

Investigation of Cluster Development and Distribution in REM Treated Stainless Steel

¹Asumadu Tabiri Kwayie
Materials Engineering Department,
Sunyani Technical University,
P. O. Box 206, Sunyani – Ghana

²Alexander Kwasi Kumi
Materials Engineering Department,
Sunyani Technical University,
P. O. Box 206, Sunyani – Ghana

³Ofori Yaw Nyantakyi
Materials Engineering Department,
Sunyani Technical University, P. O. Box 206,
Sunyani – Ghana

Abstract – Metallurgists have tried to produce the best materials for specific applications, in order to do this; they have to understand what goes on inside the plants and how best they can control the process. The removal of oxygen from the molten metal with the use of a deoxidant often produces nonmetallic inclusions that can reduce the quality of the final product if not properly removed. This project investigates the cluster characteristics in a stainless steel grade during deoxidation process with rare earth metals and also whether the samples provide authentic clusters distribution. It was found out that cluster starts forming immediately the mischmetal was added, they take time to fully develop and then they are finally removed from the system. The distribution of the clusters on the surface of the samples also provided more information on the distribution of the clusters in the liquid metal at the time of sampling. This information helps us to understand the properties of the inclusions and clusters that are produced in the steel during deoxidation process, in order to device the best methods to remove them.

KEY – Deoxidant, mischmetal, nonmetallic, cluster, inclusions

I. INTRODUCTION

The recent evolutions that are taking place in the world of materials have propelled the demand for high performance and quality materials. Every bit of strength and enhanced properties in each material is exploited to the later. Customers these days demand the best materials for specific application. It is of great importance that steel makers meet the demands of their customers in order to stay in business. Since 1950, materials engineers have known how to control the factors pertaining to steel production and have since then been able to produce quality grades of steel for all sorts of applications. The story got better after the invention of ladle technology, and this has helped steel makers to make steel of specific and controlled compositions. Clean steels have become the order of the day and each company's research and development team have targeted making steels with as low amount of impurities as possible.

Nonmetallic inclusions which form in the steel during deoxidation, desulfurization and reoxidation have been known to decrease the performance of materials for various

applications. The mechanical properties of materials are drastically reduced by the presence of these inclusions. For very sensitive applications where failure cannot be tolerated, the presence of inclusions often leads to catastrophic outcomes. Oxygen and sulfur are the two most troublesome elements when it comes to nonmetallic inclusion formation. The oxygen enters the steel during carbon removal in the converter, through contact with the top slag and also during reoxidation of the melt, whereas the sulfur enters the steel through the coke used as energy source and other raw materials.

It is against this background that deoxidants like aluminum, silicon (mostly in the form of ferrosilicate, FeSi), zirconium and titanium have been used to reduce the dissolved oxygen content of the steel before casting. These elements react with oxygen and in most cases produce a nonmetallic precipitate which is removed from the molten steel by the top slag. Rare earth metals (REM) have high affinity to oxygen and sulfur than any of these mentioned elements and they are currently been used for deoxidation and desulfurization of a wide range of steel grades. REMs offer better inclusion characteristics and relatively faster deoxidation and desulfurization processes.

The light optical microscope and the scanning electron microscope have helped us to understand the morphology, size distribution and chemical composition of these inclusions. And this project will contribute to further understanding of the characteristics of clusters formed during deoxidation of stainless steels with REMs.

B. Aim

The main aim of this project is to investigate into the deoxidation of stainless steel using rare earth metals.

1) Objectives:

- To evaluate the cluster characteristics in a stainless steel grade during deoxidation process with rare earth metals
- To assess the extent of clusters distribution in the molten steel.

C. Methodology

Both qualitative and quantitative analysis would be used for analysis in this project.

D. Scope

The choice of samples would be limited to stainless steel grades.

II. LITERATURE REVIEW

A. Stainless Steel

Harry Brearly accidentally discovered in 1913 that when chromium is added to iron up to 10% or more, the metal formed does not corrode [1]. Various grades of this steel have been developed and each one of them has tremendous resistance to corrosion and outstanding mechanical properties depending on the heat treatment. The steel's ability to resist rust formation on the surface is what gives it its name 'stain' 'less'. The corrosion properties of the steel improve significantly when 12% chromium is added. The chromium combines with oxygen in the atmosphere to form a passive chromium oxide layer that protects the surface of the materials thereby preventing further oxidation. With variations in the chromium percentage and addition of different alloying elements such as molybdenum the corrosion resistance can be enhanced. This would increase the scope of usage of the material under extreme corrosive environments.

Sufficient amount of nickel when added for alloying will stabilize the austenitic phase of the steel, this greatly enhances the mechanical properties and fabrication characteristics of the material. 8 to 10% Nickel addition improves the ductility of the stainless steel and this helps to protect it against stress corrosion cracking (SCC).^[2] Above these compositions the material becomes susceptible to SCC again. One major problem with stainless steels at the early stages of their development was their weldability but with the addition of nitrogen, the weldability significantly improves. Nitrogen also enhances resistance to pitting corrosion in austenitic stainless steels [3].

B. Stainless Steel Production

There are two main processes used in steel production, one is the use of the combination of ore and scrap as the raw materials (ore based) and the other is the use of only scrap for production (scrap based).

1) *Ore Base Steel Production:* When the ore is used for production then coke, limestone and iron ore mixture is fed into a blast furnace where reduction reactions are used to transform the iron ore into molten pig iron with a high percentage of carbon. As shown according to figure 1, from the blast furnace the molten metal can either be cast into pig iron or can further be transported to the basic oxygen furnace where scraps (with high chromium content in the case of stainless steels) can be added and the carbon content is reduced drastically with the help of oxygen blowing (oxidation reactions).

After the oxygen blowing when the required oxygen content is obtained, various alloying elements can be added to improve the properties of the steel. In the case of stainless

steels, the major alloying element is chromium and in some cases nickel. The chromium can therefore be added in lumps. The steel is then further refined to obtain the appropriate alloying compositions and the temperature is adjusted for the next casting process.

2) *Scrap Based Steel Production (Through Electric Arc Furnace):* The scrap based routine of steel making is done with the help of an electric arc furnace. This routine is the main line of production for stainless steels these days. In this process steel scraps and stainless steel scraps with high chromium content is charged into the electric arc furnace. Carbon electrodes are used to melt the scraps by producing an electric arc at their tips. The scraps melt into two distinct phases: the molten metal phase and the slag phase.

The slag formed is used to remove impurities from the molten metal. When a homogeneous molten metal is obtained, it is tapped and moved with the help of mobile ladles to the converter where the alloying composition can be corrected and the temperature adjusted for the next casting procedure.

This method consumes a lot of energy in its operations. It also relies more on the scraps with high degree of purity.

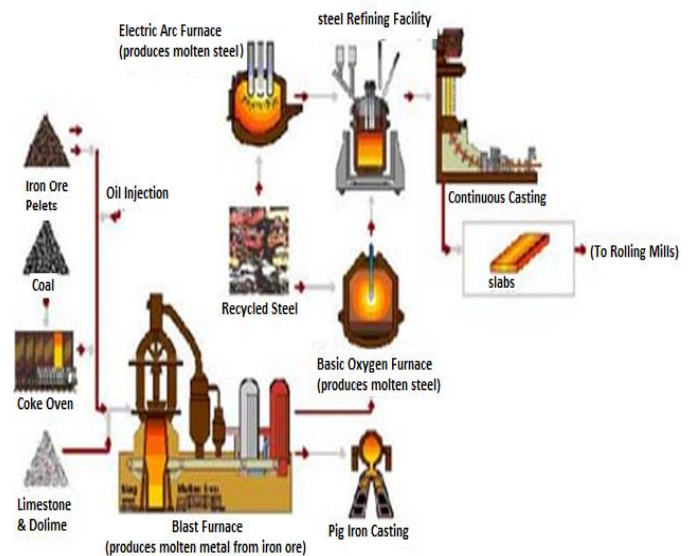


Fig. Typical steelmaking and continuous casting facility [4]

3) *Argon Oxygen Decarburization (AOD):* Different steel grades require different alloying elements that give them their distinct properties. In this process the carbon content is reduced to the appropriate composition and the various alloying elements can also be adjusted as well. This is mainly achieved by injecting oxygen into the metal melt to oxidize the carbon into carbon mono oxide (CO). In the process argon, nitrogen or mixture of the two gases are introduced into the system either for stirring or for diluting the oxygen gas. Argon and nitrogen injection also enhance inclusion removal in most cases.

4) *Casting*: There are two main processes used in casting the molten steel, the continuous casting and ingot casting. In most processing plants for stainless steels, the continuous casting process is used (this depends on the steel grade). The molten metal passes through cooling rollers and solidifies into a long metal strip, which is then cut into shorter slabs, billets or blooms depending on the size. The slabs are hot rolled into thinner and longer plates in a continuous rolling system until the appropriate thickness is obtained. This process is also accompanied by quenching procedures in stages.

Depending on the applications and customer specifications, the plates might be cold rolled to increase its yield strength. Surface smoothing might be applied by well polished rollers for applications where a higher degree of surface smoothness is required. The plates are then annealed to obtain homogeneous mechanical properties and improved microstructure. They are coiled into big metal coils and they are now ready for further processing into finished products. The billets and blooms are also processed according to their intended purposes.

C. *Deoxidation*

1) *Sources of Oxygen*: The total oxygen content of the steel is defined as the oxygen content dissolved in the steel plus the oxygen content in the form of oxides (nonmetallic inclusions) as can be seen in figure 2. In the converter oxygen is blown into the molten metal in order to reduce the carbon content of the pig iron to obtain the steel. In the process dissolved elements like Si, Mn, Mg and P gets oxidized into SiO₂, MnO, MgO, P₂O₅ respectively. These compounds formed make up the top slag which is less dense than the molten metal and therefore floats on top of it. The dissolved oxygen content of the steel also increases significantly in this process. Molten steel with high dissolved oxygen content is more likely to form nonmetallic inclusions with dissolved elements which have high affinity to oxygen, when the solubility of the oxygen in steel reduces at lower temperatures.

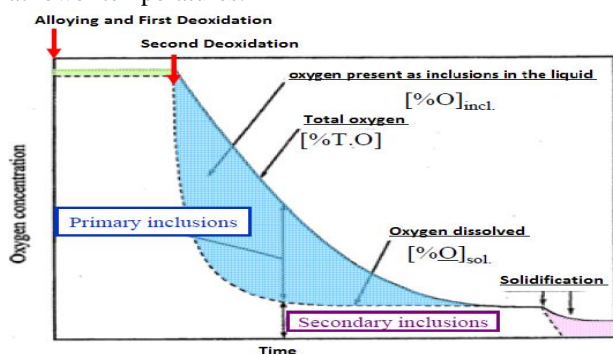


Fig. 2. Oxygen concentration of steel at a given time, this figure shows the curves for the oxygen content from the steel making process up to the solidification of the melt [5].

Another problem associated with high dissolved oxygen content is the ability of pore formation in the steel during solidification. Pores of gases form in the steel and this reduces the mechanical properties of the final product. It is therefore of great importance for the dissolved oxygen

content in the steel to be reduced. Other sources of oxygen in the steel making processes are slag, atmosphere, refractory and wet scraps.

2) *Deoxidation of steel*: Deoxidation is essentially the reaction of dissolved oxygen with dissolved elements that have a higher affinity to oxygen under the formation of nonmetallic oxides. The main purpose of deoxidation is to reduce the dissolved oxygen content of the steel to the required content. This however leads to the formation of more inclusions in the steel and they are removed later. The deoxidation process is mostly controlled by the activity of the dissolved elements, thermodynamic and kinetic conditions for the system.

3) *Thermodynamics of Deoxidation*: The deoxidation process is bounded by the thermodynamic conditions that exist in the ladle during the duration process. The solubility of oxygen in steel increases as the temperature increases. Therefore during solidification, the dissolved oxygen combines with the dissolved elements in the steel that have high affinity to oxygen.

$$xM + yO = M_xO_y \dots\dots\dots 1$$

M can be any alloying element that has an affinity to oxygen; the elements will therefore combine with the oxygen according to their oxygen potentials. The M_xO_y product formed can be solid, liquid or gas depending on the compound formed and the operation temperature in the ladle (usually 1600°C) [5]. M in most cases can be C, Al, Si, Ce, Zr, Mn or solvent Fe. Examples of solid products from this reaction are Al₂O₃ and SiO₂, CO₂ is also an example of a gaseous phase and some complex compounds of the Al-Si-Mn system also exist as liquid. The thermodynamic conditions can be put into the following equations:

$$K = \frac{a_{M_xO_y}}{a_o^y \cdot a_M^x} \dots\dots\dots 2$$

$$K = \exp \left[\frac{-\Delta G}{RT} \right] \dots\dots\dots 3$$

Where K is the equilibrium constant of the reaction which depends inversely with the temperature as can be seen in equation 3 and *a* is the activities of the respective elements. Δ*G* is the Gibbs free energy of the reaction which is also a function of temperature and R is the universal gas constant.

From equation 2, it can be deduced that in order to decrease the active concentration (activity: which is given by the interaction parameter multiplied by the concentration of dissolved oxygen) of the oxygen in the molten metal, the activity of M should be increased. This can be achieved by increasing the content of M in the liquid metal. Another point is also to decrease the activity of the product formed (M_xO_y) this is mainly done by removal of the product from the system therefore giving room for more products to be formed. Even though K depends on temperature and the Δ*G*, it usually remains constant in this case.

4) Types of Deoxidation

a) *Single Component Deoxidation:* Single component deoxidation is when an element that has a higher affinity to oxygen more than that of the alloying elements is used to reduce the oxygen content of the steel. This is mainly done to reduce the tendency of the alloying elements to form nonmetallic oxides at lower temperatures when the solubility of the dissolved oxygen reduces. The Ellingham diagram as shown in figure 3 is very helpful in choosing the right element for the deoxidation process.

The lower the element's location in the Ellingham diagram the higher its affinity to oxygen, therefore element like Al, Si and Ca are most often used for the deoxidation process. Mg and Ti is not usually used because of stability and cost respectively.

Other elements like zirconium which is just below the aluminum curve and the rare earth metals which are also below the calcium curve are not found in this figure but are also very effective deoxidizers.

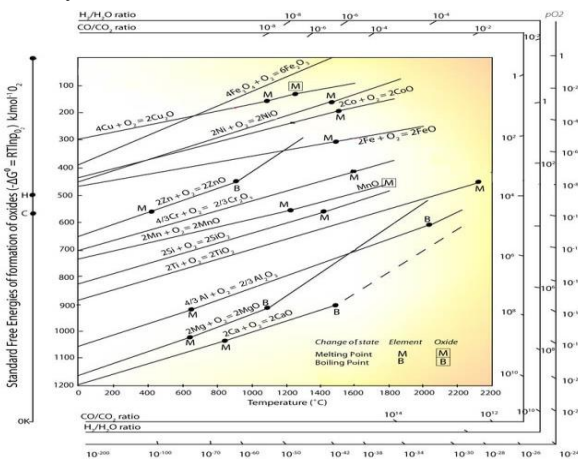


Fig. 3 Ellingham diagram, the oxygen affinity of the elements plotted against the temperatures [6].

b) *Complex deoxidation:* In order to achieve very low contents of the oxygen in the steel, different deoxidants are used for the deoxidation process. Deoxidation can be done in stages and with different combination of the deoxidizers: most often a less strong deoxidizer is used followed by a stronger one. A typical example is in the case where FeSi is used to deoxidized the melt before the aluminum killing process is done. The Si in the FeSi combines with the dissolved oxygen to form SiO₂, and the melt ends up with little amounts of dissolved Si as well. This process is followed by the addition of aluminum which further reduces the oxygen content of the melt.

These days complex combinations of Al-Mn-Si compositions are used for the deoxidation process. These are done for special steels where the oxygen content of the steel is much critical to the application of the final product.

5) *Rare Earth Metal (REM) Deoxidation:* The demand for cleaner and high strength steels in addition to good weldability and more tougher steels have fueled the quest for increasing use of various elements that have a higher affinity to oxygen for the deoxidation process. REM reacts quickly upon addition and the product formed give inclusion

properties that are different from the other problematic deoxidants search as Si and Al. The commercial sources of REM are mischmetal (which is 50-55%Ce, 25-30%La, 10-15%Nb and 4-6%Pr), neodymium metal (70-75%Nd and 15-19%Pr), rare earth silicide(30-35% REM, 30-35%Si and 30-35%Fe) and in their pure forms [7]. The yield of the REM in molten steel is mostly dependant on the melt chemistry and the method of addition. Improper addition methods can lead to the loss of a higher percentage of the REM in the slag or reoxidation by the atmosphere.

a) *Properties of REM:* REM in nature have lower melting temperatures as compared to the steel making temperature range (refer to table I). This means that dissolution of REM in the molten metal for deoxidation to start is not much of a problem. The density of the REM's are close to the density of iron and this means that REM deoxidation products would not float as the products from aluminum deoxidation would. The vapor pressure of cerium at 1600°C is 0.0023atm far lower than that for calcium(1.8atm) and magnesium(17.6atm) [8]. The other REMs also have values close to that of cerium, this means that REMs are more stable in the melt to prevent loss of mischmetal by evaporation.

The solubility of REM in steel decreases with decreasing temperature and this results in a formation of an eutectic with iron (as can be seen in figure 4). The REM's segregates at the grain boundaries where it forms the eutectic compositions [7]. This phenomenon causes hot shortness in high strength low alloy (HSLA) steels. The problem is predominant when there is a high REM residue in the steel.

TABLE I. PROPERTIES OF REM AND IRON

Element	Melting point °C	Boiling point °C	Density kg/m ³	Heat of fusion kJ/mol
Fe	1536	2859	7860	15.5
Ce	804	3599	6800	9.2
La	920	4516	6200	10.0
Nb	1024	3299	7000	10.9
Pr	935	3499	6800	10.0

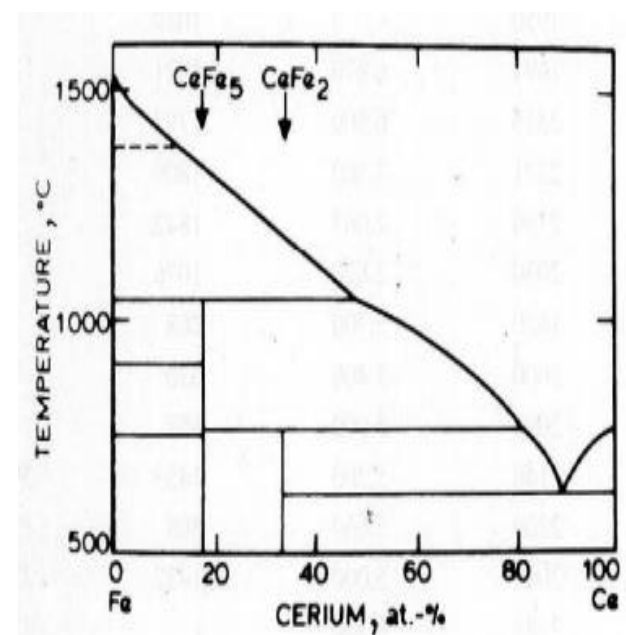
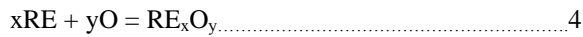


Fig. 4. Fe-Ce binary phase diagram [7]

b) *Thermodynamics of REM Deoxidation:* Under oxidizing conditions rare earth metals are very reactive and they easily react with oxygen to form oxides. The reactivity of the various metals that made up the REM; namely Ce, La, Pr and Nb are virtually similar. The standard free energy of the oxidation reactions between the REMs and oxygen is more negative than that of aluminum, magnesium and zirconium but just close to that for calcium, as can be seen in figure 5.

The higher the atomic number of the element in REM the more stable is the oxide formed. The reaction between the rare earth metal and oxygen is according to the equation below:



Where RE can be Ce, La, Nb, Pr or any of the REMs and RE_xO_y can be Ce_2O_3 , La_2O_3 etc.

The Gibbs free energy of formation of these oxides are remarkably high as compared to that for alumina, an example is that for the formation of La_2O_3 which is 841977KJ/mol O_2 and Ce_2O_3 which is 844868 KJ/mol O_2 [7]. These values are higher than that for alumina, which is 723629 KJ/mol O_2 . This explains why the REMs have high affinity for oxygen and forms more stable oxides during the deoxidation process.

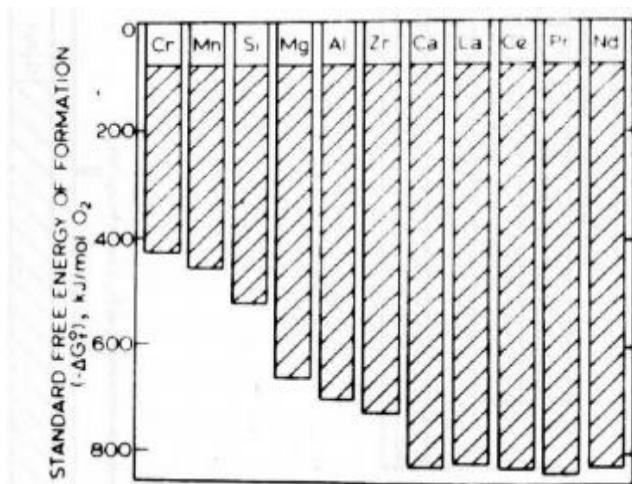


Fig. 5. Standard free energies of formation of rare earth and other oxides at 1650°C [7]

c) *REM additions and recovery :* The method of addition of REM determines the yield and recovery of on the elements in the melt. This is because the steel is fully killed upon addition of the REM since it has a very high affinity for oxygen. Another reason is because the REM reacts with oxides such as SiO_2 , FeO in the slag and reduces them. Some percentage also reacts with atmospheric oxygen and change into powered oxides.

Various methods have therefore been developed in order to improve upon the recovery of the REMs upon addition. The method that gives the highest residue of the REMs in the steel is the addition through vacuum degasser. This method is mainly used when alloying of REMs to improve toughness and ductility is required. Another method that gives the best recovery of the REM in the steel is the

plugging method. In this method the REM is delivered directly to the molten metal. The equipment is submerged below the slag level in order to avoid the reactions with the oxides in the slag. Adding the mischmetal during tapping is the method that offers the lowest recovery in the molten metal. In this method most of the REMs are lost through contact with air and slag.

Other methods also used are ladle addition during gas bubbling, before reladling, during teeming, mold addition during teeming.

D. Inclusions in Steel

Nonmetallic inclusions are products from the reactions between dissolved elements and compounds. These reactions lead to the precipitation of secondary phases in the steel. These secondary phase have different morphologies, sizes, chemical compositions and physical properties. The products formed are mostly oxides, nitrides, sulfides, carbides or a combination of any of them. Figure 1 shows some morphologies that inclusions form in steel. The mechanical properties of the final product are affected by the nature of the inclusions. REM and aluminum forms clusters in the molten steel as products from the deoxidation process. These clusters have the potential of causing clogging during casting and tapping processes. The clogging happens in narrow tubes and tapping holes. This problem can cause a stop in the casting or tapping process and which is unprofitable for companies.

Inclusions might be termed as primary inclusions if they are formed during ladle treatments or secondary inclusions if they are formed during solidification and casting processes. The primary inclusions form first and they most often serve as the secondary phases for the secondary inclusions to heterogeneously precipitate on.

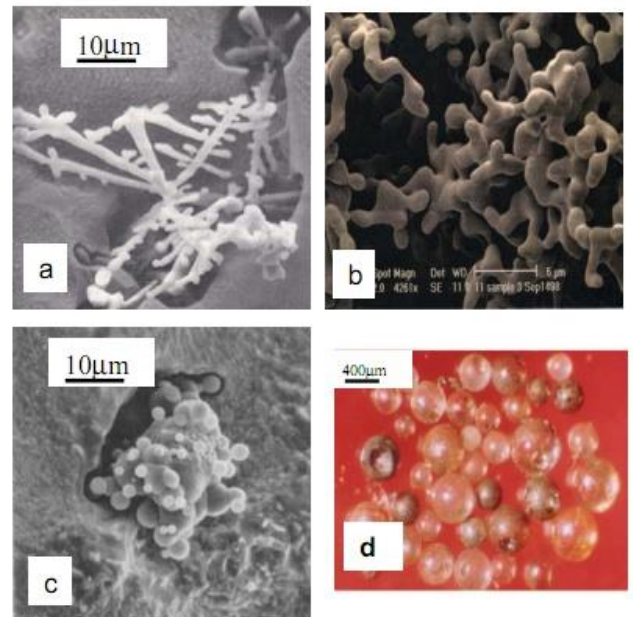


Fig. 6. Alumina inclusion morphologies: a) dendritic cluster [9] b) coral structure [10] c) alumina cluster [11], and d) slag inclusions [12][13]

III. EXPERIMENTAL WORK

A. Information about Samples

Six of the samples were taken in the ladle and one was taken in the tundish: the samples were taken as follows: 1minute before the mischmetal was added, 1minute, 5minutes, 11minutes, 15minutes (all these were taken in the ladle) and 39minutes (taking in the tundish) after the mischmetal was added, as can be shown in figure 7.

All samples taken from the ladle were taken automatically and the one taken in the tundish was taken manually. The samplers used were argon protected to preserve the composition of the molten metal. The mischmetal contained a mixture of REMs with composition: 50-55%Ce, 25-30%La, 10-15%Nb and 4-6%Pr.

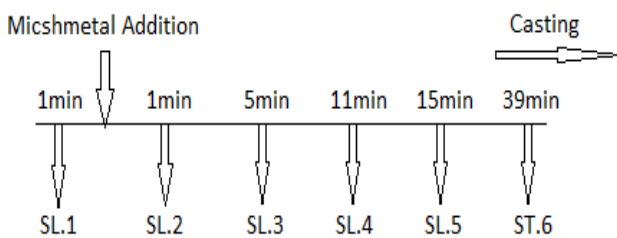


Fig. 7. Sampling time intervals

B. Sample Preparation

The samples were lollipop shaped samples (figure 8) that had been taken from a single heat. They had a diameter of about 33mm. In all, six of the samples from the same heat were analyzed for clusters with the help of Light Optical Microscope (LOM) and Scanning Electron Microscope (SEM). The surfaces of the samples were grinded in four stages and polished.



Fig. 8 The lollipop shaped sample

C. Surface Evaluation for Clusters

1) *Light Optical Microscopy*: For the LOM, the surfaces of the samples were sectioned into nine portions as can be shown in figure 9, from I to IX. The portions I, VI and VII made up the bottom part, II, V and VIII made up the middle portion and III, IV and IX made up the top part. This was done in order to evaluate the distribution of the clusters on the surface of the samples. Images of the clusters on the surface of the samples at each portion were taken with magnifications from X2.5 to X100. The user interface of the LOM was used to measure the sizes of the clusters for further analysis.

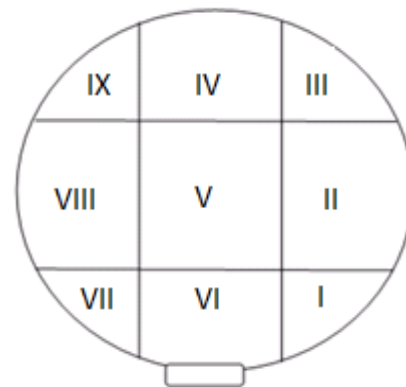


Fig. 9. Sectioning on the surface of the samples for the LOM analysis.

The length and width of the clusters were measured as shown in the figure 10. The average sizes of the clusters were then calculated according to the formula:

$$A_s = \sqrt{L \times W} \dots\dots\dots 5$$

Where A_s is the average size, L is the length and W is the width of the clusters. The number of clusters per unit area (N_A) of each zone is also calculated as follows:

$$N_A = \frac{TN_{(zone)}}{A_{(zone)}} \dots\dots\dots 6$$

Where $TN_{(zone)}$ is the total number of clusters of a particular zone and $A_{(zone)}$ is the area of the zone.

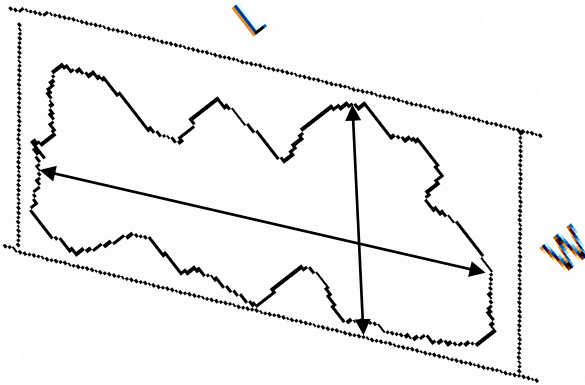


Figure 10 Length and width of the irregularly shaped clusters.

2) *Scanning Electron Microscopy*: According to the interesting results from the LOM analysis, the sample taken 11 minutes after the mischmetal was added was selected for the SEM analysis. SEM was used to evaluate the morphology of the clusters and Energy-Dispersive X-ray Spectroscopy (EDS) was used to obtain the composition.

IV. RESULTS AND ANALYSIS

A. Morphology and Composition Analysis of Clusters

The morphology of the clusters is irregularly shaped and bigger clusters are surrounded by smaller ones as can be seen in figure 11. Similar clusters were found distributed on the whole surface of the sample.

The EDS analysis of the clusters showed a significant amount of cerium and lanthanum. The cerium and lanthanum combined with oxygen to form the clusters with little amounts of the other REMs during the deoxidation process. This is evident according to the atomic percentage of oxygen, cerium and lanthanum in the clusters as shown in table II.

B. Cluster Size Investigation along the Time Intervals

There were no clusters found on the surfaces of the samples taken 1 minute before the addition of the deoxidant and 39 minutes after it was added therefore they are not represented in the result.

Figure 12 shows the average size of the clusters plotted against the frequency of the number of clusters. It can be deduced from the figure that all the curves peaked at 5µm, the curves then drop sharply. It is however conclusive from the result that, the average size of the clusters has the maximum number around 5µm.

The number of clusters that had the 5µm size 1 minute after the deoxidant was added is 30 and this number increases significantly to about 48 after 5 minutes. From 5 minutes to 15 minutes the peaks appeared to be stable and this indicates that the averages size of the clusters remain independent of time after 5 minutes of the deoxidant addition, at least up to 15 minutes.

The lower peak of the curve representing 1 minute after the mischmetal addition shows that the clusters started

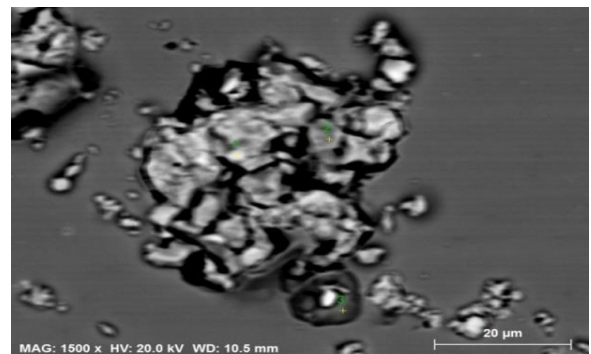
forming immediately the deoxidant is added (the kinetics nevertheless cannot be verified here). It is however lower than the peaks from 5 minutes therefore it takes a bit of time to form up to its highest number.

TABLE II. SHOWING THE COMPOSITION ANALYSIS OF CLUSTERS

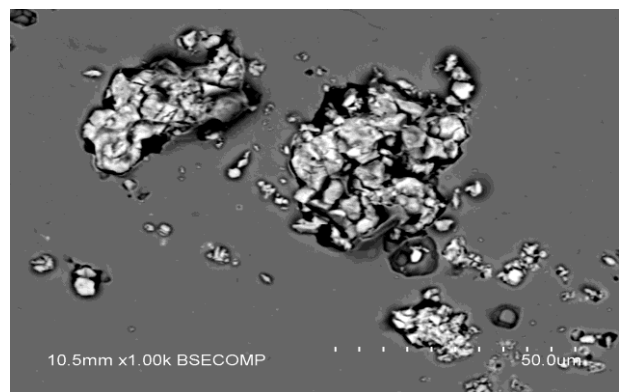
Element	Series	Norm C	Atom C
Cerium	L	30 - 42.15	25.40
Praseodymium	L	5.77	3.46
Neodymium	L	7.97	4.67
Lanthanum	L	15- 31.07	18.89
Silicon	K	0.23	0.69
Oxygen	K	6.89	36.36
Sulfur	K	0.06	0.17
Iron	K	1.83	2.77
Chromium	K	1.24	2.01
Nickel	K	0.47	0.67
Calcium	K	2.33	4.904.90

Another observation is that, the curve that represents 11 minutes after the deoxidant was added appears to have deviated a bit from the other curves and it had a peak of about 18 clusters for the sizes within the neighborhood of 12µm, this proves the coexistence of other cluster sizes as well.

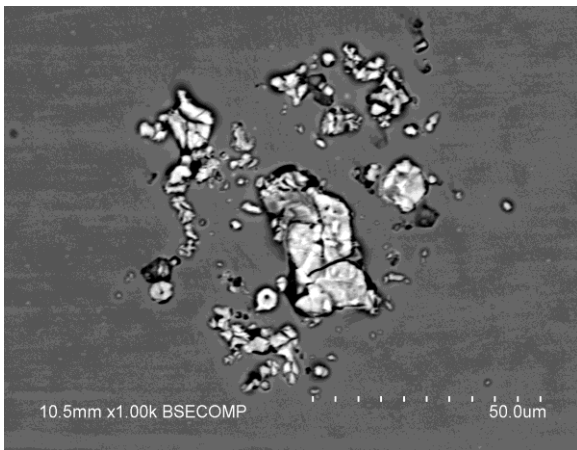
Standard deviation of the size of clusters shows (figure 14) clearly that the size of clusters is within close intervals for the various time intervals. The 1 minute time mark shows clusters having sizes within the range of 3µm - 5µm. This however reduces to 2 µm - 4µm for 5 minutes and then rises for the



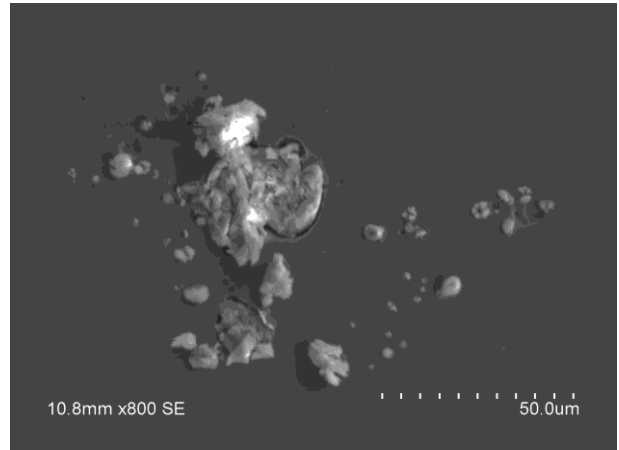
b)



b)



c)



d)

Fig. 11, SEM images for a) one of the clusters used for the EDS analysis and b), c) and d) show typical morphologies of clusters found on the surface of the sample 11minutes after the addition of the mischmetal.

11minutes mark to $4\mu\text{m} - 6\mu\text{m}$ before it decreases again to the $3\mu\text{m} - 5\mu\text{m}$ after 15minutes: this is consistent with the result from figure 12. The size of the clusters can therefore be assessed to range from $3\mu\text{m} - 6\mu\text{m}$ for the various time intervals. The existence of clusters of other sizes cannot be nevertheless ignored.

C. Evaluating the Total Number of Clusters among the Time Intervals

The total number of clusters per unit area plotted against the various time intervals according to figure 13, show a

very interesting pattern. It started rising from 1minute of the deoxidation process and got to its peak at the 11minutes mark before it started decreasing.

This means that the highest number of clusters during the deoxidation process can be found around 11minutes. When this result is combined with the results from figure 14 which indicates that the largest cluster sizes can be found around

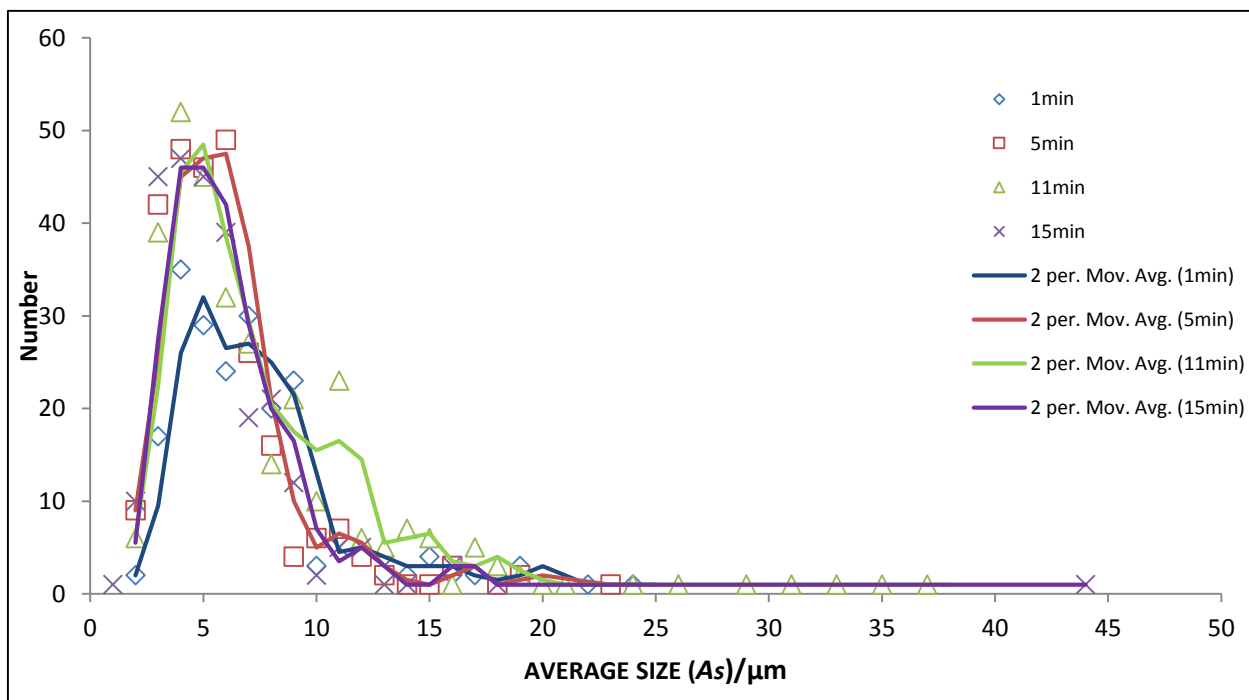


Fig. 12. The number of inclusions found on the surfaces verses average size of clusters along the time intervals from 1min to 15min.

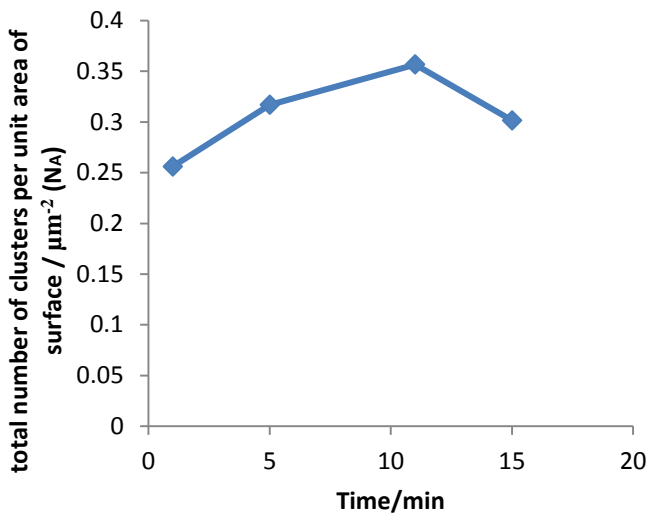


Fig. 13. The total number of clusters per unit area (μm^{-2}) of the surfaces of samples plotted against time intervals.

that same time (11minutes), it depicts that both the highest number of clusters and the largest cluster sizes can be found around 11minutes after the mischmetal is added.

The cluster characteristics seem to have gotten to their peak at 11minutes after the deoxidation process is started. It is of this background that the sample for this time was selected for the SEM and EDS analysis in order to obtain a vivid results as possible.

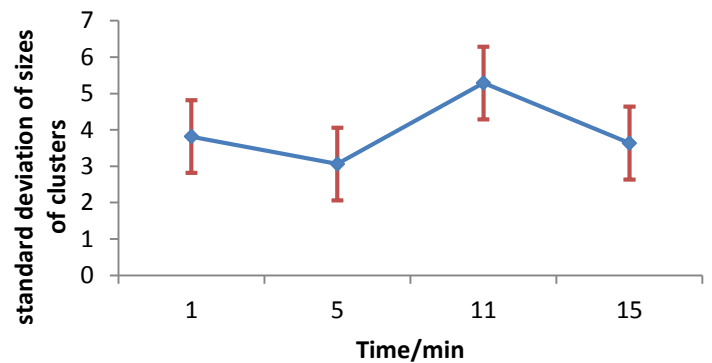


Fig. 14. The standard deviation of the size of clusters plotted against the various time intervals.

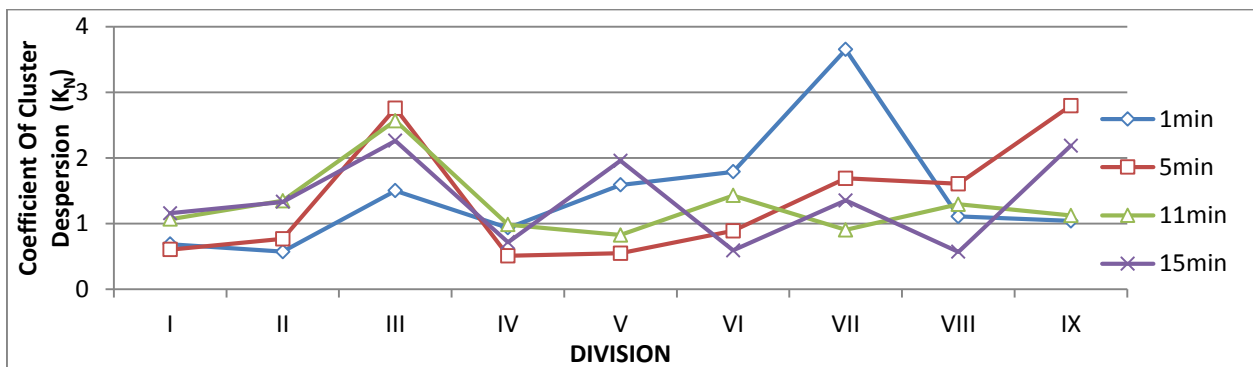


Fig. 15. K_N values for the various portions on the surface of the samples for various time intervals.

D. Distribution of Clusters on the Surface of Samples

For the distribution of the clusters on the surface of the samples, divisions were made on the samples as can be shown in figure 15. To evaluate the average cluster distribution in the liquid metal as at the sampling time, the coefficient of dispersion K_N [14] was used to evaluate the surfaces according to the formula:

$$K_N = \frac{N_A}{\bar{N}_A} \dots \dots \dots 7$$

Where N_A represents the total number of clusters per unit area of the zones (refer to equation (6) in previous section) and \bar{N}_A is the total number of clusters per unit area of the investigated surface. The K_N model can also be used to investigate the portions that the cluster can be overestimated ($K_N > 1$), reasonably estimated ($K_N \approx 1$) or underestimated ($K_N < 1$). If $K_N \approx 1$ then that portion fairly represents the distribution of the clusters in the liquid metal at the sampling time [14]. On the other hand the portions that are over estimated could be used to analyze the inclusion and cluster

characteristics such as in extraction and SEM analysis: as the majority of clusters precipitate there. From figure 15, various patterns can be deduced from the graph made from the K_N values.

The portions I, II and IV had values that were approximately equal to one, this means that these portions have cluster distribution that can be compared to the dispersion of clusters in the liquid steel. Various portions in the individual samples also show K_N values from 0.5 to 1.3 and these portions can also be evaluated.

A very interesting discovery is the curve corresponding to the sample taken 11minutes after the addition of the mischmetal. Except for the portion III which had a K_N value in the overestimated range, all the other portions met the $K_N \approx 1$ (thus from 0.8 to 1.4) criteria. This means that this sample provides the best knowledge of the cluster distribution in the liquid sample at the time of sampling.

Another pattern that needs evaluation is the values for the portion III for the curves for 5, 11 and 15minutes time

intervals and also VII for the sample representing 1minute. These portions show significantly high K_N values. The reason for the high K_N values at the III portions of the various samples might be attributed to the sampling position of the sampler as it is consistent true out all the samples.

E. Recommended Zones for Cluster Analysis

The sample taken after 11minutes of the mischmetal addition offered significant statistics in all the major topics discussed under this part of the project.

The compositional analysis of the clusters on this sample proves that the clusters were indeed REM clusters with significant amount of cerium and lanthanum.

The standard deviation of the clusters showed according to figure 13 that, this sample had average sizes ranging from $4\mu\text{m}$ - $6\mu\text{m}$, which was larger than all the other samples analyzed under the LOM. Figure 14 also shows that this sample had the highest number of clusters per unit area than all the other samples. It is however obvious that this sample has more and larger clusters, this is of great value to cluster analysis.

With the distribution of clusters on each sample, the sample showed consistent $K_N \approx 1$ values, which also makes it the best sample that gives adequate information about the dispersion of clusters in the liquid steel as at the sampling time. On the other hand, all the other samples also showed $K_N \approx 1$ values at I, II and IV and these parts can also be recommended for further investigations. Portion III on all the other samples would also be recommended for various analyses to understand cluster and inclusion characteristics, such as Extraction and SEM analysis, since it had very high K_N from figure 15.

V. CONCLUSION

The deoxidation process requires the use of an effective element that has a high affinity to oxygen to reduce the oxygen content of the steel during ladle treatments. In the process primary inclusions are formed and these inclusions depending on their chemical nature and morphology might come together to form clusters. Knowledge of how these clusters behave in the liquid steel is of great importance in order to be acquainted with some of the challenges (such as clogging) that it might pose to the steel making process line. This project however took a pace to investigate the size and distribution of REM clusters on the surface of the samples taken 1minute before the mischmetal was added and 1minute, 5minutes, 11minutes, 15minutes and 39minutes after the mischmetal was added. Two of the samples that were taken 1minute before the addition of mischmetal and 39minutes after the mischmetal was added, did not show any clusters on the surface. They were therefore given little attention to, since the purpose of the project was to evaluate cluster development on samples.

The rest of the samples that showed promising results for clusters where therefore further analyzed and investigated. From the investigation various portions could be identified and recommend for analytical work. The sample taken 11minute after the mischmetal was added stood out as the most promising sample for any type of analysis to study the characteristics of clusters both in the liquid steel (according to the K_N model) and on the solid piece (in view of the LOM analysis). The clusters can therefore be said to be evenly distributed in the liquid metal due to its equivalent density.

The project therefore could provide significant results and patterns after the statistical evaluation of data collected from the LOM analysis.

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