On the Removal of Non-Metallic Inclusions from Molten Steel through Filtration

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May 1990

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the Degree of Master of Engineering

Abstract

Non-metallic inclusions in steel such as alumina, silicates, etc. are detrimental to many steel properties. Elimination of these inclusions has long been a major target in steelmaking.

In this investigation, attempts have been made to remove these non-metallic inclusions by passing the liquid steel through a ceramic filter. It was found that this approach is very effective for removing solid non-wetting inclusions such as alumina. It appeared that liquid silicates could also be removed to some degree.

Résumé

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La présence dans l'acier, d'inclusions telles que l'alumine et les silicates etc, est néfaste pour plusieurs des propriétés de l'acier. Depuis longtemps, l'élimination de ces inclusions a été un objectif important pour l'industrie sidérurgique.

Dans le cadre de cette étude, il a été tenté d'éliminer ces inclusions nonmétalliques en faisant passer l'acier liquide à travers un filtre de céramique. Il a été démontré que cette approche est très efficace pour extraire les inclusions solides non-mouillantes. Il semble que, quant à elles, les silices liquides pourraient être aussi extraites en partie.

Acknowledgements

The author wishes to express his gratitude to his supervisor, Professor R. I. L. Guthrie for his guidance and support, and to Dr J. Herbertson for BHP's sponsoring of the work and provision of funding. The author also wishes to thank Robert Paquette, the furnace technician, who helped to carry out the liquid steel filtration experiments.

The author also wishes to thank Frank Sebo, the lab technician, François Dallaire and Vivian Lee, research assistants in the McGill Metalls Processing Center for their assistance in carrying out the water modelling experiments.

Acknowledgements are also due to Helen Campbell, a SEM expert, for her assistance in SEM analysis; M. Riendeau, for the chemical analyses; W. Van de Vrande, DOFASCO, and Roger Mc-Callum, quality control supervisor in IVACO Mills, for their assistance in total oxygen analyses; Guangbi Chen, a visiting scientist, Selçuk Kuyucak, Hyoung Chul Lee, G. Kamal, fellow students, Nobuhiro Kurokawa, research assistant, Kaike Cai, a visiting professor for useful discussions; and Ramani Sankaranarayanan, a fellow student, for his help in photo taking.

Finally, the author wishes to thank Janet Peace, Research Administrator, for her consideration about the author's health.

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Chapter 1

Introduction

1.1 The Challenge

Facing a stringent demand for better quality steels, metallurgists and steelmakers have, for many years, been trying to produce cleaner steel, i.e. to remove harmful impurities such as S, P, O, N, C and H as well as other residual elements such as Cu, Sn, Pb, Sb, As etc.. Good progress has been made and various steelmaking and refining techniques have been developed. Although Japanese steelmaking companies (e.g. Sumitomo) have claimed that steel as clean as 10 ppm total oxygen can be produced after all necessary secondary steelmaking processes such as shown in Figure 1.1 [1] have been employed, their merit hardly justify the cost and efforts involved except for some special applications.

Oxygen is removed by condensing it through reactions with dissolved aluminum and silicon to oxides of alumina and silica. The alumina inclusions within the liquid steel tend to cluster and can block the metering nozzle used in tundishes. Currently, the commonly used remedy for this is to treat aluminum killed melts

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Figure 1.1: Processes used to produce clean steel [1].

with calcium silicide, $CaSi_2$, or other calcium bearing alloy additions, so as to change alumina clusters into liquid calcium aluminates. Despite this treatment, a success rate of only 65% could be achieved in IVACO Rolling Mills[2], where 0.01 m diameter nozzles meter steel into a four strand continuous casting machine. While the larger metering nozzles of 0.02-0.03 m diameter for supplying liquid steel to large slab caster systems are less prone to complete blockage during a cast, continuous-continuous casting (i.e. back to back casting) runs into such problems, so that the battle to control and produce clean steels continues on all fronts!

1.2 Filtration Technology in Metal Processing

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Success in the development of filtration technology for the aluminium industries has encouraged steelmakers to attempt equivalent operations. Evidently, removing the nonmetallic inclusions from molten steel through filtration can provide an on-line treatment without an additional process vessel. What is needed is a little modification of existing metallurgical equipment, e.g. tundishes etc.. This is a great advantage over other refining processes, such as lime-Ca-Si injection into the teeming ladle.

Filtration technology has been available in the aluminum industries since the early 1970's. Table 1.1 lists some in-line treatment systems in aluminum industries[3].

The pioneers in the development of in-line melt treatment sys-

			Impuriti	es Renoved
System	Corpany	Description	Scluble	Inclusion
181	Alcoa	Tabular alumina aggrenate bed	No	Yes
IKR Filter	Tokyo Kakyu Razal	Tubes of a rigid ceramic material with sized pores	No	Yes
Rigid Media	Metaullica Systems	Tubes of a rigid ceramic material with sized pores	No	les
SELEE®	Consolidated Aluminum	Reficulated coromic foam filter	No	Yes
FILD	British Aluminium	Filter bed of trbular alumines bails+coated with salt, counter-current flow of gas bubbles generated by a perforated tube and molten salt flux cover over melt	163)es
469	Alcoa	Dual filter beds of tabular alumina balls and aggregate with counter-current flow of gas bubbles generated by porous media	Yes	Yes
DUF1	Alusuisse	Filter bed of petroleum coke with counter current flow of gas bubbles generated by porous media	Yes)es
SNIF	Union Carbide	Reactor chamber where small gas bubbles are generated and intimately mixed in the melt using a spinning notice with stator (fiomation process)	Yes	P•
62 2	Alcoa	Reactor chamber where fine bubbles of gas are generated and intimately mixed in the melt with a rotary vane disperset	tes	P۹
ALPUR	Pechiney	Reactor chamber where fine bubbles of gas are generated and intimately mixed in the melt using a rotary vane disperser	Yes	₽∙
HINT.	Consolidated Aluminum	Cylindrical reactor chamber where fine gas bubbles are generated by high-prossure nozzles and are dispersed by the swirling action of the metal which is then filtered through ceramic foam of SELEE® structure	Yes	Yes

Table 1.1: Commercially available in-line melt treatment systems [3].

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* No positive filtration but partial removal of inclusions by flotation

tems were Bromdyke and McDonald. Brondyke[4] developed deep bed filtration utilizing a bed of sized tabular alumina aggregate. McDonald[5] used a porous ceramic body (consisting of an inert aggregate, bonded with a glass resistant to molten aluminum) as a filtration medium to remove inclusions. The development of the ceramic foam filter by Dore, Yarwood et al[6][7][8][9] marked a milestone in metal filtration. The ease of installment, the effectiveness of removing nonmetallic inclusions and the inexpensiveness of the ceramic foam filter have greatly expanded the applications of filtration technology in the aluminum, super alloy and foundry industries. Figures 1.2 to 1.4 [10] show some of the various filtration processes employed in the aluminum industries.

In the foundry industry, the ceramic foam filter can be installed into the runner of the sand cavity, providing a last moment barrier which helps prevent dross and inclusions from entering the final products. Figure 1.5 shows the placement of a ceramic foam filter in a cope and drag sand mold. With replacement of ceramic foam filters for steel screens in a metal runner system, Mollard, et al reported that the reject factor dropped from 20% to 10% in casting rocket engine components and a 100% need for rework to remove unacceptable surface defects in 60 castings to a no need for rework in 30 castings in casting aircraft components[11].

In the steel industry, filtration techniques are still in their infancy. Many investigations have been performed using different filtering media. Happ and Frohberg[12] used a packed bed consisting of 0.0035 to 0.005 m diameter balls of alumina, mullite, and magnesia to filter low carbon steel. They reported that

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Figure 1.2: (a) Reverberatory well system with hoist attached to vessel to provide back-flushing action. (b) Vessel installed at Pride Cast Metals, Inc. with a $16^{\circ} \times 22^{\circ}$ (0.41 m×0.56 m) ladling area. Note clean metal in vessel and dross in surrounding well [10].



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Figure 1.3: (a) Stationary crucible well filter vessel. (b) Static holding well system. Filters are back-flushed by manually raising vessel in the well [10].



Figure 1.4: (a) Filtered crucible for melting/holding nonferrous alloys. (b) Crucible melter, top view of 600 lb.(272 kg) unit. Note filter mounted in paddle [10].



Figure 1.5: Horizontal placement of ceramic foam filter in cope and drag sand mold [11].

alumina bearing deoxidation products and silicate inclusions could be removed. Ali, Mutharasan and Apelian[13] used a square celled monolithic alumina filter(400 cells per square inch) to filter low carbon steel killed with aluminum. They reported that inclusions greater than 2.5 μm were totally removed [chihashi et al[14]] used a multi-hole filter of alumina(the hole diameters ranged from 2 to 5 mm) to filter silicon-aluminum killed steel. Their results showed 30-60% reduction levels in total oxygen within the filtered melt. Aubrey et al[15] used alumina foam filters to filter aluminum killed steel. Their results showed 46-97% reduction in total oxygen. Wieser[16] filtered aluminum-killed carbon steels with alumina foam filters in tundishes, observing a 30% to 50% reduction in total oxygen. D. Apelian et al[17] went on to filter manganese-silicon killed melts using Al_2O_3 and ZrO_2 foam filters. They found that total oxygens were reduced by 11-43 3% following filtration.

1.3 This Investigation

Previous investigations have focused mainly on the influences of the filter media and metal flow rates on filtration efficiency. This investigation has focussed more on the inclusion side, such as the influences of inclusion types and size distributions on the filtration efficiency, and the mechanisms of inclusion removal A further objective of this investigation was to examine the performance of the reticulated zirconia filters in molten steel applications in order to provide information for a high speed thin strip casting project wherein molten steel is to be delivered through a nozzle made of reticulated ceramic filter materials to a freezing moving substrate.

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Chapter 2

Non-Metallic Inclusions in Steel

2.1 Origin of Non-Metallic Inclusions in Steel

Non-metallic inclusions are an inevitable part of steel. Strictly speaking, steel is a highly complex matrix, consisting of iron phase (alloyed mainly with carbon) and a variety of non-metallic phases (mainly oxides, sulphides and nitrides). These inclusions can originate indigeneously as a result of melt processing operations (e g killing steels by dissolving Si or Al into the melt and precipitating oxides inclusions) or as a result of precipitation during solidification. Alternately, inclusions of an exogenous nature can originate from entrained slags and/or spalling or eroded refractories with which the molten steel contacts.

2.1.1 Formation of Inclusions during the Oxidation Period of Steelmaking

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Non-metallic inclusions begin to nucleate the moment that oxidation of molten iron commences. In this period, impurities such as silicon, manganese, etc. within the melt are oxidized to oxides, while dissolved carbon is oxidized to CO or CO_2 .

$$2Fe + O_2 = 2FeO \tag{2.1}$$

$$2FeO + Si = SiO_2 + 2Fe \tag{2.2}$$

$$FeO + Mn = MnO + Fe \tag{2.3}$$

$$SiO_2 + MnO = MnO.SiO_2 \tag{2.4}$$

$$FeO + C = Fe + CO \tag{2.5}$$

Most of these inclusions, e.g., manganese silicates, are eliminated into the slag due to their buoyancy and the strong mixing action created by the escape of CO from the molten steel. Those inclusions/oxides remaining will change their composition during the subsequent stages of steelmaking process. This is especially true in open-hearth and electric arc furnace steelmaking processes. The final composition and the characteristics of these inclusions depend upon specific melts and steelmaking practices. In this regard, Pickering's work[18] repesents a systematic investigation to which interested readers are referred.

Because most of the inclusions formed at the steelmaking stage can be eliminated, as mentioned above, they will not contribute much to the problem of inclusions in steel. That is also why they have been almost completely neglected in investigations into the origins of non-metallic inclusions. The author has included this section here only for reason of completeness.

2.1.2 Formation of Inclusions during Deoxidation

Raw liquid steel contains certain amounts of dissolved oxygen, depending on the composition of the steel concerned. The most influential element controlling the level of oxygen is dissolved carbon; the lower the carbon, the higher is the level of dissolved oxygen, [O], following pneumatic refining operation. In pure iron, the maximum dissolved oxygen is about 0.16 weight percent at $1524^{\circ}C[19]$, at which the eutectic reaction takes place:

$$2Fe_{(l)} + [O] = Fe_{(s)} + FeO_{(l)}$$
(2.6)

The following equation represents the solubility of oxygen in molten iron equilibrium with iron oxide as a function of temperature[20]:

$$\log[0\%] = -\frac{6320}{T} + 2.734 \tag{2.7}$$



Figure 2.1: FeO inclusions in non-deoxidized steel, $1000 \times$.

However, in solid iron or steel, the solubility of oxygen is essentially zero with increasing purity and lattice perfection of the metal[21]. As a result, any dissolved oxygen in liquid steel would be precipitated out as FeO inclusions during solidification if the steel were not deoxidized. Figure 2.1 shows spherical inclusions of FeO.

The dissolved oxygen in molten steel can be decreased by adding elements to the steel which have a higher affinity for oxygen than iron. Commonly used elements include manganese, silicon and aluminum. Silicon together with manganese are usually added



Figure 2.2: Deoxidation equilibria in liquid iron alloys at 1600°C [22].

to a bath of molten steel in the form of ferroalloys such as Fe-Si, FeMn, Fe-Mn. The deoxidizing power of these elements range from manganese as the weakest to aluminum as the strongest (see Figure 2.2) [22].

Deoxidation is normally carried out during tapping, at which time deoxidizers are added to the ladle. (mold deoxidation is also practised in the case of ingot casting). Deoxidation reactions take place as soon as additions melt and dissolve in the liquid steel. The result is the formation of millions of inclusions per kg of melt. The type and the whereabout of these inclusions depend on specific deoxidation practices.

Inclusions also form during cooling of liquid steel and solidification. Because the solubility of oxygen decreases as the temperature of steel decreases, the reaction: $[M] + [O] = M_x O_{y(l,s)}$ will proceed towards the right at each given temperature until equilibrium is established. These inclusions will remain in steel as there is no way for them to separate from the solid steel unless some additional remelting refining process such as electric-slag remelting process is employed.

The types and characteristics of inclusions formed during deoxidation, naturally, depend on a specific steelmaking practice and extensive investigations have been carried out in the past few decades.

(1). Si/Mn deoxidation

Both manganess and silicon are weak deoxidizers. They are usually used in conjunction to produce rimmed and capped steel in ingot casting steelmaking practice. Even though the deoxidizing power of manganese is much weaker than that of silicon, if the two elements are used together, the resultant deoxidation effect becomes much stronger than either of the two elements used alone. This is because the deoxidation product, SiO_2 , can dissolve in other oxides, MnO, thereby reducing the activities of their deoxidation products. Figure 2.3[23] shows the equilibrium data for simultaneous deoxidation with silicon and manganese at 1600°C.



Figure 2.3: Equilibrium relations for deoxidation of steel with silicon and manganese at 1600°C [23].

The deoxidation products can be pure silica or manganese silicate, depending on the activities of the oxides and the ratio of $[Si\%]/[Mn\%]^2$ in steel deduced from the equilibrium constant for the reaction:

$$[Si] + 2MnO \rightleftharpoons 2[Mn] + SiO_2 \tag{2.8}$$

$$K = \frac{[Mn\%]^2(a_{SiO_2})}{[Si\%](a_{MnO})^2} = 118.$$
(2.9)

at 1600°C [24]

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According to Turkdogan, there is a critical ratio: $[SiO_2\%]/[Mn\%]^2$ above which only solid silica forms as the deoxidation product, for which the activity of silica, $a_{SiO_2} = 1$. As Figure 2.4 [25] indicates, if the composition of steel, for a given



Figure 2.4: Critical silicon and manganese contents of iron in equilibrium with silica saturated with almost pure manganese silsicate [25].

temperature, lies above the curve, manganese does not participate in the deoxidation reaction, and only solid silica is formed. Otherwise, the deoxidation product is in the form of manganese silicate inclusions.

(2). Al/Si/Mn deoxidation

This deoxidation practice is mainly employed to produce semikilled steels, the residual dissolved oxygen in the range of 30 to 60 ppm is obtained by simultaneous deoxidation with Al, Si and Mn[26]. The deoxidation products can be corundum ($\alpha - Al_2O_3$), mullite ($3Al_2O_3.2SiO_2$), galaxite ($MnO.Al_2O_3$) or liquid aluminosilicate depending on the concentration of the three elements dissolved in liquid steel. Fujisawa and Sakao[27] have calculated the equilibrium relations for this complex deoxidation from the free energy data for the oxides and the activities of the constituent ox-

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Figure 2.5: Equilibrium relations for deoxidation of liquid steel with Al-Si-Mn for %Si + %Mn = 1 (wt%) [27].

ides in the $MnO - SiO_2 - Al_2O_3$ system. Figure 2.5[27] shows their calculated equilibrium relations for 1550°C and 1650°C under the condition: Si% + Mn% = 1. The equilibrium oxygen activity as a function of aluminum content at different ratio of [Mn%]/[Si%] in liquid steel at 1550°C is shown in Figure 2.6[27].

(3). Aluminum - lime deoxidation

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Aluminum is a strong deoxidizer and usually used to produce killed steel. The deoxidation constant, $k = [Al\%]^2 \times [O\%]^3$, from the



Figure 2.6: Equilibrium oxygen activity as a function of %Al and Mn/%Si ratio in liquid steel at 1550°C [27].

reaction: $2[Al] + 3[O] = Al_2O_{3(s)}$, for aluminum and oxygen in solution in the steel phase has been determined to be about 10^{-14} [28] at 1600°C. The deoxidation products are mainly $\alpha - Al_2O_3$ (corundum) when the soluble Al exceeds 0.005%. Below this value iron-manganese aluminates, $(FeO, MnO).Al_2O_3$ will form[28]. These solid alumina particles, with a size range of 1-5 μm , tend to form clusters in molten steel due to the high interfacial tension between alumina and liquid steel. Although studies have shown that these inclusions have a higher floating out rate than predicted according to Stokes' Law and that most of the primary formed alumina clusters can separate from steel, those still remaining and those formed during the cooling of liquid steel are quite sufficient to block tundish nozzles in continuous casting, particularly the smaller diameter nozzles associated with billet casting operations.

When burnt lime is added together with aluminum, the deoxidation products will become molten calcium aluminates provided the proportions of the two are appropriate:

$$12CaO + 14[Al] + 21[O] = 12CaO.7Al_2O_3$$
(2.10)

Figure 2.7 [29] shows the $CaO - Al_2O_3$ system. It is to be noted that molten deoxidation products improve the effectiveness of the deoxidation; for instance, the steel deoxidized with aluminum alone to a level of 4 ppm oxygen (activity) will contain 0.02% Al as residual aluminum in solution, while with the mixture of aluminum and lime deoxidation, forming lime-saturated calcium aluminates liquid reaction product, the same level of deoxidation will be achieved with only 0.001% Al left in solution[24].



Figure 2.7: Phase diagram for the $CaO - Al_2O_3$ system [29].

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Molten inclusions are also desirable from hydrodynamic point of view since they tend to rise more rapidly out of a steel melt and clearly separate. Similarly, being liquid they are less inclined to block up metering nozzles.

2.1.3 Formation of Inclusions during Desulphurization

The presence of excess sulphur in steel can cause hot-shortness. This usually occurs within the temperature range 900°C to 1100°C. Figure 2.8 [20] shows the iron side of Fe-S phase diagram. It can be predicted that pure iron-sulphur alloys containing less than 100 ppm S should not be subject to hot-shortness during entire hot-working operation. On the other hand, if the sulphur content exceeds this value, a liquid phase will form along grain boundaries as the temperature of steel falls below 1100°C. This will cause weakness in the steel (hot-shortness) during hot rolling operations. If oxygen is present, a liquid oxy-sulphide will form in γ -iron at lower sulphur contents and lower temperatures. To avoid this, sulphur must be removed to a certain degree depending on the content of other elements (mainly Mn and O) in the melt.

Sulphur can be removed by forming highly basic and reducing slags according to the following reaction:

$$CaO + FeS = CaS + FeO \tag{2.11}$$

Most of the calcium sulphide inclusions can be absorbed into the slag, while the remaining may react or join other types of in-



Figure 2.8: Iron rich side of Fe-S phase diagram [20].

clusions, forming complex or multiphase inclusions. The presence of [O] will hinder desulphurization since calcium has a stronger affinity for oxygen than sulphur. The following reaction therefore tends to occur:

$$CaS + [O]_{Fe} \rightleftharpoons CaO + [S]_{Fe}$$
 (2.12)

$$K = \frac{a_S}{a_O} \tag{2.13}$$

If a_0 is high, a_S must be high in order to maintain K constant for a given temperature. K = 28 at 1600°C [30]. [O] can be controlled by adjusting [AI].

The presence of manganese can avoid hot-shortness by the formation of manganese sulphides which usually form along grain boundaries or precipitate onto existing inclusions during solidification.

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During calcium treatment with a synthetic flux, e.g. calcium aluminate, sulphur can dissolve into aluminates saturated with calcium [31]

2.1.4 Effects of Kinetics on the Formation of Inclusions

In practice, the final form of inclusions is far more complicated than that suggested by the forgoing text. This is because the kinetics involved in the reaction of inclusion formation and various parameters of steelmaking affect the type, size distribution and final destination of inclusions.

In general, the formation of inclusions in liquid steel, like any other new phase formation, includes nucleation and subsequent growth by diffusion. Homogeneous nucleation will result in inclusions with a smaller and more or less uniform size compared to those formed under heterogeneous nucleation. Nucleation in liquids requires certain supersaturation, the magnitude of which largely depends on the specific free interfacial energy at the nucleus/liquid interface. Studies have concluded that homogeneous nucleation of oxides of strong deoxidizing elements such as Al, Ti, Zr, etc. is possible[32]. Heterogeneous nucleation needs substrates (impurities) on which the new phase (inclusions) precipitate. It is believed that inclusions of weaker deoxidizers, such as Si, Mn etc. form by heterogeneous nucleation. Weak deoxidizers' ferroalloys usually contain a trace of Ca, AI, Ti, etc.. These elements have a strong affinity for oxygen. Thus they will preferentially react with oxygen, forming nuclei by homogeneous nucleation on which the weak deoxidizer's oxides can precipitate. It has been observed that inclusions formed in Si-killed steel contain a trace of Ca, Al, and Ti (see Figure 4.43).

Once the nucleation process finishes, the nuclei will grow by precipitation through diffusion and/or by the physical process of coalescence or agglomeration or aggregation as a result of collisions of inclusions. Turkdogan has shown that the number of nuclei has pronounced effect on the growth of oxides inclusions. The more the nuclei, the smaller the size of inclusions. Figure 2.9[25] shows the effect of number of nuclei in melt on the rate of growth of oxides as they rise in the melt, for $[\% O_i] = 0.05$ and $[\% O_e]^1$ =0. According to Turkdogan, there is a critical value of nuclei, Z_m ; if the number, Z, is less than a critical value, Z_m , inclusions will grow large enough to float out of the melt quickly, leaving behind a high residual oxygen level in the melt. However, if the number of nuclei, Z, is greater than Z_m , inclusions will attain their full growth in a relatively short period of time, i.e. the residual oxygen in solution approaches equilibrium. In this case, the inclusions are small in size, and hence their separation from the melt takes a longer time.

The growth of inclusions is very fast. According to Bergh's study[21], for a melt of 400 ppm dissolved oxygen killed by silicon, the mean distance between inclusions would be about 30-35 μm if the mean particle diameter was about 5 μm . If such a particle had grown by diffusion, the time for this growth was about 0.5 seconds.

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¹i and e denote initial and equilibrium respectively



Figure 2.9: Effect of number of nuclei in melt on the rate of growth of oxide inclusions [25].

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In view of the elimination of inclusions, some researchers[32] have suggested that steelmaking practice should be conducted so that it promote the growth of inclusions to such a size that they are able to float out of the melt. This could be done by introducing artificial nuclei into the melt. However, it should be borne in mind that the rate of separation of inclusions does not merely depend on Stokes' Law. Interfacial phenomena between inclusions and molten steel also play a role, in that slightly wetted inclusions are probably less readily ejected at a melt/slag interface than more strongly ferrophobic inclusions such as alumina.

Figure 2.10[33] shows the process of the growth of silica inclusions during deoxidation.



Figure 2.10: Characteristic process of growth of silica inclusions during deoxidation [33].

2.1.5 Inclusions from Slag and Refractories

Aside from indigenous sources of inclusions, i.e. from the reactions in steelmaking, other major sources of inclusions (termed exogenous) include slags and refractories. Inclusions from these sources are characterized by their sporadic occurrence, irregular shape and large size. However, there is no clear distinction between exogenous and indigenous inclusions. Small particles of slag or refractories may act as nuclei for the precipitation of indigenous inclusions. Reactions may take place between indigenous inclusions and exogenous inclusions. As a result, the final forms of inclusions met with in a solid steel matrix are usually very complex; and often multicomponent and/or multiphase.

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Slag can be entrained into steel during tapping or teeming, resulting in exogenous inclusions[34]. In general, these inclusions are characterized by the presence of calcium. Refractories, with which molten steel is in contact during the whole steelmaking process can be eroded or corroded and thus entrained into steel. These inclusions usually contain traces of MgO, TiO_2 and K_2O [35].

The compositions of inclusions arising from both slag and refractories are usually different from those of the original slag and refractories. This is because these exogenous particles interact with indigenous inclusions from the moment they enter the molten steel and therefore continuously change their composition.

2.1.6 Inclusions from Reoxidation

Reoxidation means that a deoxidized melt (low in dissolved oxygen) picks up oxygen as a result of its exposure to the atmosphere during the processing of molten steel. The increased oxygen will react with residual deoxidizer elements (solutes) within the melt to form inclusions which have less chance to separate than those formed earlier during deoxidation. Furthermore, increased dissolved oxygen (if there is insufficent time for the deoxidation reactions to reach equilibrium) will worsen segregation during solidification due to the enrichment of oxygen in the liquid phase at the solidification front.

2.2 The Type, Number and Size Distribution of Inclusions

2.2.1 Types of Inclusions

The types of inclusions in steel are mainly oxides, sulphides and nitrides. As mentioned earlier, these particles can exist in steel as pure oxides such as Al_2O_3 (corundum), as single phase multicomponent, or multiphase inclusions, depending on specific steelmaking practices. Commonly encountered oxides are FeO, Al_2O_3 , SiO_2 , MnO, MgO, Cr_2O_3 , TiO_2 , CaO, ZrO_2 etc.. Except for Al_2O_3 , all others usually exist in the form of multicomponent and/or multiphase particles in normal steelmaking practice. Figure 2.11 provides EDS spectra of inclusions in IVACO steel samples.

Commonly encountered sulphides are FeS, CaS, MnS, MgS etc.. Based on thermodynamic analysis, sulphides can not form if dissolved oxygen levels are very high within the steel bath. When the oxygen level is low, sulphides will form, as is the case in desulphurization of hot metal (pig iron). Based on the analysis of the [Ca]-[S]-[O]-[Fe] system, Shalimov[31] worked out an equilibrium relationship for the activities of oxygen and sulphur:

$$\log a_o = -\frac{5150}{T} + 1.195 + \log a_s \tag{2.14}$$

Ca, Mg, rare earth sulphides, precipitating sooner than (Fe,Mn)S, while the steel cools, are solid at their moment of formation. They are small and well dispersed in the iron matrix [30]. MnS usually precipitates out during solidification on inclusions already existing ł

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within the melt and/or along grain boundaries. When Ca, Mg and rare earths exist, they can be substituted wholly or partly for MnS and consequently modify the morphology and characteristics of MnS. Because these mixed sulphides are harder and less deformable than manganese sulphides, the substitution gives the treated steel better isotropy with respect to mechanical properties than steels which only contain (Fe,Mn)S [30].

The commonly encountered nitrides are TiN, AIN, ZrN, etc.. As with sulphides, nitrides can only form when oxygen levels are low (or low in microlocations) because oxygen has a higher affinity for Ti, AI and Zr than does nitrogen and sulphur. Figure 2.12 [36] shows the changes of free energies, $\Delta(\Delta G)$, for the formation of sulphides or nitrides from their corresponding oxides. As can be seen, except for K_2S and Na_2S , all other sulphides and nitrides are less stable than their corresponding oxides. However, in practice, nitrides may form even when the overall oxygen content is higher than the value necessary for their formation. This can be attributed to micro inhomogeneities in melt composition. In some micro-locations, the activities of nitrogen may be high enough to meet the thermodynamic conditions needed for their formation. Generally, however nitrides are largely precipitated out along grain boundaries during solidification².

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²This accounts for the reason for Al being able to restrict the grain coarsening of Austenite.



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Figure 2.12: Standard free energy changes for the formation of sulphides, nitrides from their corresponding oxides under standard state conditions [36].

Table	2.1:	Chemical	composition	of six	IVACO	samples
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Heat Code	Chemistry											
	С	Mn	P	S	Si	Cu	Ni	Cr	Mo	Sn	Al	Ca
B25728	0 35	0.82	0 0 0 7	0 01 2	0 21	019	0.08	0.06	0 02	0 10	0 004	
B25857	018	074	0 011	0 002	0 20	013	0 07	0.06	0 03	0 005	0 014	
A24830	017	079	0 0 0 8	0 01 5	0 20	0 1 0	0 06	0.04	0 0 2	0 007	0 0 0 0	
A24671	016	067	0 0 0 8	0 0 0 4	0 18	011	0 06	0.05	0 0 2	0 005	0 0 2 5	0 00 33
A24430	0.18	070	0 0 0 7	0 0 0 3	018	011	0 06	0 05	0 0 2	0 004	0 01 3	
B25724	0 20	0 82	0 0 0 9	0 002	0 17	0 1 1	0.06	0.04	0 0 2	0 003	0 01 2	0 0020

2.2.2 Number of Inclusions

The typical numbers of inclusions in steel are remarkably large. Calculations made by Bergh has shown that there were about 2.5×10^7 inclusions larger than 2.5 μm per cubic cm at an oxygen content of 400 ppm in a silicon-killed melt[21]. The author's analysis of some silicon-killed samples for IVACO showed these contained about 10^8 inclusions per cubic cm with a size range of 1-5 μm . Figure 2.13 shows the number and size distributions of inclusions in 6 samples. Table 2.1 lists the corresponding chemical compositions.

2.2.3 Size Distributions of Inclusions in Steel

The sizes of inclusions can range from the smallest of about 300 Å[37] to about a few hundred microns. The larger inclusions are usually exogenously entrained slag or refractories or agglomerates of indigenous inclusions. The size of these inclusions can sometimes be as large as few mm — visible with naked eye.



Figure 2.13: Number and size distribution of inclusions in IVACO steels.

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2.3 Harmful Effects of Non-Metallic Inclusions on Steel Properties

Non-metallic inclusions existing in a steel matrix as a second phase with totally different properties from that of steel inevitably affect the mechanical properties of steel. However, quantitative evaluation can be rather complex. Different types of inclusions or the same type with different parameters may have different effects on certain properties. Some parameters may act in favor of some properties of the steel but may be harmful to other properties in the same time.

2.3.1 Deformability of Inclusions

The major parameter influencing steel properties is the deformability or plasticity of the various inclusions. If the plasticity of an inclusion is different from that of steel during all steelworking operations—rolling, forging, forming etc., it will be a potential source of further defects in the finished steel products. For instance, if, during steel deformation, the non-metallic inclusions lengthen less than the steel, stresses will be built up which may lead to cracking or other discontinuities between the inclusions and the steel phase. Figure 2.14[38] shows the formation of a conical gap at the steel/inclusion interface after rolling. On the other hand, if the plasticity of the non-metallic inclusions is comparable to that of steel, the inclusions will lengthen in the same way as the steel, the binding forces at the inclusion/steel interface will not be broken and no discontinuities will occur. In addition, this type of inclusion may be advantageous for some steel

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Figure 2.14: Conical gaps at a calcium aluminate inclusion/steel interface [38].

properties such as machinability by their ability to participate in the plastic flow of the steel phase (e.g. MnS)as already noted. However, this type of inclusion is harmful to the isotropic properties by forming stringers or plates along the rolling direction, thus creating line defects. Also, visual defects on surface are unacceptable for exposed applications.

Thanks to the work done by Pickering, Malkiewicz and Rudnik[38], a relative measurement of an inclusion's deformability has been developed, ν being the index of deformability:

$$\nu = \frac{\epsilon_i}{\epsilon_s} = \frac{2\ln\lambda}{3\ln h} \tag{2.15}$$

where $\epsilon_i = \ln \lambda = \ln \frac{b}{a}$ is a measure of the true elongation of the inclusions, $\epsilon_s = \frac{2}{3} \ln h = \frac{2}{3} \ln \frac{F_0}{F}$ is an expression for the true elongation of the steel, where b, a are the length and the width of a cross section of an inclusion parallel to the rolling direction;

 F_0 is the initial cross-section of the steel specimen and F is the cross-section of the specimen after working the steel. The index of deformability, ν , ranges from 0, for non-deformable inclusions, to unity for inclusions which elongate equally with the steel. (Even values greater than unity are possible for inclusions which elongate to a greater degree than steel).

The deformabilities of inclusions not only depend on the chemical compositions of the inclusions, but also on working temperatures, rates and degrees of deformation, and steel composition.

In general, corundum $(M_2O_3, e.g. Al_2O_3)$ and spinel $(MO.M_2O_3, e.g., CaO.Al_2O_3)$ type inclusions are hard and undeformable at normal working temperatures for steel. The deformability index, ν , of these inclusions is therefore 0.

Silicates are brittle at lower temperatures but deformable at higher temperatures, depending on their composition. Pure silica is generally brittle even at higher temperatures. An increase in SiO_2 content in silicates will decrease the deformability of the silicates, while an increase of MnO content will increase their deformability.

Sulphide inclusions can deform plastically, independent of temperature, in the range of $-80^{\circ}C$ - $1260^{\circ}C$ [38]. In this range, their values of ν are about 1.

Calcium aluminates in the form of $CaO.Al_2O_3$, $CaO.2Al_2O_3$ and $CaO.6Al_2O_3$ are hard and undeformable, their deformability index, ν , is 0. However, inclusions belonging to $CaO - SiO_2 -$ Al_2O_3 system can deform plastically over a comparatively wide temperature range[38]

2.3.2 Effect of Inclusions on Fatigue Properties

Inclusions with a low deformability index are harmful to steel's fatigue properties. These inclusions are unable to transmit stresses existing in the steel matrix. As a result, stresses around these inclusions will be built-up and cracks may be initiated in these locations, leading to fatigue failure during the service of a steel component. Figure 2.15[39] shows a fatigue failure due to a large inclusion. Also as mentioned earlier, during the working or forming of the steel, cavities or microcracks may be created at the inclusion/steel interfaces or within the inclusion itself. These defects will be the origin of further defects leading to fatigue failure. The tendency for fatigue failure increases when the size and the number of these inclusions become greater.

However, inclusions with a high index of deformability have little harmful effect on steel's fatigue properties.

2.3.3 Effect of Inclusions on the Isotropic Properties of Steel

As mentioned earlier, deformable inclusions such as MnS and silicates will form stringers or plates during rolling. This will lead to anisotropy, which will give rise to the well known decreases in through-thickness ductility in plates of structural steel and is



Figure 2.15: Fatigue failure from a large Ca inclusion (10 mm) [39].

also related to the phenomenon of Pamellar tearing in welding[40].

2.3.4 Effect of Inclusions on Other Properties

The presence of undeformable inclusions in steel has a tendency to initiate cracks either during working or service of the steel. As a result, various properties of the steel will be impaired. Studies have shown that tensile strength and impact resistance decreases as the amount of inclusions increases (see Figure 2.16 [41]).

In addition, the presence of non-metallic inclusions will affect machinability (e.g. MnS will enhance machinability while hard alumina will shorten the life of cutting tools), surface quality, weldability, etc..



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Figure 2.16: Decreases in the elastic limit, ultimate tensile strength and ductility of in sintered iron as a result of increases in the volume fraction of Al_2O_3 inclusions (with a size range of 15-35 μm) [41].

Chapter 3

Production of Clean Steel

The ultimate objective of much of the research in steelmaking is to optimize the steekmaking process so that the steel produced can satisfy the requirements of its intended application. A knowledge of the behaviour of non-metallic inclusions serves as a basic guideline in searching for possible ways to produce cleaner steel.

3.1 Cleanness of Steel

The concept of steel cleanness is rather complicated. In general, the lower the contents of impurities (i.e. O, N, etc.), the cleaner the steel. Since large inclusions are more harmful than smaller ones, the size of inclusions must also be taken into account when an assessment of steel cleanness is made. With the same oxygen content, the steel may be regarded as clean if the inclusions are small or not clean if the inclusions are big. Therefore, for a given application, a critical size exists beyond which the inclusions are regarded as being detrimental to the application. In addition, the shape of inclusions is also an important parameter in assessing the harmfulness of the inclusions, e.g. it has been shown previously

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that dendrites or stringers will affect the transverse and isotropic properties of steel. Clearly, the criteria for different applications are different. Therefore, all the parameters: application, contents of impurities, types and size distributions of inclusions, etc. must be known before one can decide whether the steel is clean, or not.

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3.2 Optimization of Deoxidation Process

Deoxidation processes directly affect the cleanness of steel. In general, a good deoxidation practice should be one that brings the oxygen down to a minimum and leads to products of deoxidation that are either easily able to separate from the steel or are less harmful to the steel properties desired. The generally recognized practice is complex deoxidation. Since in this case, the deoxidation products are in a molten state in the liquid steel, so that the chance of their separation is higher than for solid particles (because liquid inclusions coalesce more easily to become bigger in size and consequently have a higher Stoke's rising velocity). Furthermore, the activities of the deoxidation products are reduced (< 1) as a result of the formation of complex liquid inclusions, therefore, the power of the deoxidants added will be increased relative to when they are used separately.

3.3 Secondary Steelmaking Processes

Secondary steelmaking processes are refining processes carried out in ladles, tundishes or other vessels after the molten steel leaves the primary furnace. These mainly include argon stirring, vacuum degassing, flux injection, cored wire injection and REM canister treatments. The overall objectives are: to lower the dissolved gases such as oxygen and hydrogen; to lower sulphur content; to remove non-metallic inclusions; to modify the shape of the inclusions into less harmful form and to produce special steel such as ultra-low carbon steels. Figure 3.1 [42] shows various processes and their functions.

3.3.1 Argon Stirring

Blowing argon into the ladle during reheating, alloying, deoxidation or injection refining process can aid homogenization of temperature and composition and floatation of non-metallic inclusions.

3.3.2 Vacuum Degassing Processes

The primary purpose of these processes is to remove the dissolved gases such as oxygen and hydrogen by subjecting the liquid steel to vacuum. Oxygen is removed by reaction with carbon, forming CO, according to

$$[O] + [C] = CO (3.1)$$

When the pressure is lowered to 0.01 atmosphere, the deoxidizing power of carbon becomes even stronger than Al[42]. This is also called carbon deoxidation. The same principle is used in

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Figure 3.1: Various secondary steelmaking processes and their functions [42].

producing ultra-low carbon steel.

Hydrogen in steel can cause thermal flakes, embrittlement and low ductility. Thick plate products are particularly susceptable owing to the long diffusion distances for hydrogen to migrate to the surface and escap vis-à-vis strip products. Hydrogen can be removed according to Sievert's Law:

$$[H]\% = k\sqrt{P_{H_2}} \tag{3.2}$$

where k is Sievert's constant, equal to 0.002 at 1600°C and 1 atm..

Since nitrogen tends to form stable nitrides, it is not readily removed by the degassing process[42]. Even at low oxygen levels, when the surface active effects of oxygen in limiting nitrogen desorption are much less, nitrogen removal is typically no more than 20% at most.

The most commonly used vacuum degassing process is the RH vessel. It consists of a vacuum vessel with two legs and a vacuum system. During operation, the two legs are immersed into the steel in the ladle, inert gas is introduced into one of the two legs, causing steel to rise up to the vacuum vessel and recirculate back to the ladle through the down leg. The vacuum can reach 0.3 to 0.6 Torr or even lower[42].

Recent developments have incorporated many other metallurgical features into RH process such as alloying by adding alloys through a hopper, blowing oxygen to aid decarburisation, adding

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Figure 3.2: Schematic illustration of RH-OB process [42].

synthetic flux to absorb inclusions in steel, or even reheating by blowing aluminum powder and oxygen, etc.. Figure 3.2 shows the RH-OB process.

3.3.3 Injection

Injection is a process by which synthetic flux, calcium alloys or Rare Earth Metals are injected into molten steel. Many merits can be obtained from such processes. For instance, desulphurization, shape modification of inclusions, absorption of inclusions etc. are possible.

(1). Powder injection

The powder injection technique was first developed in 1969 at



Figure 3.3: Installation of injection process [43].

Thyssen Niederrhein AG works and has since become known as the TN process. In this process, powdered treatment agents such as lime or calcium, calcium aluminate slags, calcium silicide or calcium carbide are injected into the melt to absorb inclusions and sulphur or to modify the shape of inclusions. In the presence of lime or calcium, sulphur will dissolve into a lime-saturated calcium aluminate. This process has been found effective in desulphurization, deoxidation and shape modification of inclusions. This process is carried out in the teeming ladle (see Figure 3.3)[43].

(2). Cored wire or canister injection

Calcium bearing alloys or Rare Earth Metals can be added into the melt in the form of cored wire or canister to facilitate the effectiveness of the addition (see Figure 3.4) [42]. Rare Earth Metals are very effective in the modification of sulphide inclusions.



Figure 3.4: Plunging method for adding rare earth metals [42].

Addition of these elements to aluminum-killed melt converts almost all the residual oxygen to rare earth oxides, Re_2O_3 , or more likely, to rare earth aluminates, which will react with dissolved sulphur to form oxysulphides, Re_2O_2S , during cooling and solidification of the steel, thereby preventing intergranular MnS (which will lead to anisotropy) from forming.

According to Turkdogan[44], a sulphur content of 0.006%-0.002% in aluminum-killed melts is suitable for rare earth treatment. Below 0.002%, there is no precipitation of MnS during solidification.

3.4 Prevention of Reoxidation

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Many studies have shown that reoxidation after the final refining process can degrade steel quality. Liquid steel streams during pouring or teeming from a ladle to a tundish or from a tundish to a mold will absorb or entrain air into the steel if these streams of steel are not protected from exposure to the atmosphere. In their studies, Lindenberg et al[45] found that total oxygen doubled after removing shrouding of the steel stream from ladle to tundish. The increased oxygen reacts with residual aluminum in Al-killed melt, forming Al_2O_3 , and increasing the tendency of nozzle clogging during continuous casting.

Air can enter steel in two ways; one is direct dissolution, the other is entrainment by the falling stream (see Figure 3.5 [46]) followed by absorption. The former is a diffusion related phenomenon, the lower the bulk level of dissolved oxygen in the steel, the faster the diffusion. As a result, completely killed steels are more prone to reoxidation. Direct entrainment is created by turbulence both in the falling stream and its juncture region with steel in the ladle or tundish. In these processes, nitrogen contents may also increase, leading to more nitride inclusions. The author observed an increase in nitrogen contents after the steel was poured through a filter assembly without protection.

Nowadays, good steelmaking practices require the steel stream to be shrouded by refractory tubes through which argon is passed as a shroud gas to the stream.



Figure 3.5: Air entrained from falling stream [46].

3.5 Prevention of Slag Carryover and Employment of Better Quality Refractories

The prevention of carryover oxidizing slag from the furnace into the ladle greatly facilitates deoxidation and desulphurization treatments within the ladle and improve the cleanness of steel.

Another important aspect in producing clean steel is the quality of refractories. Improvement in both thermal and chemical stability of the refractories helps minimize corrosion and erosion problems. This inevitably minimizes the chance of large exogenous inclusions occuring in the final steel products.

3.6 Control of Flow Conditions

Flow condition within a ladle or tundish can significantly affect the separation of inclusions (e.g. vortices will entrain inclusions). It is therefore important to understand and control flow conditions so

that the separation of non-metallic inclusions can be maximized. Mathematical modelling is an useful tool to predict flow conditions. Joo and Guthrie have modeled steel flow phenomena in tundish for a wide variety of conditions. It was predicted that the separation of inclusions in the size range of 50-120 μm can be increased by as much as 50% [47] using flow modification devices such as weirs and dams within the tundish.

3.7 Filtration

In this process, liquid steel passes through a filtering medium during which the non-metallic inclusions may be removed. It has been demonstrated experimentally in this investigation that filtration is a very effective way to remove non-wetting solid inclusions. The major advantage of this process is that it can remove even very small ($\sim 1\mu m$) solid particles. These small inclusions are difficult to separate from steel in those refining processes which are based on separation by floatation. Although this process is not commercially available in tonnage applications, many industrial trials have been attempted[48]. Figure 3.6 shows the filtration set-up in tundish conducted by SELEE. Perhaps it is not too optimistic to say that it may become an in-line refining process in the near future, analogous to filtration techniques in the aluminum industries.

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Figure 3.6: A SELEE Filtration set-up in tundish for continuous casting [48].

Chapter 4

Filtration of Molten Steel

4.1 Filtration Theory

4.1.1 Classification of Filtration

Filtration processes can be classified into three categories: screening, cake and depth filtration (see Figure 4.1).

In screening filtration, the mechanism for the retention of particles is one of mechanical entrapment. All particles larger than the pore size of the filter medium will be retained, while particles smaller than the pore size will go through the filter. In this sense, the filter behaves as a sieve. This process is suitable for situations when it is required that absolutely no particles greater than a given size should pass.

In cake filtration, the particles are retained by a layer of accumulated particles (cake) on the filter surface. At the start of filtration, particles are retained according to the screening filtration mechanism Once the cake is formed, the cake itself serves as the filter medium to retain further inclusions. As the cake becomes thicker and thicker, the pressure drop across the cake becomes greater and greater. The process will be stoped when the permeability becomes too low to maintain the operation. This process is suitable for filtering fluids with concentrated suspensions.

In depth or deep bed filtration, the particles to be removed are usually much smaller than the pore size of the filter medium. They can be removed by depositing or adhering to the surfaces of the filter. The filter medium is usually either a bed of granular material or a porous solid in which tortuous channels usually exist. The mechanism for the retention of particles depends on many factors and will be discussed later on. The process is suitable for the removal of small quantities of particles.

4.1.2 Fluid Flow Characteristics

(1). Darcy's Law

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Flow through a porous medium, under low pressure conditions, i.e., when the velocity is low, obeys Darcy,s Law[49]:

$$Q = \frac{K \cdot A \cdot \Delta P}{L} \tag{4.1}$$

where Q is flow rate (m^3/s) , A, cross-sectional area (m^2) , K, a constant $(m^4/N.s)$, its value depends on both the liquid and the porous medium characteristics, ΔP the pressure drop across the bed, L the thickness of the bed.



Screening filtration



Cake filtration



Deep bed filtration

Figure 4.1: Filtration processes.

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a. Permeability

The constant K is further defined as $K = k/\mu$. k is referred to as the specific permeability (or permeability) of the porous medium. μ is the viscosity of the fluid. k has the unit of length squared:

$$k = K.\mu = \left(\frac{m^4}{N.s}\right)\left(\frac{N.s}{m^2}\right) = m^2 \tag{4.2}$$

This procedure allows the influence of the porous medium and fluid to be evaluated separately.

Specific permeability depends on the properties of a given porous medium such as capillary pressure curves, internal surface area, etc.. All these properties are manifestations of the geometrical arrangement of the pores.

Another important parameter of the porous medium is the porosity ε , defined as the fraction of volume of the bed not occupied by solid material (also known as the fractional voidage or voidage). Porosity is one of the major factors on which permeability depends. Many models have been developed which attempt to find an empirical correlation between the two For example, in a straight capillary model, where a bundle of straight, parallel capillaries of with uniform diameter d_0 are regarded as a porous medium, and the correlation was found to be[50] (for Darcian flow):

$$k = \frac{\varepsilon \, d_0^2}{32} \tag{4.3}$$

A detailed discussion can be found in reference [50].

b. Filter velocity and pore velocity

The ratio of the flow rate, Q, to the overall cross-sectional area of the porous medium, A, is called the *seepage*, *superficial* or *filter* velocity u_f :

$$u_f = \frac{Q}{A} = \frac{1}{A} \frac{dv}{dt} \tag{4.4}$$

It follows that then the average pore velocity, \overline{u}_p , is:

$$\overline{u}_p = \frac{u_f}{\varepsilon} \tag{4.5}$$

c. Blake-Kozeny equation

For flow through packed beds of length L and particulates giving a porosity ε , Darcy's Law takes the form:

$$u_f = \frac{1}{4.2} \frac{\Delta P}{L\mu S_0^2} \frac{\varepsilon^3}{(1-\varepsilon)^2}$$
(4.6)

This is known as Blake-Kozeny equation[49] which is valid for laminar flow conditions $R_c^1 \simeq 2$, where S_0 is the total surface area of particulates per unit volume.

 ${}^{1}R_{c} = \frac{\rho u_{f}}{\mu(1-\epsilon)S_{0}}$

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For highly porous media such as the reticulated ceramic filter used in this investigation, the appropriate equation may be those derived on the basis of *drag theory*, where the walls of the pores or the surfaces of the filter webs are treated as *obstacles* to an otherwise uniformly straight flow of the viscous fluid. The drag of the fluid on each portion of the walls (surfaces) is estimated from the Navier-Stokes equation, and the sum of all drag is thought to be equal to the resistance of the porous medium to flow[50]

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Analyses based on this approach, assuming the *dragging* obstacles are fibres perpendicular to the flow, leads to the following equation[50]:

$$\frac{\Delta P}{L} = \frac{16\mu u_p (1-\varepsilon) (4-\ln(Re))}{3 \delta^2 (2-\ln(Re))}$$
(4.7)

where δ is the fibre's or web's thickness, $Re = \frac{\rho u_p \delta}{\mu}$. By comparing equation 4.7 with Darcy's Law, noting $Q/A = u_f = u_p \varepsilon$, one obtains the permeability:

$$k = \frac{3}{16} \frac{\delta^2 \varepsilon}{(1-\varepsilon)} \frac{(2-\ln(Re))}{(4-\ln(Re))} \tag{4.8}$$

Here k varies with flow velocity, which is a characteristic of viscous flow.



Figure 4.2: Schematic curves for non-Darcian flow [50].

(2). Non-Darcian flow

As mentioned earlier, Darcy's Law is only valid over a certain *seepage* velocity domain, for which a linear relationship between the filtration velocity (*seepage* velocity) and the pressure gradient (Darcy's Law can be expressed as differential form) exists. Outside this domain, the flow is termed as *non-Darcian flow* (see Figure 4.2).

Many investigations have been directed towards finding the range of Reynolds numbers over which Darcy's Law is valid. However, there is a great discrepancy among the different investigators

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regarding the *universal* Reynolds number above which Darcy's Law would no longer be valid. These values range from 0.1 to 75 [50]

There are numerous proposed heuristic correlations and theoretical models that attempt to describe non-Darcian flow phenomena in porous media. Forchheimer[50] added a second-order term in the velocity to Darcy equation:

$$\frac{\Delta P}{L} = au + bu^2 \tag{4.9}$$

where a, b, are constants.

White and Missbach [50] proposed an equation:

$$\frac{\Delta P}{L} = au^m \tag{4.10}$$

where a is a constant, and m ranges between 1 to 2. When m approaches 1, the flow becomes Darcian flow.

Correlations between the friction factor f and Reynolds number have also been attempted. In this case, when f and Re are inversely proportional, the flow is subject to Darcy's Law:

$$f = \frac{C}{Re} \tag{4.11}$$

where C is a constant.

otherwise, the flow is non-Darcian. A detailed discussion can be

found in reference[50].

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Ergun's Equation:

For flow through packed bed of uniform spheres, the non-Darcian flow can be described by Ergun's equation [49]:

$$\frac{\Delta P}{L} = \frac{150\mu u_f}{d^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} + \frac{1.75\rho u_f^2(1-\varepsilon)}{d\varepsilon^3}$$
(4.12)

where d is the diameter of the spheres, other parameters are the same as defined before.

If the friction factor is defined for this case as f_E :

$$f_E = \frac{d \cdot \Delta P \cdot \varepsilon^3}{L\rho u_f^2 (1 - \varepsilon)}$$
(4.13)

and the Reynolds number as Re_E :

$$Re_E = \frac{d\rho u_f}{\mu(1-\varepsilon)} \tag{4.14}$$

then, in dimensionless form, equation 4.12 becomes :

$$f_E = \frac{150}{Re_E} + 1.75 \tag{4.15}$$

For packed beds of nonspherical particulates, Ergun's equation evolves into:

$$\frac{\Delta P}{L} = \frac{150\mu u_f \lambda^2}{\overline{d}_{vs}^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} + \frac{1.75\rho u_f^2 \lambda}{\overline{d}_{vs}} \frac{(1-\varepsilon)}{\varepsilon^3}$$
(4.16)

where λ is defined as a shape factor by:

$$S_0 = \frac{6\lambda}{d} \tag{4.17}$$

and \overline{d}_{vs} is the volume-surface mean diameter:

$$S_0 = \frac{6}{\overline{d}_{vs}} \tag{4.18}$$

4.2 Filter Media

4.2.1 General Consideration

Due to the high temperature of liquid steel, the only candidates for filter media are ceramic materials. The physical and mechanical properties of the ceramic filter media must be adjusted so that they can withstand thermal shock during priming and the mechanical stresses imposed by the impact (momentum) of the steel stream during filtration Further they should neither corrode nor erode as a result of metal-slag or inclusion-filter interactions

Since most of the inclusions in steel are small in comparison with the pore size of the filter media permeable to liquid steel, the deep bed filtration mechanism largely applies. The structure of the filter should be constructed so that it would enhance the transportation of the inclusions to the surfaces of the filter and thus promote retention of inclusions.

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From a process point of view, the filter media should be sufficiently permeable to allow the liquid steel to flow through at a speed which satisfies the normal industrial operations.

(1). Thermal stresses (shock)

Thermal stress is caused by thermal expansion on heating or cooling of an object when the expansion is restrained in one way or another. There are two cases where thermal stresses can occur. One is when the object is dimensionally (physically) restrained. In this case, there is no leeway for the object to change its dimensions, i.e., the thermal expansion is restrained. The other is when the object is subjected to severe temperature gradients. In this case, the expansions of the different volume elements of the object are different due to the temperature gradient. The expansion of the volume elements which are in higher temperature zone will be restrained by its neighboring volume elements which are in the lower temperature zone. The result is compressive stresses in the volume elements in the higher temperature zone, and tensile stresses in the volume elements in the lower temperature zone.

The magnitude of these stresses depends on the temperature difference, ΔT , Young's elastic modulus E, the coefficient of thermal expansion α , Poisson's ratio γ and the geometry of the object. For a long hollow cylinder, (to some extent similar to the structure of the reticulated filter webs) if its surface temperature is instantly raised to T_s , without changing the average temperature from its

initial value, the compressive tresses on the surfaces and tensile stresses in the center are given by the following equations [51]:

Surface:

$$\sigma_r = 0 \tag{4.19}$$

$$\sigma_{\theta} = \sigma_z = \frac{E\alpha}{1 - \gamma} (T_a - T_s) \tag{4.20}$$

Center:

$$\sigma_r = 0 \tag{4.21}$$

$$\sigma_{\theta} = \sigma_z = \frac{E\alpha}{1 - \gamma} (T_a - T_c) \tag{4.22}$$

where $\sigma_r, \sigma_{\theta}, \sigma_z$ are stresses in r, θ and z directions, T_a, T_s, T_c are the average, surface and center temperatures of the long hollow cylinder respectively.

If the average temperature of the cylinder changes along with the surface temperature, the analytical calculations become more difficult and depend on Biot's modulus, Bi, which is defined as the product of the surface-heat-transfer, h, and the characteristic heat transfer length, l_h , to the thermal conductivity, k.

$$Bi = \frac{l_h h}{k} \tag{4.23}$$

when Bi is equal to or greater than 20[51], then the stress calculation can be approximated to the former case.

When the stresses reach the fracture stress of the material, fracture will occur. The corresponding temperature difference ΔT_f can be determined from the equation:

$$\Delta T_f = \frac{\sigma_f (1 - \gamma)}{E\alpha} \tag{4.24}$$

or for other shapes[51]:

$$\Delta T_f = \frac{\sigma_f (1 - \gamma)}{E\alpha} \cdot S \tag{4.25}$$

where S is a shape factor, σ_f is the fracture stress. These equations are valid only under the assumptions made above.

According to Hasselman[52], for a sphere subjected to transient heating or cooling, assuming convective heat transfer, ΔT_f can be determined from the following equation:

$$\Delta T_f = \frac{2.5\sigma_f(1-\gamma)}{E\alpha}(1+\frac{2}{B}) \tag{4.26}$$

These criteria refer only to the fracture initiation in ideally elastic ceramic materials. For other ceramic materials, initiation of cracks may not necessarily mean a failure, because they may be stopped by a pore or grain boundary. For this case, it is the propagation of cracks that leads to a failure. A detailed discussion of these matters goes beyond the scope of the present topic.

(2). Mechanical stresses

Mechanical stresses are caused by the head pressure and the kinetic impact. These stresses can also lead to failure during priming or filtration. The mechanical strength of a foam filter can be increased by increasing the thickness of the webs, but this may not be good for thermal shock resistance. Also, the structure must



Figure 4.3: Temperature dependence of forced convection corrosion of alumina, mullite, and fused silica in the slag system of $40CaO - 20Al_2O_3 - 40SiO_2$ [53].

be subject to other considerations such as pressure drop, pore size requirements and chilling effects. The mechanical stresses can be minimized by appropriate arrangement of the filter so that the impact of the steel stream and metallostatic head pressure can be reduced without impairing other filtration parameters.

(3). Corrosion and erosion

The filter medium is unavoidably subject to slag attack during filtration. This requires that the filter medium should be stable enough, i.e., no corrosion due to the interactions between the filter medium and the slag. Obviously, the stability of a filter medium depends on both its and the slag's compositions as well as temperature. Figure 4.3[53] shows the dependence of the corrosion rate of alumina, mullite and fused silica in a slag with a composition of $40\% CaO - 20\% Al_2O_3 - 40\% SiO_2$ at different temperatures.

In order to minimize the slag attack, considerations should be made to avoid direct contact between filter and slag during filtration. For instance, the filter should be totally submerged into molten steel as soon as possible, as the slag is concentrated on the surface. This attack is escalated by the combined effect of the thermal shock and the momentum of the impacting jet and associated turbulence during priming.

In addition, the filter must not creep excessively during filtration period.

4.2.2 Types of Filter Media

The filter media commonly used in metal processing can be classified into three types: tabular ceramic particulates (bonded or unbonded), ceramic monoliths and ceramic foams.

(1). Ceramic particulate

In this case, the filter medium consists of ceramic particulates, e.g., alumina tabs and /or balls, with variety of sizes and shapes depending on a specific application. In the unbonded case, the particulates are packed together and very often referred to as a packed bed. In the bonded case, the particulates are bonded

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Figure 4.4: (a) Unbonded, (b) bonded, ceramic particulates [54]

together by a ceramic binder. The pore size, porosity and permeability of the filter medium can be regulated by selecting the ceramic particulates and the amount of binder. Figure 4.4[54](a), (b) show the unbonded and bonded ceramic particulates respectively.

(2). Ceramic monoliths

This type of filter consists of regular cells. The shape and size of the cells can be changed for different applications. The material can be mullite, zirconia, alumina, etc.. Figure 4.5 shows square-celled and triangular celled monoliths respectively.



Figure 4.5. Ceramic monoliths [54].

(3). Ceramic foam

This is the most delicate type of ceramic filters for metal processing. They are produced by immersing a polymeric foam precursor into a ceramic slurry and then fired. During firing the precursor vaporizes, leaving a positive ceramic replica of the original foam. A variety of foam filters is available with different ceramic material, pore size and dimensions for different applications. Table 4.1 lists the specifications of some Hi-Tech foam filters[55]. The pore size is measured by numbers of pores per linear inch (ppi). Figure 4.6 shows the typical structure of the Hi-Tech foam filters[77].

In some cases, woven ceramic fibers are also used.

Table 4.1: Physical, mechanical and thermal properties of Hi-Tech foam materials [55].

Material	Pore	Calc.	Avg	Peak Pore	Web	Unit Bulk	Unit	iner	Modulus of	Compress	Creep
	Size	Pore Size	Pore Dia	Dia.(3)	Thick	Density	Porosity	Shock	Rupture(5)	Strength	Def
	(pp1)	(ppi)	um(001")	um(001")	um(001")	(g/cc)	(%)	(am)(4)	mPa (ps1)	mPa(psi)	(1)(6)
NCL Mullite	10(1)	13.7(2)	1194 47	1287 51	686 27	0 46	78	4 5	1 40 203	2 29 333	0 205
	20	20.3	737 29	678 27	508 20	0 47	77	10 5	1 57 228	3 06 445	0 136
	30	28 3	610 24	591 23	279 11	0 45	81	2 4	1 16 160	0 74 108	0 595
98A1203	10	13 9	1321 52	1521 60	508 20	0 51	82	4 1	1 50 217	2 23 323	0 226
	20	21.9	838 33	800 32	356 14	0 61	80	8 1	3 25 472	2 83 411	0 074
	30	31 5	559 22	564 22	254 10	0 66	77	6.0	2 88 418	2 08 301	0 139
ZTA A1203	10	16.1	1143 45	1193 47	432 17	0 57	85	03	1 16 169	2 45 356	0 151
	20	21 9	838 33	813 32	330 13	0 61	83	03	1 78 258	2 18 317	0 375
	30	33 6	533 21	50J 20	229 9	0 69	80	10	1 03 150	1 25 181	0 7 4
PSZ ZrO _Z LD"	10	13 7	1346 53	1411 56	508 20	0 72	85	1 2	1 10 160	1 40 203	0 185
	20	23 4	737 29	690 27	356 14	0 74	84	2 1	1 48 215	1 37 199	0 262
	30	30 0	610 24	600 24	254 10	0 84	82	0 2	1 77 256	1 01 146	0 276
PSZ ZrO _Z HD•	10	13.6	1397 55	1237 49	457 18	0 93	81	10	2 23 324	2 51 365	0 114
	20	21 3	838 33	622 24	356 14	1 18	77	22	3 37 489	1 96 285	0 249
	30	30.2	584 23	616 24	254 10	1 1?	76	63	2 32 336	1 84 267	0 397

LD = Low Density HD = High Density
(1) Pore size, pp1 = No. of pores per linear inch.
(2) Pore size, calculated pp1 based on avg pore dia. and web thickness.
(3) Peak pore dia, determined from pore size distribution curve
(4) Thermal thock resistance, wt. loss after sample was rapidly heated to 1150°C (2100°F) and cooled to RT
(5) MOR, 3 point bend test.
(6) Percent compressive deformation, %/hr for 3 hrs under 5 psi (0 034 mPa) loading at 1500°C (2732°F)

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A. Lines

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Figure 4.6: Typical structure of Hi-Tech filters [77].

4.2.3 Characteristics of Filter Media

The characteristics of the filter media will presumably affect the filtration efficiency and operating parameters. Apelian et al[54] have evaluated some of the aforementioned types of filter media in terms of micro-topography, surface area, micropore distribution and flow dispersion coefficient. They found that the surface properties, e.g., roughness, is closely related to the manufacturing process. The same type of filters may have quite different surface properties.

(1). Surface area

By measuring the specific surface area via the B.E.T. method (multimolecular absorption theory first described by Brunauer, Emmett and Teller[56]), Apelian et al found that in general, the ceramic foam filter media possess the largest surface area while the bonded ceramic particulates had the lowest surface area amongst the generic types (ceramic particulates, monolith, foam and woven fibres) evaluated.

(2). Micropore distribution

Micropores refer to those porous of the surfaces of the filter media (a reflection of surface characteristics). Although, these micropores do not contribute to fluid flow, they affect the local drag coefficient and act as inclusion capture sites and thus influence inclusion retention. In Apelian's study, except for the catalyst substrate (unbonded alumina balls), the bonded ceramic foam



Figure 4.7: Micropore distributions of bonded ceramic foam [54].

filters were found to have a higher value of microporosity than other types of filter media. Figure 4.7 [54] shows the micropore distributions of bonded ceramic foams.

(3). Porosity

Porosity refers to the percent of void volume present in the porous medium and is defined as:

$$\varepsilon = 1 - \frac{\rho_b}{\rho} \tag{4.27}$$

where ε is the porosity or total porosity, ρ_b is the bulk density and ρ is the density of a given filter medium. ε is the sum of the macro and microporosity. Only macroporosity contributes to fluid flow, so that any increase in macroporosity will decrease head loss across the filter. Once again, the ceramic foam filters were found to have the highest porosity in Apelian's study.

(4). Flow dispersion coefficient

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One of the major characteristics of a filter medium is its dispersivity. This dispersion of fluid (or mixing) by the filter medium will enhance the transport of inclusions to the filter surface. Apelian et al measured the mixing level, or dispersion, of several filter media by introducing a dye into the flow stream to the filter and subsequently measured the concentration of the dye in the outflow stream whereby the characteristic response time, τ , termed the dispersion coefficient, was determined. Figure 4.8 [54] illustrates the definition of τ , and dispersion coefficients of various filter media, as a function of Reynolds number.

According to their results, the dispersion coefficients decrease with an increase in Reynolds number. It was argued that at high Reynolds number, the asperities and crevices in the medium would become dead volumes and the liquid volumes trapped at these sites are not renewed by the flowing fluid.

It turned out that the extruded monolith and ceramic foam exhibited a higher dispersion. It should be pointed out that higher dispersion τ indicates a greater probability of inclusion transportation to the filter surfaces. However, it should not be simply interpreted as a higher filtration efficiency since inclusion retention depends on other factors as well.



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Figure 4.8: The definition of τ , where τ_D is the delay time [54].

4.3 Mechanisms of Inclusion Removal

4.3.1 Mechanical Entrapment (Screening)

For solid inclusions larger than the pores of the filter media, they can be simply mechanically trapped by the filter. This mechanism applies to those exogenous inclusions in steel such as entrained slag droplets or spalling refractories, as they usually are relatively large. In iron casting, dross is also removed according to this mechanism of mechanical entrapment.

4.3.2 Inclusion Retention in Deep Bed Filters

Since inclusions in steel are usually much smaller than the pore size of the filter media (see Figure 4.9 [78]), they must be removed



Figure 4.9: Relative sizes of filter pores and inclusions [78].

by deep bed filtration. There are two steps for an inclusion to be retained by the filter. First, the inclusion must be transported to the vicinity of filter surfaces. Second, it must be stabilized on the surfaces according to either a force balance or by other interactions such as sintering.

(1). Transportation processes

a. Interception

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When a fluid flows around a solid body, i.e., filter, a boundary layer will form, within which exists a velocity gradient with a zero velocity on the surface of the solid body. If an inclusion in the fluid is in such a position that the distance from its center to the surface of the filter during its passage through the latter is less than the collision diameter, i.e., $d_t/2$, it will contact the surface of the filter and be intercepted. This process is termed as interception.

b. Diffusion

Small inclusions (less than 10 $\mu m[57]$) will experience a random diffusional movement due to collisional energy transfer by the molecules of the suspending fluid, i.e., molten steel. This is termed as Brownian diffusion. The diffusion coefficient D_B can be expressed as follows[58]:

$$D_B = \frac{KT}{3\pi\mu d_i} \tag{4.28}$$

where K is Boltzmann's constant. T is the absolute temperature and μ is the viscosity of the fluid. d_i is the diameter of the inclusion.

c. Hydrodynamic effects

Inclusions within the boundary layer will be subject to a shear gradient. Under these conditions, particles, i.e., inclusions will experience a difference in drag form from one side to another. This causes the particle to rotate, creating a spherical flow field and resulting in a lateral pressure difference acting upon the particle. As a result, the particle will move towards lower velocity region, i.e., the surfaces of the filter.

d. Inertia impaction

Inertia impaction occurs when a particle has sufficient inertia to maintain its trajectory as the flow streamline diverge around the filter media. In this case the particle has a greater density than the fluid in which it is suspended. (in steel filtration, this does not apply).

e. Sedimentation or floatation

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When the density difference between the particles suspended and the fluid is substantial, the particle will experience a different velocity than the fluid, as a result, it has a tendency to deviate from the streamline to contact the filter media.

Figure 4.10 shows schematic representation of the transportation processes.

The hydrodynamic action, inertial impaction and sedimentation or floatation are enhanced by increasing particle size Conversely, diffusion is enhanced by decreasing particle size Consequently, the efficiency of a depth filtration process may show some minimum at a particle size intermediate between those for these mechanisms. Yao[59] has demonstrated in his gas filtration study that this minimum occured at $1\mu m$ with plastic spheres

(2). Stabilization

a. Surface tension

The interfacial tensions between non-metallic inclusions and molten steel, non-metallic inclusions and filter media and filter media and molten steel play an important role in the retention of inclusions

Interfacial tension and contact angle are related by Young's force balance equation:

$$\sigma_{l-s} = \sigma_{s-g} - \sigma_{l-g} \cos \theta \tag{4.29}$$



Figure 4.10: Schematic representation of inclusion transportation processes.

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Figure 4.11: Schematic of contact angle - sessile drop.

where θ is the equilibrium contact angle determined by the shape of a liquid droplet on a solid surface, σ_{l-s} , σ_{l-g} and σ_{s-g} are the interfacial tensions between liquid and solid, liquid and gas and solid and gas respectively. θ is a measure of the ability of a liquid to wet a solid. Its value ranges from 0°, where the ' quid wets the solid completely, to 180°, where the liquid does not wet the solid at all. Usually, contact angles which are less than 90° are regarded as wetting and greater than 90° as non-wetting.

When a liquid droplet is placed upon another liquid, a lens will form if the liquids are immiscible due to the displacement of the denser liquid by the lighter droplet.

The interfacial tensions are related by the visible contact angle ψ by Neumann's relation[60], if horizontal equilibrium is considered:



Figure 4.12: Schematic of a liquid lens.

$$(\sigma_{l_1-l_2})^2 = (\sigma_{l_1-g})^2 + (\sigma_{l_2-g})^2 - 2\sigma_{l_1-g}\sigma_{l_2-g}\cos\psi \qquad (4.30)$$

and

$$\sigma_{l_1-l_2}\sin(\theta-\psi) = \sigma_{l_1-g}\sin\psi \qquad (4.31)$$

if vertical equilibrium is considered.

Here, according to Archimedes' principle, the contact angle θ is larger than the visible contact angle ψ .

Cramb et al[60] have provided a good review of contact angles and interfacial tensions among liquid steel, refractories and slags. these are cited in Tables 4.2-4.4.

Liquid steel is non-wetting with respect to alumina, silica, lime, zirconia, magnesia and titanium nitride and wetting respect to

Refractory	Temp. (°C)	Contact Angle	Steel Type
ALO. 98%	1 520	105	0.4%C'
ALO.	1,600	144	pure*
ALO.	1.600	112	3.4 % C ³
A1.0.	1.600	135	pure'
SiO.	1.600	115	pure*
SIO.	1.550	110	pure
CaO	1.600	132	pure*
CaO	1.550	121	pure*1
TIO.	1.600	84	pure'
Cr.O.	1.600	88	pure*
ZrO, 89%	1.520	108	0 16%C'
ŹrÓ.	1.550	119	pure*
ZrO.	1,550	122	pure'
MoO 95%	1.520	111	0 16%C'
MaO	1,600	125	pure'
MaO	1,550	128	pure
MnO	1,550	113	pure
SIC 91%	1,500	60	0.16%C'
Graphite	1,460	120	0.16%C'
TIN	1,550	132	pure*
BN	1,550	112	pure**
CaS	1,550	87	pure*
CaO-MgO-SIO,	1,450	104-120	NI-Cr steel ¹⁴
CaO-SIO, A1,O,	1,450	96-114	Ni-Cr steel ¹⁴

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Table 4.2: Contact angles between refractories and liquid steel [60].

Table 4.3: Interfacial tensions between some pure systems [60].

System	Temp. (°C)	y mN/m 93023	
AI.O.(s)	1,475		
AI.O. Fe(I)	1.570	2,300"	
MoO Fe(l)	1,725	1,600"	
MoO(s)	25	1,000"	
Fell)	1,600	1,890**	
d Fe(s)	1,400	2,150"	
CaO SiO,	1,600	485*	
FeO	1,600	570 **	
CaO SiO, AI.O.	1,550	500**	
CaO AI.O.	1,550	600 **	
CaF.	1,550	280 **	
CaO CaF, 20/80	1,550	310**	
CaO AI,O,-CaF, 40/40/20	1.550	400**	
CaO·AI,O, CaF, 20/20/60	1,550	300**	

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Siag Type	Refractory Type	Temp. (°C)	Contact Angle
Fe0 SiO, 70/30	alumina	1,250	< 10"
FeO-MnO-CaO SIO, ALO,	zirconia	1.500	5-20'
FeD-MnO CaO SIO, ALO,	alumina	1.500	< 10'
FeO MnO CaO SIO, AI,O,	SIC	1,500	104-122
FeO-MnO CaO SiO, Al,O,	graphite	1 500	110-132
CaO-S1O, Al, O, 40/40/20	MgÖ	1,400	9-32"
CaO SIO, MgO 10/56/34	SI,N.	1,550	50**
Na.O StO. MgO	SI.N.	1.550	20**
Mold slag	Steel	1,400	0-30"
CaO-SIO, Al, O, 40/40/20/	iron	1,450	30-60**
CaO SiO, Al,O, FeO	iron	1,450	0-60**

Table 4.4: Contact angles between liquid slags and solid surfaces [60].

titania, chromium oxide, calcium sulphide and silicon carbide. The wettability will increase when there is a tendency for reaction or dissolution between the liquid and solid. For example, a drop of low carbon steel wets graphite initially, but as the carbon content increases, the wettability decreases and eventually the droplet becomes non-wetting.

Dissolved oxygen, sulphur, selenium and tellurium in steel influence the wettability between inclusions or refractories and the molten steel. The wettability of liquid steel with respect to alumina increases with increase in oxygen content and decreases with increase in selenium or tellurium contents. Sulphur has little effect on wettability of oxides and liquid steel.

Liquid steelmaking slags wet liquid or solid steel and their wettability increases with increasing silica and FeO content in the slag and decreases with increasing sulphur content in the metal and alumina content in the slag. According to Iguchi[62] et al, a slag with 28 mole percent FeO will wet solid iron completely.

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If complex inclusions have a similar composition to a steelmaking slag, they will be wettable with respect to liquid steel.

Liquid slags wet most refractories (except for silicon carbide or graphite), Their wettability increases with increasing FeO contents in the slag. Therefore, a slag can absorb inclusions at the steel-slag interfaces or during any intermixing of slag and steel during argon stirring or flux injection.

Interfacial tensions and contact angles are related through Young's or Neumann's equations. The interfacial tensions of non-wettable interfaces are greater than either of the component surface tensions, while that of wettable interfaces are lower than either of the component surface tensions. For instance, the interfacial tension between solid alumina and liquid iron at 1600°C is about 2300 mN/m [60], while that of solid alumina and pure iron are 930 mN/m and 1890 mN/m respectively (in this case, the contact angle is about 140°).

When the contact angle is less than 20° , both Young's and Neumann's equations are approximated by Antonow's relation[60]:

$$\sigma_{metal-slag} = \sigma_{metal-gas} - \sigma_{slag-gas} \tag{4.32}$$

Cramb et al proposed the following relation[61]:



Figure 4.13: Iso- ϕ lines in $CaO - SiO_2 - Al_2O_3$ ternary at 1600°C [61].

$$\sigma_{metal-slag} = \sigma_{metal-gas} + \sigma_{slag-gas} - 2\phi (\sigma_{metal-gas} - \sigma_{slag-gas})^{0.5}$$
(4.33)

 ϕ is defined as

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$$\phi = -\frac{\Delta G^a_{metal-slag}}{\sqrt{\Delta G^c_{metal-gas} \Delta G^c_{slag-gas}}}$$

where $\Delta G^a_{metal-slag}$ is the free energy of adhesion for the interface between phases of liquid metal and slag, and $\Delta G^c_{metal-gas}$ and $\Delta G^c_{slag-gas}$ are the free energy of cohesion for liquid metal phase and liquid slag phase respectively. ϕ is characteristic of a system. Its value varies with the composition of the slag. Figure 4.13 [61] shows ϕ values in the $CaO - SiO_2 - Al_2O_3$ system at 1600°C.

b. Thermodynamic condition

An analysis of interfacial energies between inclusions, liquid steel and slag or filter media can predict the possibility of inclusion removal by the filter media in the case of filtration or by the slag in the case of slag-steel mixing.

For an inclusion to be attached to the surfaces of the filter media or walls of ladle or tundish, the change in the Gibbs free energy of the system at constant temperature and pressure can be simply calculated through interfacial energies:

$$\Delta G = A\sigma_{inclusion-filter} - A\sigma_{inclusion-steel} - A\sigma_{steel-filter} \quad (4.34)$$

where A is the contact area between the inclusion and the filter or refractory wall.

If $\Delta G < 0$, the inclusion can be stabilized on the surface of the filter or the wall of ladle or tundish, if no other forces exist.

When molten steel does not wet non-metallic inclusions nor the filter media, i.e., $\theta > 90^{\circ}$, the values of $\sigma_{inclusion-steel}$ and $\sigma_{steel-filter}$ are high, and ΔG will become more negative.

If the steel wets the inclusions, i.e., $\theta < 90^{\circ}$, e.g., titania, $\sigma_{steel-inclusion}$ will be lower than the case of non-wetting and ΔG will become less negative. Presumably, the chance of removing these inclusions by the filter media is less than that of those of non-wetting inclusions.

In the case of filtration of aluminum-killed steel with alumina filter media, equation 4.34 becomes:

$$\Delta G = A\sigma_{alumina-alumina} - 2A\sigma_{alumina-steel} \tag{4.35}$$

since

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$$\sigma_{alumina-alumina} = 2\sigma_{alumina-gas} \tag{4.36}$$

equation 4.35 becomes:

$$\Delta G = 2A(\sigma_{alumina-gas} - \sigma_{alumina-steel}) \tag{4.37}$$

and, alumina is non-wetting, $\sigma_{alumina-gas} < \sigma_{alumina-steel}$, i.e., $\Delta G < 0$.

If the inclusions are sintered to the filter, then:

$$\Delta G = -2A(\sigma_{alumma-steel}) \tag{4.38}$$

The above principle also applies to inclusion absorption by slags.

c. Kinetic considerations

Thermodynamic analysis only can predict the possibility of inclusion separation from molten steel onto the filter surfaces The rate of this separation is controlled by kinetics. When an inclusion is transported to the surfaces of the filter or the metal-slag interfaces, it cannot instantaneously contact the surfaces or be absorbed by the slag. Time is needed for the thin metal film trapped between the inclusion and the surfaces to drain out before actual contact can occur. This time interval is termed as the rest time, t_{rest} . According to lyengar[60], if there are no repulsive forces and buoyancy is the cause for droplet movement, t_{rest} at the metal-slag interface can be expressed as following:

$$t_{rest} = K\Delta\rho\mu gr_i^5 (\sigma_{inclusion-metal})^{-2} \delta^{-2}$$
(4.39)

where μ is the metal viscosity, r_i is the inclusion radius and K is a constant, $\Delta \rho$ is density difference between the metal and the absorbing slag, δ is the critical film thickness.

As can be seen, for a given system, t_{rest} decreases with an increase in interfacial tension between the metal and inclusions and with any decrease in inclusion size, i.e., the rate of separation of inclusions is favoured, from kinetic point of view, when the interfacial energy between the inclusion and the metal is high and the size of inclusions is small. Solid inclusions with a dendritic nature (i.e. very small radius of curvature at dentrite point²), t_{rest} should be small.

d. Sintering

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Once a solid inclusion contacts the filter surface, at high temperature, sintering can occur. Sintering is a process in which solid particles bind togecher under high temperature and/or pressure as a result of mass interchange processes between particles. The driving force is the high surface energy of the fine powders (particles). During sintering, the high energy interfaces between contacting particles are replaced by lower energy grain boundaries or atomic bonds, leading to an overall reduction in the free energy

²The radius of curvature at the tip of an alumina dentrite is less than 2 microns.

of the whole system.

The mechanisms for interchaging mass among particles during sintering can be: evaporation and condensation, viscous or plastic flow, volume diffusion and surface diffusion. Evaporation and condensation take place due to vapour pressures at surface asperities with small radii of curvatures. Areas of surfaces where there is a positive radius of curvature have a higher vapor pressure than those areas with a flat surface or even concave, or negative radius of curvature[63]. Consider two spherical particles which are intimately in contact with each other. After initial bonding through atom diffusion, a neck is formed. Because the vapor pressure in the neck (with a radius of r') is lower than that in the bulk, atoms will, as a result, evaporate from the bulk and condense on the neck area. This is in accordance with thermodynamic analysis. As the neck grows, the overall surface area decreases, i.e., the free energy of the system decreases.

The rate of mass transfer can be calculated. Kuczynski[64], by substituting the pressure difference ΔP , into the Langmuir equation, obtained the following expression:

$$\frac{x^3}{r} = (9\pi/2MRT)^{1/2} V_0 \sigma P_0 t \tag{4.40}$$

where M, V_0, σ is the molecular weight, molar volume and surface tension of the solid particle respectively, P_0 is the vapor pressure over a flat surface, R is the ideal gas constant, T is the absolute temperature, and t is the sintering time.



Figure 4.14: Schematic of sintering of two particles.

Kingery et al[63] have derived a similar equation:

$$\frac{x}{r} = \left(\frac{3\sqrt{\pi}\sigma M^{3/2}P_0}{\sqrt{2R^{3/2}T^{3/2}\rho^2}}\right)^{1/3}r^{-2/3}t^{1/3}$$
(4.41)

where ρ is the density.

Viscous or plastic flow is a mass transport phenomenon during sintering as a result of stresses. The stress $\sigma_{r'}$ in the neck can be expressed as follows:

$$\sigma_{r'} = -\frac{\sigma}{r'} \tag{4.42}$$

If viscous flow is the dominant mechanism, the rate of neck growth can be expressed by the following equation:

$$\frac{x^2}{r} = \frac{3\sigma}{2\mu}t\tag{4.43}$$

where μ is the viscosity, σ is the surface tension.

Volume diffusion refers to the movement of atoms or vacancies within the solid crystalline material. If this movement of atoms or vacancies take place mainly on the surfaces of the sintered particles, the process is then called surface diffusion. The concentrations of vacancies are higher at grain boundaries, interfaces or surfaces and lower in the bulk. As a result, vacancies will diffuse into the bulk and the atoms will diffuse in the opposite direction In the neck area, the concentration of vacancies can be expressed as follows:

$$\frac{\Delta C}{C_0} = \frac{\sigma V_0}{RTr'} \tag{4.44}$$

where C_0 is the equilibrium concentration vacancies under a flat surface and ΔC the excess concentration of vacancies in the neck region. Using Fick's first law of diffusion, Kuczynski obtained the following expression:

$$\frac{x^5}{r^2} = \frac{K\sigma V_0}{RT} D_r t \tag{4.45}$$

where D_v is volume self-diffusion coefficient, and K is a dimensionless constant

Where the surface to volume ratio of a system is high, surface diffusion may dominate. According to Kuczynski, for the sintering

of two spheres, the rate of sintering under such circumstances can be expressed as follows:

$$\frac{x^7}{r^3} = \frac{56\sigma V_0 \delta}{RT} D_s t \tag{4.46}$$

where δ is the interatomic distance in the solid and D_s is surface self-diffusion coefficient.

Sintering is a complex process. Any of the above mechanisms may act simultaneously for a given system.

The initial process of sintering is bonding. This process is very fast, especially at high temperature.

e. Shear stress

Inclusions on the surfaces of the filter media also experience shear stresses created by the flowing liquid steel.

If μ is the viscosity of the molten steel, $\frac{\partial v_x}{\partial y}$ is the velocity gradient in the boundary layer, then the shear stress τ_{yx} at the solid surface can be expressed as follows:



f. Other forces

The forces of attraction – Van der Waals' forces, between the molecules of closely abutting particles (inclusions and the filter media) also contribute to the stabilization of the particles within the filter. According to Ives and Gregory's [65] study of the capture of particles within rapid filters³ in relation to the forces considered in the DLVO⁴ theory of colloid stability, it appears that Van der Waals' forces are sufficient to account for the observed retention

In addition, polyelectrolyte bridging between particles and the filter medium may also occur.

The stabilization of inclusions on the surfaces of the filter depends on the resultant forces mentioned above. However, a quantitative analysis of the resultant forces for a given system may be too complex in practice to accomplish.

4.4 Experimental Work

4.4.1 Experimental Set-up

The experimental set-up is illustrated schematically in Figure 4 15 It consisted of an induction furnace with a capacity of 11 kg of steel and a filter-funnel assembly (the dimensions of the filterfunnel assembly are shown in Figure 4.17) The filter was housed inside the funnel which was joined by a crucible with a metering nozzle set in its bottom (see Figure 4.16) The flow rate of the liq-

³Flow rates through the filters are in the range of 9.43×10^{-6} to $1.18 \times 10^{-5} m^3/s.m^2$ ⁴Derjagum, Landau, Verwey, Overbeek theory of colloid stability
uid steel could be adjusted by changing the diameter of the nozzle.

The filters used were Partially Stabilized Zirconia (PSZ) filters made by Hi-Tech Ceramics, Inc., New York. Their chemical composition is: 97% ZrO_2 , 3% MgO. Further technical parameters can be found in Table 4.1, labeled LD (low density). Figure 4.18 shows a picture of a 20 ppi filter.

In this investigation, 4 different pore size filters were used, i.e., 10, 15, 20 and 30 ppi with a dimension of $5.08 \times 10^{-2}m$ in diameter and 2.54×10^{-2} in thickness.

4.4.2 Water Modelling

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(1). Flow rate measurement

Full-scale water modelling was carried out to measure the flow rate of steel through the system. From this, the steel velocity (nominal) through the filter could be readily calculated.

In steady state, the exiting velocity, u_e , of steel from the metering nozzle set in the lower crucible can, according to Bernoulli's equation, be expressed as:

$$u_e = C\sqrt{2gh} \tag{4.48}$$

where C is a discharge coefficient, h is the hydrostatic (metallostatic) head, and g is the gravitational acceleration. By measuring the flow rate Q, u_e is known:



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Figure 4.15: Schematic illustration of experimental system.



Figure 4.16: Filter-funnel assembly; (a) top view, (b) bottom view.



Figure 4.17: Physical dimensions of the filter-funnel assembly.

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Figure 4.18: Photograph of a 20 ppi filter employed for the research work.

$$Q = \pi (\frac{d_e}{2})^2 u_e \tag{4.49}$$

were d_e is the diameter of the exit hole in the bottom of the crucible. The average measured Q was found to be $6.1 \times 10^{-5} m^3/s$, with $d_e = 7.0 \times 10^{-3} m$. Thus u_e should be:

$$u_e = rac{Q}{\pi(rac{d_e}{2})^2} = rac{61}{\pi(rac{0.7}{2})^2} = 1.56m/s$$

Since h = 0.18m, therefore, C should be:

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$$C = \frac{u_e}{\sqrt{2gh}} = \frac{1.56}{\sqrt{2 \times 9.8 \times 0.18}} = 0.83$$

The filter velocity u_f at the filter should be:

$$u_f = \frac{Q}{A_f} = \frac{Q}{\pi (\frac{d_f}{2})^2}$$
(4.50)

where $d_f = 5.08 \times 10^{-2} m$, the diameter of the filter. Typically, then:

$$\overline{u}_f = rac{6.1 imes 10^{-5}}{\pi (rac{5.08 imes 10^{-2}}{2})^2} = 3 imes 10^{-2} m/s$$

Taking the macroporosity, ε_m , as 50% [54], then, the average pore velocity \overline{u}_p :

$$\overline{u}_p = \frac{\overline{u}_f}{\varepsilon} = \frac{3 \times 10^{-2}}{0.5} = 6.0 \times 10^{-2} m/s$$

Taking the density of molten steel at 1600^{o} C as $7000 \ kg/m^{3}$, its viscosity as $6.7 \times 10^{-3} kg/ms$, and the average pore diameter, \overline{d}_{p} , as $7.0 \times 10^{-4}m$, then:

$$Re = \frac{\rho \overline{u}_p \overline{d}_p}{\mu} = \frac{7000 \times 6.0 \times 10^{-2} \times 7 \times 10^{-4}}{6.7 \times 10^{-3}} = 44$$

Assuming Darcy's Law is valid⁵, the permeability of the filter or the pressure drop can be estimated according to equation 4.8 (it is an estimation since the model is not quite applicable for the filter used), where $Re = \rho \overline{u}_p \delta / \mu$. δ is about $4.0 \times 10^{-4} m$ for 20 ppi filters, then for liquid steel Re = 25, $k = 2.46 \times 10^{-7} m^2$ and $\Delta P/L = 1373 kg/m^2 s^2 (N/m^3)$. The pressure drop across the filter should be: $1373 \times 2.54 \times 10^{-2} = 34.9N/m^2$. For water, Re = 23, $k = 2.07 \times 10^{-7} m^2$, $\Delta P/L = 256N/m^3$, then $\Delta P = 6.5N/m^2$.

(2). Check on possibility of floatout

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There was some speculation that, given the experimental set-up designed, whether or not inclusions have a chance to float up during filtration. If so, the filtered samples taken from the exiting stream may not represent the true effect of filtration. In order to clarify this, full scale water modelling was carried out, with hollow glass microspheres simulating the inclusions in steel. The

⁵It is not certain whether Darcy's Law can be observed

numbers and size distributions of glass bubbles were measured by using Electric Sensing Zone (ESZ) technique developed at McGill University[66][67].

a. Modelling criteria

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The inclusion floating velocity in a steel vessel can be estimated by invoking Stokes' Law:

$$u_s = \frac{\Delta \rho g d_i^2}{18\mu} \tag{4.51}$$

where $\Delta \rho$ is the density difference between the liquid steel and the inclusion ($\rho_{steel} - \rho_{inclusion}$), d_i , inclusion diameter, μ , steel viscosity.

For the full-scale water model system, the following equation should be valid:

$$u_{s,w} = u_{s,s} \tag{4.52}$$

where $u_{s,w}$ is Stokes' velocity of the glass bubbles in water modelling, $u_{s,s}$ of the inclusions in liquid steel.

The viscosity of water at 18° C is $1.05 \times 10^{-3} kg/ms$, and of steel at 1600° C $6.7 \times 10^{-3} kg/ms$. Taking the density of glass bubbles, inclusions (Al_2O_3 or SiO_2) and steel as 340 kg/m^3 [68], 3000 kg/m^3 and 7000 kg/m^3 respectively, then:

$$\frac{(\rho_{water} - \rho_{glass})gd_{g,w}^2}{18\mu_w} = \frac{(\rho_{steel} - \rho_{inclusion})gd_{i,s}^2}{18\mu_s}$$
(4.53)

Substituting the corresponding values into the above equation, we obtain

$$d_{g,w} = 0.98 d_{i,s} \tag{4.54}$$

where $d_{g,w}$ represents the diameter of the glass bubbles in water modelling, and $d_{i,s}$ the inclusion diameter in steel.

Therefore, the floating effect of inclusions in steel can be predicted by the full-scale water modelling using the size conversion given by equation 4.54.

(b). E.S.Z. technique

The Electric Sensing Zone technique (also referred as Resistive Pulse Technique) was first developed by Dr. Wallace Coulter[69] for blood cell counting. The principle is quite simple a voltage is maintained between two electrodes which are suspended in an aqueous system and circuited through a small orifice in an electrically insulated glass tube — termed as *probe*, When a non-conductive particle passes through the orifice, the voltage across the two electrodes increases (a pulse) due to the increases in resistance in the circuit. The amplitude of the voltage pulse is, to a first approximation, proportional to the volume of the particle. Therefore, by counting the number and measuring the amplitude of the pulses, the concentration and the size distribution of the particles suspended in the fluid can be known. Figure 4.19 is a

schematic illustrating the principle of particle detection[67]. A detailed description can be found in references[66][67].

(c). Experimental

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Figure 4.20 shows the experimental assembly. Water with entrained glass bubbles, was introduced from a tank into the filter assembly through a siphon. Two ESZ probes, one above the filter and one immediately below the filter, were used to detect the glass bubbles. Water flowed through the orifice into the tube and down to a container placed below driven by the siphon effect. The pulses detected were processed through a preamplifier, a log amplifier and displayed on a Multi-Channel Analyzer (MCA) used in its Pulse Height Analyzer (PHA) mode. The signals were also transferred to a computer where the counts and size distribution of detected particles could be directly displayed on the CRT screen.

(d). Results and discussions

The results are shown in Figure 4.21. As can be seen that there is no substantial difference between the two probe readings. This indicates the glass bubbles had no chance to float up during filtration. Neither could they be retained by the high porous filter, as these glass bubbles are hydrophillic and can not, therefore, be stabilized to accumulate on the surfaces of the filter under steady state conditions.



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Figure 4.19: Schematic of particle detection principle via the ESZ technique [67].





Figure 4.20: Experimental assembly for ESZ.



Figure 4.21: Number and size distributions of glass particles detected by the ESZ probes

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Figure 4.22: Pore size distribution of Hi-Tech filters [55].

4.4.3 Filtration of Aluminum-killed Melts

In order to examine the filtration of alumina — the most troublesome type inclusions, aluminum-killed heats were filtered with 10, 15, 20 and 30 ppi Hi-Tech filters. Figure 4.22 shows the pore size distribution of these filters[55].

(1). Preparation of Steel Melts

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For each test, 25 lbs (11 kg) of Armco iron (to simulate low carbon steel) would be melted in a Tocco induction furnace. When the temperature reached 1600°C, aluminum rod or wire (its chemical composition is listed in Table 4.6) with a diameter of 3/8 in $(9.525 \times 10^{-3} \text{ m})$ or 1/8 inch $(3.175 \times 10^{-3} \text{ m})$ was injected into the melt. The dissolved oxygen was measured both before

Table 4.5: Chemical composition of Armco iron.

		С	Mn	P	S	Si	Cu	Ni	Cr	V	Mo
	%	0.000	0.075	0.007	0.009	0.000	0.019	0.000	0.000	0.000	0.000

Table 4.6: Chemical composition of aluminum used in deoxidation

%	rod (dia. 3/8 in)	wire (dia. 1/8 in)		
Si	0.091	0.04		
Fe	0.06	0.077		
Cu	0.014	0.014		
Mn	0.013	0.026		
Mg	0.001	< 0.001		
Ni	0.014	0.045		
Zr	0.18	0.10		
Ti	~ 1	0.019		
V	0.082	0.003		
Cr	0.11	0.094		

and after aluminum addition using an oxygen probe Celox/2 or Celox/3 (both of which contain a reference Cr/Cr_2O_3 cell). The dissolved oxygen before the aluminum addition was found to be about 0.14%. The aluminum addition was monitored indirectly by using the oxygen probe. The amount added was adjusted so that a completely deoxidized melt could be produced.

(2). Aluminum deoxidation

The aluminum deoxidation constant, $[\% Al]^2 \cdot [\% O]^3$ is, at 1600°C, about 10^{-14} . Assuming pure Al_2O_3 was formed according to

 $2[Al] + 3[O] = Al_2O_3$, the amount of reacted $[Al]_{reacted}$ and $[O]_{reacted}$ should, on a wt% basis, be:

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$$[Al]_{reacted} : [O]_{reacted} = 2 \times 27 : 3 \times 16$$
$$[Al]_{reacted} = 1.125[O]_{reacted} \qquad (4.55)$$

Assuming the residual dissolved [O] to be 1 ppm, for an 11 kg bath with an initial oxygen of 0.14%, $[O]_{reacted} = 11 \times (0.14\% - 0.0001\%) = 0.016$ kg. The corresponding reacted aluminum $[Al]_{reacted} = 1.125 \times 0.016 = 0.018$ kg. The residual aluminum [Al] in the bath should be:

$$[\%Al] = \sqrt{\frac{10^{-14}}{[\%O]^3}} = \sqrt{\frac{10^{-14}}{0.0001^3}} = 0.1$$

Therefore, for a residual aluminum content of 0.1 wt%, the extra aluminum required is: $[AI] = 11 \times 0.1\% = 0.011$ kg. The stoichiometric amount of aluminum added should be 0.029 kg.

In practice, it was found that it needed about 0.08 kg (276% of the stoichiometric amount) to reach the aimed oxygen level. This is in agreement with Olga Repetylo et al's [70] findings (200% - 500%). The reason being, firstly, the melting was carried out under atmospheric conditions with no slag protection on the surface. This oxygen depletion due to Al-O reaction will be accompanied by the continuous dissolving of oxygen from the atmosphere. Secondly, according to Guthrie et al [71], additives will encounter thermal and fluid-dynamic contacting resistances. The added aluminum will generally refloat before complete dissolution



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Figure 4.23: Change in dissolved oxygen content following aluminum additions

in the bath, even when projected with high entry velocities such as via bullet shooting methods. In the present experiments, even though aluminum was plunged into the melt, subsequent melted droplets of aluminum may have had a chance to float up to the surface. In addition, the nature of electromagnetic stirring produced by the induction furnace would also increase the rate of oxygen absorption and the chance of aluminum resurfacing.

Figure 4.23 shows the change in dissolved oxygen content with time following the aluminum addition.

Assuming the controlling step of oxygen transfer is in the liquid phase and that the steel bath is well stirred (see Figure 4.24), then:

$$\dot{N}''A = \begin{pmatrix} rate \\ of \\ oxygen \\ consumption \\ due \\ to \\ reaction \end{pmatrix} + V \frac{dC}{dt}$$
(4.56)

where \dot{N}'' is the rate of oxygen dissolving per unit area, A, V are the surface area and volume of the steel bath respectively, and C is the concentration of dissolved oxygen in the steel bath.

If we ignore oxygen depletion due to reaction with dissolved aluminum noting that V = Ah, h is the depth of the steel bath, then:

$$k_l(C_0 - C) = h \frac{dC}{dt}$$

where k_l is mass transfer coefficient in the liquid phase, C_0 is the saturation concentration at the interface. Integrating with boundary condition: t = 0, C = 1ppm, t = t, C = C then

$$rac{k_l}{h}\int_0^t dt = \int_{1ppm}^C rac{dC}{C_0-C}$$

$$\frac{k_l}{h}t = -\ln(\frac{C_0 - C}{C_0 - 0.0001})$$

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Figure 4.24: Schematic of oxygen gradient in a well stirred steel bath.

$$\frac{C_0 - C}{C_0 - 0.0001} = e^{-\frac{K_1}{h}t}$$

since $C_0{}^6 \gg 0.0001\%$, hence

$$\frac{C}{C_0} = 1 - e^{-\frac{k_I}{\hbar}t}$$

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$$C = C_0 (1 - e^{-\frac{k_l}{\hbar}t}) \tag{4.57}$$

 ${}^{6}C_{0}$ is, at 1600°, about 0.14%.

The dotted line in Figure 4.23 represents equation 4.57 with k_l taken as 5×10^{-4} m/s and h as 0.20 m.

(3). Products of deoxidation

The deoxidation products were found to be corundum (α -alumina). As is well known, these alumina inclusions form clusters in steel. Viewed under lower magnification, they look like pieces of cloud (see Figure 4.25). Under higher magnification, these clusters consist of very fine particles with a typical size range of 1 - 5 μm . The size evaluation of these clusters is somewhat of controversial. Braun et al[72] have evaluated alumina clusters by measuring their mean diameters determined by their projected areas.

It should be pointed out that clusters, or *pieces of cloud* are different from aggregates or agglomerates. The former, if viewed under high magnification on a cross section, show the particles to be still well separated. Aggregates, if viewed under low magnification, look like a piece of solid inclusions, under high magnification, they consist of individual particles with no steel in between (see Figure 4.26). The reason for the formation of clusters or aggregates is due to the high interfacial energy between the alumina and molten steel— formation of aggregates will reduce the area of the interfaces, while the magnetic stirring of the induction furnace provided the kinetic conditions needed—collision of inclusions. As can be seen from Figure 4.26, the steel was pushed or squeezed out from between the alumina particles due to the high interfacial tension. Figure 4.27 illustrates the schematic of this phenomenon.



(a)



Figure 4.25: Alumina clusters; (a) optical micrograph, (b) SEM micrograph, the sample was deep etched with bromine-ethanol solution.



(a)



(b)

Figure 4.26: Alumina aggregates, (a) optical $50\times$, (b) SEM micrograph.

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Figure 4.27: Schematic of empty gap formation between alumina pariticles.

Taking the gap between alumina particles as $1\mu m$ and the interfacial tension σ as 2300 mN/m, then

$$\Delta P = \sigma(\frac{1}{r_1} + \frac{1}{r_2})$$
 (4.58)

where r_1, r_2 are principle radii curvature, ΔP is the pressure difference across the meniscus. If the curvature is close to that of a sphere, then

$$\Delta P = \sigma(\frac{2}{r})$$
(4.59)
= 2300($\frac{2}{10^{-6}}$) = 4.6 × 10⁶ N/m²

 ΔP

If we equate ΔP with ρgh , this pressure difference corresponds to 67m metallostatic head of liquid steel! This means that these aggregates (with no steel in between) can form in any steelmaking or processing vessels since there are no vessels deeper than 67 m!

In some melts deoxidized with aluminum containing titanium $(\sim 1\%)$, titania (TiO_2) or $Al_2O_3 - TiO_2$ inclusions were also found (see Figure 4.28). Unlike alumina, titania inclusions did not form clusters (see Figure 4.29). This is because the interfacial energy between titania and molten steel is much lower than that of alumina. Since aluminum has a stronger affinity for oxygen than titanium, [O] will reacts with [AI] preferentially until [AI] and [O] is reduced to such a level that $\Delta G_{Al_2O_3} > \Delta G_{TiO_2}$.

$$2[Al] + 3[O] = (Al_2O_3)_s \tag{4.60}$$

$$[Ti] + 2[O] = (TiO_2)_s \tag{4.61}$$

$$\Delta G_{Al_2O_3} = \Delta G^o_{Al_2O_3} + RT \ln \frac{1}{a^2_{Al} \cdot a^3_O}$$
(4.62)

$$\Delta G_{T_i O_2} = \Delta G^o_{T_i O_2} + RT \ln \frac{a_{T_i O_2}}{a_{T_i} \cdot a_O^2}$$
(4.63)

then, [Ti] will begin to react with [O], forming TiO_2 or $TiO_2 - Al_2O_3$ inclusions.

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Figure 4.28: EDS spectra of titanium oxides.



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Figure 4.29: Titania inclusions.

(4). Process Parameters

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A few heats were run in order to establish process parameters. It was found that the minimum diameter of the exiting hole on the bottom of the crucible should be about $7 \times 10^{-3}m$ (1/4 in drill). A trial with $5 \times 10^{-3}m$ diameter did not succeed, the steel quickly froze in the exiting hole and blocked the flow.

It was found that the filter assembly must be preheated to about 900°C in order to assure successful operation. In a trial with a cold filter assembly, the funnel became cracked owing to thermal shock and steel leaked out. In addition, the nozzle (7mm) also froze up, and little steel passed through. Furthermore, the steel only went through the center part of the filter.

The pouring temperature was about 1600°C.

(5). Procedure

Shortly after the aluminum addition (within 3 minutes), the melt was poured into the preheated filter assembly which had been just taken out of a resistance furnace. A metallostatic head of about 0.05m was maintained above the filter.

(6). Filter priming

The initiation of the filtration process is called priming. It involves two stages[73]: first, the liquid steel enters the filter pores, and then flow the full length of the pores to exit from the filter. The

priming process requires the expenditure of energy to overcome the surface tension, the liquid steel being non-wetting relative to the filter material and the filter pores offering resistance to steel flow.

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If the filter is at the same temperature as the liquid steel, the energy needed to overcome the surface tension can be predicted:

$$h = \frac{2\sigma\cos\theta}{\rho rg} \tag{4.64}$$

where h is the metallostatic head, σ is the surface tension of liquid steel, θ is the contact angle between liquid steel and the filter, ρ , the density of liquid steel, r, the radius of the filter pores.

In the case of direct pouring, the charging velocity needed to overcome the surface tension for instant priming should be:

$$u_c \ge 2\sqrt{\frac{\sigma\cos\theta}{r\rho}} \tag{4.65}$$

where u_c is the charging velocity, which can be calculated from equation 4.48 (C = 1 in this case):

$$u_c = \sqrt{2gl}$$

where l is the height of the charging stream.

If the filter can not be instantly primed by the kinetic energy, it may be fully primed later on, once a metallostatic head has been built up. If the filter is at a lower temperature than the liquid steel at the point of priming, the metallostatic head or the charging velocity may be higher than the value predicted by equation 4.64 or equation 4.65. If the temperature of the filter is lower than the liquidus temperature of steel, freezing may occur on the filter surfaces at the beginning, and if there is insufficient superheat, the temperature drop of the steel due to heating the filter can exceed the superheat available, and priming failure may occur.

In the present set of experiments, it was found provided the filter assembly was preheated beyond 900°C, liquid steel would prime the filter without any problems except for the case of the 30 ppi filter. Filtration started almost instantly.

Given l, the height of the charging stream, as about 0.1 m, then $u_c = 1.40$ m/s. Taking σ as 1890 mN/m, θ as 120° (for a zirconia filter), r as $7.0 \times 10^{-5}m$ (10 ppi filter), $3.5 \times 10^{-5}m$ (20 ppi) and $3.0 \times 10^{-5}m$ (30 ppi), then according to equation 4.65, $u_c = 0.88m/s, 1.24m/s, 1.34m/s$. These represent the required charging velocities for instantly priming 10, 20 and 30 ppi filters respectively, if the filter temperature is the same as the liquid steel.

Since the temperature of the filter was lower than that of the liquid steel in the experiments, priming failures in the case of the 30 ppi filters were not surprising.

When the filter assembly was not preheated, it was found that although steel primed the center part of the filter, the exit nozzle would quickly freeze up due to the chilling effect.

(7). Metal flow rates

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The metal flow rate did not remain constant, but rather decreased gradually as a result of deposition of inclusions within the filter. The initial flow rate should, according to water modelling, be $6.1 \times 10^{-5} m^3/s \times 7000 kg/m^3 = 0.427 kg/s$. If this flow rate were maintained and no clogging occurred, it would take about 26 seconds to filtrate 11 kg of steel through the filter.

(8). Sampling

Unfiltered samples were taken in the induction furnace at the moment of pouring, using fused silica tubes or sampling crucibles. Samples of filtered steel were taken from the stream of steel exiting the nozzle set in the bottom of the crucible of the filter assembly (see Figure 4.15), using sampling crucibles. The samples were quenched in water. Seeing that inclusions within the metal bath (induction furnace) may not be evenly distributed, sampling was carried out in such a way that both unfiltered and filtered samples were taken from the same bulk metal. This was effected by taking the filtered samples at the very early (within 3 seconds) period of filtration, corresponding to the top layer of metal in the furnace where the unfiltered samples were taken.

(9). Analyses

Both microscopic and total oxygen analyses were carried out on the filtered and unfiltered samples. Clogged filters were examined with a Scanning Electron Microscope (SEM). The microscopic analysis with both the optical and SEM techniques provide information on the reduction in inclusion population, the type and morphology of inclusions, and the attachment of inclusions to the filter surfaces. Total oxygen analyses were carried out with STROHLEIN's instruments - ON.MAT 822. The advantage of this instrument is that it can produce an oxygen-temperature-time spectrum (i.e. the amount of oxygen released from a sample as a function of temperature). This information can help the types of inclusions to be deduced. Figure 4.30 shows such a spectrum.

The filtration efficiency based on total oxygen analysis can be expressed as follows:

$$\eta = \frac{O_{UF} - O_F}{O_{UF}} \times 100\%$$
(4.66)

where η is the filtration efficiency, O_{UF} , O_F represent the total oxygen contents (wt%) in unfiltered and filtered samples respectively.

(10). Results and discussion

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> It was found that the filter can successfully remove alumina inclusions. As can be seen from Figure 4.31, there is a dramatic reduction in inclusion population after filtration. Figure 4.32 shows the inclusions trapped inside the filter (20 ppi). The total oxygen analysis showed, in this case, a 90% reduction (1044 ppm before filtration, 140 ppm after filtration).

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Figure 4.30: An oxygen spectrum produced by STROHLEIN's instruments - ON.MAT 822.

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Figure 4.31: Optical micrograph of; (a) unfiltered and (b) filtered, samples, $10\times$.



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Figure 4.32: Optical micrograph of clogged filter showing the trapped alumina inclusions, $50 \times$.

a). Mechanisms for alumina retention by filter

As can be seen from Figure 4.33, the alumina inclusions appear to be sintered to the surfaces of the filter. Once such inclusions are sintered to the surfaces of the filter they will become part of it. On coming inclusions can either sintered to the filter surfaces or to the inclusions already sintered, thus forming a sort of network inside the filter. This will significantly reduce the porosity available for flow and eventually block the filter. This observation is in accordance with the thermodynamic analysis made in Section 4.3.2. Thus the high interfacial energy between the alumina and the molten steel, the high temperature and the small size of the alumina particles, all facilitate the sintering process.

b). Pore size dependence

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It was found that filtration efficiency increases with decreasing pore size (see Figure 4.35). This is because filters with a smaller pore size will enhance the inclusion transportation processes of interception, diffusion and hydrodynamic effects by narrowing the steel streams inside the pores.

c). Inclusion size dependence

It seems there was no size dependence on inclusion (alumina) capture. This can be explained as being due to the large driving force for sintering; that is, as long as the inclusions are transported to the surfaces of the filter, they should be captured. In other words, whether or not an inclusion can be captured depends only on whether or not it can be transported to the solid surfaces of the filter or already sintered inclusions. As discussed earlier, small sizes (< $10\mu m$ in aqueous liquids[57]) will facilitate



(a)

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(b)

Figure 4.33: (a) SEM micrograph shows the alumina sintered to the filter surface, (b) the networks inside the filter. Samples were deep etched with Bromine-Ethanol solution.



Figure 4.34: Schematic of alumina networking inside the filter.

Brownian diffusion process, while large sizes will enhance hydrodynamic action. This means both large and small inclusions can be transported to solid surfaces according to different mechanisms.

d). Inclusion type dependence

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Microanalysis showed that TiO_2 inclusions were hardly removed (see Figure 4.36). Unlike alumina, these titania inclusions were not clustered. They were more or less evenly distributed within the solidified melt. This is because the interfacial energy between titania and molten steel is much lower than that of alumina. The contact angle between TiO_2 and liquid steel at 1600° C is about 84° . As discussed in the thermodynamic analysis, the separation of wetting inclusions from molten steel is less favoured than nonwetting inclusions.


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Figure 4.35: Dependence of filtration efficiency on filter pore size.



Figure 4.36: Number and size distributions of titanium oxides.

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e). Filter thickness dependence

Three heats were run to check the influence of filter thickness on filtration efficiency. The 1-in $(2.54 \times 10^{-2}m)$ thick filter was cut into two 0.5-in thick filters. One of them was used as a 0.5-in thick filter and the other was combined with the normal filter and served as a 1.5-in thick filter. The results of the experiment with these three different filters in thickness are shown in Figure 4.37. It turned out that the filtration efficiency with 0.5-in thick filter was much lower than that of the normal (1-in) filter. However, the 1.5-in thick filter hardly showed any improvement in inclusion removal. This could mean that the dependence of inclusion capture on the depth of the filter may have a limit for a given filter beyond which there would be no further improvement in inclusion capture.

f). Filtering time dependence

It was found that the total oxygen in filtered steel decreases with filtering times. This is because the attachment of alumina inclusions to the surfaces of the filter would decrease the effective pore size of the filter and thus increase the chance of inclusion capture, over the time period of these experiments.

g). Initial oxygen dependence

In order to lower the initial levels of dissolved oxygen, a steel melt comprising 7 kg of 0.45 C steel and 4 kg of low carbon steel was tested. (see Table 4.7 for detailed chemical compositions). In this case, the dissolved oxygen before the addition of aluminum, was found to be 42 ppm, and practically zero ppm following addition. By comparison, the total oxygen was found to be 63 ppm

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Figure 4.37: Dependence of filtration efficiency on filter thickness.



Figure 4.38: Dependence of filtration efficiency on filtering time.

Table 4.7: Chemical composition of carbon steel.

	С	Mn	Р	S	Si	Cu	Ni	Cr	Mo
%	0.29	0.66	0.005	0.079	0.14	0.095	< 0.001	0.092	0 001



Figure 4 39[.] MnS inclusions.

before filtration and 54 ppm after filtration, corresponding to a filtration efficiency of 14% (10ppi filter). However, microscopic analysis showed MnS to be the dominating species of inclusions (see Figure 4.39).

h). Filter clogging

In all experiments with high initial dissolved oxygen melts, the filters became clogged. The longest filtering time was about 15

seconds before clogging of the coarsest filter (10 ppi). For the case of melts of low initial oxygen levels, the filters were not clogged at all (see figure 4.40).

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As mentioned earlier, the clogging of the filter is due to the fact that the formation of alumina networks inside the filter reduces the effective macroporosity available for the flow of liquid steel. For a given system, when the networking inside the filter reaches certain degree, the flow through the filter would stop.

Presumably, the clogging of a filter should be a function of metallostatic head above the filter, steel cleanness, the amount of steel filtered, the way the networks of alumina inclusions form inside the filter and the structure of the filter materials. It is probably premature to estimate the occurrence of filter clogging in filtering lower level oxygen steels based on the results obtained from this investigation alone. Consequently, the oversimplified model developed in the following is only meant to serve as a rough estimate.

Let us consider, therefore, a similar case to this set of experiments, i.e., given ferrostatic head being about $5.1 \times 10^{-2}m$, and filter material being Hi-Tech reticulated structure. After neglecting the influence of how alumina networks form, the main factors which affect filter clogging would be the cleanness and the quantity of the steel filtered.

The model is based on the assumption that when the volume fraction of alumina inclusions deposited inside the filter reaches





Figure 4.40: (a) Clogged filter, (b) filter not clogged.

certain level, the filter would become clogged.

In this set of experiments, clogging occurred after about six kg of steel with an oxygen level of 1400 ppm had been filtered through a 10 ppi filter.

According to S. Kuyucak[74], the volume fraction (ppm) of alumina equals 4.25 times the oxygen (ppm) in steel. Then the volume fraction of alumina inclusions in unfiltered steel should be: $4.25 \times 1400 = 5950 ppm(0.595\%)$. In six kg of such steel, the total volume of alumina inclusions should be: $\frac{6}{7000} \times 0.595\% =$ $5.1 \times 10^{-6}m^3$. Assuming 90% of the alumina inclusions are retained by the filter, the volume of the alumina inclusions deposited inside the filter should be: $4.59 \times 10^{-6}m^3$. The total volume of the macro pores inside the filter should be: $(2.54 \times 10^{-2})^2 \cdot \pi \cdot 2.54 \times 10^{-2} \cdot 50\% = 2.57 \times 10^{-5}m^3$. Therefore, the volume fraction of alumina inclusions inside the macro pores at clogging should be: 4.59/25.7 = 18%.

Assuming that clogging occurs when the total volume of alumina inclusions deposited reaches 18% of the total volume of the macro pores of the filter, for an unit volume of such filter materials (with a macroporosity of 50%), the following equation should be valid:

$$4.25 \times 10^{-6} \cdot O \cdot \frac{X}{7000} \times 90\% = 1 \times 50\% \times 18\%$$

or

$$X = 1.6470588 \times 10^8 \frac{1}{O} \tag{4.67}$$

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Figure 4.41: Nitrogen increase after filtration.

where X (kg) is the amount of steel filtered, O is the oxygen level (ppm) in steel. For example, when the oxygen level is 400 ppm, a unit volume $(1m^3)$ of filter material should be able to filter about 412 tons of steel before clogging occurs under the conditions mentioned above.

I). Reoxidation during pouring

It should be pointed out that under the experimental set-up, there would be reoxidation during filtration since the steel stream was not shrouded. According to Figure 4.41⁷, the nitrogen content

⁷Q: quenched, AC: air cooled.

heat e			ffar cren	ther size	dia of		daaonved (ppn	loxygen 1)	pouring T.	totai o) (ppr	n)	fitnetion	clogging	remarks
	(25 ba)	(gram)	*c	(4442)	ext hole (mm)	(cranara)	before Al addition	after Ai addition	•c	beture Altration	after fitration	(1)		
1	Armco	50	901	20	35	takro	1402	19.2	1586					filler was cryned but nozzie was troen
2	Armoo iran	30	945	20	5	lukro			1600					filler was crimed but nozzie was trosen
3	Animcia Iran	80	950	20	7	ок	1489	< 2.5	1650	1586	121	9275	yes	
4	Armoo Iran	80	950	20	7	ок			1600	1044	140	90%	yes	
5	Armou iron	no	950	20	7	ок			1600				no	
6	Annco Iran	80	980	10	7	ок			1610	793	193	76%	yes	
7	Armon Iron	80	no (Ireh	10	7	failure			1600					furmui cracked
8	oerbon steel	56	975	10	7	ок	42	ο	1600	63	54	14%	no	
9	Annoo Iran	80	920	15	7	ок	1292	< 3	1650	1057	211	80%	yes	
10	Annoo Iran	80	950	30	7	tekre			1600					filler waan'i prmed
11	Annoo Iran	80	950	10	7	ок			1600	1056	241	77%	yes	1 5∼n thak fiter
12	Armoo Iran	80	950	10	7	ок			1600	1068	363	66%	yes	0 5-in thick filter

Table 4.8: Summary of experimental conditions.

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	C	Mn	Р	S	Si	Ni	Cr	Mo	V	Nb	Al
%	0.10	0.25	0.011	0.077	>2	0.025	0.082	0.001	0.001	0.003	0.001

Table 4.9: Chemical composition of carbon steel.

was increased by 33% (47 ppm before filtration, 70 ppm after filtration) in the case of quenched samples. This clearly indicates that air dissolved into the steel during pouring. Therefore, the actual oxygen removal will be slightly higher than those indicated above, since the reoxidation aspect was not taken into account in its calculation.

4.4.4 Filtration of Silicon-killed Melts

(1). Preparation of Melts

Two melts of Armco iron and one melt of carbon steel (see Table 4.9 for the chemical composition) were tested with different amounts of ferrosilicon additions. The melts were made in the induction furnace. The ferroalloys were added at 1600°C. The dissolved oxygen was measured with an oxygen probe before and after the additions.

(2). Si deoxidation

The solubility constant for silicon deoxidation, $[\%Si][\%O]^2$, is about 2.7 × 10⁻⁵ at 1600°C[75], assuming $a_{SiO_2} = 1$ and $f_o^2 f_{Si} = 1^8$. If the dissolved oxygen is reduced from 0.14% down

⁸When [Si] < 2%, $f_o^2 f_{S_1} \simeq 1$

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to 0.01% for the case of Armco iron melts, the reacted $[Si]_{reacted}$ should be:

$$0.13 \times \frac{28}{32} = 0.1138\%$$

The residual [Si] in equilibrium with [O] is:

$$[\%Si] = \frac{2.7 \times 10^{-5}}{[\%O]^2} = \frac{2.7 \times 10^{-5}}{0.01} = 0.27$$

So silicon needed in an 11 kg bath is

$$11 \times (0.27\% + 0.1138\%) = 0.042kg$$

The ferrosilicon used contains 75% Si. Therefore the stoichiometric amount of ferroalloy needed should be 0.056 kg.

The amount of ferrosilicon actually added and the dissolved oxygen before and shortly after the alloy addition can be found in Table 4.10. Since the additives were dropped into the furnace as small lumps, the low efficiency of the addition's usage was expected for such a practice.

(3). The deoxidation products

In the heat with Armco iron and 0.2 kg ferrosilicon addition, the inclusions were found to be silica⁹. Judging from their spherical shape, they were in molten state before steel solidification. In principle, if there are no other deoxidizers, pure silica should form and this is in solid state at 1600° C. However this evidently did not happen. The reason for this could be due to the presence

⁹It could be silicate with trace of other oxides

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of traces of other elements such as manganese (the Armco iron contains 0.075% Mn), Al, Ca, etc. in the melt or ferroalloy, even though the EDS spectrum does not show their presence¹⁰ Another possible reason could be due to the kinetic conditions of the alloy addition's dissolution patterns; for instance, if the actual content of [Si] does not reach the aim level everywhere within the bath at the same time, then, in some locations, the [Si] content may not be high enough to meet the conditions for the formation of pure silica.

In the heats of Armco iron and carbon steel, 0.5 kg ferrosilicon addition, the inclusions were found to be complex. EDS analysis showed that they belonged to the $SiO_2 - Al_2O_3 - CaO$ system with a trace of Ti (see Figure 4.43). These inclusions were much smaller than those found in the melt with a 0.2 kg ferrosilicon addition. Perhaps, the large silica or silicates floated out of the melts due to increased the coalescence of inclusions as a result of the large amount of ferrosilicon addition. In all cases, inclusions floating up was, indeed, observed during operation.

(4). Operational parameters

The process parameters and flow rates for these silicon-killed heats were the same as those used for filtering Al-killed melts. The operation and sampling processes were carried out in the same manner as those described in 4.4.3.

¹⁰Probably, due to the low resolution of the EDS





Figure 4.42: (a) An EDS spectrum of, (b) silicon and iron scans on, a silica inclusion.



Figure 4.43: An EDS spectrum of silicate inclusions.

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Figure 4.44: (a) Silica inclusions found in a melt of 11 kg deoxidized by 0.2 kg ferrosilicon, (b) Silicates found in a similar melt deoxidized by 0.5 kg ferrosilicon. 148

(5). Results and discussion

The total oxygen analyses revealed a 35%-54% reduction following filtration of Si-killed melts. Microscopic analysis showed that the number of larger inclusions was reduced, while the number of smaller inclusions was increased (see Figure 4.45). Wieser[76] also reported that the number of *nodule* (inclusions) counts after filtration was increased. The reason for this is probably due to the re-formation of the liquid inclusions after they passed the filter; (in other words, the larger inclusions were probably broken up into smaller particle droplets by the filter). On the other hand, Wieser reasoned that the filter refractory may be abraded by the metal stream, thereby providing an increase in nuclei and nucleation sites within the filtered steel. Alternatively he argued that some substances which might be poison to the existing nuclei within the steel entering the filter were retained by it thereby activating the potential nuclei in the filtered steel.

a). Proposed mechanism for the retention of molten inclusions

It is probable that molten inclusions were removed by forming layers on the filter surfaces. This is especially true when the inclusions are wetting with respect to the filter material and nonwetting with respect to liquid steel. The steady state thickness of the layer of inclusions on the filter surfaces will depend upon the nature of the inclusions, the filter materials, the composition of liquid steel and the pore velocity. Since the liquid layer is deformable under shear stress, there will, for a given pore velocity, exist a critical thickness beyond which on coming inclusions cannot be stabilized on it, instead, they will be torn away by shear

Table 4.10:	Experimental	results.

heat	No.	1	2	3
steel type	(11 kg)	Armco iron	Armco iron	carbon steel
filter size	(ppi)	20	15	15
dia. of exist	hole (mm)	7	7	7
filter preh.	temp. °C	975	975	975
pouring temp.	°C	1676	1600	1600
Si added	(kg)	0.2	0.5	0.5
dissolved [O]	before Si add.	1150	1198	293
(ppm)	after Si add.	60	15	10
total O_t	before filt.	250	488	115
(ppm)	after filt.	163	226	56
η	%	35	54	51
priming		OK	OK	OK
clogging		No	No	No

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Figure 4.45: Inclusion counts and size distributions.



Figure 4.46: Schematic of molten inclusion retention.

stresses.

Based on the above reasoning, the removal of molten inclusions by filtration on an industrial scale may not be practical.

b). Selective removal

Based on the oxygen spectrum analyses of the filtered and unfiltered samples of silicon-killed steels, it seems that inclusions or components of complex inclusions with the higher melting points (corresponding to the peaks in the higher temperature regions, probably Al_2O_3 , CaO, etc.) were removed more than those with the lower melting points (corresponding to the peaks in the lower temperature regions see Figure 4.47 - 4.49). These high melting point inclusions may exist as separate solid inclusions and/or as components of molten complex inclusions. If these inclusion types

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existed separately, the higher removal efficiency observed could be explained by the same mechanism as that for alumina removal. If they existed as components of molten inclusions, this could mean that the filter was able to selectively remove different components of molten complex inclusions.

c). Pore size dependence

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It seems there was no pore size dependence on inclusion removal. This could indicate that different mechanism is involved compared to that applying during the filtration of aluminum-killed melts. In the present case, although transport phenomena would be enhanced in finer filters, the inclusions may not be able to stabilize on the filter surfaces even if they were transported to them since the velocity domain may act to cause relatively higher shear stresses infavorable to stabilization.

d). Filter performance

In all experiments, the filters performed well, no apparent degradation was observed. The filters were not clogged at all, and all steel passed through. Figure 4.50 shows the filter assembly used. The filter appeared to remain totally intact.

e). Dependence on filtering time

It was found that the total oxygen of the filtered samples remained almost constant with filtering time (see Figure 4.38). This is because the deposition of molten inclusions did not act in a synergistic way to improve inclusion retention.

f). The floating-off of molten inclusions

The large differences between dissolved oxygen before deoxidation

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Figure 4.47: An oxygen spectrum from an unfiltered sample

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#:A050 D:27.09.89 T:16.24 W:0.31090 C:00000001302 AT:02.51 н 0:0.0157 % 1005/0.00000 % 1174/0.0010 % 1408/0.0006 % 1505/0.0101 %

1904/0.0012 % 1967/0.0001 % 2004/0.0007 % 2091/0.0000 % 2097/0.0001 % 2101/0.0000 % /0.0000 % /0.0000 %

Figure 4.48: An oxygen spectrum from a filtered sample



Figure 4.49: Selective removal of inclusions.

and total oxygen before filtration (see Table 4.10) indicate that most of the molten inclusions floated off quickly (within 3 minutes, see operation parameters).

4.4.5 Filtration of Si-Al-killed Melts

(1). Melt preparation

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11 kg of Armco iron was melted in the induction furnace. When the temperature reached about 1600°C, 0.3 kg of ferrosilicon was added. The dissolved oxygen was found to be 1365 ppm before and 22 ppm after, the addition. Aluminum wire was, within 3 minutes of the ferrosilicon addition, then thrust into the melt. The oxygen probe reading then indicated that the dissolved oxygen approached 0 ppm.



Figure 4.50: Used filter-assembly, (a) top view, (b) bottom view

(2). Deoxidation products

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The inclusions appeared to be very similar to alumina clusters (see Figure 4.51). Closer examination revealed that these inclusions consist of a core of silica or silicates in the molten state and an alumina or $Al_2O_3 - SiO_2$ shell, in the solid or semi-solid state in molten steel. Individual alumina particles were also observed in the clusters of these inclusions.

The above observation clearly indicates that the deoxidation took place separately (or sequentially), i.e., before the aluminum addition, the reaction: $[Si] + [O] = SiO_2$ was completed. The added aluminum reacted with residual [O] and/or silicates to form alumina or alumino-silicates. The controlling step for the reaction between [Al] and silicates presumably is the diffusion of Al through the Al_2O_3 or $Al_2O_3 - SiO_2$ shell. This process can be expected to be diffusion-limited, and therefore slow. This probably explains how the double layer inclusions were formed.

(3). Characteristics of Si-Al deoxidation practice

Because of the distinct characteristics of the deoxidation products, they behaved differently in molten steel from both silicate and alumina inclusions. They combined the advantages of, (a) easier coalescence of molten silicates allowing them to increase in size (the big individual globular particles are about 40 μ m) prior to Al addition, and (b) the non-wetting effects of alumina, allowing them to form clusters. Both effects enhanced inclusion float



(a)



(b)

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Figure 4.51: Inclusions in Si-Al-killed steel. (a) SEM (BE), (b) SEM (SE) micrograph.



(a)



Figure 4.52: Double layer inclusions, (a) aluminum scan. (b) silicon scan.

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out! Indeed, the total oxygen was found to be only 65 ppm in the unfiltered samples, compared to 1365 ppm dissolved oxygen prior to deoxidation, meaning that 95% of the inclusions formed had floated off!

This deoxidation practice is strongly recommended for further investigation. As it appears that clean steel can be made by merely adjusting the deoxidation processes, which may be sufficient to avoid expensive secondary or tertiary refining processes for inclusion removal.

(4). Results and discussion

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The total oxygen analysis showed 60% reduction after filtration. The filtered steel was very clean, only 26 ppm total oxygen. This merit may be brought about by both filtration and the deoxidation practice as mentioned above.

steel type	25 lbs. Armco	
filter size	10 ppi	
dia. of exist hole	7 mm	
filter preh. temp.	975°C	
pouring temp.	1560°C	
Si added	0.3 kg	
Al added	0.04 kg	
dissolved [O]	before Si addition	1365 ppm
	after Si addition	22 ppm
	after Al addition	0 ppm
total O _t	before filtration	65 ppm
	after filtration	26 ppm
η		60 %

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Table 4.11: Experimental results and conditions

Chapter 5

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Final Remarks

5.1 Conclusions

1. The Hi-Tech Partially Stabilized Zirconia filters can successfully remove alumina inclusions in molten steel. The removal efficiency can reach over 90%.

2. Finer filters improve the removal efficiency of alumina inclusions.

3. Alumina inclusions sinter to the surfaces of the filter or to alumina inclusions already sintered, forming networks inside the filter thus reducing the effective pore size and eventually leading to the filter blockage.

4. Titania inclusions were hardly removed by the zirconia filter.

5. Total oxygen analyses showed about 50% reduction following filtration of silicon-killed melts. Because the molten inclusions are deformable, they did not block the filter. 6. To avoid a filter's blocking when used as a flow control device for liquid steel, the melt must be largely free of solid, non-wetting, inclusions.

7. The Hi-Tech PSZ filters used in this research work performed very well under the experimental conditions applying to this investigation.

5.2 Claims to Originality

1. This is the first time the sintered boundary between alumina inclusions and filter surfaces has been revealed (shown in Figure 4.33).

2. This is the first report of titania inclusions being hardly removed by the Partially Stabilized Zirconia filters.

3. This is the first time that a condition for instant priming, in the case of direct charging of liquid steel onto a filter of the same temperature, has been proposed:

$$u_c \ge 2\sqrt{\frac{\sigma\cos\theta}{r
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