
1 Introduction

1.1 HISTORY OF SECONDARY STEELMAKING

Prior to 1950 or so, after steel was made in furnaces such as open hearths, converters, and electric furnaces, its treatment in a ladle was limited in scope and consisted of deoxidation, carburization by addition of coke or ferrocake as required, and some minor alloying. However, more stringent demands on steel quality and consistency in its properties require controls that are beyond the capability of the steelmaking furnaces. This is especially true for superior-quality steel products in sophisticated applications. This requirement has led to the development of various kinds of treatments of liquid steel in ladles, besides deoxidation. These have witnessed massive growth and, as a result, have come to be variously known as *secondary steelmaking*, *ladle metallurgy*, *secondary processing of liquid steel*, or *secondary refining of liquid steel*. However, the name *secondary steelmaking* has more or less received widest acceptance and hence has been adopted here.

Secondary steelmaking has become an integral feature of modern steel plants. The advent of the continuous casting process, which requires more stringent quality control, is an added reason for the growth of secondary steelmaking. Steelmaking in furnaces, also redesignated now as *primary steelmaking*, is therefore increasingly employed only for speedy scrap melting and gross refining, leaving further refining and control to secondary steelmaking. There are processes, such as *vacuum arc refining (VAR)* and *electroslag remelting (ESR)*, that also perform some secondary refining. However, they start with solidified steel and remelt it. Hence, by convention, these are not included in secondary steelmaking.

Harmful impurities in steel are sulfur, phosphorus, oxygen, hydrogen, and nitrogen. They occupy interstitial sites in an iron lattice and hence are known as *interstitials*. The principal effects of these impurities in steel are loss of ductility, impact strength, and corrosion resistance. When it comes to detailed consideration, each element has its own characteristic influence on steel properties. These will be briefly mentioned in subsequent chapters associated with them. Oxygen and sulfur are also constituents of nonmetallic particles in steel, known as *inclusions*. These particles are also harmful to properties of steel and should be removed as much as possible. Carbon is also present as interstitial in iron lattice. However, unlike the other interstitials, it is generally not considered to be harmful impurity and should be present in steel as per specification. But, today, there are grades of steel in which carbon also should be as low as possible.

Historically, the Perrin process, invented in 1933, is the forerunner of modern secondary steelmaking. Treatment of molten steel with synthetic slag was the approach. *Vacuum degassing (VD)* processes came in the decade of 1950–1960. The initial objective was to lower the hydrogen content of liquid steel to prevent cracks in large forging-quality ingots. Later on, its objective also included lowering of nitrogen and oxygen contents. Purging with inert gas (Ar) in a ladle using porous bricks or tuyeres (*IGP*) came later. Its primary objective was stirring, with consequent homogenization of temperature and composition of melt. It offered the additional advantage of faster floating out of nonmetallic particles. It was also found possible to lower carbon to a very low value in stainless steel by treatment of the melt with oxygen under vacuum or along with an

argon stream. This led to development of *vacuum-oxygen decarburization (VOD)* and *argon-oxygen decarburization (AOD)*.

Synthetic slag treatment and powder injection processes of molten steel in a ladle were started in late 1960s and early 1970s with the objective of lowering the sulfur content of steel to the very low level demanded by many applications. This led to the development of what is known as *injection metallurgy (IM)*. Injection of powders of calcium bearing reagents, typically calcium silicide, was also found to prevent nozzle clogging by Al_2O_3 and lead to inclusion modification, which are of crucial importance in continuous casting as well as for improved properties.

The growth of secondary steelmaking is intimately associated with that of continuous casting of steel. Up to the decade of the 1960s, ingot casting was dominant. Now, most of world's steel is cast via the continuous casting route. The tolerance levels of interstitial impurities and inclusions are lower in continuous casting than in ingot casting, and this has made secondary refining more important. For good quality finished steel, proper macrostructure of the casting is also important, in addition to the impurity level. This requires close control of the temperature of molten steel prior to teeming into the continuous casting mold.

In traditional pitside practice, without ladle metallurgical operations, the temperature drop of molten steel from furnace to mold is around 20–40°C. An additional temperature drop of about 30–50°C occurs during secondary steelmaking. Continuous casting uses pouring through a tundish, causing some further drop of 10–15°C. Therefore, provisions for heating and temperature adjustment during secondary steelmaking are very desirable. This has led to the development of special furnaces such as the *vacuum arc degasser (VAD)*, *ladle furnace (LF)*, and *ASEA-SKF ladle furnace*. These are very versatile units, capable of performing various operations. There have been further developments in this direction recently. Efforts are being made to install one unit only and even then achieve a flexible manufacturing program.

Table 1.1 summarizes the features of various processes.¹ It shows the capabilities of each. However, it is to be borne in mind that some versatile units of today are really combinations of several processes. For example, some modern vacuum degassers have provisions for oxygen blowing and powder injection. Hence, good desulfurization and decarburization also can be attained in them. It ought to be noted here that a significant fraction of sulfur in blast furnace hot metal is removed by pretreatment in a ladle during transfer to steelmaking shop. Similarly, phosphorus is removed primarily in a basic oxygen furnace and to some extent during pretreatment of hot metal. Shima² has reviewed the development of steelmaking technology in Japan, dealing broadly with these.

1.2 TRENDS IN STEEL QUALITY DEMANDS

The world steel market was somewhat stagnant and did not witness significant growth during the decade of the 1980s. Scholey³ has discussed this with special emphasis on Europe. **Table 1.2** presents world consumption of steel products in 1990 and predictions of the same for A.D. 2000 as per statistics prepared by the International Iron and Steel Institute (IISI).⁴

Table 1.2 shows that predicted growth of consumption is large in Asia but either insignificant or negative in other countries. However, according to IISI, lack of tonnage growth does not indicate stagnancy. With continuous improvement in quality, less and less quantity of steel is being consumed for the same applications. If this point is taken into consideration, then there has been remarkable progress in steel technology on the quality front, and also improved yield. **Figure 1.1** shows the change in product mix in the U.S.A. from 1925 to 1990, as compiled by Stubble.⁵ It demonstrates a massive shift in favor of sheet and strip; so much so that, in 1990, more than 50% of the product was in this shape, as compared to about 20% in 1925. This is the worldwide trend also. It is to be recognized that this shift was technologically possible to a large extent due to improvement in steel quality through secondary steelmaking. Near net shape casting, which is commercially expected in the near future, will require even more stringent control of impurities and inclusions.

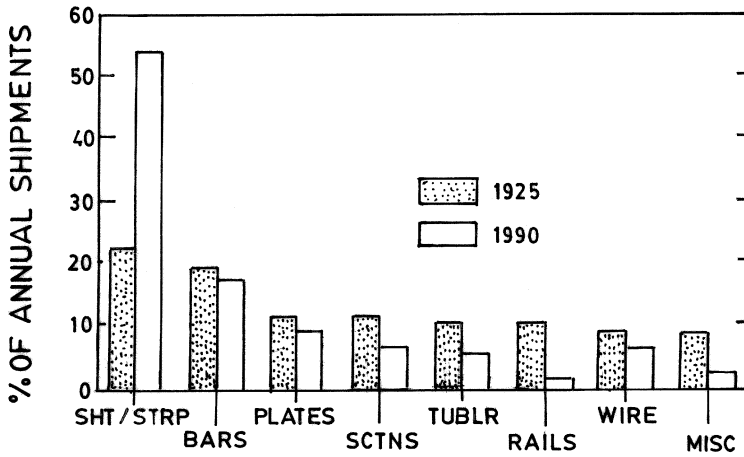


FIGURE 1.1 Product mix in the United States of America: 1925 vs. 1980⁵ (reprinted by permission of Iron & Steel Society, Warrendale, PA, U.S.A.).

TABLE 1.1
Various Secondary Steelmaking Processes and Their Capabilities

Item	Processes							
	VD	VOD	IGP	IM	VAD	LF	ASEA-SKF	
Desulfurization	minor	minor	minor	yes	yes	yes	yes	
Deoxidation	yes	yes	yes	yes	yes	yes	yes	
Decarburization	minor	yes	no	no	no	no	yes	
Heating	no/yes	yes*	no	no	yes	yes	yes	
Alloying	minor	yes	minor	minor	yes	yes	yes	
Degassing	yes	yes	no	no	yes	no	yes	
Homogenization	yes	yes	yes	yes	yes	yes	yes	
Achieving more cleanliness (i.e., less inclusions)	yes	yes	yes	yes	yes	yes	yes	
Inclusion modification	no	no	minor	yes	yes	yes	yes	

*chemical heating only

Source: data primarily from Ref. 1.

With the passage of time, customers are demanding better and better quality steels, which means

1. fewer impurities
2. more cleanliness (i.e., lower inclusion content)
3. more stringent quality control, i.e., less variation from cast to cast
4. microalloying to impart better properties (for plain carbon and low alloy steels)
5. better surface quality and homogeneity

The above demands, combined with other requirements such as (a) the need for cost reduction in view of competition from polymers etc., (b) environmental pollution control, and (c) a relatively stagnant world steel market, pose enormous challenge to the steelmaking community. Before any

TABLE 1.2
World Steel Consumption

	Millions of Metric Tonnes of Steel Products	
	1990 (actual)	2000 (predicted)
North America	96.5	99
European Community	115.5	117
Japan	92.6	85
Latin America	22.3	35
P. R. China	54.9	80
Other Asian countries	78.6	120
Africa	8.6	9
Former USSR and Eastern Europe	148.5	100
Others	36.4	41
Total	653.9	686

Source: data from Ref. 4.

secondary steelmaking treatment, the lowest levels of impurities attainable with present-day practices, including a metal pretreatment facility, would be approximately as follows:

sulfur:	100 ppm
phosphorus:	20 ppm
nitrogen:	40 ppm
hydrogen:	5 ppm
carbon:	400 ppm
oxygen:	variable

Upon traditional deoxidation in a ladle, oxygen can be brought down to lower than 30 ppm. Thus, the minimum total of S + O + P + N would be about 200 ppm, and including carbon about 600 ppm.

Changing demands on quality may be illustrated with the example of line pipe steel for North Sea gas.⁶

Year	Maximum ppm in Steel, by Element					
	C	S	P	H	N	O
1983	400–600	20	150	–	100	–
1990		10	15	–	35	20
Long-term	S + O + P + N = 45 ppm					

Ramaswamy⁶ has reviewed the subject and has outlined some of the quality requirements of line pipe steel for sour gas applications, steels for offshore platforms, bearing steels, steel for the rod and wire industry, and for power plant rotors. Figure 1.2 shows the trends in residuals attained by Japanese Steel Works.⁷ A special mention may be made of a recent spurt in demand for *ultra-low carbon steel* (C < 30 ppm or so) for the manufacture of thin sheets by cold rolling with continuous annealing for automobiles. These steels not only have ultra-low C but have other residuals also at ultra-low levels, e.g., N < 15 ppm, S < 10 ppm, P < 15 ppm, H < 2 ppm. In addition, inclusion contents are also drastically lower as compared to regular steels. An expansion

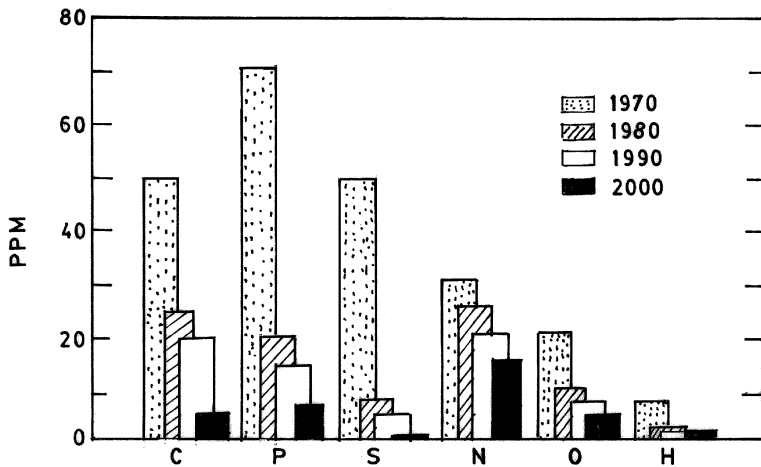


FIGURE 1.2 Minimum residual levels in steel in Japan.⁷

of the market for fine steels by approximately a factor of three has been predicted from 1985 to year 2000 by Japan's fine steel study group.⁷

As shown in Table 1.1, all kinds of secondary steelmaking operations are capable of yielding steels with more cleanliness. Inclusions are generally harmful to the mechanical properties and corrosion resistance of steels. The choice of deoxidation practice combined with proper stirring is one of the measures to remove inclusions. However, a more serious source of harmful inclusions (i.e., larger sizes) is erosion of refractory lining. In addition, reaction of lining with the melt is a source of impurity at such low impurity levels. Therefore, the success of secondary steelmaking processes is intimately linked with the development or use of newer refractory materials such as those high in alumina, zircon, magnesia, dolomite, etc.

The cleanliness consciousness has increased to such an extent that trials are going on for filtering molten steel through ceramic filters to remove nonmetallic inclusions. The technique is still in the experimental stages.

Inclusion modification is one of the techniques to render inclusions less harmful to the properties of steel. Injection of calcium into the melt is done for this purpose. Sometimes, rare earths are also employed.

1.3 SCIENTIFIC FUNDAMENTALS

The application of scientific fundamentals is an important contributing factor to the progress of secondary steelmaking technology. This has been possible due to growth of applied sciences, including metallurgical sciences, and their application.

The laws of thermodynamics had been well laid out by the turn of the 19th century. However, their application to high-temperature systems had to wait because of a lack of thermochemical data. Collection of such data had started on a modest scale by the beginning of this century. The pace accelerated as years went by, and it began on a really massive scale after the 1940s. By about 1970, fairly reliable data were available on most of the systems and reactions of interest in pyrometallurgy.

Equilibrium process calculations call for experimental data on activity vs. composition relationships in liquids that may be broadly grouped into metallic solutions, SiO₂-based slag solutions, etc. Most of these solutions are multicomponent ones. The development of metallurgical thermodynamics called for new techniques to handle them. The participation of renowned physical chemists other than metallurgists made these possible.

Kinetics is a late comer as compared to the thermodynamics of pyrometallurgical reactions. Scientific investigations were started after 1950. However, they picked up quickly and, for the last three decades, the field has been pursued vigorously. As a result, kinetics of pyrometallurgical reactions and processes is a subject of engineering science in its own right. Knowledge already available in chemical engineering has been instrumental in its development.

It had been recognized several decades back that lack of proper mixing in the liquid bath adversely affects the efficiency of steelmaking processes. Many investigations have been carried out on mixing, especially in the last two decades. Again, mixing, mass transfer, and phase dispersions depend on fluid flow in the bath. Such a flow is turbulent in steelmaking processes. Turbulence is a very complex phenomenon. Scientists and engineers in a variety of disciplines are concerned with the solution of problems involving turbulent flow.

Experimental investigations on fluid flow and mixing at steelmaking temperatures are difficult. In this connection, water modeling (i.e., cold modeling or physical modeling) has contributed significantly to our understanding of these aspects. Here, water typically simulates liquid metal. Transparent perspex or glass vessels allow flow visualization. Similarity criteria have been employed to various extents.

A quantitative approach in the area of fluid flow, mixing, and mass transfer is based on fluid mechanics—especially as related to turbulent flow. Such computations involve computer-oriented numerical methods. Considerable advances have been made in this direction—so much so that these are being employed for interpretation of results, design, and process prediction.

1.4 PROCESS CONTROL

A variety of process control measures must be adopted if desirable benefits are to be obtained from secondary steelmaking. It is neither possible nor necessary to list all these. Only some will be briefly mentioned below in view of their special significance.

1.4.1 IMMERSION OXYGEN SENSOR

Dissolved oxygen in molten steel is a key scientific as well as quality parameter in secondary steelmaking. Its measurement has been possible due to development of immersion oxygen sensor over the last two decades or so. It is actually an oxygen concentration cell with a solid electrolyte (typically $\text{ZrO}_2 + \text{MgO}$ or $\text{ZrO}_2 + \text{CaO}$ variety). The EMF of the cell allows estimation of dissolved oxygen content through thermodynamic relations. Since the signal is electrical and obtained within 15 s of immersion, it is widely used to measure and control oxygen in molten steel. Through thermodynamic relations, it allows us also to know the soluble aluminum content of steel, which again is another valuable piece of information that steelmakers desire.

An immersion oxygen sensor has also been widely employed in a variety of scientific and technological investigations related to deoxidation reactions and behavior of oxygen at different stages of steelmaking. The pioneering contribution of Kiukkola and Wagner (1956), who first set up such a cell for thermodynamic measurements in laboratory, is to be recognized. Iwase and McLean⁸ have reviewed sensors for iron and steelmaking. It may be noted that immersion electrochemical sensors for other elements, such as silicon and phosphorus, are being developed but are essentially based on oxygen sensors.

1.4.2 SOME OTHER PROCESS CONTROL MEASURES

Gases such as oxygen and nitrogen are picked up from surrounding air during teeming and pouring. This can significantly increase gas contents in liquid steel. Unless this is prevented, most secondary steelmaking operations will not provide any benefit. For continuous casting, the use of either a *submerged nozzle* or shrouding of the nozzle by inert gas is the solution. For ingot casting, this is difficult to practice; in this case, management of teeming stream is the strategy.

For efficient deoxidation, synthetic slag treatment, and injection processes, it is essential to prevent too much slag from primary steelmaking furnaces from being carried over into ladles. All steelmakers know the associated difficulties if we wish to avoid lots of metal being left out untapped. Therefore, through considerable efforts, significant advances have been made in techniques of tapping with a very low quantity of slag. It is then modified by suitable additions for further processing.

In traditional ladles, refractory lined stoppers were employed for flow control during teeming through the nozzle. A major development has been *slide gate*, which is superior as a flow control device.

The traditional method of addition of aluminum to liquid steel as ingots or shots makes the efficiency of aluminum deoxidation poor as well as irreproducible, leading to serious control problems. The technology of mechanized feeding of aluminum wire is a significant improvement in this connection. Today, many plants have facilities for feeding wires consisting of Ca or CaSi powders clad in steel as well. This is an alternative to the injection of these powders into the melt by injection metallurgy techniques.

Fruehan⁹ has reviewed some of these topics in a concise fashion. Of course, advances in instrumentation as well as the use of computers have contributed significantly, as in all other fields. The modern installations employ extensive computer control. Increasing efforts are being made to employ software based on mathematical models, as well as expert control systems by application of artificial intelligence techniques. The review by Bozenhardt and Shafer provides some information.¹⁰

Good process control is not possible without fast and reliable chemical analysis techniques. There have been considerable advances in this direction. Emphasis is also being given to in-situ analysis without the need of transferring samples to a separate analytical unit. These advances are being utilized not only in secondary steelmaking but in other areas as well.

Stirring is an integral part of secondary steelmaking. It is done primarily by gas purging. However, *electromagnetic stirring* is an alternative. Electromagnetic (EM) stirring during induction furnace melting of steel has been known from the beginning of 20th century. A major application of EM stirring from the 1970s was in continuous casting. EM devices are also being employed increasingly in recent years in the secondary steelmaking area not only for stirring, but also for flow control, slag control, etc. This offers many advantages, including flexibility in the nature and intensity of fluid motion.

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