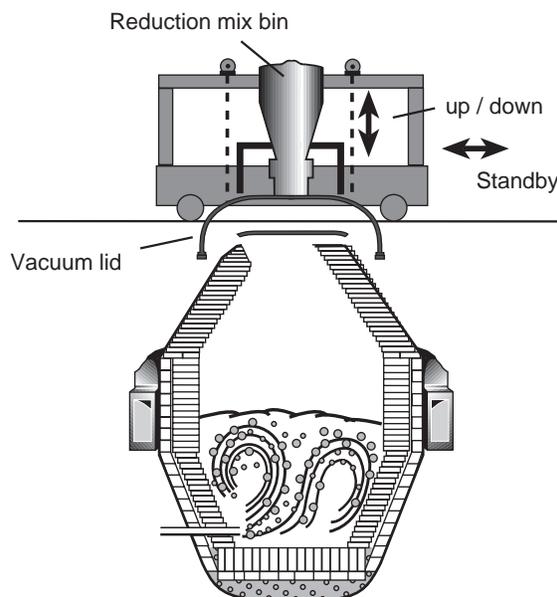


Fig. 12.5 AOD/VCR vessel.

treatment for final decarburization, final trimming, homogenization and flotation of inclusions before the ladle is taken to the teeming operation. In almost all of these triplex processes, vacuum processing steels in the teeming ladle is the final step before casting. The vacuum oxygen decarburization (VOD) process was developed by Thyssen in West Germany.¹⁵ The other processes using vacuum include the use of RH-OB for making stainless steels at Nippon Steel Corporation¹⁶ and the use of an SS-VOD process¹⁷ by Kawasaki Steel Corporation. These processes are shown in Fig. 12.6.

With all these developments over several decades, now there are many different processes to make stainless steels. The available processes can be divided into three groups: the converter processes, converter with vacuum processes, and vacuum processes. Table 12.1 shows the variety of processes.

Table 12.1 Different Process Routes for Making Stainless Steels

Process	Tuyere Location	Bottom Gases	Top Gases
AOD	Side	O ₂ , N ₂ , Ar, Air, CO ₂	O ₂ , N ₂ , Ar
KCB-S	Side	O ₂ , N ₂ , Ar	O ₂ , N ₂ , Ar
K-BOP/K-OBM-S	Bottom or Side	O ₂ , N ₂ , Ar, Hydrocarbons	O ₂ , N ₂ , Ar
MRP, ASM	Bottom	O ₂ , N ₂ , Ar	
CLU	Bottom	O ₂ , Steam, N ₂ , Ar	O ₂ , N ₂ , Ar
AOD-VCR (vacuum)	Side	O ₂ , N, Ar ₂ , N ₂ , Ar	
VOD (vacuum)	Bottom (bubbler)	Ar, O ₂	

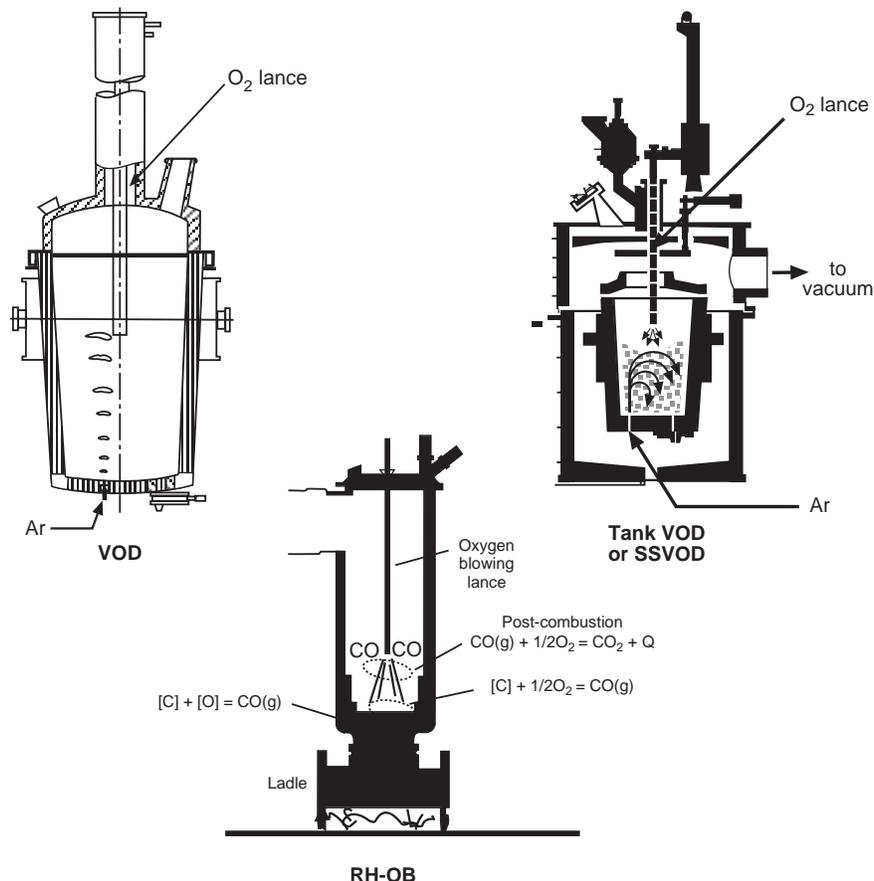


Fig. 12.6 Vacuum processes for refining stainless steel.