IZMIR KATIP CELEBI UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

INVESTIGATION OF CHANGES IN THE FORMATION AND TYPES OF NON-METALLIC INCLUSIONS IN THE STEEL PRODUCTION PROCESS

M.Sc. THESIS

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(Y130111026)

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Thesis Advisor: Assoc. Prof. Dr. Husnugul YILMAZ ATAY

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İZMİR KATİP ÇELEBİ ÜNİVERSİTESİ

FEN BİLİMLERİ ENSTİTÜSÜ

ÇELİK ÜRETİM SÜRECİNDE OLUŞAN METAL OLMAYAN KALINTILARIN OLUŞUMU VE DEĞİŞİMLERİNİN İNCELENMESİ

YÜKSEK LİSANS

İbrahim BAKAR

(Y130111026)

Malzeme Bilimi ve Mühendisliği Ana Bilim Dalı

Tez Danışmanı: Dç. Dr. Hüsnügül YILMAZ ATAY

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Ibrahim BAKAR, a **M.Sc.** student of **IKCU Graduate School Of Natural And Applied Sciences**, successfully defended the thesis entitled "Investigation Of Changes In The Formation And Types Of Non-Metallic Inclusions In The Steel Production Process", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :

         Assoc. Prof. Dr. Husnugul YILMAZ ATAY

         İzmir Katip Çelebi University

Jury Members :

         Prof. Dr.   ....

         İzmir Katip Çelebi University

         Prof. Dr.   ....

         Ege University

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ABBREVIATIONS

Alt	**:** Total Al
Alsol	**:** Dissolved Al
Alins	**:** Undisolved Al
Ototal	**:** Total Oxygen
ASTM	**:** Amerikan Society for Testing and Materials
EN	**:** Euro Norm
EAF	**:** Electric Arc Furnace
LF	**:** Ladele Furnace
VD	**:** Vacuum De-gassing
CCM	**:** Continuous Casting Machine
CA6	**:** CaO.6Al2O3
CA2	**:** CaO.2Al2O3
CA	**:** CaO.Al2O3
C12A7	**:** 12CaO.7Al2O3
C3A	**:** 3CaO.Al2O3
CaSi	**:** Calcium silicon
K	**:** Reaction Equilibrium Coefficient
OES	**:** Optical Emission Spectroscopy
ppm	**:** Parts Per Million
SEM	**:** Scanning Electron Microscope.
SEN	**:** Submerged Entry Nozzle
BSE	**:** Backscattered Electron
EDS	**:** Energy Dispersive Spectrometry
wt%	**:** Weight percent
XRF	**:** X-Ray Fluorescence
Al_2O_3	**:** Alumina
SiO_2	**:** Silica
MnO	**:** Manganosite
$MnO\text{-}Al_2O_3$	**:** Galaxite
$CaO\text{-}Al_2O_3$	**:** Calcium aluminate
$CaO\text{-}SiO_2$	**:** Calcium silicate
$CaO\text{-}Al_2O_3\text{-}SiO_2$	**:** Calcium aluminosilicate
MnS	**:** Manganese sulphide
BCC	**:** Body centered cube
FCC	**:** Face centered cube

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INVESTIGATION OF CHANGES IN THE FORMATION AND TYPES OF NON-METALLIC INCLUSIONS IN THE STEEL PRODUCTION PROCESS

ABSTRACT

It is not possible to produce steel without inclusions as the process for steel production requires. Based on this fact, the researches on clean steel are concentrated on the reduction of inclusions and transformation of inclusions into harmless state by modification. The definition of steel cleanness is related to final product application. Non-metallic inclusion, in the liquid steel, causing many problems and production lost in steel production process and final application. Aluminum killed steels mostly contain Al_2O_3 and MnS inclusions. Al_2O_3 inclusions are formed during de-oxidation or re-oxidation steps in steel making and continuous casting process. Alumina inclusions cause nozzle clogging in the continuous casting machine and show dendritic fracture during hot rolling.

During solidification of steel in continuous casting machine, Mn and S are refused from the solidifying dendrites, causing an increase in their concentration in the remaining liquid steel, which finally leads to MnS precipitation in the interdendritic spaces towards the end of solidification. MnS inclusions can be easily deformed during hot rolling process, thus gets elongated to long stringers, causing anisotropy in mechanical properties of hot rolled steel products.

Final product mechanical properties and physical properties are affected adversely by Al_2O_3 and MnS none-metallic inclusions in liquid steel. Non-metallic inclusions are causing cracking, fracture, tearing, surface defects etc. during forming and welding. To prevent these problems, the inclusions are modified to a more harmless form by feeding calcium wire during steel production. This process is called calcium treatment application.

Ca treatment application is used to reduce the harmful effects of the Al_2O_3 and MnS inclusions. Ca can modify oxide and sulfide inclusions. But insufficient Ca addition leads to incomplete modification of alumina inclusions and resultant formation of solid calcium aluminates having high melting points in steel making temperature.

These types of inclusions are detrimental to castability of steel. Ca addition is very important consideration in steel production. As mentioned above insufficient ca addition, inadequate calcium addition produces high temperature soluble aluminas, excessive calcium addition leads to the formation of CaS and C_3A (calcium aluminate) compounds. CaS and C_3A inclusions are detrimental to castability of steel in continuous casting machine besides harmful effect on physical and mechanical properties of final product.

When calcium is fed to liquid steel, it will first react with oxygen and sulfur and modifies the sulfide inclusions. At well deoxidized steel by aluminum, taking into account very low level of free oxygen CaO reaction is negligible (1.1). In steels containing low sulfur, transformation of alumina inclusions will take place as soon as calcium addition (1.3). Calcium reacts with the Al_2O_3 inclusions, aluminum is released into the steel melt and the formed CaO is dissolved into the alumina

inclusions. If the steel contains high sulphur, the desulphurisation reaction (1.2) becomes significant and competes with the oxide modifying reaction (1.3). The critical question is whether or not calcium added to steel will react with sulfur by reaction (1.2) and form CaS or modify Al_2O_3 to liquid calcium aluminates by reaction (1.3). The degree for modification of Al_2O_3 inclusions by calcium treatment depends on the competitive reaction between O and S with Ca in liquid steel.

$$Ca + O \rightarrow CaO \tag{1.1}$$

$$Ca + S \rightarrow CaS \tag{1.2}$$

$$Ca + (x + 1/3)Al_2O_3 \rightarrow CaO.xAl_2O_3 + 2/3[Al] \tag{1.3}$$

$$Ca + MnS \rightarrow (Ca.Mn)S \tag{1.4}$$
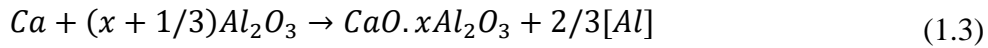
As a result of the research done so far, it has been found that there are five types of calcium aluminate CA_6, CA_2, CA, $C_{12}A_7$, and C_3A. Among them, $C_{12}A_7$ has the lowest melting point and liquid during until steel solidification temperatures. Liquid calcium aluminate inclusions have high CaO content and the inclusion has high sulfide capacity, they can absorb significant amount of sulfur. When the steel cools the solubility of sulfur in the inclusion decreases and CaS precipitates, resulting in a duplex inclusion of CaS or (Ca, Mn)S and calcium aluminate.

Consequently, calcium will convert solid alumina (Al_2O_3) inclusions into lower melting point calcium aluminates ($C_{12}A_7$), which will help prevent the clogging of the casting nozzles.

For successful calcium treatment, the sulfur value in the liquid steel must be sufficiently low that the calcium must not react with the sulfur, but instead must react with the aluminum inclusions. However, calcium treatment is not efficient for high sulphur steels as calcium reacts with sulphur to form solid calcium sulphide instead of liquefying the alumina. As mentioned about the formation of calcium sulfide can occur if calcium and sulfur contents are sufficiently high. Since calcium has higher affinity for oxygen than for sulfur, the addition of calcium initially results in a more or less pronounced conversion of the alumina into calcium aluminates until the formation of calcium sulfides starts as the addition of calcium continues. Calcium sulfides are solids at steelmaking temperatures and they also cause nozzle clogging in the continuous casting machine like alumina.

The remaining sulfur without making any compounds in liquid steel, during casting and solidification it reacts with manganese to form manganese sulfide inclusions in steel (1.4). For most steels Mn and S levels are not high enough for the formation of MnS inclusions in the ladle or tundish. Therefore, MnS inclusion is commonly not found in liquid steel. As the steel solidifies, Mn and S are rejected from the solidifying dendrites, causing an increase in their concentration in the remaining liquid, which finally leads to MnS precipitation in the interdendritic spaces towards the end of solidification. This described situation occurs in the continuous casting

machine in liquid steel production. The calcium aluminate inclusions retained in liquid steel suppress the formation of MnS stringers during solidification of steel. Instead of elongated MnS stringers, spherical inclusions can be obtained by calcium treatment which is called sulphide shape control.

In this thesis, the formation of non-metallic inclusions in vacuum process applied aluminum killed High Strength Low Alloy steel and how to change from ladle furnace to final product were examined at Ozkan Steel. In the experimental section, first of all the samples were subjected to chemical analysis in optical emission spectrometry. At a later stage, the samples were examined using a special program on an optical microscope. Finally, the samples were examined in SEM.

ÇELİK ÜRETİM SÜRECİNDE OLUŞAN METAL OLMAYAN KALINTILARIN OLUŞUMU VE DEĞİŞİMLERİNİN İNCELENMESİ

ÖZET

Çelik üretiminin süreci gereği inklüzyonsuz çelik üretmek mümkün değildir. Bu gerçekten yola çıkan araştırmacılar, daha temiz çelik üretmek için inklüzyonların sayısını azaltmak ve daha zararlı yapılara dönüştürmeye odaklanmışlardır. Çeliğin temizliği en son kullanılacağı ürünle ilgilidir. Sıvı çelik bünyesinde ki inklüzyonlar üretim sürecinde üretim kayıplarına neden olurken, nihai üründe de birçok sebeb olurlar. Al elementi ile deokside çeliklerde çoğunlukla Al_2O_3 ve MnS inklüzyonları görülür. Al_2O_3 inklüzyonları deoksidasyon ve reoksidasyon aşamlarının olduğu çelik üretimi süreci ve sürekli döküm sürecinde oluşur. Alümina inklüzyonları sürekli döküm sürecinde nozul tıkanmalarına sebeb olurlarken, haddeleme sürecince dentiritik kırılmalar gösterirler.

Sürekli döküm makinasında sıvı çeliğin soğuması aşamasında Mn ve S elementleri dentritik yapıdan ayrılırlar. Bu durum yoğunluklarının kalan kısımdan daha yüksek olmasına neden olur. Sonuçta MnS olarak arayüzlerde çökelmeye başlarlar. MnS inklüzyonları haddeleme sürecinde kolaylıkla deforme edilebilir. Bu durum haddelenmiş mamulün mekanik özelliklerinde anisotropiye neden olur.

Nihai ürünün fiziksel ve mekanik özellikleri Al_2O_3 ve MnS inklüzyonlarından kötü yönde etkilenir. Kalıntılar nihai üründe şekil verme kaynaklama süreçlerinde çatlak, yırtılma ve yüzey kurlarına sebeb olabilir. Bu tip sorunları önlemek için sıvı çelik üretimi aşamasında Ca tel besleme yapılarak kalıntılar daha zararsız formlara dönüştürülür. Bu işlem Ca uygulaması olarak adlandırılır.

Kalsiyum uygulaması Al_2O_3 ve MnS inklüzyonlarının çelik üzerindeki zararlı etkilerini azaltmak için yapılır. Ama yetersiz kalsiyum uygulaması tam olarak tamamlanmamış alüminyum modifikasyonlarına neden olur. Böylesi bir durumun sonucunda çelik yapım aşamasında ergime noktası yüksek kalsiyum alüminatlar oluşur. Bu tip kalıntılar çeliğim sürekli döküm makinasında çeliğin çekilebilirğinide kötü etkiler. Ca ilavesi çelik üretimi için çok önemli bir konudur. Yukarıda da belirtildiği gibi yetersiz Ca ilavesi yüksek sıcaklıkta ergime noktasına sahip katı alümina oluşmasına, fazla Ca ilavesi ise CaS ve C_3A oluşmasına neden olur. CaS ve C_3A inklüzyonları nihai üründe fiziksel ve mekanik özelliklere zararlı etkilerinin yanında çeliğin dökülebilirliğinide kötü yönde etkilerler.

Sıvı çeliğe kalsiyum beslendiğinde, ilk olarak oksijen ve sülfür ile reaksiyona girerek süfürü modifide eder. Al ile iyi deokside edilmiş çeliklerde serbest oksijen miktatı çok düşük olduğundan CaO oluşumu göz ardı edilebilir(1.1). Düşük kükürt seviyesine sahip çeliklerde Ca ilavesi yapılır yapılmaz, alümina inklüzyonlarının modifikasyonu başlar (1.3). Ca sıvı çelikteki alümina inklüzyonları ile reaksiyona girerek sıvı çeliğe alümünyum salınır. Oluşan CaO, alümina inklüzyonları içinde çözünür. Eğer yüksek sülfür konsantrasyonuna sahipse, sülfür giderme reaksiyonu

(1.2) önem kazanır ve oksit giderme reaksiyonu ile yarışır (1.3). Ca uygulamasıyla, Al_2O_3 inklüzyonlarının modifikasyon derecesi O ve S elemetlerinin Ca ile bileşik yapma rekabetine bağlıdır.

$$Ca + O \rightarrow CaO \tag{1.1}$$

$$Ca + S \rightarrow CaS \tag{1.2}$$

$$Ca + (x + 1/3)Al_2O_3 \rightarrow CaO.xAl_2O_3 + 2/3[Al] \tag{1.3}$$

$$Ca + MnS \rightarrow (Ca.Mn)S \tag{1.4}$$
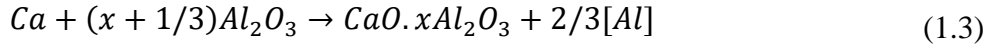
Bugüne kadar yapılan araştırmalar sonunda 5 tip kalsiyum alüminat tespit edilmiştir CA_6, CA_2, CA, $C_{12}A_7$, C_3A. Aralarında $C_{12}A_7$ çelik yapım sıcaklığında en düşük ergime sıcaklığına sahip olandır. Sıvı kalsiyum aluminate inklüzyonları yüksek derecede CaO içerir ve yüksek derecede sülfit absorplama capasitesine sahiptir. Sıvı çelik soğurken inklüzdaki S çözünürlüğü düşer CaS olarak çökelirken dupleks CaS veya (Ca, Mn)S inklüzyonları oluşur.

Sonuç olarak kalsiyum katı alüminaları (Al_2O_3), ergime noktası daha düşük kalsiyum alüminatlara ($C_{12}A_7$) çevirdiği için sürekli döküm makinesinde nozul tıkanmalarında önler.

Başarılı bir kalsiyum uygulaması için, sıvı çelik içerisindeki sülfür miktarı mutlaka çok düşük olmalıdır. Kalsiyum sülfür ile tepkimeye girmesin ve alümina inklüzyonlarıyla tepkimeye girsin. Ancak sıvı çelikteki sülfür yüksek ise kalsiyum sülfür ile reksiyona girerek, sıvı $C_{12}A_7$ yerine katı CaS oluşturur. Yukarıda da belirtildiği gibi CaS ancak sıvı çelikte Ca ve S değerleri yüksek olduğunda gerçekleşir. Kalsiyumun, oksijen için sülfürden daha yüksek afiniteye sahip olması nedeniyle, başlangıçta yapılan kalsiyum ilavesi, alüminanın kalsiyum alüminatlara az veya çok belirgin bir şekilde dönüşmesine neden olur. Kalsiyum ilavesi devam ettikçe CaS oluşumu gerçekleşir. CaS çelik yapım sıcaklığında katı olduğundan sürekli döküm makinesinde nozul tıkanmalarına neden olur.

Sıvı çelikte herhangi bir bileşik yapmadan kalan kükürt, döküm çekilirken ve katılaşma sırasında manganez sülfür inklüzyonları oluşturmak için manganez ile reaksiyona girer (1.4). Çoğu çelik için Mn ve S seviyeleri, pota veya tandişte MnS inklüzyonlarının oluşumu için yeterince yüksek değildir. Bu nedenle, MnS inklüzyon genellikle sıvı çelikte bulunmaz. Sıvı çelik katılaşırken, Mn ve S soğuyarak katılaşan dentritlerin arasından itilir böylece yoğunlukları çeliğin geri kalanına göre daha yüksek olur. Sonunda MnS inklüzyonları dentritlerin arasındaki boşluklarda çökelirler. Bu açıklanan durum, sıvı çelik üretiminde sürekli döküm makinesinde gerçekleşir. Sıvı çelikte bulunan kalsiyum alüminat inklüzyonları, çeliğin katılaşması sırasında MnS kalıntıların boyuna ipliksi oluşumunu bastırır. Kalsiyum ilevesi ile sülfür şekil kontrolü olarak MnS ipliksi boyuna uzatılmış inklüzyonları yerine, küresel şekle sahip inklüzyonlar elde edililir.

Bu tez çalışmasında alüminyumla deokside edilmiş vakum işlemi uygulanmış düşük alaşımlı yüksek mukavemetli çeliklerdeki metal olmayan kalıntıların oluşumları pota ocağından mamüle kadar değişimleri incelenmiştir. Deneysel kısımda örnekler önce optik emission spekrometresinde kimyasal analizi yapıldı. Daha sonraki aşamalar da özel bir program içeren optik mikroskopta incelendi. Son olarak örnekler SEM de incelendi.

1. INTRODUCTION

1.1 General Information About Non-metallic Inclusions

Non-metallic residue formed during steel production and continuous casting processes oxide, sulfur and nitrile compounds are called inclusions. Inclusions in steel, depending on the quality type and size, cause problems such as nozzle clogging and flow interruption during continuous casting, surface defects during rolling processes, deterioration of mechanical properties in the final product, and cracking, tearing, fracture and etc.

The effects on the steel of the inclusions will change according to the end use of the steel. Clean steel production has become important as the areas of use of final steel products become more specific. By nature of the steel production processes are impossible to produce completely non-inclusion steel. For this reason, researches in this area, is concentrated on the reduction of inclusions in the steel, and modifying it into harmless inclusions.

The processes in which the inclusions of steel production are formed should be well determined and necessary precautions should be taken to avoid them. Until the liquid steel is tapping from the electric arc furnace (EAF) to the solidifying in the continuous casting machine (CCM), there are too many processes that interact.

The main ones are;

- In the process of ladle furnace (LF), steel-slag, steel-refractory lining, steel-reoxidant element, etc. interaction.

- In the process of vacuum degassing (VD), steel-slag, steel-refractory lining, steel-reoxidant element, etc. interaction.

- In the proses of CCM, steel-tundih slag, steel-mould powder, etc. interaction.

The most harmful inclusion types in Al-deoxidized steels are Al_2O_3 and MnS inclusions. The formation of Al_2O_3 inclusions is due to deoxidation and reoxidation starting from the ladle furnace process and continuing through the continuous casting

process. MnS inclusions occur during solidification in the continuous casting process. Calcium treatment is applied in the LF, alumina inclusions in solid phase in steel production conditions are modified to inclusions of liquid calcium aluminate and MnS inclusions formation are also prevented. The calcium treatment process converts the Al_2O_3 and MnS inclusions into a harmless spherical form. So that these inclusions can be removed from the steel by floating.

For the effective inclusion cleaning, the chemical composition of the steel to be produced should be well analyzed and calcium should be applied considering the amount of dissolved oxygen and sulfur in the liquid steel during production.

The perpose of thesis study, the formation of non-metallic inclusions in vacuum treatment aluminum killed High Strength Low Alloy steel and how to change from ladle treatment to final product will be examined at Ozkan Steel. In this study, inclusions, which caused a problem at product, will be searched and analyzed. The source of these inclusions will be detected and will be taken precautions in order to decrease production losses.

1.2 The Structure of Steel

The metal structure is in crystalline form. The atoms in the solid are arranged in regular, repeated models. The smallest group of atoms that define atomic arrangement in a crystal is called a crystal lattice. There are many cage structures. However, pure iron has two cage structures: a body centered cube and a face centered cube (Fig. 1.1).
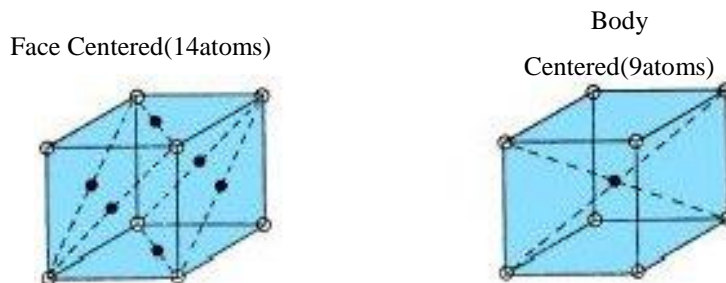
Figure 1.1: Pure iron structures [1].

Liquid steel does not contain a pattern like solid form. Liquid phases of metals have irregular atomic order. When the liquid is cooled to freezing temperature, crystals

start to form. When pure iron is cooled to 1530^0C degrees, a body-centered lattice structure consisting of nine atoms coming together is formed (one atom at each corner and one in the center). Other atoms then start to repeat the pattern around the cube. Thousands of crystals start growing at about the same time. But the atoms have to reduce their kinetic energy in order to be stable in the crystal structure. The mass of liquid must pass that surplus energy onto its surroundings, and that takes time. Atoms become solid as they lose their energy and the race starts to take place in the crystal structure among them. When freezing is complete, and every atom of liquid has become part of a crystal, the crystals themselves are not arranged in any kind of an over-all pattern. When pure iron reaches room temperature from freezing point, crystal structure also changes. This is slightly different situation. At a temperature of 1400^0C the crystal lattice pattern changes from its original body-centered form to the face-centered form. At 910^0C the lattice reverts to the body-centered form. These temperatures are termed critical temperatures. The freezing temperature drops when each element of pure liquid iron is added. The freezing phenomenon is actually not a single point temperature but a certain temperature range. Between the limits of this range, the metal is neither solid nor liquid; it is mushy or pasty. For some jobs this is a very important phase, for example welders.

Iron freezing temperature range up to 2% carbon content. Then it narrow to 4.3% carbon and finally disappears completely. An alloy of 95.7% iron and 4.3% carbon freezes completely at a temperature of 1130^0C and is called a eutectic alloy. After this point it is useful the iron-iron-carbide equilibrium diagram will be looked at. A simple figure of this fiction is shown in Figure 1.2. The two thick lines at the top of the diagram show the freezing point range for iron carbon alloys.
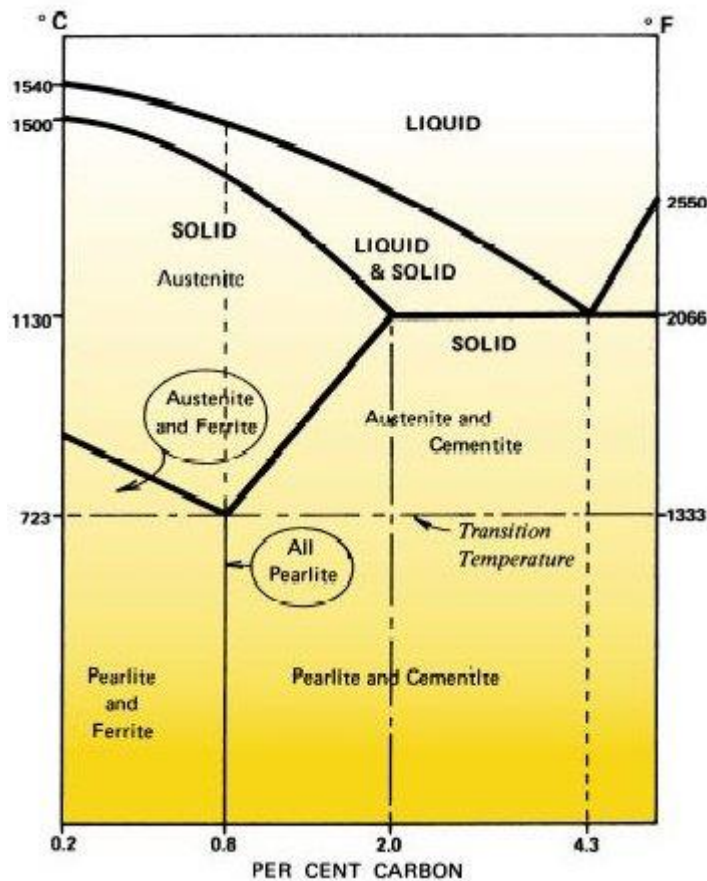
Figure 1.2: Weight percentage of carbon [1]

In the vertical line, which corresponds to 0.8% carbon content in the diagram, the alloy begins to freeze at about 1500^{0}C. Crystals of almost pure iron form in the face-centered pattern. (In pure iron, the crystals first formed in the body-centered pattern, but changed over to the face-centered pattern at a temperature a bit above 1500^{0}C). The carbon atoms keep moving around in the liquid, until the iron has crystallized. The liquid disappears when the temperature drops to a little over 1389^{0}C. The carbon has gone into what is termed 'solid solution' in the mass of iron crystals. The carbon atoms load themselves in the center of the surface-centered structure. They remain in the structure same position until the temperature of the solid metal has dropped to 723^{0}C. At that temperature, the iron crystals change from the face-centered form to the body-centered form. In the body-centered structure, there's not enough space for a carbon atom. As a result most of the carbon atoms linked with iron atoms to form a crystalline compound named iron carbide ($Fe_{3}C$). If cooling is slow, this iron carbide forms plates between plates of pure body-centered iron. If the sample taken from

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steel is cut etched and polished after it has cooled completely, and examine it under a optical microscope, almost all of the structure is formed of pearlite grains.

As can be seen in Figure 1.2, the phase called austenite has a face-centered grain structure, with carbon in solid solution. The austenite structure cannot be examined microscopic in ordinary carbon steel, (for the reason of temperature), but some alloy steels retain this structure at room temperature and in them it can be examined. The ferrite phase, the carbon content below 0.80% by weight in the iron carbon balance diagram and the phase seen below the eutectoid zone. Cementite refers to crystalline iron carbide (Fe_3C) which forms between the grains of pearlite in a slowly-cooled steel which has more than 0.80% carbon. Martensitic, which describes a structure formed in carbon steels when the steel is cooled rapidly (not shown on the equilibrium diagram). When steel is slowly cooled, all of the carbon in the steel appears as iron carbide layers within the pearlite grains. At even slower cooling conditions, thicker iron carbide layers occur. On the contrary, if the cooling rate is slightly increased, the layers of iron carbide in the pearlite become thinner. The grains of pearlite appear to become larger, and all grains of ferrite become smaller.

If the steel in the austenite phase at high temperature is cooled rapidly, by actually quenching in water, brine, or oil; the martensite transformation begins at certain regions within the austenite grains, in the form of martensite phase layers. This initial temperature, which is formed by the martensite layers, is called the martensite start temperature. As the sample continues to cool, the number of these martensite plates continues to increase. When the temperature falls below a certain value, no more martensite layers can be formed. In this temperature, where the transformation is completed, martensite finish temperature is called. The apparent reason for the formation of martensite is this: That it takes time for the carbon in the face-centered crystals of iron (austenite) to move out of the face-centered crystals and form crystals of iron carbide.

Martensite is a phase change that occurs without precipitation. When austenite with a surface-centered cubic structure is cooled rapidly below the martensite formation temperature, martensite is formed in the atoms without any diffusion. Martensitic is an extremely saturated iron solid solution to carbon. If the carbon ratio of the steel is

less than 0.25%, it is in the form of body centered cube, and if it is more than the volume centered tetragonal cube cage structure. If the carbon ratio of steel is less than 0.25%, it is in bct structure. If the carbon content of the steel is greater than 0.25%, the body centered tetragonal cage structure. Depending on the carbon ratio of steel, the martensite structure may be needle-shaped or plate-shaped. In steels with a carbon content less than 0.50%, martensite is seen as bundles of needles. If the carbon ratio exceeds 1%, it appears as lens-like plates. Martensite is hard, brittle and strong (Fig. 1.3). This is because of small grain size, dense dislocation density and internal stresses.

Figure 1.3: A martensitic structure, formedwhen medium-or high-carbon steel isquenched, looks something like this when examined under the microscope [1].

A steel containing 0.80% carbon is classified as high-carbon steel, and is seldom use in welding works. One of the terms of metallurgy is eutectoid steel, it can form a structure that is 100% pearlite. A welder is almost always working on hypoeutectoid steels. These steels are containing usually less than 0.80% carbon (the steels with more than 0.80% carbon are termed hypereutectoid).

Most of the steels used to form sheet contain 0.13% carbon or less; extra-low-carbon sheet may contain as little as 0.03% carbon. Steels in the upper part of this range (0.08 to 0.13%C), when allowed to cool slowly, usually contain some grains of pearlite, although the grains of pearlite are much smaller than the grains of ferrite. The mechanical properties of the product are affected by the size and shape of the ferrite grains.

Steels used in steel plate, tubing and steel pipe production mostly contain more than 0.13% carbon. Unless it has been given special heat-treatment at the steel mill after rolling, carbon steel plate will usually show a mixture of ferrite and pearlite grains,

with the pearlite grains smaller than the ferrite grains. However, this structure can be modified greatly by heat treatment (Fig. 1.4).

Figure 1.4: A photomicrograph of a piece ofsteel containing about 0.30% carbon will look something like this, showing a mixture offerrite grains (white) and pearlite grains [1].

1.3 Imperfection

It has been long assumed that the materials are of a perfect structure on an atomic scale. But in fact it's not like that. All contain large numbers of various defect or imperfection. Actually many of the characteristics of materials are extremely sensitive to deviation from crystalline perfection. These imperfections do not always produce bad results. Maybe deliberately loaded onto the materials during structural disturbances to achieve certain special characteristics.

Classification of crystalline imperfection is frequently made according to geometry or dimensionally of the defect; according to geometry point, line or plane; dimension defect.

1.3.1 Type of defect

• Point Defect: The defects which arise due to the irregularity or deviations from ideal arrangement of atoms around a point or on atom in a crystalline substance are called point defect or atomic imperfections.

• Line Defect: The defects which arise due to irregularities or deviations from ideal arrangement in entire row of lattice point are called line defects.
These irregularities are called crystal defects or crystal imperfections.

1.3.1.1 Point defect in solids

Vacancy defects

The simplest term the lack of the atoms in the crystal structure of the substance that should be. All solid crystalline structure contains vacancies, in fact, it is not possible to create or find vacancies free materials.

Self-interstitials defects

An interstitial is an atom that occupies a place outside the normal lattice position. It may be the same type of atom as the others (self interstitial) or an impurity atom (Fig. 1.5).
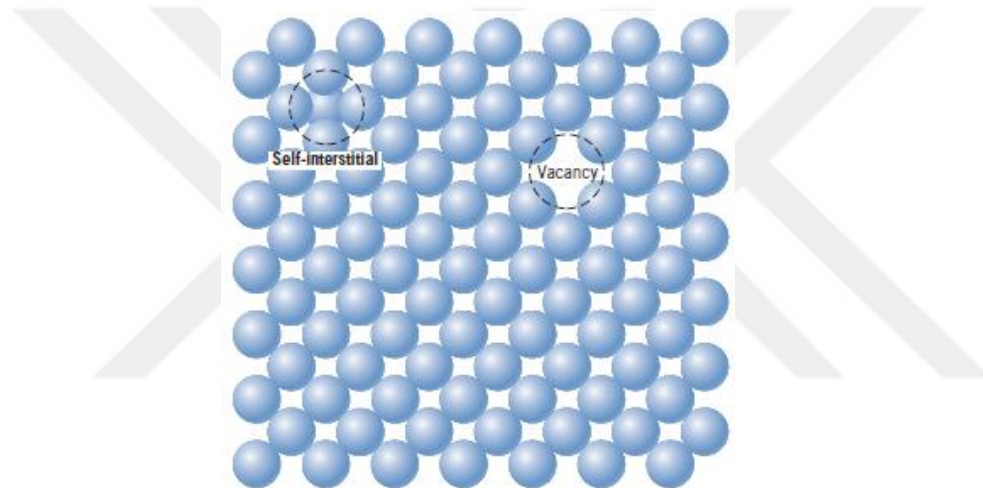
Figure 1.5: Two-dimensional representations of a vacancy and aself-interstitial. (Adapted from W. G.Moffatt, G.W. Pearsall, and J.Wulff, The Structure and Properties of Materials, Vol. I, Structure, p. 77. Copyright © 1964 by John Wiley & Sons, New Yor1.3.1.2 Impurities in solid)[2].

Pure metals consist of atoms of only one type of. But this is impossible, impurities or foreign atom will always be present. And having a diffrent element in pure metal not always a bad situation. For example sterling silver is a 92.5% silver-7.5% copper alloy. In normal ambient environment is highlt corrosion resistant but also very soft. Alloying with copper significantly increase the mechanical strength without decreaseing the corrosion resistance appreciably (Fig. 1.6).
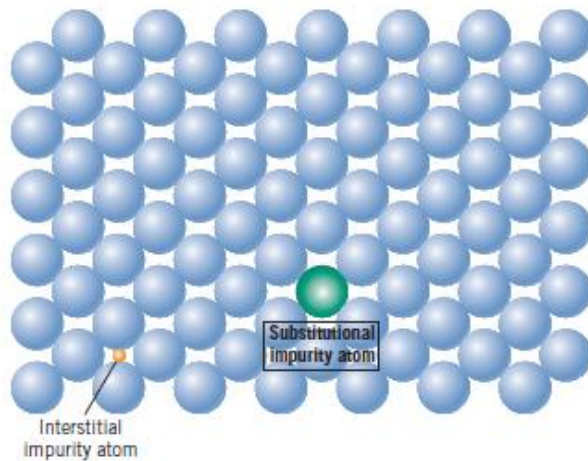
Figure 1.6: Two-dimensionalschematic representations of substitutional and interstitial impurity atoms. (Adapted from W. G. Moffatt, G.W. Pearsall, and J.Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 77. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)[2].

1.3.1.3 Miscellaneous imperfection

Dislocations-Linear defect

A dislocation is a defect caused by misaligned some atoms a linear or one-dimensional.

Edge dislocation

Edge dislocation is a linear defect which has its burger vector perpendicular to the dislocation line (Fig. 1.7).
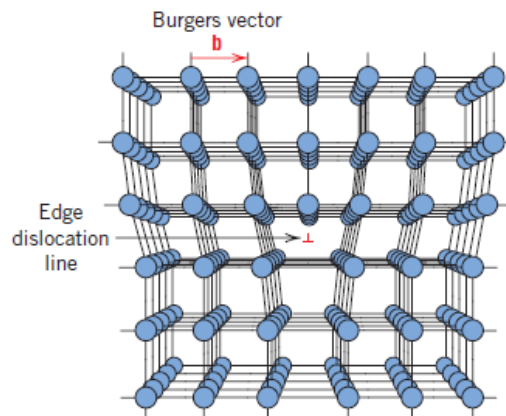
Figure 1.7: The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective. (Adapted from A. G. Guy, *Essentials of Materials Science,* McGraw-Hill Book Company, New York, 1976, p. 153.)[3].

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Screw dislocation

Another type of dislocation is named screw dislocation. Screw dislocation is more complex then edge dislocation. Burger vector is parallel to dislocation line.

Mixed dislocation

Mixed dislocation is a dislocation which has both edge and screw component.

1.3.1.4 Interfacial defects

Interfecial defects are boundaries that have two dimensions and normally separate regions of the materials that have different crystal structure and crystallographic orientations. These imperfections include external surface, grain boundariesi twin boundaries.

1.3.1.5 Bulk defects

There are many more defects in the materials than described above. For example pores, cracks, foreign inclusions, and other phases. The results of these defects are more evident during processing and fabrication.

1.3.1.6 Atomic vibrations

Every atom in a solid material is vibrating very rapidly about its lattice position within the crystal. In a sense, these atomic vibrations may be thought of as imperfections or defects.

1.4 Modern Steel Making

Modern steelmaking can be examined in six steps:

a) Ironmaking: In the first step, the raw inputs iron ore, coke, and lime are melted in a blast furnace. The resulting molten iron - also referred to as 'hot metal' - still contains high carbon(4-4.5%) and other impurities that make it brittle.

b) Primary Steelmaking: There are differences between BOS and EAF process from Primary steelmaking methods. BOS methods add recycled scrap steel to the molten iron in a converter. At high temperatures, oxygen is blown through the metal, which reduces the carbon from 4-4.5% content to 0-1.5% content. However in EAF methods, feed recycled steel scrap through use high power electric arcs (temperatures up to 1650 °C) to melt the metal and convert it to high-quality steel. The carbon ratio in the eaf method is lower than the bos method. But it is more difficult to manage the residual elements in the steel, since only scrap steel is used to produce liquid steel.

c) Secondary Steelmaking: Secondary steelmaking involves treating the molten steel produced from both BOS and EAF routes to adjust the steel composition. Secondary steelmaking process, to obtain the desired steel qualities, involves adjusting steel temperature, adding or removing certain elements. Depending on the types of steel required, the following secondary steelmaking processes can be used:

- stirring
- ladle furnace
- ladle injection
- vacuum degassing

d) Continuous Casting: In this step, the molten steel is cast into copper mould which cooled by circulating water from the surrounding area. A thin shell is formed around the liquid steel which is poured into the copper mold. The shell strand is withdrawn using guided rolls and fully cooled and solidified. The strand is cut into desired lengths or weight depending on application; slabs for flat products (plate and strip), blooms for sections (beams), billets for long products (wires) or thin strips.

e) Primary Forming: the steels cast in various shapes and sizes are subjected to the hot rolling process, so that the products are intended to have a stable inner structure, a smooth outer surface. It is also aimed to reduce the elimination of casting defects.

1.4.1 Steelmaking process and steel cleanliness

1.4.1.1 The steelmaking process

Iron making primary and secondary steelmaking, casting and hot rolling form main steps for steel production.

Producing liquid iron which is referred as hot metal from iron ore is included in ironmaking [5,6]. Molten pig iron is produced in blast furnace where sintered iron ore, coke and other fluxes are fed and iron oxide is reduced by carbon and CO gas. There are 4 to 5 wt %C and other impurities such as Mn, Si, P and S after blast furnace operation, which make improper for most engineering applications.

Primary steelmaking process is them main process where raw steel is produced [5,6, 7]. Iron route (pig iron route) and scrap recycling are two different technologies which is utilized for producing steel. Basic oxygen furnace (BOF) or converter are used for reducing carbon content or scrap metal or fluxes aand blowing oxygen are added to scrap metal. This process is know Basic Oxygen Steel making. .Carbon is burnt by oxygen and CO, CO_2 and Mn, Si and P impurities are generated and then they are collected in slag. Using Electric Arc Furnace (EAF)for melting to recycle steel from scrap iron and steel is an alternative method.

Adjustment is required in temperature, composition and cleanliness of steel for obtaining necessary properties of steel. Secondary steelmaking process is the stage where refining treatments are implemented. In Several elements are added or removed in ladle where raw steel is transferred for adjusting composition according to final grade specification. Operations which are implemented in secondary steel making process are summarized as following [5,6,8,9].

• Oxygen Control: Dissolved Oxygen content in steel is high after BOS process (400 to 1000 ppm). Formation of COS gas bubbles (boiling of metal) can be prevented by removal of oxygen. Otherwise it may lead distruption, excessive porosity, or big amount precipitation of FeO during solidification of steel. High amount of difference in oxygen solubility together with temperature cause this fact. Liquid iron has 0.2284 wt % (Fe(l)-FeO equilibrium), oxygen solubility at 1600 ^{0}C temperature. However oxygen solubility is 54 ppm t 1390 ^{0}C and 2 ppm at 900 ^{0}C.

Elements which have high relation with oxygen are added to hot metal for removing dissolved oxygen. Ferromanganese, ferrosilicon, silicomanganese and aluminum are most popular deoxidizers. Steel grade and residual dissolved oxygen determines the selection for the amount of deoxidants. Oxide inclusions which floats out of molten steel surface for deoxidation products which are captured by slag.

- Alloying: Spficific properties of final product is obtained by adding alloying elements such as Ca, Ti, Se, Te and Nb. Generally those alloys are injected to steel. Ca, CaS and CaAl alloys, C, Mg and S are covered by steel cover and added to steel as cored wire. Deoxidation can be implemented by wirefeeders however Al can be added to steel as solid wire.

- Removal of Impurities: In the event that sulphure remains inside raw steel after BOS or EAF operation it will lead detrimental properties over steel. Slag metal reactions under reducing conditions which require deoxidation of before sulphure removal is used for removing sulphure. Sulphure is transferred from steel to Slag under presence of CaO and Al in desulphurization process. Necessary desulphurization level is obtained by carefully controlling the composition of the slag.

- Stirring and homogenization: homogenization of bath composition and temperature and improving slag metal reactions and enhancing inclusion removal are main objectives of ladle stirring. Bubbling Ar gas by submerged lance or porous plugs from bottom are used for implementing stirring or electromagnetic stirrer is used for stirring.

- Degassing: RH process (Ruhrstahl-Heraeus) and tank degasser are used for vacuum degassing. Hydrogen removal, carbon deoxidation and decarburization, vacuum alloying and steel carburization are implemented in vacuum treatment. Vigorous stirring which is implemented in vacuum treatment significantly improves desulphurization of steel.

- Heating: Temperature may decrease during alloying, flux addition and degassing and this loss may be significant and may lead reheating of steel. Steel is heated and steel composition homogenized again in ladle furnace by using Ar bubbling too. Some steel mills are performing vacuum degassing by presetting the

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temperature at which the liquid steel will lose during the vacuum degassing process. CAS-OB (Composition Adjustment by Sealed Argon Bubbling – Oxygen Blowing) where AL and O_2 gas added at the same time by means of top lance is used for chemical reheating. Steel is heated by Al and O_2 exothermic reaction where Al_2O_3 is formed.

Before casting steel Completed steel is transferred from ladle to tundish for adjusting steel composition, temperature and cleanlimess after secondary steel making process. Continuous casting machines are generally used for casting steel (Presented in Fig. 1.8). Liquid steel is distributed continuous casting moulds by tundish which serves as reservoir during ladle changes [10]. Steel is delivered from ladle to inlet section of tundish which is lined with refractory and steel is delivered to mould from outlet section of tundish through nozzles. Flow of liquid which is teemed into mould is controlled by stopper rod or sliding nozzles which control opening. Dams are other flow control equipments.
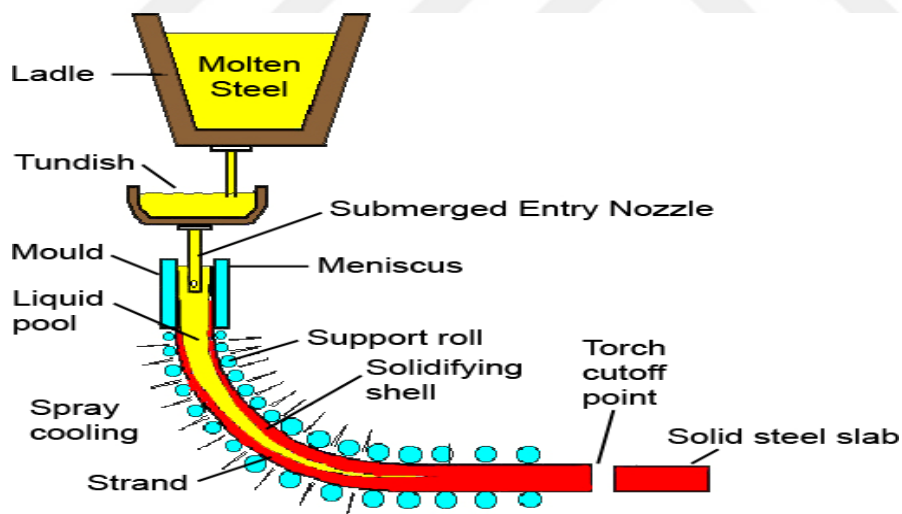
Figure 1.8: Schematic lay-out of the ladle, tundish, SEN and casting mould for curved continuous casting [4].

Inclusions can be removed by decantation in tundish for improving steel cleanliness as longs as there is not reoxidation in tundish.

Liquid steel starts to solidify in water cooled copper mould and forms strand (Fig. 1.8). Water sprays are used for cooling strand at exit of mould and formation of bulges until strand is completely solidified is prevented by supporting with rolls. Then accordingly with final applicatın (slabi, bloom, or billet) strand is cut into desired measurements. Hot rolling method is used for obtaining finished products such as ingot, slab, bloom or billet. Material is reheated to 1200-1300 ^{0}C again and moved forward and reverse between rolls for a few times. Steel is shaped in to required size and its mechanical properties are improved by hot rolling.

1.4.1.2 Steel cleanliness

There is increasing demand for high quality steel in steel industry. Final product should have high performance, high reliability and durability and also there demands regarding with cost reduction, energy saving and environmental issues should be met for steel makers to be in competition. Microstructure heavily influences the properties of material. Non-metallic inclusions are particles that are embedded in the matrix of steel. Oxides, sulphides, nitrides and carbides are main form of inclusions. Some sulphide inclusions and large oxides may present in molten steel where as last three types of inclusion precipitated during cooling and solidification stage. Certain properties of final product may be influenced significantly due to metallic inclusions in completed steel. Thereby as cleanliness of steel depends on presence of nonmetallic inclusions and other impurities which may effect over final product, steelmaking industry aims to produce cleaner products.

1.5 Classification of Inclusions

Sources of nonmetallic inclusions are used for their classification [11,12]. Indigenous and exogenous inclusions are two main types. Deoxidation stage, cooling and solidification periods of hot metal are main stages where indigenous inclusions occur. The former are called primary inclusions and the latter secondary inclusions or precipitates. Reaction between dissolved oxygen in liquid Fe and addition of deoxidant such as Al or Si cause formation of inclusion. Oxygen inclusion is from

internal to metal in this case. Deoxidation products create most of indigenous inclusions

Reactions beween deoxidized steel and environment cause exogeneous inclusion. Indigenous inclusions can be obtained on demand however unintended mechanical and chemical reactions between hot metal cause exogenous reactions. Large size, irregular shapes and isolated occurrence of exogenous inclusions cause detrimental effect [12]. Reoxidation products, refractory lining erosion and slag capture form main reasons for exogenous inclusions. Mechanical reactions during turbulent mixture of slag and metal cause exogenous inclusion. Emulsificatiıon of Slag which generally has large and spherical shape due to liquid phase at steel making process cause exogenous inclusion [12]. Erosion of refractory and formation of macroinclusions may be caused from high speed of hot metal close to refractory walls and keeping at tank for long time period. Reaction between hot metal and surrounding cause reoxidation inclusions.

1.5.1 The influence of inclusions on steel properties

Generally Mechanical properties of steel are influenced badly from non metallic inclusions. Plasticity, thermal coefficient properties are different in inclusions with respect to steel matrix and this lead different mechanical and thermal stresses in inclusions with respect to steel matrixes [14]. Presence of harmful inclusions effect ductile fracture, toughness, fatigue and machinability properties badly [14,15].

Causing formation, enlargening and coalescence of void and crack propagation by forming nucleation site may effect ductile fraction badly [16]. Ductile matrix is forced to be deformed by void formation and this creates higher stress and decohesion in areas close to inclusiın [17]. Volume of fraction and inclusion forms effect strain which may lead ductile fracture [15,16]. Anisotropy behavior of elongated inclusions and orientation due to working direction makes them harmful for ductility. In conclusion impact and fracture will be effected badly from existence of soft inclusions such as sulphide, MnS since their high plasticitiy (type D and in Fig. 1.9) will deform their steel matrix.

Premature fracture may occur as steel formability reduced due to elongated inclusions. Fatigue strength may reduce significantly due to inclusions ad they increase tensile strength significantly [18]. Alumina and calcium inclusions and similar oxide inclusions increase stress because of their expansion coefficient which is lower than steel. The behaviour of hard non deformable inclusions of the type globular silicate, crystalline high alumina calcium aluminate and Al_2O_3 cluster during rolling is illustrated in, respectively, Figure 1.9 (a), (b) and (c). Cracks starts to occur in interface between inclusion and metal matrix due to tensile stresss. Once formed, the crack propagates into the steel matrix, eventually causing fatigue failure. Most sulphide inclusions have higher tensile stress than steel which cause them not to effect fatigue strength badly.

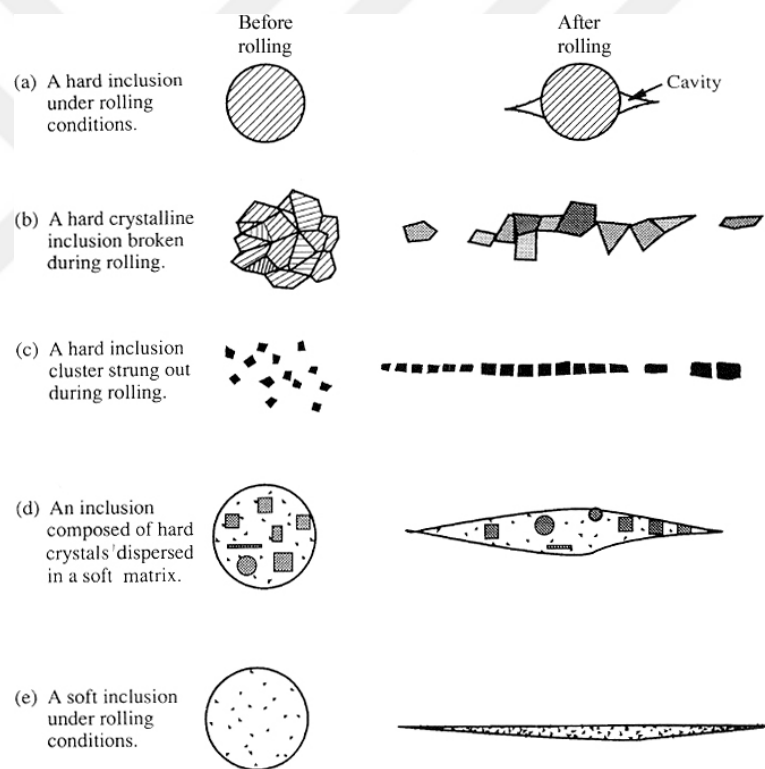**Figure 1.9:** Schematic representation of inclusion shapes before and after deformation (from Engh [17]).

Increase in number and size of inclusions are used for observing detrimental effects over properties. Additionally surface properties may be influenced from inclusions significantl which leads inferior surface appearance and poor polishability, reduce in corrosion resistance and coating adherence [15].

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Machinability is improved by sulphide inclusions but it gets worse by oxide inclusions [15]. Carbides and oxides, such as aluminates and silicates, are hard and abrasive, resulting in high wear of the cutting tool. Machinability is improved by large sulphide inclusions which act as lubricant and chip breaker.

Table 1.1: Typical steel cleanliness requirements for high performance steels [19, 20].

Application	Critical inclusion size (μm)	Critical impurity content (ppm)
Automotive and deep-drawing sheet	100	$C \leq 30$; $N \leq 30$
Deep drawing and ironing can sheet	20	$C \leq 30$; $N \leq 30$, Tot. $O \leq 20$
Ball bearings	15	Tot. $O \leq 10$
Tire cord	10~20	$H \leq 2$; $N \leq 40$, Tot. $O \leq 15$
Wire	20	$N \leq 60$; Tot. $O \leq 30$
Sour gas* pipe	Shape control	$P \leq 50$; $S \leq 10$

Harmful effects over steel properties can be reduced by controlling inclusion shape in addition to inclusion size. Inclusion modification is adding allowing element during secondary steel production process and there by inclusion population is modified. Composition and inclusion shapes are widely modified by calcium treatment. Al_2O_3 inclusions are modified in low melting calcium aluminates by calcium treatment in Al killed steels and this make those steels globular and less abrasive with respect to Al_2O_3 at rolling temperatures.

Occurrence of clogging at tundish and submerged entry Nozzles (SEN) makes non metallic inclusions harmful for the productivity of steel production process. Accumulation of solid and semi solid material during flow of material from tundish to mould cause SEN clogging (Fig. 1.9). Thereby internal nozzle diameter gets smaller which cause steel flow reduction that leads clogging of nozzle. Additionally there may be significant loss in quality of steel due to breaking free of accretion layer

and entering into steel flow. Moreover irregular or asymmetric flow models through nozzle may lead slag entrapment and surface defects [20].

There may be premature interruption of continuous casting process, expensive repair and rejections due to occurrence of non metallic inclusion during casting. It is determined that deposit results reoxidation rather than build up of inclusions according to results of microscobic examinations. As it is shown by Sasai [22], presence of FeO which is caused from steel reoxidation promotes inclusions in continuous caster nozzle. The mechanism of the deposit build-up is not fully understood. Parameters which influence capability for casting steel may include steel composition, casting temperature, nozzle refractory material and geometry.

Non-metallic inclusions can have beneficial effects on the properties of the final product by promoting the formation of a fine-grained structure during phase transformation. It is known that several Ti containing oxides acts as potential nucleation site for acicular ferrite formatıon which improves toughness [23,24] Ti stabilized Interstital Free If steels are produced by adding Ti as alloying element during secondary steel making process. All inclusions do not act as effective nucleation sites for acicular ferrite. Non-metallic inclusions with specific composition and size must be selected. Microstructure refinements which are called as dispersoids for being differentiated with harmful inclusions are formed or added into melt [25]. Dispersoids are created within system as result of deoxidation and desulphurization and alloy containing reactive element Ce and Zr are added into melt for creating them. Alloy containing high number of dispersoids are used for transferring dispersoid population in second concept. Strict control of secondary steel production practices and adequate alloy design and alloying sequence are required in microstructure refinement. Existence of nonmetallic inclusions is closely related with performance of finished steel. Strict control of inclusion characteristics is required in highly demanding practices. Understanding mechanism of inclusion is very important for steelmaker for controlling their existence and improving quality of product.

1.6 Aluminum Deoxidation

The aluminum oxygen tendency is at the head of the strongest elements and can react very quickly with oxygen to form highly stable compounds. The driving force of the deoxidation reaction $3Al + 2O \rightarrow Al_2O_3$ is given by the Gibbs free energy change of the reaction, in J mol^{-1} [26].

$$2Al + 3O \rightarrow Al_2O_3 \quad \Delta G^0 = 1209400 - 391{,}2877T \quad K = \frac{a_{Al_2O_3}}{(a_{Al}^2).(a_O^3)} \quad (1.5)$$

With aluminum it is possible to reduce the oxygen solubility to below the critical value. However, when the oxygen solubility is low, the amount of aluminum dissolved in the steel is increased according to the above equation. In continuous casting machines with open casting, the aluminum dissolved in the steel causes the formation of alumina (Al_2O_3), which reacts with the air to cause clogging of the ladle and tundish nozzle. For this reason, the aluminum value is limited to $Al \leq 0.006$ in open-cast machines.

Table 1.2: Steel Grafe and dissolved oxygen value

Steel Grade	Deoxidation Element	Dissolved Oxygen
Rimmed Steel	Mn	100-200 ppm
Semi-killed Steel	Si/Mn	50-70 ppm
	Si/Mn/Al	25-40 ppm
	Si/Mn/Ca	15-20 ppm
Fully-killed Steel	Al	2-4 ppm

Magnesium and silicon alone do not adequately de-oxidize the liquid steel. Aluminum has to be used under control even though it is a strong de-oxidant. For this reason, aluminum, silicon and manganese are used together in practice. In this

case, deoxidation products are complex Al_2O_3-SiO_2-MnO compounds so that provide better oxygen removal.

Oxygen removal is very important in steel production. For this purpose, devices that measure the amount of oxygen in liquid steel are used and the amount of aluminum and silicon to be added is given according to this value.

If oxygen removal is not sufficient;

- Gas bubbles form during solidification. These defects can adversely affect the mechanical properties of the steel by impairing the semi-finished and finished surface quality
- Yields of ferroalloy and carbon drop, consumption of these materials increases.
- Control of production process becomes more difficult.
- Refractor wear increases.
- During the carbon addition, the overflow may occur in the ladle.

1.7 Reoxidation of Liquid Steel

One of the main causes of exogenous inclusions in the steel production is reoxidation. It is a very complex process that can occur at different places at the same time after the deoxidation stage. The reason of reoxidation is the different oxygen potential between the steel and its environment. For example in aluminum deoxidized steels, the free aluminum remaining from deoxidation stage can be oxidized. So that unintended exogenous inclusions are produced. These exogenous inclusions are deteriorating the internal steel cleanliness drastically. The reoxidation process in steel production is mainly studied in the ladle and the tandish (re-oxidation in the copper mold will be examined in tundish). As regards to the ladle (Fig. 1.10), the oxygen sources considered relevant in the reoxidation process of liquid steel are the air atmosphere, ladle slag, ladle glaze, alloying purity, and refractory lining materials [12,15,20,28]. In the tundish, the following factors are responsible for steel reoxidation [29]: air ingression due to leaks, at joints or breaches made in the tundish and/or through the refractory brick, exposure with air at tundish inlet and bath

surface; ladle well packing material; tundish cover powder; tundish residual slag and ladle slag; and tundish refractories.
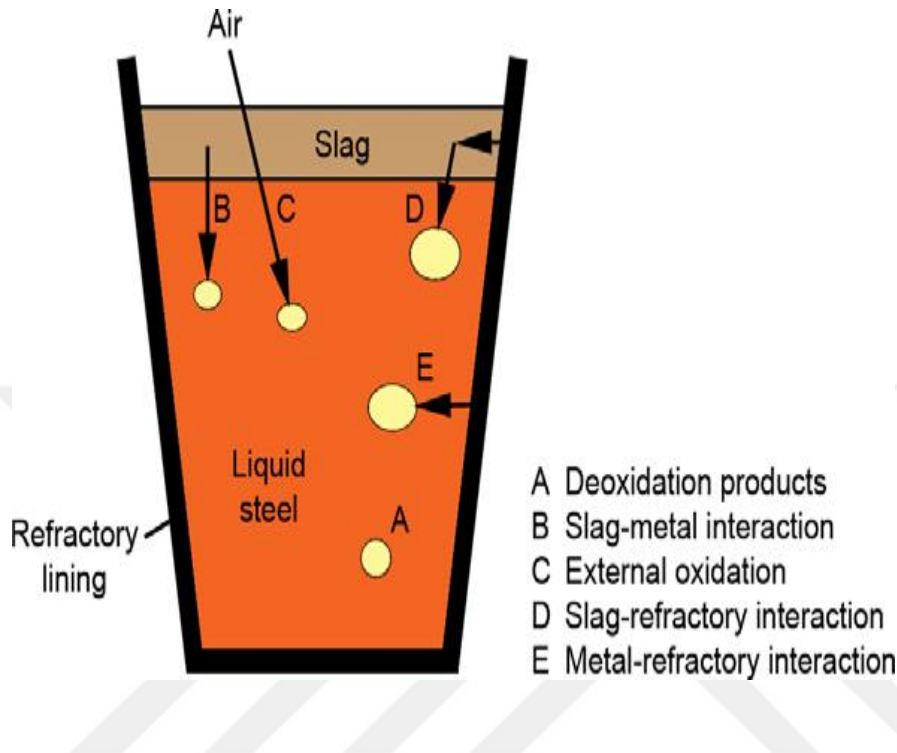
Figure 1.10: Sources of inclusions in the ladle (adapted from Dyson et al. [28]).

1.7.1 Reoxidation by exposure to air

Exposure of molten steel to air leads to the formation of oxides at the surface of the liquid metal (Fig. 1.10, arrow C).The exposure of liquid steel to air continues not only on the surface of the ladle, but also when the liquid steel is poured from the ladle to tundish and poured from tundish to mould. With the oxygen absorption and steel reoxidation, the steel and subsequently the inclusion composition change. Due to the high oxygen affinity of aluminum, inclusion of Al_2O_3 in aluminum killed steels is expected. But the level of oxygen in the steel increases due to air exposure of the liquid steel. In this case besides the Al_2O_3 inclusions, SiO_2, MnO and FeO inclusions are observed.

Some methods have been developed to prevent inclusions formation that can form after deoxidation. The steel can be protected by shrouding the nozzles with Ar gas

for the transfer from ladle to tundish and tundish to mould, purging the tundish with Ar gas prior to ladle opening, using a protective cover for the tundish and tundish cover dust, carefully sealing joints in the shrouds, performing Ar injection to pressurize the shrouds, injecting Ar at the stopper rod or sliding gate, controlling the stirring intensity to avoid the formation of a slag eye (covering slag is pushed to the side due to the gas bubbling, forming an open-eye of molten metal exposed to atmosphere), using tight air covering flux, employing high viscosity and surface tension slags for ladle and tundish, etc.

1.7.2 Reoxidation caused by slag

Interactions between steel and slag can lead to the formation of exogenous inclusions in liquid steel (Fig. 1.10, arrow B). The reaction of reoxidation mechanism is shown in Equation 1.5. According to this reaction, oxide compounds in the slag phase such as FeO, SiO, MnO eq. When they react with aluminum, aluminum is oxidized as they are reduced (Eq. 1.6 [8]). Because, when the ellingham diagram is examined, the reaction proceeds to the right side of the equation due to the high oxygen affinity of the aluminum.

$$3/2 Si_2O + 3FeO + 3MnO + 2Al \rightarrow 3/2 Si + 3Fe + 3Mn + Al_2O_3 \qquad (1.6)$$
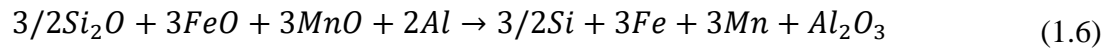
Slag control is very important in order to prevent inclusions due to reoxidation at the slag-metal interface. It is recommended to lower the MnO, FeO and SiO_2 contents in ladle, tundish and mould slags to less than 1 wt%. Also an increase of the CaO/SiO_2 ratio results in a decrease of the number of Al_2O_3 inclusions.

1.7.3 Reoxidation caused by refractory materials

Refractory lining materials may contribute to inclusion formation both by mechanical and chemical erosion (Figure 1.10, arrows D and E). An inert gas is generally blown under the ladle to mix liquid steel. During mixing, mechanical erosion is observed in areas with turbulent flow and high shear velocity, causing the detachment of refractory macro-inclusions into liquid steel. In contact with Al-killed

low alloyed steel, residual water in tundish refractory material which originated from being repaired or originated from failed preheating process, SiO_2, MnO and Fe_tO present in dolomite and MgO-based refractories can be directly reduced by Al in liquid steel. the inclusions formed from liquid steel refractory interactions are generally spinel structure.

The slag refractor interaction at different stages of the process may also cause the formation of inclusions. (Fig. 1.10, arrow D). The mechanism consists in the penetration and the attack of the refractory by the slag and the fluxing of the refractory hot zone, causing the breakdown of the refractory structure [28]. The interaction between infiltrated slag and refractory components results usually in the formation of low melting point phases that initiate erosion of the refractory grains into the slag. The elements constituting the brick, including O, are leached out and may promote oxide formation through reoxidation of the liquid steel.

To avoid reoxidation of the liquid steel, it is therefore crucial to choose non-reactive refractory linings with a high resistance to wear. The chemical stability of the refractory should be investigated both with the slag systems and with the steel grade. Ladle wall for clean steel production is made of high quality refractories, such as high Al_2O_3 bricks with low SiO_2 contents [13]. To reduce reoxidation, the refractories should be fired at 1200 °C to remove water [30].

1.7.4 Reoxidation by ladle glaze

When draining the ladle, a film of slag adheres to the ladle wall and penetrates into the ladle refractory pores (Fig. 1.11 (a)). This slag film, known as ladle glaze [31, 35]. Until the next heat, the slag film in the ladle wall becomes solid. During the next heat, the ladle glaze melts, penetrates to the spaces in the refractory bricks and reacts with the lining components (Fig. 1.11 (b)). The outer layer of the glaze is partially removed in the liquid steel after filling of the ladle. the glaze fragments in the liquid steel form inclusions. In addition, due to the reaction of the liquid steel and the ladle glaze, the SiO, FeO and MgO is reduced while the Al precipitates to form inclusions. (Eq. (1.5)). The reaction with the refractory components causes a modification in inclusion chemistry compared to the glaze composition. As the refractory lining is

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subjected to fluxing by the ladle glaze, the refractory structure is broken down, causing the detachment and the release of refractory grains into liquid steel under strong stirring conditions [32,33] (Figure 1.11 (d)). The contribution of the glaze to the number of inclusions is increasing with the ladle treatment duration [32] and the ladle age [32,34], as the infiltrated layer grows thicker and becomes more porous, enhancing its detachment. This mechanism was confirmed as a source of inclusions in liquid steel by using BaO tracers in ladle slag [36]. Inclusions containing BaO were found in heats processed with the same ladle where the BaO-doped slag had been previously added.
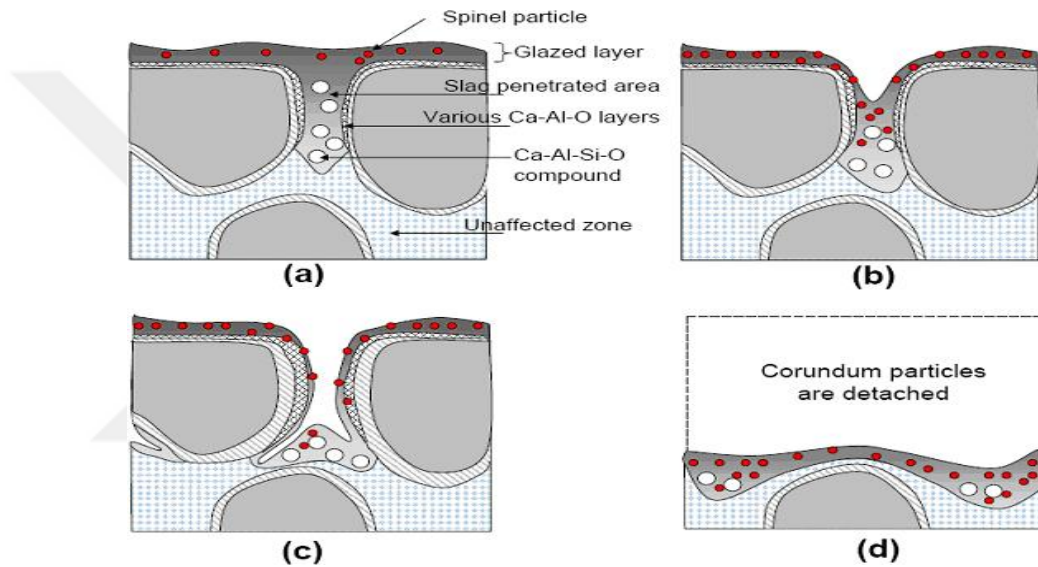
Figure 1.11: Erosion process of the glazed refractory of a high alumina refractory lining during the secondary steelmaking process. (a) Formation of glazed refractory, (b) pitting of glazed refractory, (c) severe erosion at the interface of corundum particle and spinel matrix, and (d) detachment of corundum particle barrier layer [37].

Tripathi [34] concluded from the investigation of industrial samples taken at various stages of the ladle treatment that the ladle glaze was the most important source of inclusions in tool steel. In order to control the glaze layer, Thunman [35] indicated that the composition of the ladle slag and the cooling rate of the glaze can significantly influence the composition and the structure of the ladle glaze. Also, the studies of Beskow [32,33] emphasized the importance of optimized stirring conditions, and degassing and flotation time on the number of inclusions supplied by ladle glaze.

1.8 Minimization of Macroinclusion Number

Macro inclusions are a source of many problems during casting, or even during use. So elimination or reduction of macro-inclusion in steel making is very important issue. The number and formation of macro-inclusion can be reduced by making ladle and tandish design.

As seen in Figure 1.12, Clean Steel technologies are developed and introduced during the ladle and tundish operations to limit steel reoxidation and to enhance inclusion removal before the steel is teemed in the mould. Clean steel making process include suitable slag making, improvement of the ladle process, tundish and nozzle refractories, use of long nozzle, inert gas shrouding, melt flow control devices, appropriate temperature adjustment to steel quality, etc. [10]. Steel deoxidation is generally performed in two stages [14]. Steel deoxidation process begins with the added of deoxidant during taping in the ladle, where efficient stirring promotes inclusion growth and removal and homogenise the melt bath. The second addition is performed in the ladle furnace where gentle stirring is sufficient to achieve a good deoxidation. At the end of the deoxidation process, gentle purging should be conducted to avoid slag entrapment, exposure to air and refractory erosion prior to steel teeming.
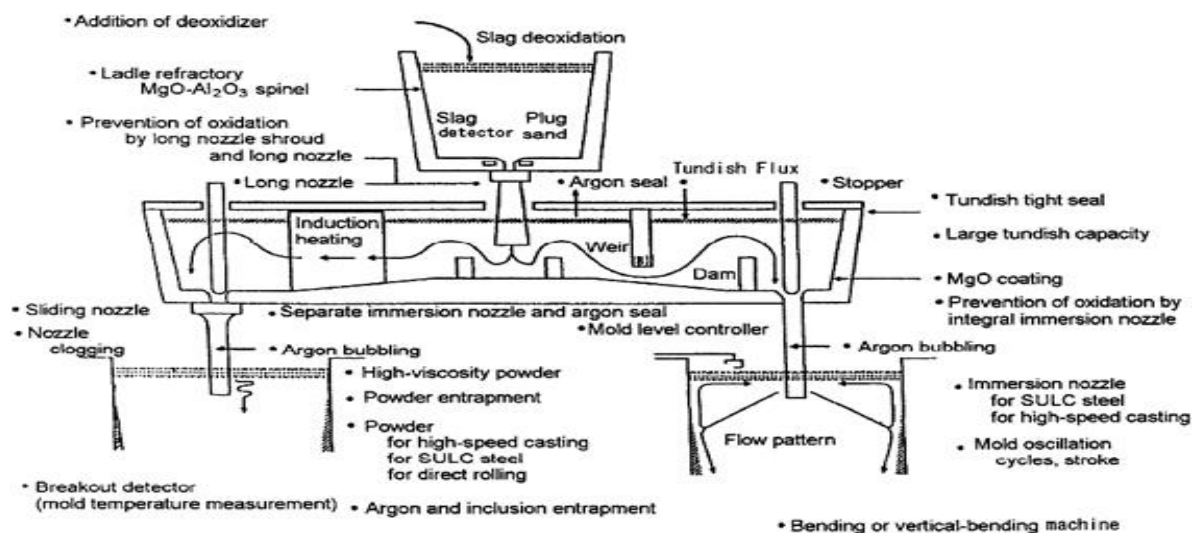

Figure 1.12: Continuous casting system (ladle, tundish and moulds) with all devices and precautions for casting clean steel (SULC = Super Ultra Low Carbon steel) [10].

26

There are multiple macro-inclusion source in the continuous casting process such as residues from the tundish refracteries, liquid steel level changes in the mold soslag entrapment in the mold, slag entrapment in the tundish eg. Macro inclusions also occur as a result of reoxidation of the liquid steel. These inclusions are transported with the steel flow, collide and coalesce to form large aggregates. Upon late formation, these aggregates have no time to float out of the melt, causing casting problems and loss of final product quality.

1.9 Inclusion Modification

The demand for clean steel is increasing ever day. The criterion of clean steel is about where it use. To be able to produce high performance steels, inclusions engineering is developed day by day. Removal of inclusions in steel production is based on two basic approaches. The first approach consists in the minimisation of the harmful effect of the residual inclusions on the steel product by modifying, in the liquid steel, their chemical composition towards harmless compounds. But the effects on the final product properties of the inclusions for this should be well known.

Some of those used in steel production can be given like a sample. Sulphide inclusions are not detrimental to fatigue since their coefficient of thermal expansion is larger than of the steel matrix. MnS inlusions reduces to harmful effect of Al_2O_3 inclusions by covering them with a layer. The composition of non deformable inclusions can be modified towards low melting point compounds. Owing to their higher deformability, the modified inclusions become elongated during hot rolling, forming long stringers. During cold rolling, the modified inclusions are brittle, resulting in the breaking of the thin stringers into small pieces that are not detrimental to steel properties[10]. The most suitable eample described is manganese silicate glass.

Another example of inclusion modification, which is widely used in continually casting steel, is the calcium treatment [8]. Ca is fed into the molten steel as CaSi, CaFe metalwire. Calcium has very high vapour pressure. Therefore when used alone, the yield lost very high. To prevent this stuation commonly is used with silisyum as Ca-Si wire. Silicon, increase the yield of calcium by lowering vapour pressure.

Calcium addition decrease of the oxygen content in the steel and the improvement of steel de-sulphurization. Calcium treatment is used to transform solid and harmful Al_2O_3 inclusions into liquid $12CaO \cdot 7Al_2O_3$ inclusion at steel making temperature. Many calcium aluminium compounds form during calcium treatment. But only the $12CaO \cdot 7Al_2O_3$ form is liquid at steel casting temperature. The modification from solid to liquid inclusions at steelmaking temperature provides globular-shaped inclusions, which are less harmful to steel properties and increase steel castability by reducing SEN clogging events.

Another method for ultra clean steel production is to use deoxidation with silica and manganese instead of aluminum [38].

The second approach is to use inclusions to enhance the mechanical properties of steel. It is not macro inclusions described herein. There are detrimental to steel properties. But in contrast with macro inclusions, microinclusions which are in the 1 μm range, can enhance mechanical properties of the steel. Oxides such as FeO, MnO, TiO_x, $MnO \cdot SiO_2$, $Fe(Mn)O \cdot Al_2O_3$, etc. act as nucleation sites for a variety of precipitates such as sulphides, nitrides and carbides. These precipitates prevent grain growth during hot rolling process. A very fine, narrow size distribution of the nucleating particles should be the aim.

1.10 Classification of Inclusion Morphologies

The classification which is used in this work follows that presented by Braun [27] and Dekkers [43-45]. The five morphology types which are clustered and dendritic, faceted, plate-like, spherical and aggregated, are not exclusive. The characteristics of more than one type can be found in an inclusion. They co-exist in the liquid steel from the ladle to the mould. Their relative frequency depends on the different treatments after the deoxidation stage. In this section, the essential morphologies of Al_2O_3 inclusions will be described briefly. The description focuses mainly on studies reporting inclusion morphologies after extraction of the inclusions from the metal matrix, as this method is believed to provide the most appropriate way to observe

inclusion morphologies compared to the traditional examination of polished cross sections.

1.10.1 Spherical inclusion

Spherical inclusions are singular and have spherical shape (Fig. 1.13 (a)). Many of them can be found in industrial steel samples. Their size is less than 1 μm [44, 45]. Larger spherical inclusions, 2 to 5 μm diameter, are not found frequently. The formation mechanism of spherical inclusions is subject of discussion yet. There are several formation mechanisms proposed.
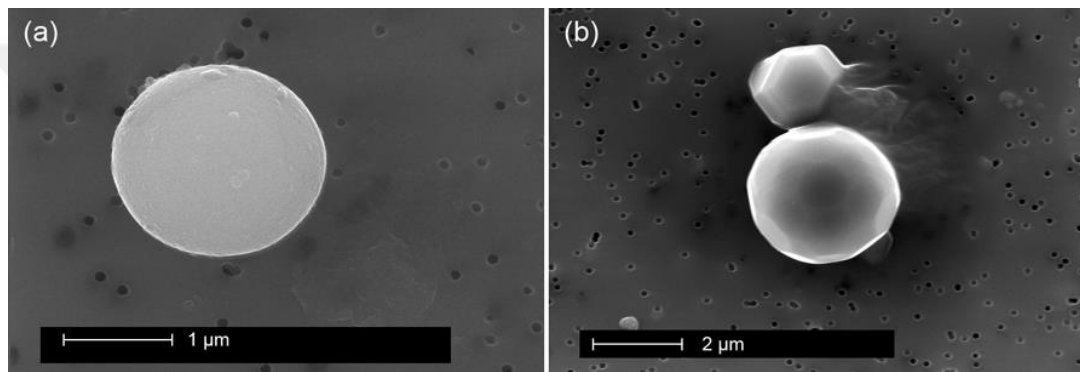

Figure 1.13: Spherical Al_2O_3 inclusions [44].

Due to their spherical shape, some authors [11, 47] propose that these inclusions were liquid or partly liquid at steelmaking temperature. In order to have liquid inclusions local temperature in the steel bath should exceed the melting point of Al_2O_3 at 2072 °C [47]. The exothermic reaction between Al and O [11,47] during the deoxidation stage would release the necessary heat.

Flemings [49,50] and Robinson [42] proposed that spherical inclusions are originated coarsening and breaking of dendrites arm. Dendrites and other high surface area inclusions are unstable because of high surface energy. They will have tendency to become coarse to reduce their surface area. As a result, dendrites arms can melt or dissolve off completely in the melt. They can be carried away in the melt and formed new inclusions. This process, shown schematically in Figure 1.14, is called as dendrite multiplication and is promoted with melt stirring [49].
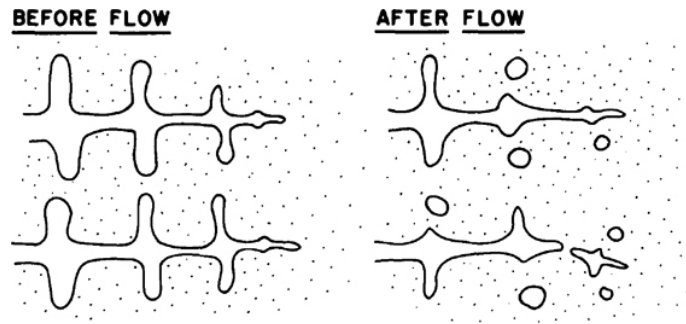
Figure 1.14: "Dendrite multiplication" resulting from convection and associated thermal pulses (from Flemings [49]).

The crystal can have a spherical shape under an adhesive-type growth mechanism (rough interface). High supersaturation (large driving force) and continous suply of mass to the crystal can lead to growth of spherical crystals. Dekkers [43,44] observed that the size and number of the small spherical inclusions did not change dramatically in samples taken from liquid steel between the ladle and tundish. Dekker determined that these inclusions were formed during the steel sampling. Rapid cooling of liquid steel could provide necessary conditions which are high supersaturation with respect to Al and O and continous suply of mass to the crystal. Similarly, Wasai [51] reported a change in size of the small spherical inclusions with the sample cooling rate. He came to a conclusion that these are secondary inclusions. However, they both noted that larger spherical inclusions are most probably primary inclusions. The development of facets of spherical inclusions, as depicted in Figure 1.13 (b), was due to a decrease in supersaturation [43,45].

In addition, Al_2O_3 has many polymorphic forms. α-Al_2O_3 or corundum is the stable crystal phase at steelmaking temperature. However, other phases of the Al_2O_3 which are γ, δ, θ and κ phases has been observed in Al- killed steels by X-ray diffraction analysis [51]. Wasai observed δ- and γ-Al_2O_3 as secondary inclusions formed during cooling.

Among them, the small spherical inclusions were identified mainly as γ-Al_2O_3, possibly mixed with δ-Al_2O_3. He based his argument on the Ostwald Step Rule [52] to explain the presence of metastable phases. Ostwald Step rule states that the first phase to form is not necessarily the thermodynamically most stable. Instead, the phase with the lowest free-energy barrier of formation will nucleate rather than the

phase that is globally stable under the prevailing conditions [53].Therefore these metastable phases would be formed during the solidification of a supercooled liquid phase. In addition, according to the basis of the Ostwald rule and homogeneous nucleation theories, Wasai [54] concluded that the nucleation of liquid and metastable δ- and γ-Al_2O_3 from liquid Fe at 1600 °C was possible above a critical value of supersaturation. The critical supersaturated state could be achieved upon cooling of Fe owing to the lower O solubility in solid Fe pushing the O at the solidification front.

No evidence has been revealed for the presence of liquid Al_2O_3 after the deoxidation process. In Wasai's study [54], the possibility of liquid Al_2O_3 formation was supported by the observation of amorphous spherical SiO_2 inclusions in Al-deoxidised Fe, These amorphous spherical SiO2 inclusions would form from liquid SiO_2. Other mechanism to get amorphous solid which is condensation of vapour phase to an amorphous solid were not considered.

1.10.2 Faceted inclusions

Inclusion with well developed facet planes and a three-dimensional character are classified as faceted inclusions (Fig. 1.15). There are many faceted inclusions in industrial samples. Their size changes from a few μm to few tens μm [39, 44, 51]. In the work of Dekkers [43,45], faceted inclusions are further classified as octahedral (Fig. 1.15 (a)) or non-octahedral (Fig. 1.15 (b)). The reason is the belief that corundum, which cannot develop an octahedral habit, is not the only Al_2O_3 phase present in liquid steel. Other Al_2O_3 polymorphs could explain the presence of octahedral inclusions.

The facets appear in the crystal structure habit due to slower growth rate, and the subsequent ability of the crystal to arrange the incoming growth units in the configuration that minimises the surface energy. Accordingly, faceted inclusions cannot be formed during cooling [43,45]. In addition, the cooling rate of the Fe does not any effect on the size of the polygonal inclusions [51]. As a result of different

supersaturation degrees during the growth of the polyhedral crystal, flat, concave or hopper faces (Fig. 1-15c) on the octahedral inclusions were observed [43, 45].

The sintering and densification processes of aggregates can lead to large faceted inclusions. Overgrowth of plate-like inclusions or dendrites was not observed frequently on small octahedral inclusions [43, 45].
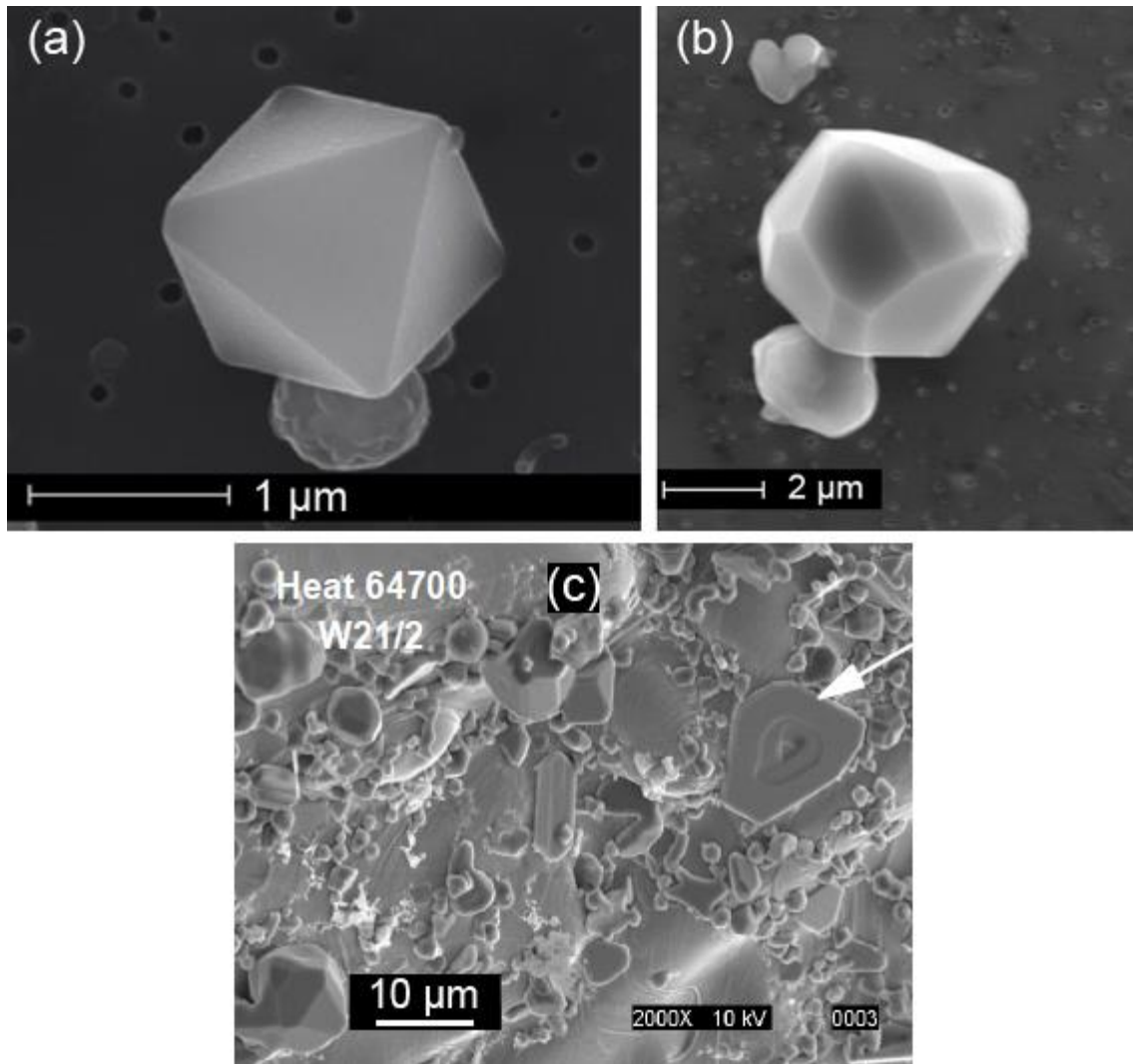

Figure 1.15: Examples of faceted Al_2O_3 inclusion: (a) octahedral (from [45]); (b) non-octahedral; (c) hopper morphologies (indicated by the arrow, from [46]).

1.10.3 Plate-like inclusions

A large surface to volume ratio is the main characteristics of Plate-like inclusions are They appear as two-dimensional, flat plates. Like faceted type, they have well-developed facet planes.

Plate-like inclusions can develop as singular platelets (Fig. 1.16a) or dendritically. Their shapes can vary, but they mostly exhibit a trigonal or hexagonal structure. For this reason they are called flower, star or maple-like inclusions (Fig. 1.16b and c). Elongated plate-like inclusions can also be found (Fig. 1.16d). They are assumed to be the result of layer growth following convection streams and governed by one-directional supply of components at one side of the crystal [45].
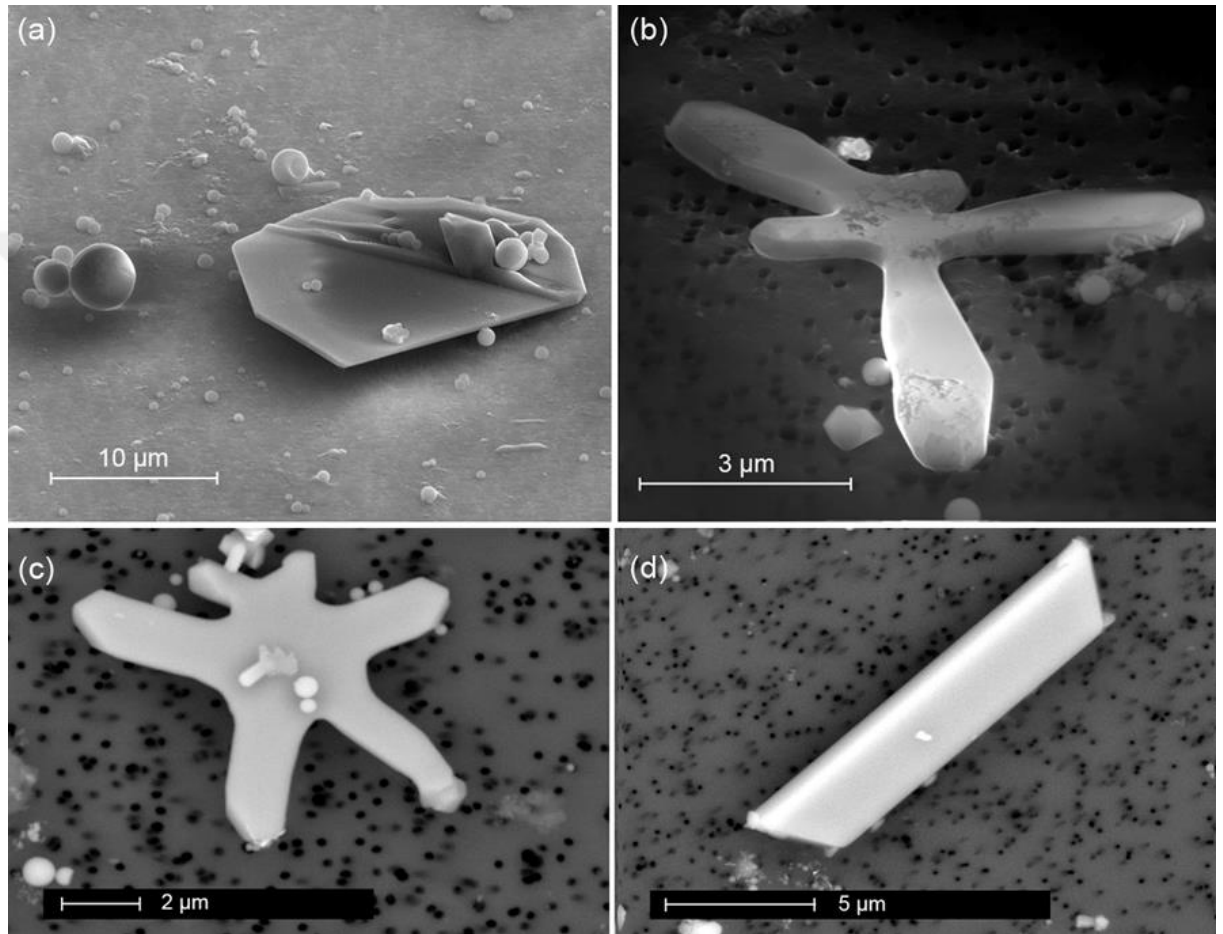

Figure 1.16: (a) Singular plate-like inclusions; (b) and (c) plate-like inclusions growing dendritically; (d) elongated platelet (bar-like) [45].

The origin of plate-like inclusions has not been fully understood. Dekkers [45] suggested that the <111> plane of corundum can be preferentially affected by supersaturation or the presence of impurities compared to the other planes faces, giving this typical plate-like structure to corundum [55].

1.10.4 Dendrites and clusters

Dendrite inclusions which are developing a symmetrically branching and multi-branching form is shown in Figure 1.17. Dendritic particles are due to growth along the supersaturation gradient. High supersaturation is driving force for the unstable growth since the rate of component supply to the crystal exceeds the rate at which the crystal accommodates the coming growth units. At the corners of the Al_2O_3 particles, the high supply rates is seen and maintained. They leads to dendritic growth, formation of needles and dendrites [49,56,57]. At large growth velocities, instabilities develop near the tip, generating the dendritic side-branches (Fig. 1.18a).
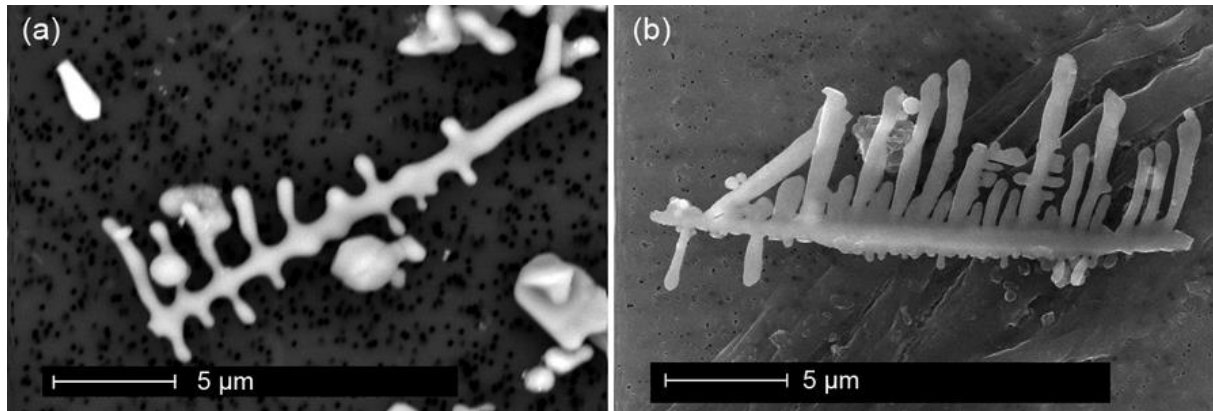

Figure 1.17: Dendritic Al_2O_3 inclusion, showing the primary arm and side branching. Coarsening of dendrites causes neck formation at the base of the dendrite arms, possibly leading to the dismembering of the arm [49,56,57].
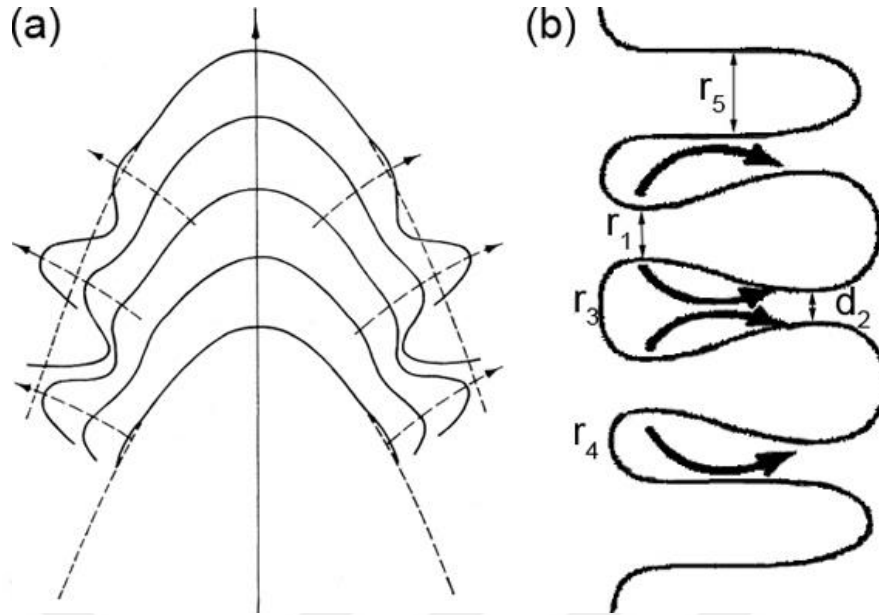
Figure 1.18: (a) Mechanism of side branching formation. The dendrite tip is shown in five successive positions as the dendrite moves up. The dashed lines indication approximate growth paths for the secondary tips (from [57]). (b) Material transport for tear-shaped arms of the dendrite as a result of coarsening, leading to the separation of dendrite arms [56].

In more turbulent conditions, clusters appear as the result of dendritic growth while the directions of the supersaturation gradient are changing. Therefore, irregular shapes are observed. They form an open network of Al_2O_3. The presence or absence of turbulences gives rise to dendrites or clusters. Like dendrites [42], clusters results from growth of one single Al_2O_3 crystal. Steinmetz [40,41] showed that the clusters are monocrystalline α-Al_2O_3, which demonstrates that they originate from growth of one single crystal. Coral-like, dendritic or plate-like shaped clusters may be observed in structure.

The tip of dendrites and clusters can exhibit a different shape than the rest of the crystal body. As supersaturation decreases, growth rate will be slower. This mechanism can result formation of facets on dendrites tip. In some cases, agglomerates of rounded particles were observed at the end of dendrite or cluster tips (Fig. 1.19a), due to the densification of the cluster or the dendrite [45]. Dendrites and clusters can undergo agglomeration and coagulation with other inclusions in the melt [27]. Their large size and subsequent larger effective collision volume is effective on phenomenon.
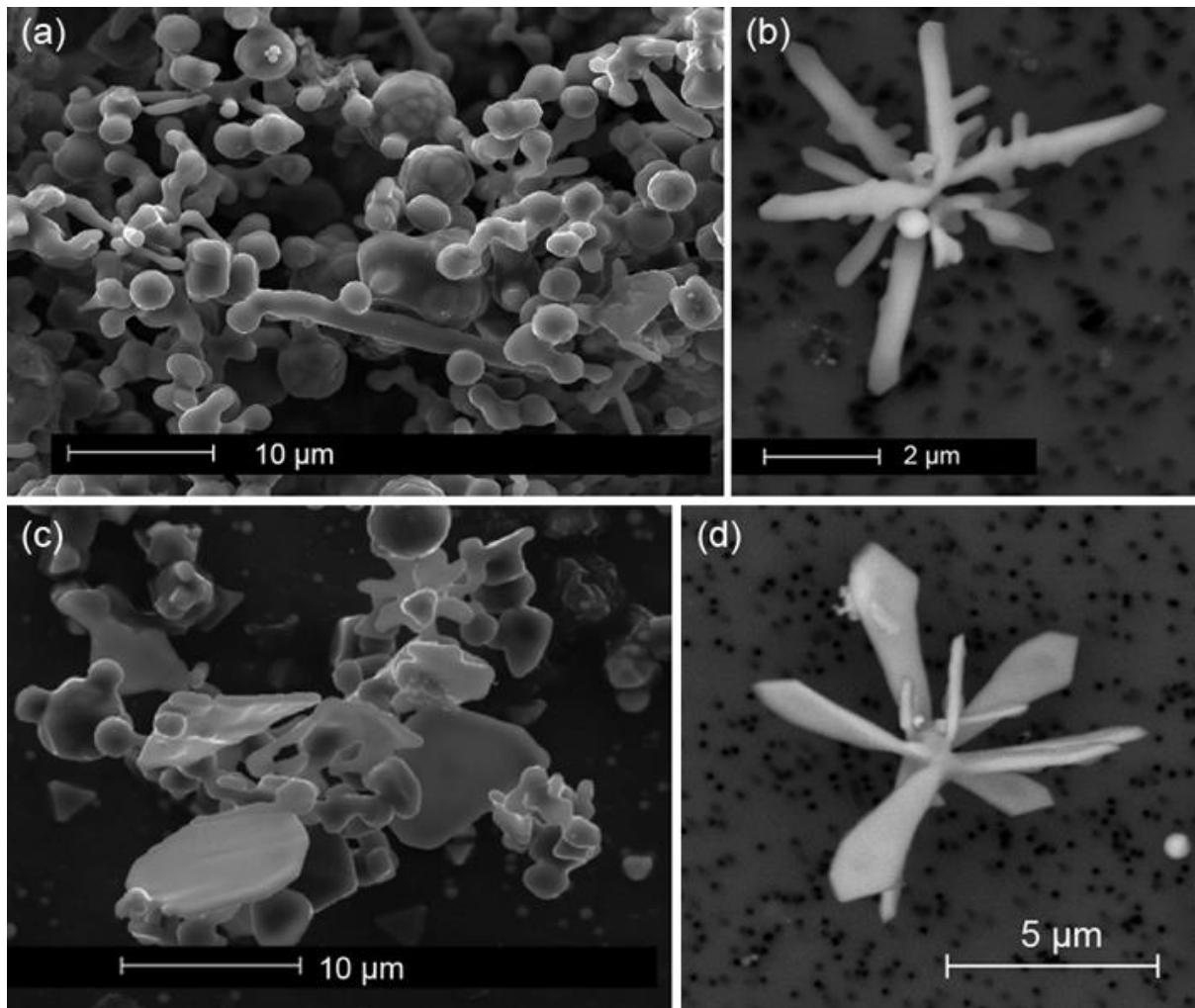
Figure 1.19: Clusters may occur with (a) coral-like, (b) dendritic, or (c) and (d) plate-like structure ((a) is taken from [26] and (c) from [45]).

Due to large surface to volume ratio, dendrites and clusters are unstable growth shapes. They are energetically unstable and prone to spontaneous surface rearrangements to lower their surface area. This phenomenon can lead to the dismembering of dendrites through coarsening, during which the material is transported from the base where the curvature radius is small to the tip, where the radius is large. The dendrite arms are tear-shaped, with the formation of a neck at the basis (Fig. 1.18b and Fig. 1.17a). At the end, the arm detaches and separates from the main body (Fig. 1.14). Densification of the cluster and the appearance of facets with minimum surface energy occur upon sintering which is also a direct consequence of surface reordering.

1.10.5 Aggregates

Collision and agglomeration of several inclusions creates aggregates. In many studies, aggregates are also referred to as clusters. However, the growth mechanism of aggregates and clusters are different. Aggregates results from collisions between several inclusions and is polycrystalline by nature [39], while clusters forms by growth of aOwing to the high surface tension between Al_2O_3 and liquid iron, the liquid iron film formed in between two approaching Al_2O_3 inclusions will disappear immediately.

The surfaces forces tend to maintain the particles together and sintering proceeds between the colliding inclusions through the formation of a neck or bridge between the particles [27]. At the beginning of attachment, inclusions which form an aggregate are individually definable (Fig. 1.20 a through c). For that reason, different morphology types canbe seen on aggregates depending on that of the single particles forming the aggregate. However, sintering, leading to the densification of the aggregate and the formation of large polyhedral inclusions occurs due to longer holding time. Driving force for sintering is minimization of surface energy. In some cases, liquid metal entrapped between the sintering crystals and formed holes or cavities [42,43,45], as depicted in Figure 1.20d.
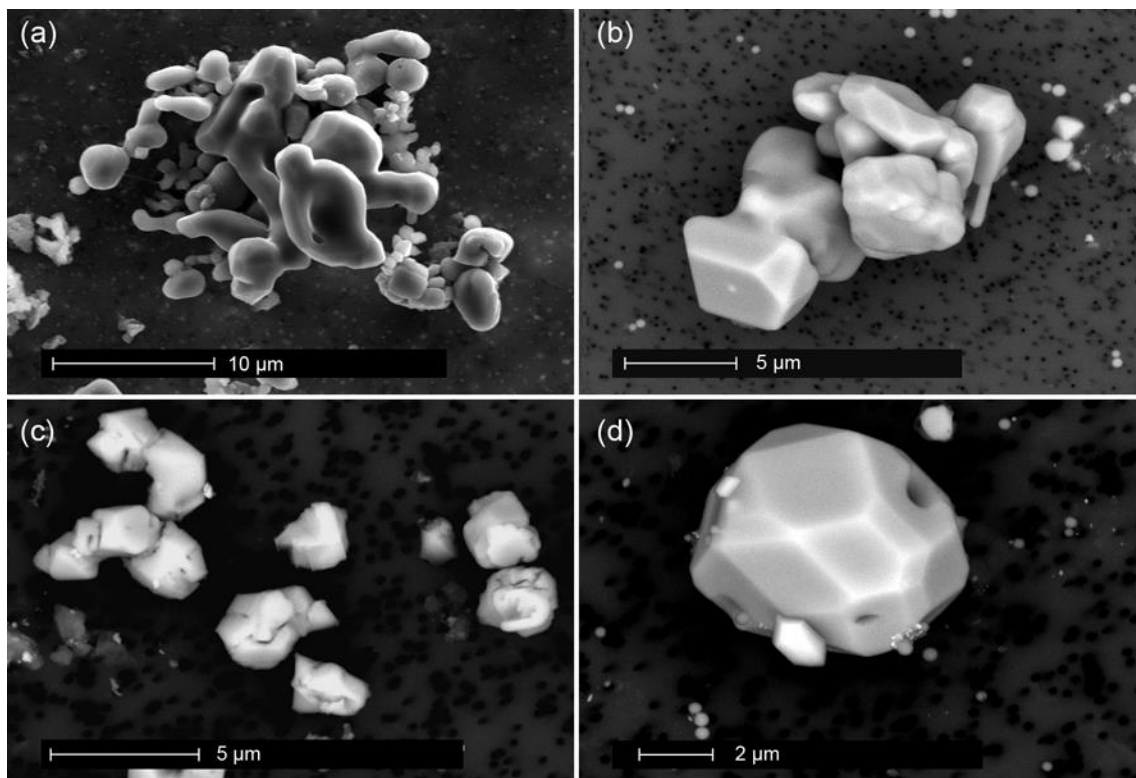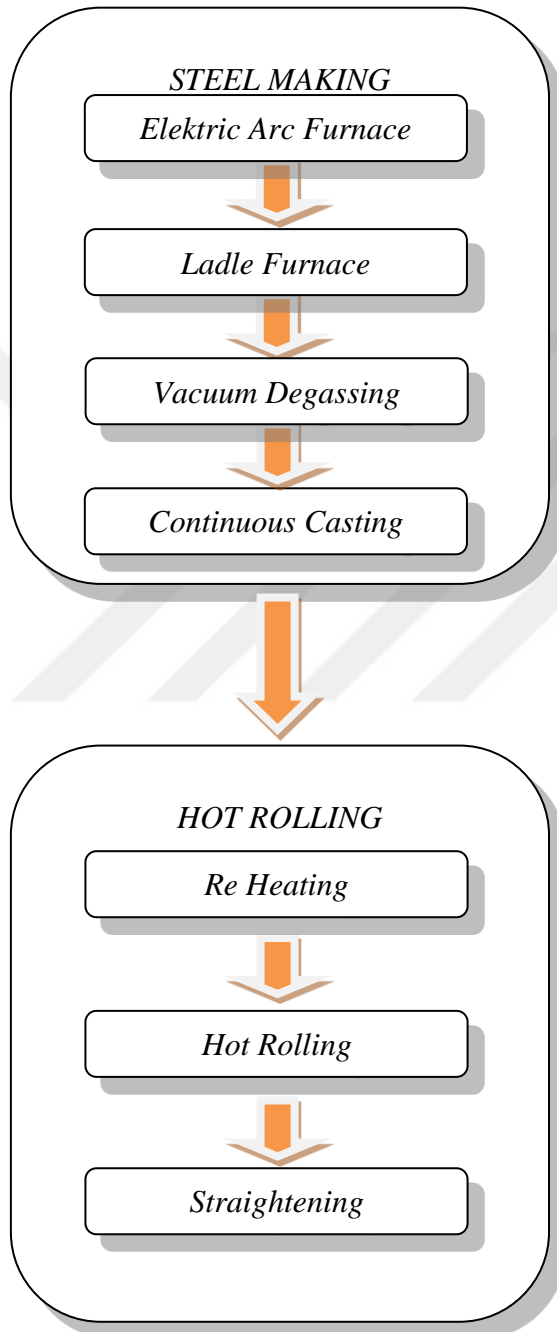
Figure 1.20: Aggregates of Al_2O_3 inclusions, originating from collisions and coagulation of two or more inclusions. Sintering induces the densification of the aggregate, forming polyhedral inclusions [42,43,45].

1.11 Ozkan Meltshop

1.11.1 Main production facilities

STEEL MAKING

Elektric Arc Furnace

↓

Ladle Furnace

↓

Vacuum Degassing

↓

Continuous Casting

↓

HOT ROLLING

Re Heating

↓

Hot Rolling

↓

Straightening

1.11.2 Manufacturing process
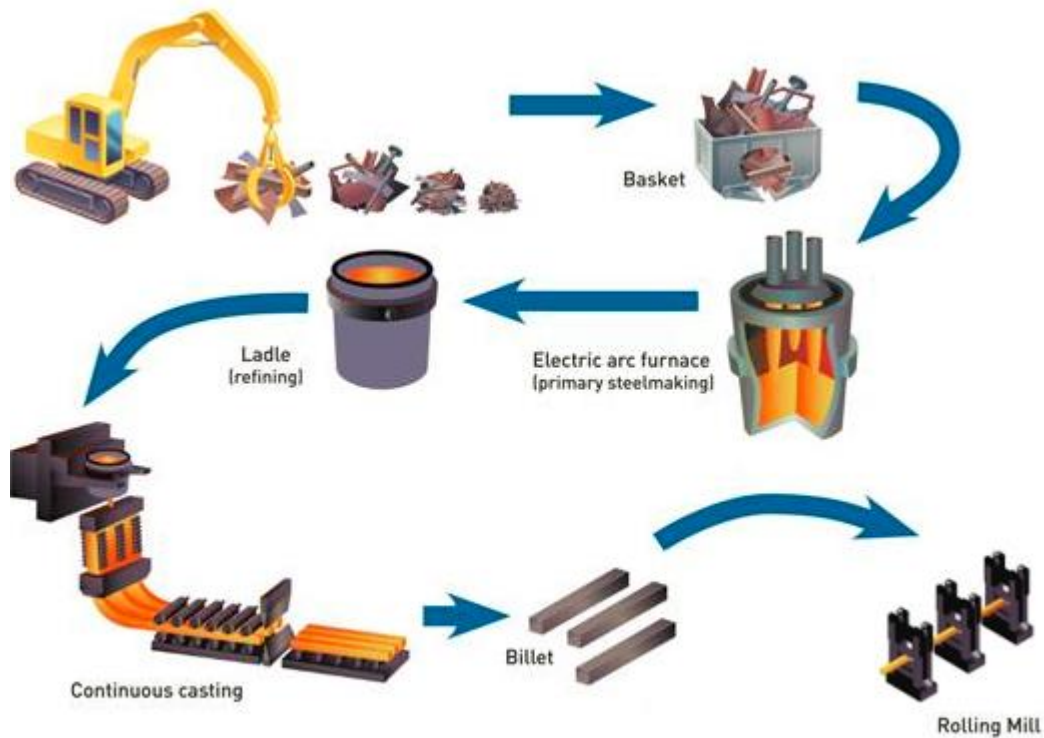
1.11.2.1 Steel making process

Figure 1.21: Steel making process [58].

1.11.2.2 Raw materials

Raw materials making steel are basically molten iron which is made by scrap melting in electric arc furnace process and subsidiary alloying materials such as FeSi, FeSiMn, FeMn, FeV, FeB, FeTi, FeNb, FeMo, FeCr, Al wire, CaSi wire etc.

Scrap and alloying elements are mainly imported. Alloying end slag maker elements are tested at the Quality Control Laboratory for suitability before unloading in the plant.

1.11.2.3 Hot metal treatment (Electric Arc Furnace)

Electric arc furnace is used to melting of scrap and also P level of hot metal is reduced in electric arc furnace (Fig. 1.22). Scrap is melted with electric energy (it is passed to the scrap with graphite electrode) and chemical energy (it is passed to the burners). Purpose of the oxidation reactions are calibrate to C and P level in liquid steel.
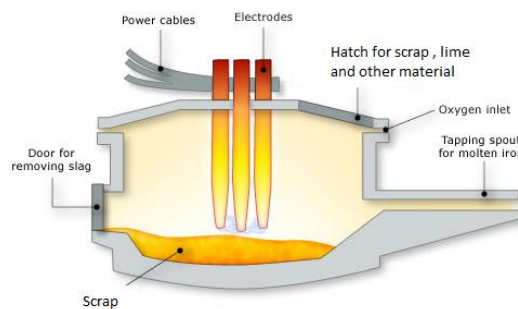

Figure 1.22: Electric arc furnace [58].

When the temperature is 1620 ºC and the chemical composition is ok the furnace is ready for tapping. (liquid steel transfer fromfurnace to ladle) During the tapping Al / FeSi / FeSiMn are added to liquid steel for de-oxidation and alloying. To keep liquid steel temperature stable and homogenous mixing of added elements argon gas is blown under the ladle.

1.11.2.4 Steel refining

S level of hot metal is reduced in ladle furnace. Steel quality, alloying and de-oxidation are made also made in ladle furnace [LF] (Fig. 1.23).
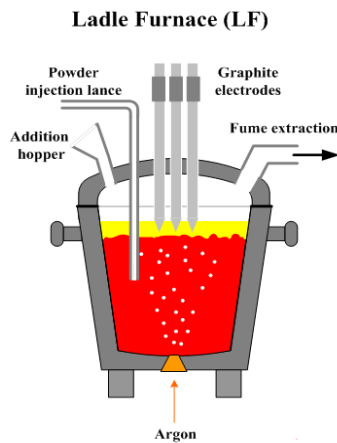
Ladle Furnace (LF)

Powder
injection lance

Graphite
electrodes

Addition
hopper

Fume extraction

Argon

Figure 1.23: Ladle furnace [58].

Nonmetallic impurities are consisting during de-oxidation process. NonmetaLlic impurities are through passing to the slag with argon blowing under of the ladle furnace.

Chemical composition of liquid steel is controlled with optic emission spectrometer. CaSi wire feed for reducing and being under control of Sulfide and Oxide impurities when the steel temperature is 1600 ~ 1610 ºC.

1.11.2.5 Vacuum degassing

Gas impurities (hydrogen and partly nitrogen) are removed from the liquid steel by using inert gas, such as argon, in the vacuum degassing system. This process also helps removing nonmetallic inclusions to have clean steel (Fig. 1.24).
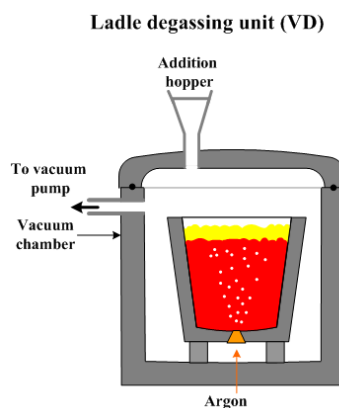
Ladle degassing unit (VD)

Addition
hopper

To vacuum
pump

Vacuum
chamber

Argon

Figure 1.24: Vacuum de-gassing unit [58].

1.11.2.6 Continuous casting process

The ladle sits in the ladle turret and the turret is rotated 180 degrees to the Casting position. Steel temperature in tundish is about 1545° C (-15/+25 °C) To avoid any contamination (pickup of oxygen and the ladle sits in the ladle turret and the turret is rotated 180 degrees to the Casting position. Steel temperature in tundish is about 1545° C (-15/+25 °C). To avoid any contamination (pickup of oxygen and nitrogen) from the atmosphere, shrouding is used from ladle to tundish and from tundish to mould. Between tundish and the mould a submerged entry shroud (SES) of alumina graphite is used. The SES dips ~140 mm into the liquid steel in the mould. The liquid steel in the mould is covered with a mould powder, which prevents contact of liquid steel with air.

Billets/blooms are continuously cast in caster with 5 strands. The process of continuous casting is as follows (Fig. 1.25):
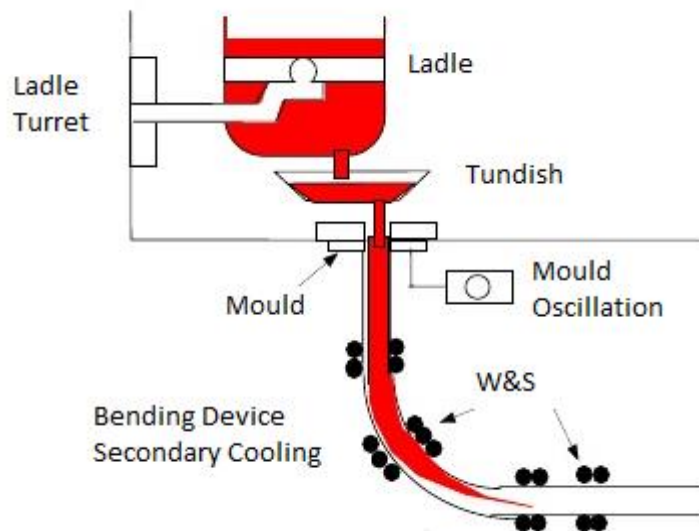

Figure 1.25: Continues casting machine [58].

Tundish preheating

Appropriate preheating is essential for trouble free casting and satisfactory quality. Too cold a tundish, cools the first incoming liquid steel so that it freezes in the SES or causes skulling on the outside of submerged nozzle. Excessive tundish preheating

may damage the refractory material or melt the tundish lids so causing inclusions in slabs. Preheating is normally done for about 2.0~3.0 hrs and temperature of 1150 °C ~ 1350 °C. Liquid steel in the tundish is covered with tundish covering powder to prevent contact with air and temperature loss.

Idendification and traceability

Chemical composition on cold sample is tested. Visual inspection is performed for surface discontinuities and dimensional control is performed length, sizes and straightening. In addition, full traceability of the products is provided by printing hot stamps and hot label is interlacking on each billet or bloom produced by Ozkan Steel company.

2. MATERIAL and METHODS

2.1 Overwiew

The main purpose of this study was to characterize the non-metallic inclusions found in high strength low alloy steel for structural applications and to track the alteration of inclusions throughout the melting operations, casting operations and final product. In the experimental section, first of all the samples were subjected to chemical analysis in optical emission spectrometry. At a later stage, the samples were examined using a special program on an optical microscope. Finally, the samples were examined in SEM (Fig. 2.1). The operations performed in the following sections will be explained in detail.

Figure 2.1: SEM Jeol JSM-5600

The samples which were taken from the liquid steel in the steel production process were sent to the spectrometer laboratory. Elemental analysis was performed with Thermo Arl 4460 optical emission device (Fig. 2.2).

Figure 2.2: Thermo Arl 4460 OES

The samples which were subjected to elemental analysis were examined under an optical microscope using a special program called Clemex (Fig. 2.3a-b). Firstly predetermined areas over specimens are scanned by this program and images from specimen surface are taken periodically. If the inclusion images were captured in taken pictures, these inclusions are classified in this program according to their shapes and they are reported according to desired standard.

Figure 2.3a: Optical microscope with clemex program

Figure 2.3b: Optical microscope with clemex program

Ferro alloys analysis was performed in Thermo Arl OptimX instrument (Fig. 2.4).

Figure 2.4: Thermo Arl OptimX XRF instrument

The samples examined in this thesis are given the code number for clarity.

Table 2.1: Sample description

Code Number	Description
151361BV	Sample taken prior to vacuum degassing process from 151361 heat
151361AV	Sample taken after to vacuum degassing process from 151361 heat
151361PP	Sample taken after rolling process from 151361 heat product
160693BV	Sample taken prior to vacuum degassing process from 160693 heat
160693AV	Sample taken after to vacuum degassing process from 160693 heat
160693PP	Sample taken after rolling process from 160693 heat product

Heat number is the unique number stamped on each billet to refer to a particular electric arc furnace treatment in a meltshop. Heat number is very important for traceability. There are two segments in a heat number. The first two digits indicate the year of the casting and the last of four digits describe the number of casting. A number like 181234 indicates that the billet came from in the year 2018 and it was the 1234th melt for that electric arc furnace that year. This information corresponds to a record the manufacturer keeps for future reference.

2.2 Microscopic Examination

First of all, samples were examined in clemex program on an optical microscope. This program is operated with a optical microscope. Certain areas were automatically scanned on the sample according to the standards, while pictures were taken at the same time. The pictures which were taken were examined by the Clemex program. If inclusions were seen in the pictures, inclusions are classified in program according to their shapes.

The standard DIN 50602 is used for the assessment of the non-metallic inclusions. The examination of special steels for non-metallic inclusions of sulfidic and oxidic nature are described in this standard. As noted above, this study was performed with a special microscope system. This system had a microscope, a high-resolution camera and an automatic scanning program. There are tables showing the shapes, sizes and frequencies of non-metallic inclusions in the standard.

In DIN 50602 standard, inclusions are classified into four main groups according to their shape in rolled products:

- Inclusion type SS: sulfide inclusions of elongated type

- Inclusion type OA: oxide inclusions of fragmented type (aluminium oxides)

- Inclusion type OS: oxide inclusions of elongated(silicates)

- Inclusion type OG: oxide inclusions of globular type.

3. RESULTS and DISCUSSION

In this thesis the examinations in the experimental section will be according to the heat number.

In this study, two castings which were produced in Ozkan Steel will be examined. The qualities of the castings produced, analyzes and the production processes from where samples were taken are summarized in following table (Table 3.1).

Table 3.1: % Chemical composition of heats

Heat No	Grade	Proses	% CHEMICAL COMPOSITION									
			C	Si	Mn	S	Cr	Mo	Al	V	Ti	Ca PPM
151361 V	16MnCr5	EAF										
		LF 1	0.11	0.09	0.99	0.220	0.86	0.013	0.085	0.006	0.002	
		LF 2	0.14	0.18	1.15	0.010	1.00	0.013	0.045	0.007	0.002	
		LF 3	0.15	0.18	1.22	0.004	1.04	0.013	0.044	0.007	0.002	
		LF 4 BEFORE VD	0.15	0.18	1.22	0.004	1.05	0.013	0.045	0.007	0.002	
		AFTER VD	0.16	0.22	1.17	0.002	1.06	0.013	0.029	0.007	0.002	26
		BILLET	0.17	0.21	1.17	0.004	1.07	0.023	0.026	0.007	0.002	14
160693 V	42CrMoS4	EAF	0.11	0.01	0.09	0.030	0.04	0.014		0.002	0.001	
		LF 1	0.27	0.16	0.70	0.023	0.83	0.141	0.039	0.004	0.003	
		LF 2	0.34	0.20	0.83	0.014	0.94	0.157	0.048	0.005	0.004	
		LF 3 BEFORE VD	0.40	0.22	0.86	0.012	0.94	0.200	0.043	0.005	0.004	
		AFTER VD	0.40	0.21	0.87	0.025	0.99	0.194	0.026	0.005	0.004	14
		BILLET	0.40	0.21	0.86	0.025	0.98	0.202	0.020	0.004	0.003	9

3.1 151361 Heat Number 16MnCr5 Steel Grades

16MnCr5 steel grade is the member of case hardening steel group. Its chemical properties are defined in BS EN 10084 standard. During the steel production proses samples are taken from pre-vacuum, after vacuum and product. Samples which were taken were first examined in the optical microscope and then in the SEM (Fig. 3.1, Fig. 3.2, Fig. 3.3, Fig. 3.4, Fig. 3.5, Fig. 3.6).
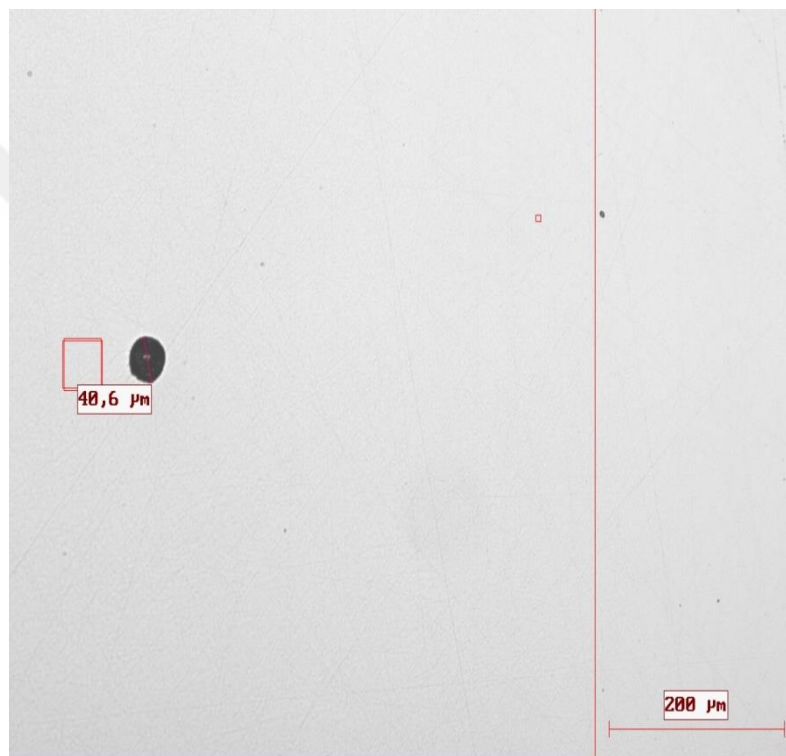

Figure 3.1: 151361BV (microscope image)

Figure 3.2: 151361BV (microscope image)

Figure 3.3: 151361BV (microscope image)
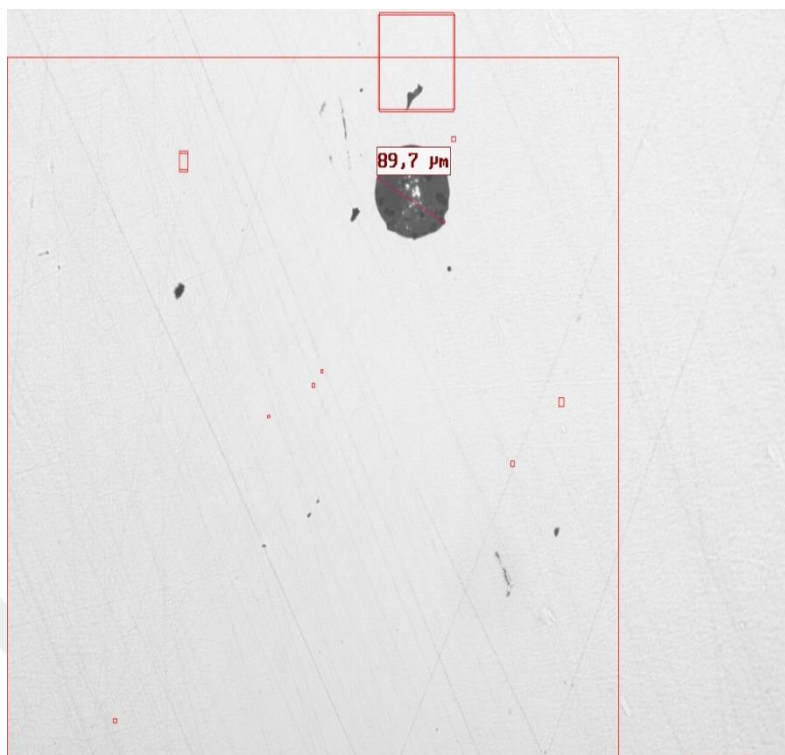
Figure 3.4: 151361AV (microscope image)
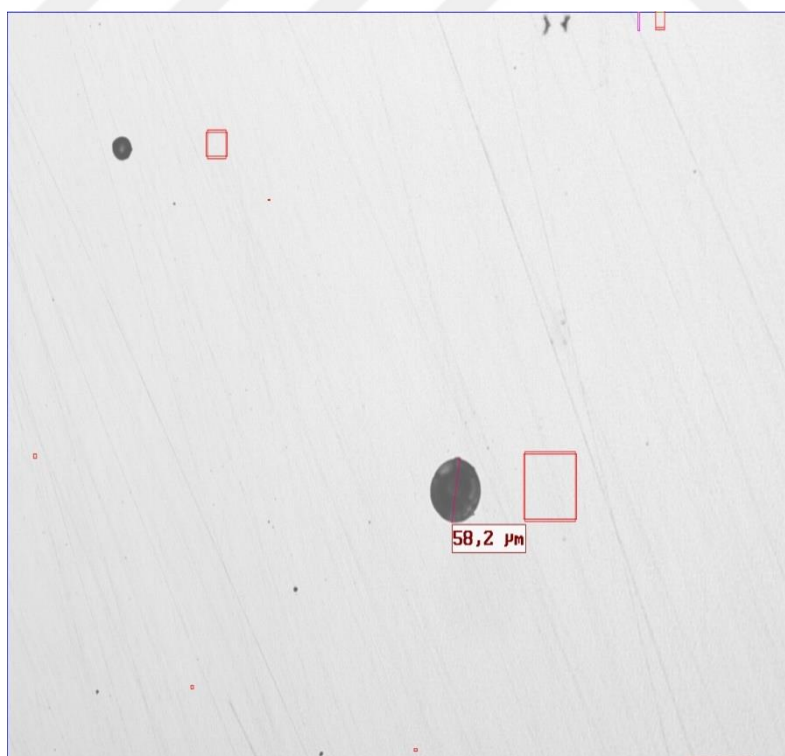
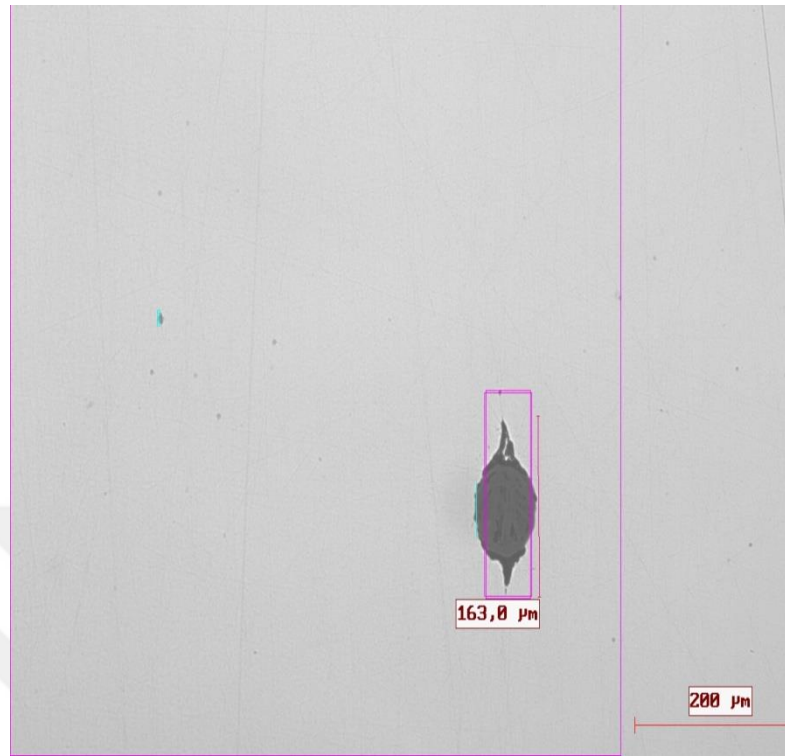**Figure 3.5:** 151361AV (microscope image)

Figure 3.6: 151361PP (microscope image)

When the samples which were taken during the steel production were microscopically examined, various sizes of globular structure non-metallic inclusion were observed. The presence of globular inclusions suggests that there is liquid when it was taken. Looking at the specimens before the vacuum degassing, the second image (Fig. 3.2) shows close-in inclusions of 20 microns in length. Looking at the other two images, the appearance of inclusions of 40 microns in diameter suggests that agglomeration continues. It is difficult to tell the chemical properties of non-metallic inclusions observed in microscopic specimens taken from liquid steel. Because in liquid steel different types of non-metallic inclusions are present in globular morphology. The inclusions in the oxide structure are mostly globular shape in molten steel. For example Al_2O_3(Alumina), SiO_2(Silica-Rhodonite), MnO(Manganosite), $MnO-SiO_2$(Rhodonite), $MnO-Al_2O_3$(Galaxite), $CaO-Al_2O_3$(Calcium aluminate), $CaO-SiO_2$(Calcium Silicate), $CaO-Al_2O_3-SiO_2$(Calcium aluminasilicate) and MnS non-metallic inclusion have globular morphology in molten steel Globular oxides were also detected at the microscope examination of the samples taken from the product. But it can be said that the globular oxides detected

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in the rolled product are calcium aluminates modified with calcium according to the shape. There is a non-metallic inclusion index report of the rolled products produced from the billets of the following casting (Table 3.2).

Table 3.2: 151361 heat number non-metallic inclusion ındex reports.

151361 16MnCr5		NON-METALLIC INCLUSIONS INDEX (According to DIN 50602)											Multiplication and first subtotal	
Specimen No	Area of polished section evaluated, in mm²	Types of inclusion as in diagram plate No.1	0	1	2	3	4	5	6	7	8			
							Factor f_g							
			0,05	0,1	0,2	0,5	1	2	5	10	20	S *)	O *)
1	246,86	SS					0	0	0	0	0	0,0	
		OA					0	0	0	0	0		1,0
		OS					0	0	0	0	0		
		OG					1	0	0	0	0		
2	246,86	SS					0	0	0	0	0	0,0	
		OA					0	0	0	0	0		0,0
		OS					0	0	0	0	0		
		OG					0	0	0	0	0		
3	308,22	SS					0	0	0	0	0	0,0	
		OA					0	0	0	0	0		2,0
		OS					0	0	0	0	0		
		OG					2	0	0	0	0		
4	246,86	SS					0	0	0	0	0	0,0	
		OA					0	0	1	0	0		5,0
		OS					0	0	0	0	0		
		OG					0	0	0	0	0		
5	246,86	SS					0	0	0	0	0	0,0	
		OA					0	0	0	0	0		0,0
		OS					0	0	0	0	0		
		OG					0	0	0	0	0		
6	211,59	SS					2	0	0	0	0	2,0	
		OA					0	0	0	0	0		0,0
		OS					0	0	0	0	0		
		OG					0	0	0	0	0		
Total	**1507**						Second subtotal					S : 2,0	O : 8,0
							Total index K 4 **)					S : 1,3	O : 5,3
							Overall total index K 4					**6,6**	
							Specification					*	

SS : Sulfides, elongated form
OA : Oxides, fragmented form (aluminium oxides)
OS : Oxides, elongated form (silicates)
OG : Oxides, globular form

*) S : Sulfides
*) O : Oxides
**) Converted to a polished section area of 1000 mm² and rounded to the nearest whole numbers.

As will be seen when the report was examined, a large non-metallic inclusion at level 6 was detected in sample number 4. For this reason, sample number 4 was selected for SEM examination.

As already mentioned above, calcium metal has commonly been utilized in inclusion shape control. In aluminum-killed steel, calcium addition can readily convert the solid alumina inclusions to liquid calcium aluminates. In this work, 16MnCr5 grade steel selected to investigate was first deoxidized with aluminum, and after that add calcium metal to molten steel for modifying and controlling non-metallic inclusions (Tab. 3.3). Calcium-containing inclusions were observed to be binary oxides and ternary oxides.

Table 3.3: 161361, 16MnCr5 chemical composition

Heat No	Grade	Proses	(%) Chemical Composition										
			C	Si	Mn	Cr	Ni	Cu	Al	V	Ti	N_{PPM}	Ca_{PPM}
151361 V	16MnCr5	EAF											
		LF 1	0.11	0.09	0.99	0.86	0.09	0.19	0.085	0.006	0.002	62	
		LF 2	0.14	0.18	1.15	1.00	0.09	0.18	0.045	0.007	0.002	64	
		LF 3	0.15	0.18	1.22	1.04	0.09	0.18	0.044	0.007	0.002	65	
		LF 4 BEFORE VD	0.15	0.18	1.22	1.05	0.09	0.18	0.045	0.007	0.002	66	
		AFTER VD	0.16	0.22	1.17	1.06	0.09	0.18	0.029	0.007	0.002	55	26
		BILLET	0.17	0.21	1.17	1.07	0.09	0.18	0.026	0.007	0.002	66	14

The addition of calcium metal to the molten steel is done by wire feeding. It is expected that the calcium aluminate inclusion will begin to appear in the liquid steel after this step. But the images which were obtained from samples taken before the vacuum degassing, calcium aluminate inclusions were observed despite the absence of calcium wire feeding (Fig. 3.7a-c; 3.10a-b). Iron alloys are added to obtain the desired chemical composition of the liquid iron. These iron alloys sometimes contain 2.5% calcium element in their construction. The results of the chemical analysis of

the ferrosilicon alloy in XRF are shown in table 3.4. Trace amount of calcium that comes from the other sources is thought to form calcium aluminate by reacting with the aluminum found in the steel.

Table 3.4: Chemical Composition of FeSi alloy

FERRO ALLOYS	CHEMICAL COMPOSITION (%)					
	Al	Ca	Mn	P	Si	Fe
FeSi	3.04	2.01	0.27	0.07	72.23	22.08
FeSi	3.24	2.25	0.63	0.08	71.80	21.80
FeSi	1.56	1.59	0.25	0.03	76.27	19.97
FeSi	3.36	1.86	0.15	0.06	70.62	23.73
FeSi	2.96	1.82	0.60	0.06	71.10	23.20
FeSi	0.81	1.53	0.53	0.02	73.92	22.98
FeSi	1.16	1.89	0.60	0.02	71.87	23.98
FeSi	1.53	2.35	0.24	0.04	77.03	18.67
FeSi	1.43	1.54	0.10	0.00	78.25	18.52
FeSi	2.56	1.54	0.26	0.01	72.19	23.26

900µm
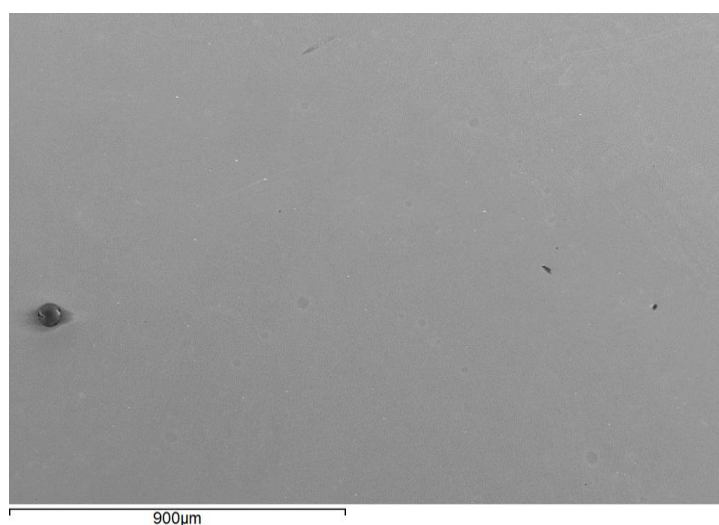
Figure 3.7a: 151361BV SEM

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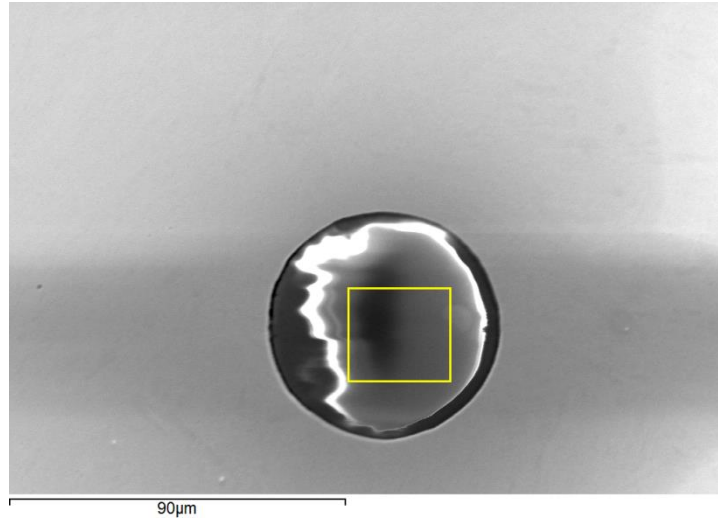
Figure 3.7b: 151361BV SEM
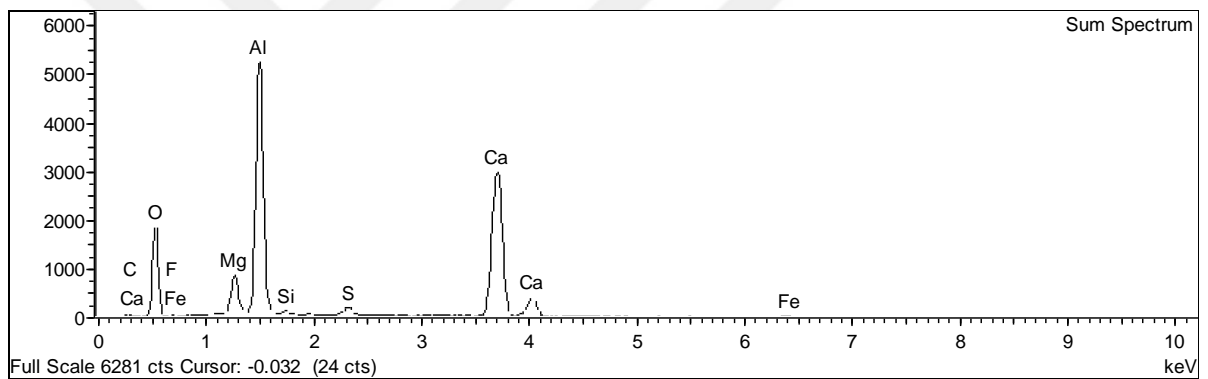
Figure 3.7c: 151361BV SEM migrograph

When SEM images of 16MnCr5 steel grade are taken before vacuum, it can be said that the inclusions in Figure 3.7a-c and figure 3.10a-b were calcium aluminate. As mentioned above, such inclusions types were expected to be seen after calcium wire feeding (Fig. 3.13a-b, Fig. 3.14a-b, Fig. 3.16a-b, Fig. 3.17a-b).

Figures 3.8a-c and Figures 3.9a-b of pre-vacuum images were examined. The morphology of inclusions was found alumina (Al_2O_3). Aluminum is one of the most effective deoxidizers used for steel deoxidation. In aluminum deoxidized steel, there are generally two species of de-oxidation products: solid hercynite (FeO-Al2O3 spinel) and solid corundum (Al2O3, α-modification). In this study iron peaks were seen beside the aluminum inclusions (Fig 3.10a-b). 0.045% metallic aluminum was measured in pre-vacuum analysis of the sample (Table 3.3).

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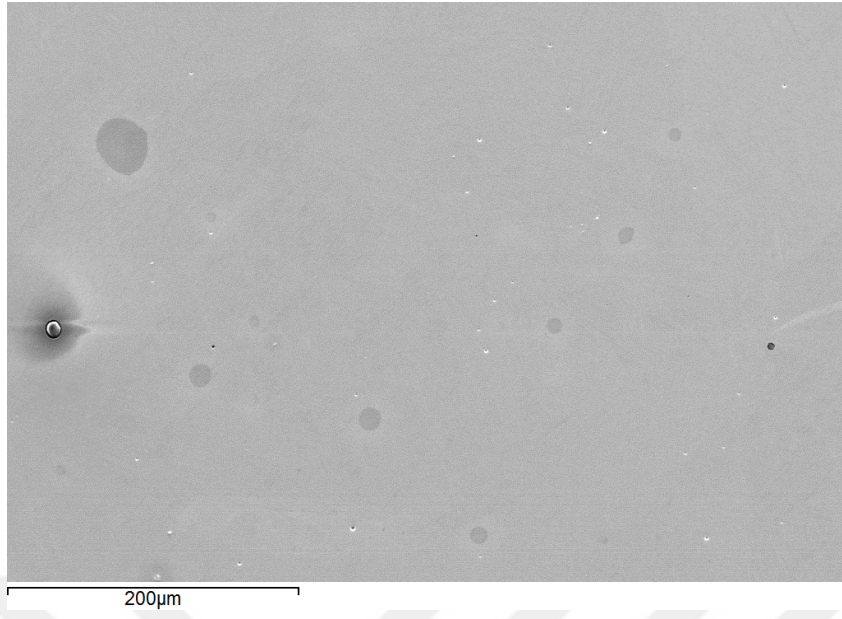
Figure 3.8a: 151361BV SEM
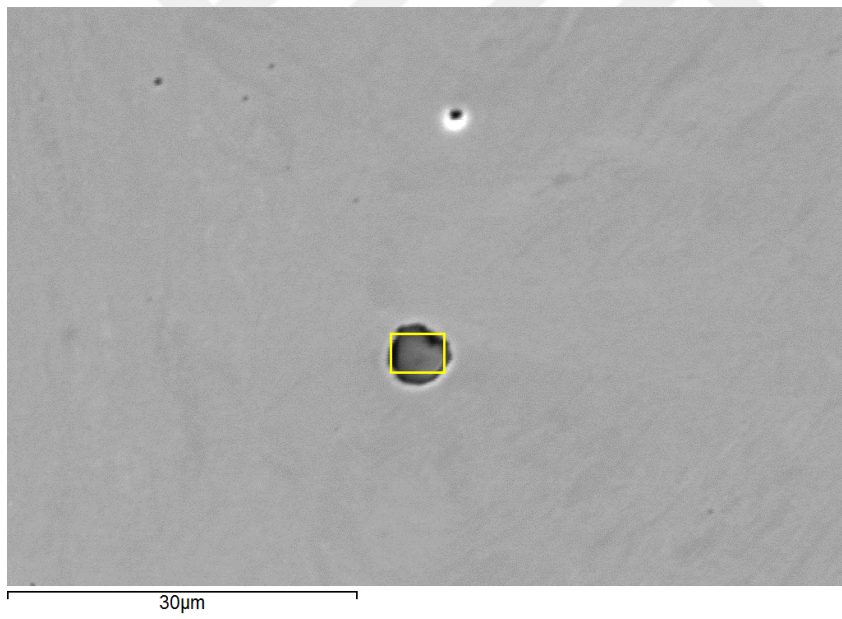
Figure 3.8b: 151361BV SEM

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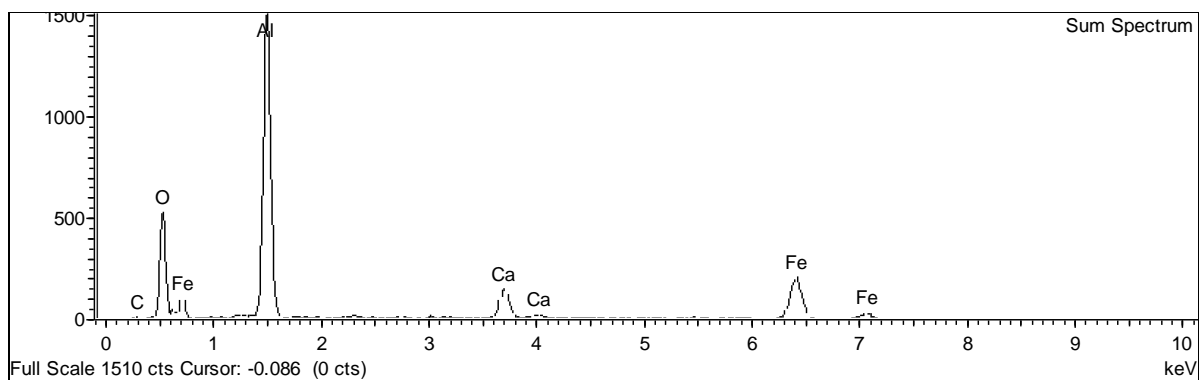
Figure 3.8c: 151361BV SEM migrograph
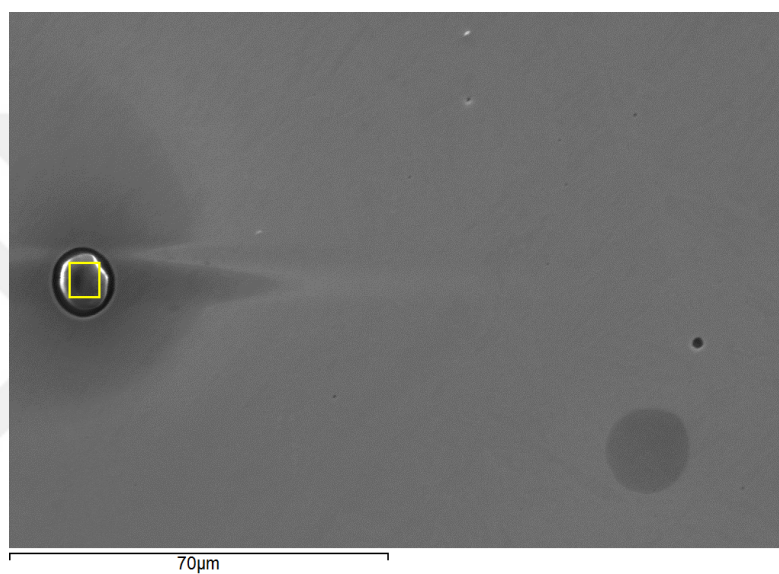
Figure 3.9a: 151361BV SEM
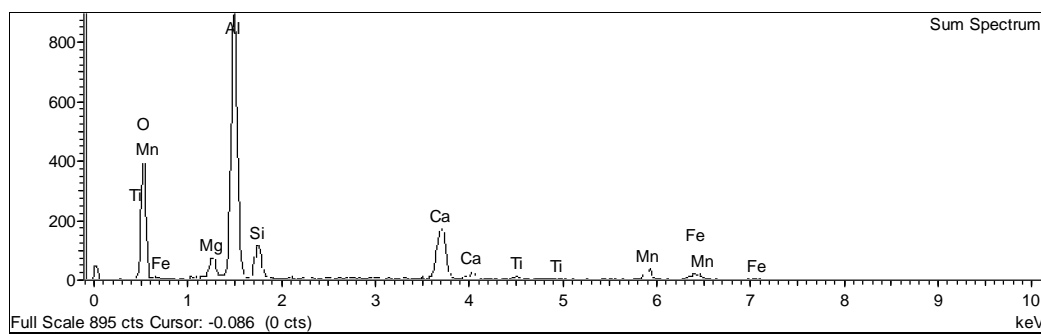
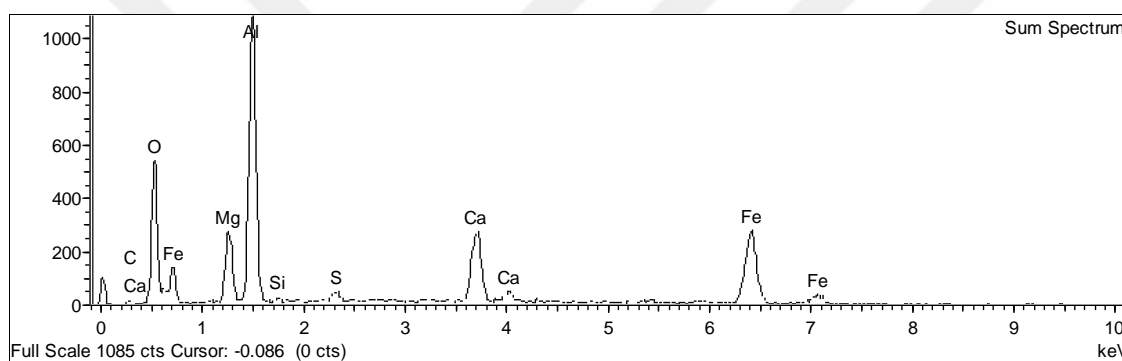**Figure 3.9b:** 151361BV SEM migrograph
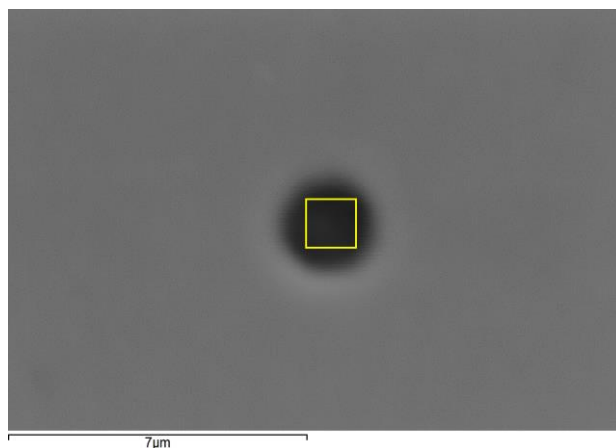
Figure 3.10a: 151361BV SEM

Figure 3.10b: 151361BV SEM migrograph

The presence of calcium, MgO in calcium aluminate inclusions often indicates the external source since calcium containing de-oxidant materials do not contain magnesium (Fig. 3.11c). Calcium aluminate inclusions containing high MgO, either as a result of refractory erosion or as a reaction between refractory and slag. The raw material which is charged into the EAF for making the current steel samples is mainly scrap steel containing trace MgO, therefore this may contribute to the trace MgO detected in the inclusions. In addition, the ingot aluminum added to the steel for de-oxidation during tapping may also contain a small amount of magnesium.
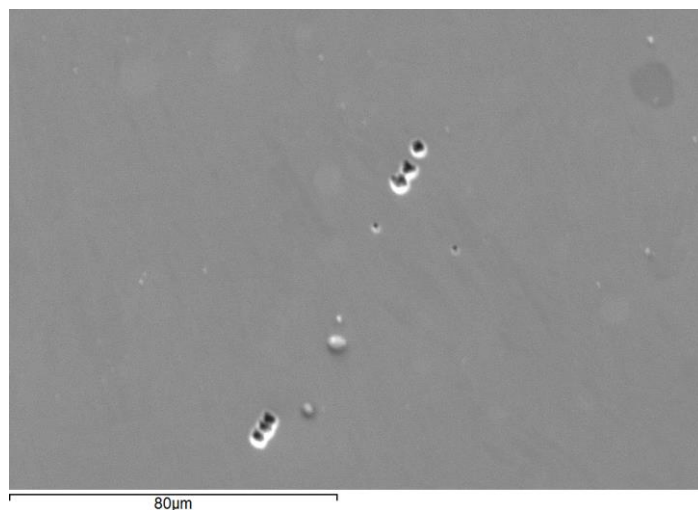
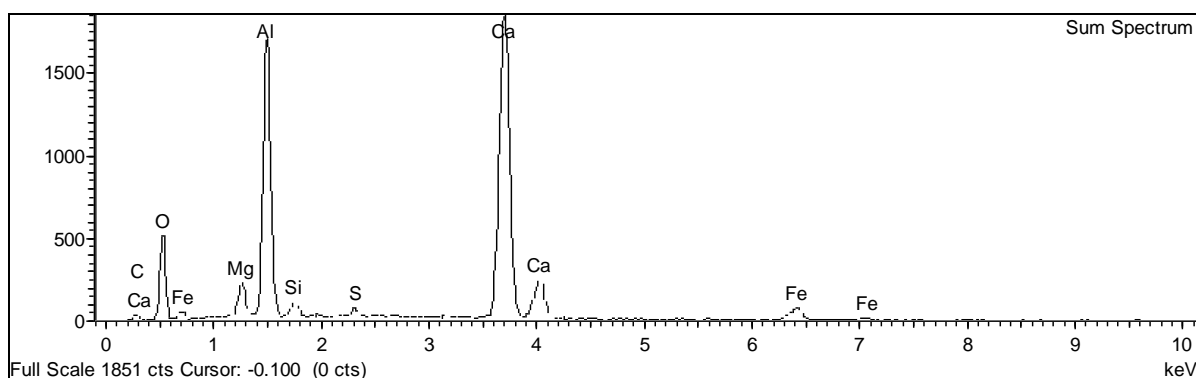**Figure 3.11a:** 151361AV SEM
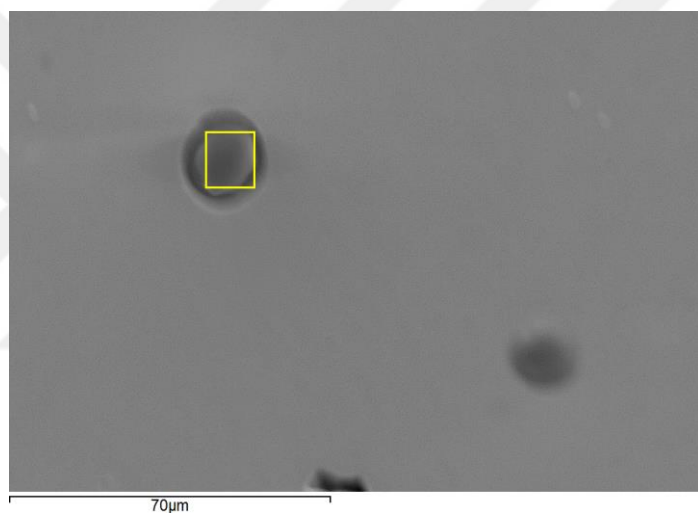
Figure 3.11b: 151361AV SEM

Figure 3.11c: 151361AV SEM migrograph

In this research, no pure form of MnO was observed in current steel samples. As a reaction product of a relatively weak deoxidizer, MnO tends to be reduced by

stronger deoxidizers upon formation or simply form solid solution with other oxides, thereby lowering the melting point of the product thus improving the extent of de-oxidation. Mn is often introduced to steel in the form of low C or high C ferroalloy. Low-carbon ferro manganese alloy is used when producing low-carbon high-manganese steel grades, while high-carbon ferro-magnesium alloy is used when producing high-carbon steels. Because high-carbon manganese ferro alloy is more cheaper. Mn and Fe will both participate in the de-oxidation reaction forming MnO-FeO product in liquid or solid solutions (Fig. 3.12a-b).
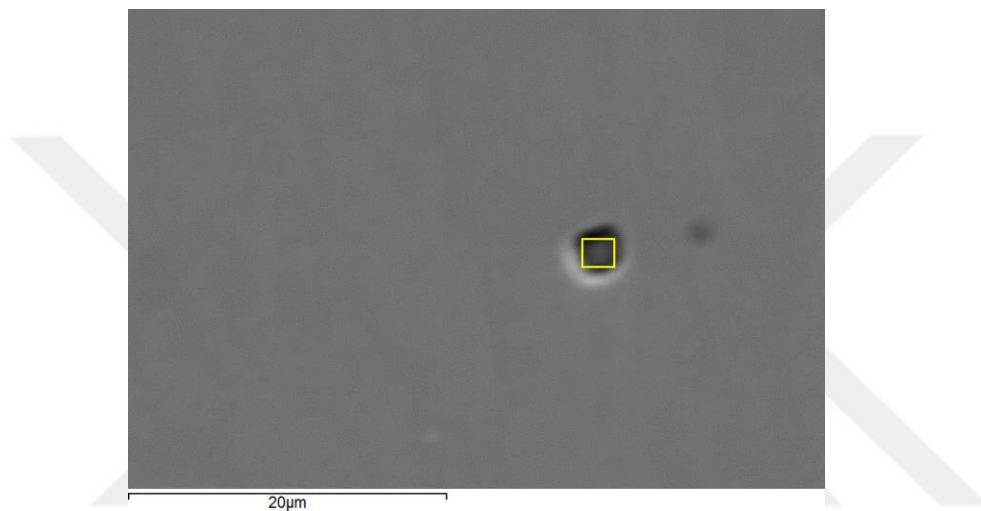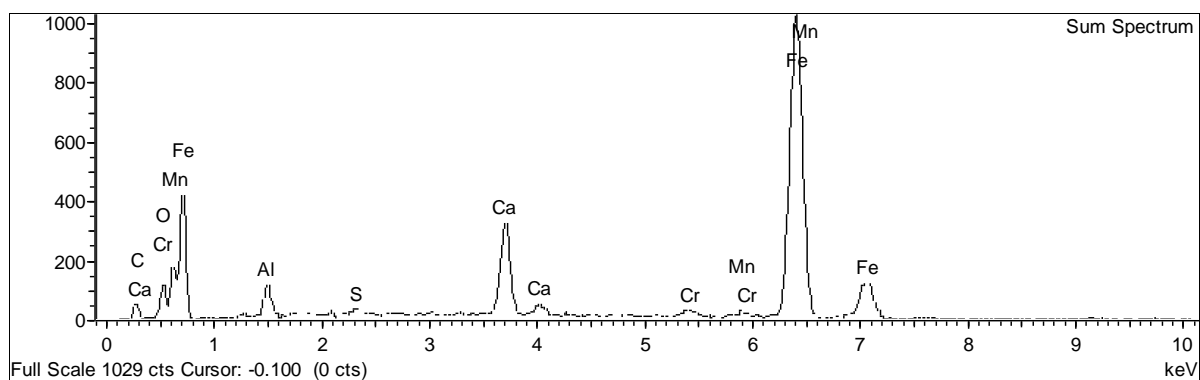

Figure 3.12a: 151361AV SEM
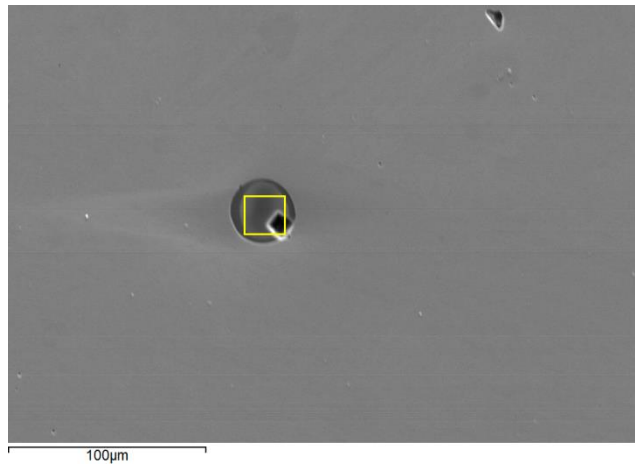

Figure 3.12b: 151361AV SEM migrograph

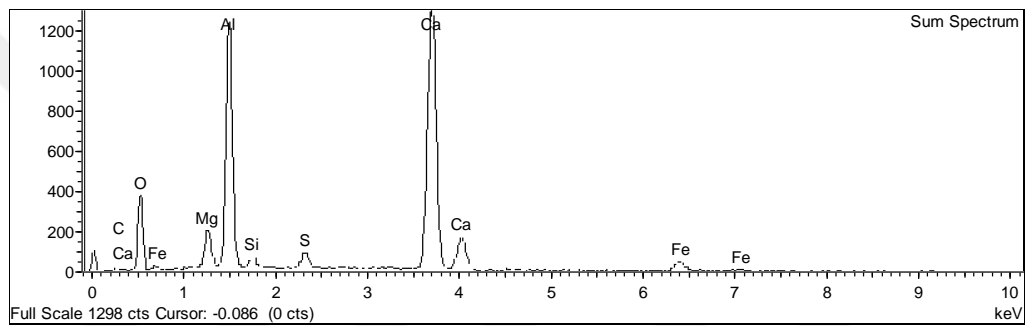62

Figure 3.13a: 151361AV SEM

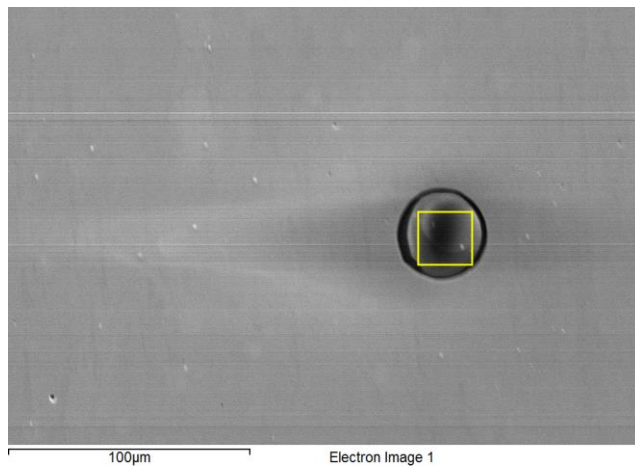**Figure 3.13b:** 151361AV SEM migrograph
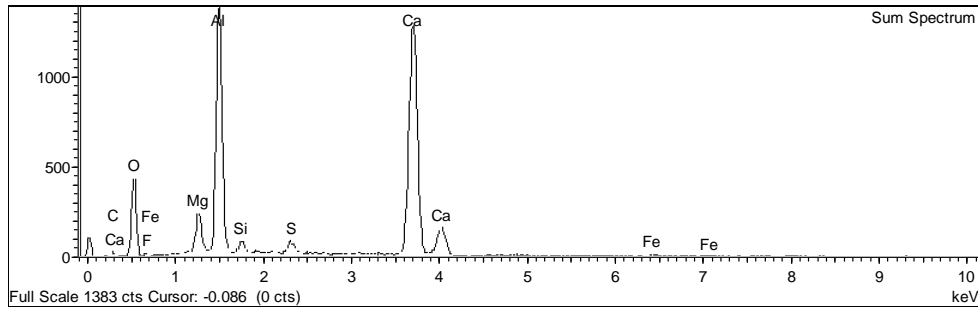

Figure 3.14a: 151361AV SEM

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Figure 3.14b: 151361AV SEM migrograph

In molten steel, manganese and silicon de-oxidation products as well as emulsified furnace slag and eroded refractories can serve as low-energy sites for Al_2O_3 inclusions to nucleate without reaching super-saturation. Multiphase inclusions occur as a result of the process described above. It is assumed that the multi-phase inclusions shown in Figure 3.15a-b were examples of corundum nucleation in molten manganese aluminosilicate.
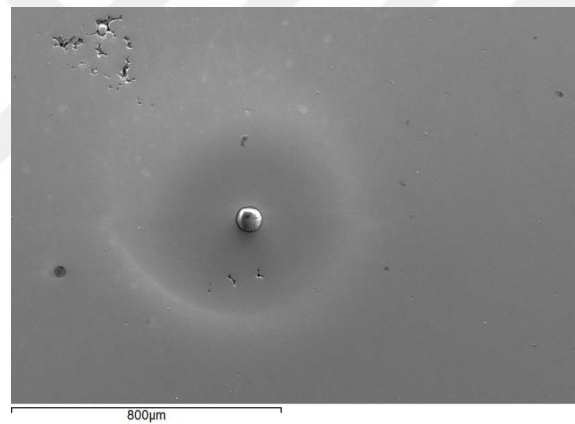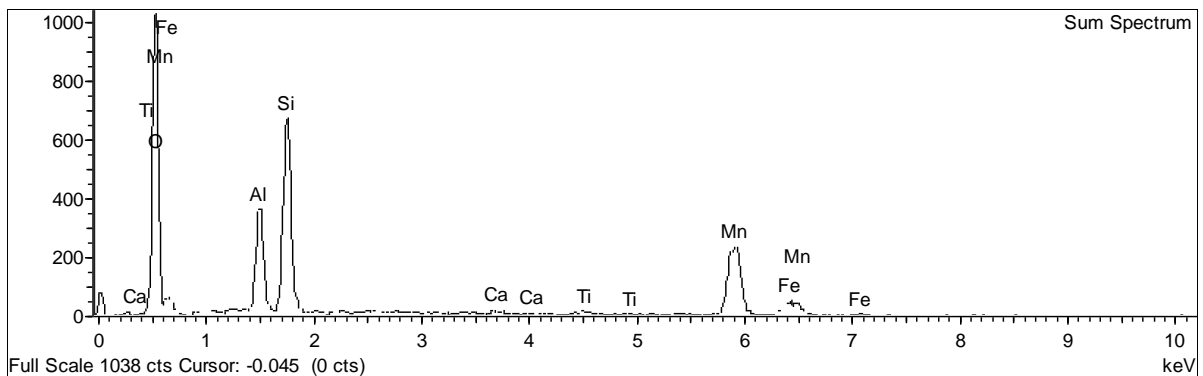

Figure 3.15a: 151361AV SEM
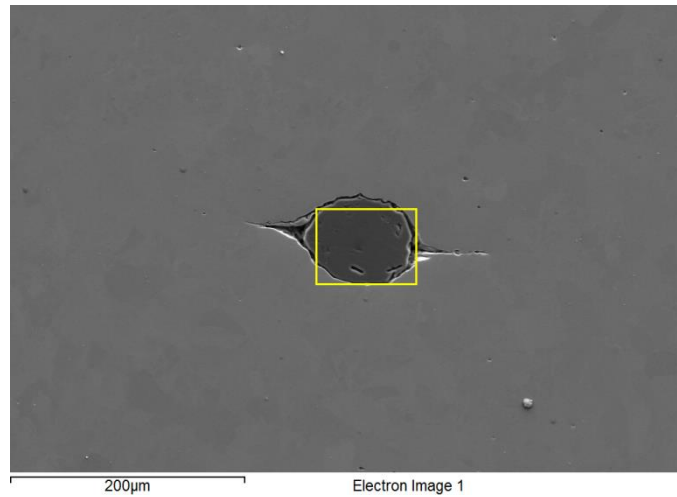

Figure 3.15b: 151361AV SEM migrograph
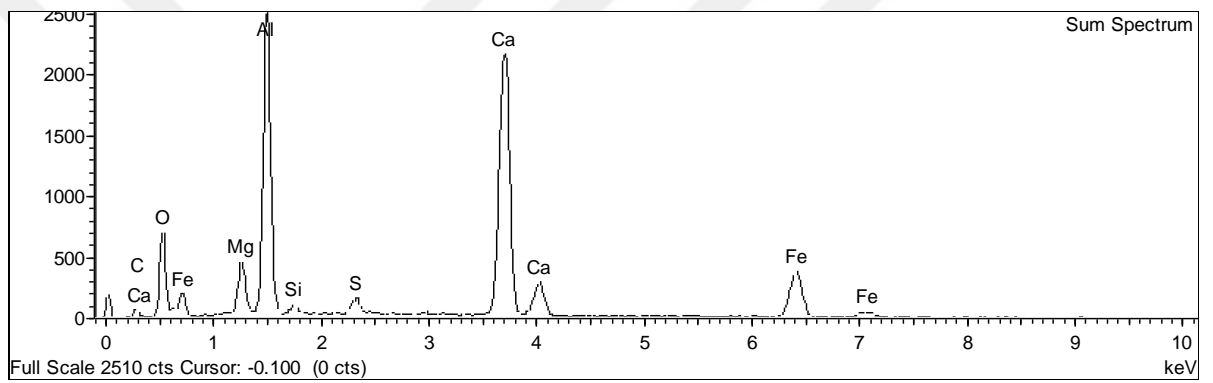
Figure 3.16a: 151361PP SEM

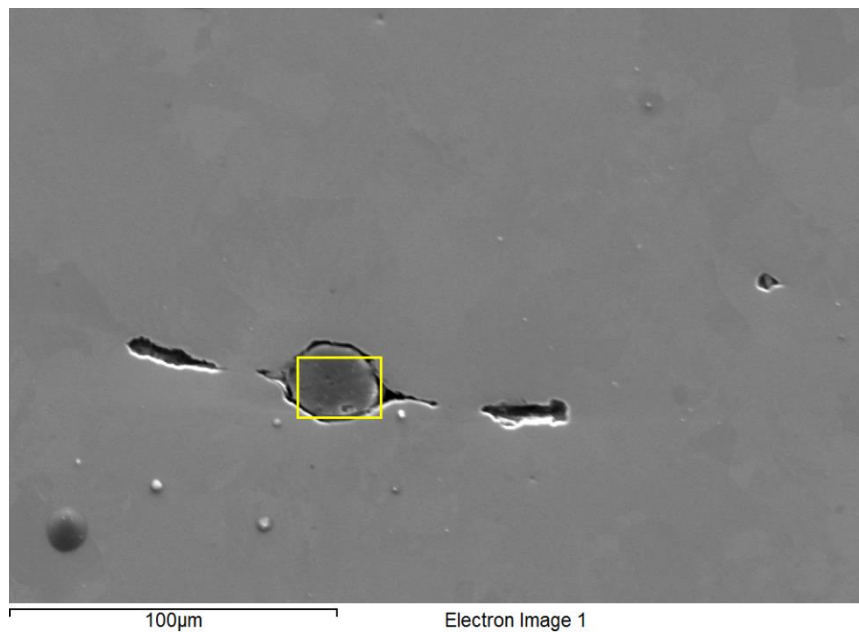**Figure 3.16b:** 151361PP SEM migrograph

Figure 3.17a: 151361PP SEM

Figure 3.17b: 151361PP SEM migrograph

Figure 3.18a-b and figure 3.19a-b were examined and the following results were reached. The peak of the calcium element in the graph was not very strong. This situation suggested that the inclusion was not due to slag. The inclusions were considered to be calcium aluminate and manganese sulphide. It has been reported by Kiessling and Westman [59] that MnS phase has extended solubility of vanadium, chromium, iron and cobalt as well as small amount of titanium and nickel. The chrome peak points in the figures were interpreted as chromium elements dissolved in the manganese sulfur inclusion.
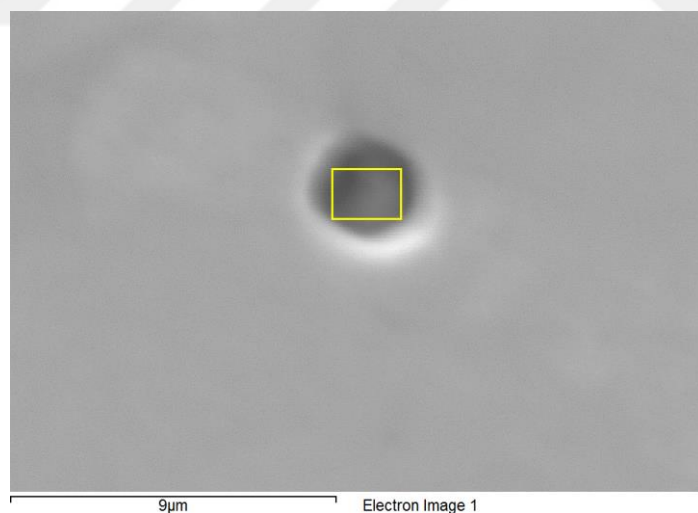
Figure 3.18a: 151361PP SEM

Figure 3.18b: 151361PP SEM migrograph
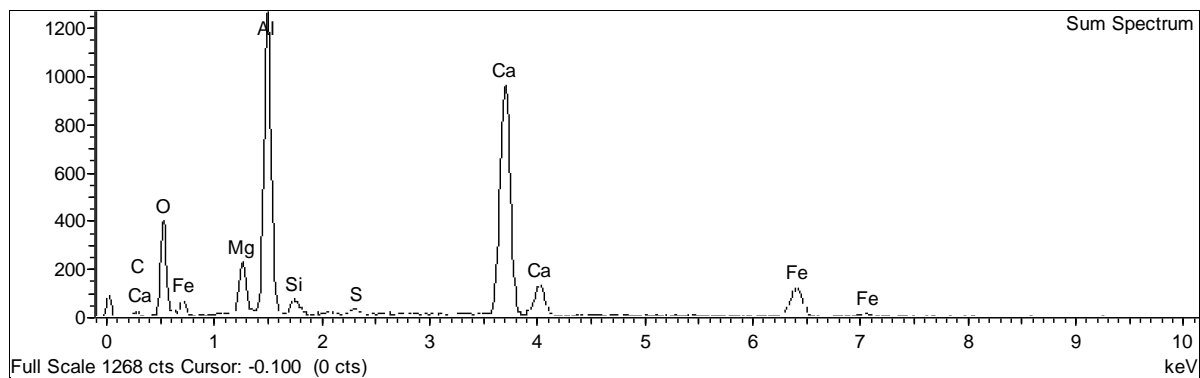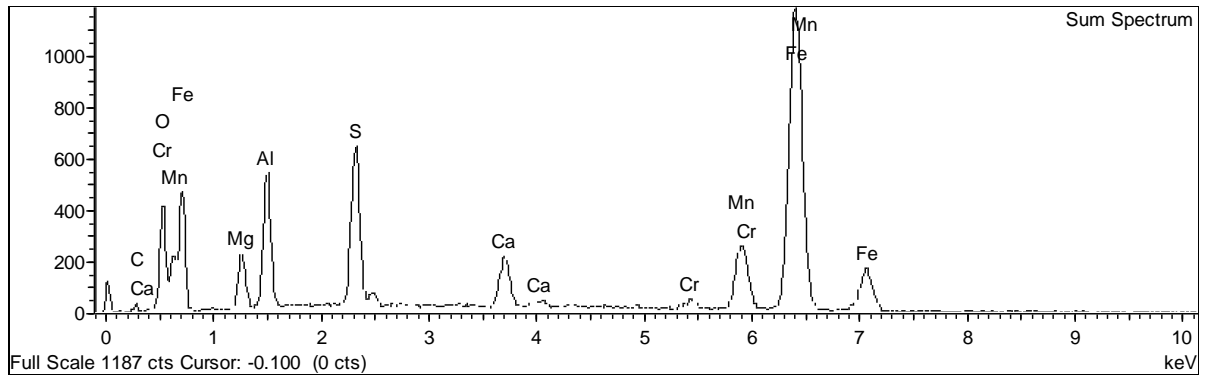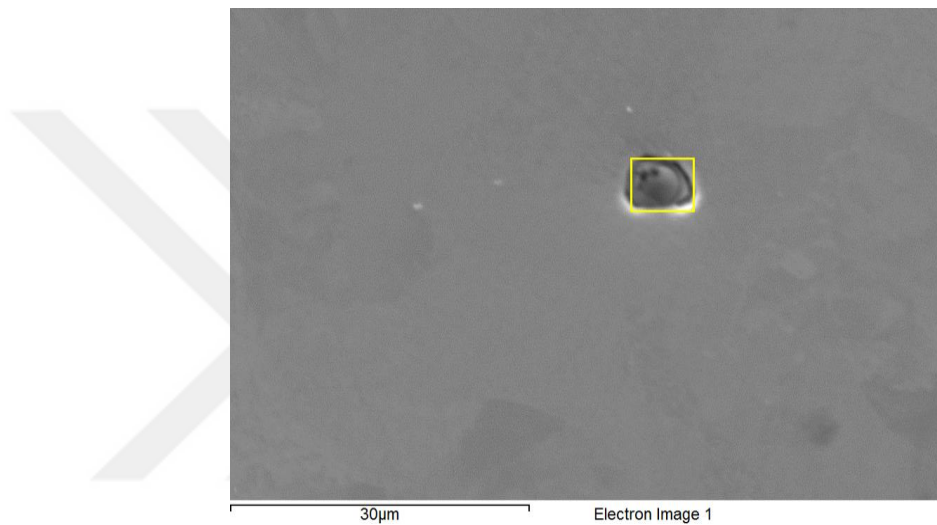

Figure 3.19a: 151361PP SEM
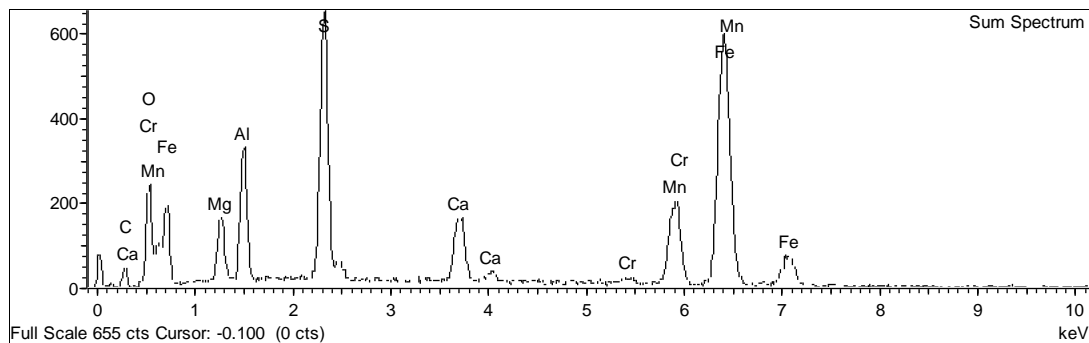
Figure 3.19b: 151361PP SEM migrograph

3.2 160693 Heat Number 42CrMoS4 Steel Grades

42CrMoS4 steel grade is the member of steels for quenching and tempering steel group. Its chemical properties are defined in BS EN 10083-3 standard. During the steel production proses samples are taken from pre-vacuum, after vacuum and

product. Samples which were taken were first examined in the optical microscope and then in the SEM.

A large nonmetallic inclusion was detected in the sample taken before the vacuum degassing process (Fig. 3.20). In this stage, it was accepted that inclusions with this size were externally sourced since there was no calcium wire feed in the liquid steel yet. Floating bigger inclusions after Ca wire feeding after vacuum de-gassing is easier due to Stokes Law. Therefore big inclusions were not expected to be seen in product sample.
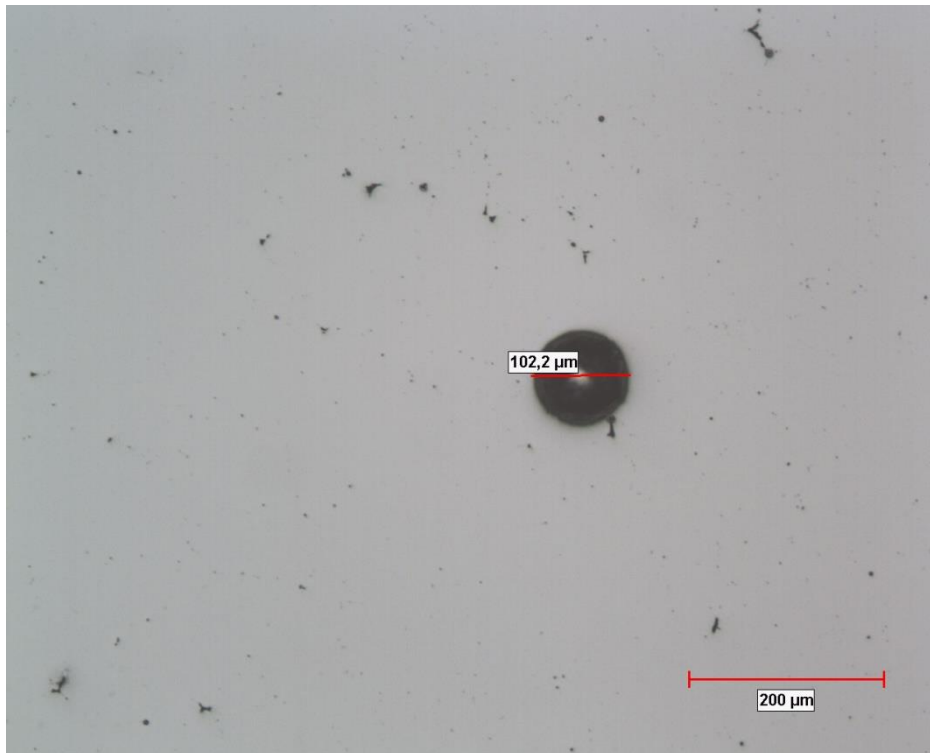
Figure 3.20: 160693BV (microscope image)

When the images of sample taken after vacuum de-gassing were examined small globular inclusions were observed. In this stage as Ca and S wire was fed into molten steel, inclusions which were seen Figure 3.21 were considered to be calcium aluminate and calcium sulfide. Some micro cracks were seen in the images due to sudden cooling of the sample (Fig. 3.21).
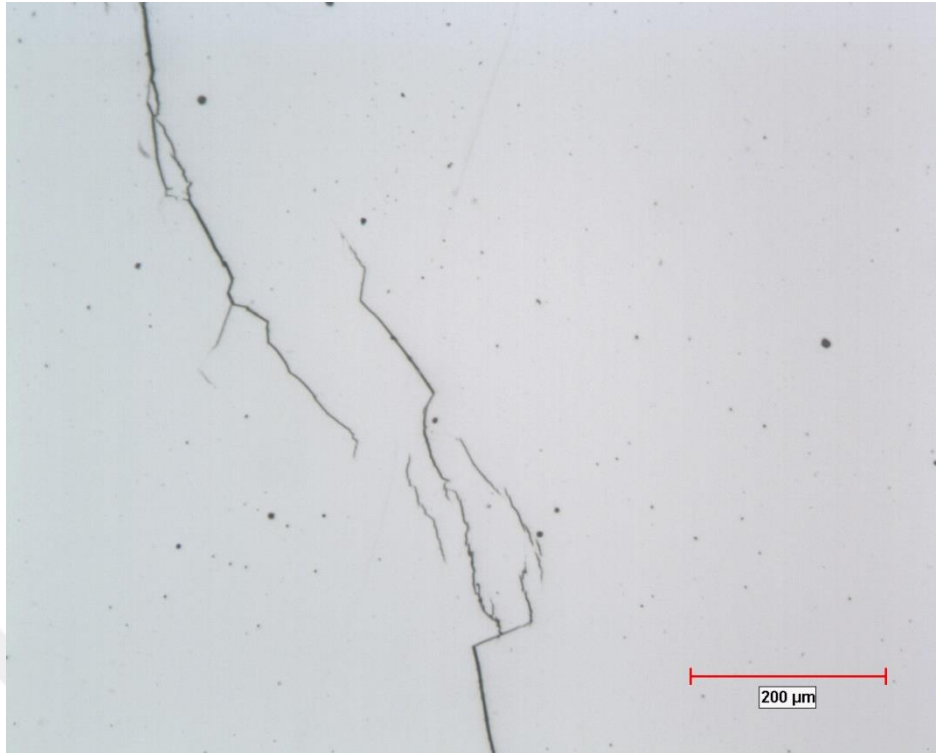
Figure 3.21: 160693AV (optical microscope)

In the optical microscope images of the specimen belonging to the product, inclusions in the vermicular structure which were extended in rolling direction were observed (Fig. 3.22). Those were considered to be typical manganese sulphide inclusions.

Figure 3.22: 160693PP (optical microscope)

The non-metallic inclusion report, which belongs to the number 160693, has been observed to be densely extended sulphite inclusion at K3 level (Table 3.5). It was expected that these types of inclusion would be seen on the samples. Because in the production of 42CrMoS4 steel grade, ferro-sulfur was added to molten steel to obtain the desired chemical analysis. When the non-metallic inclusion index report was examined, most of the inclusions were detected in sample number 4. The sample number 4 was selected for the SEM examination.

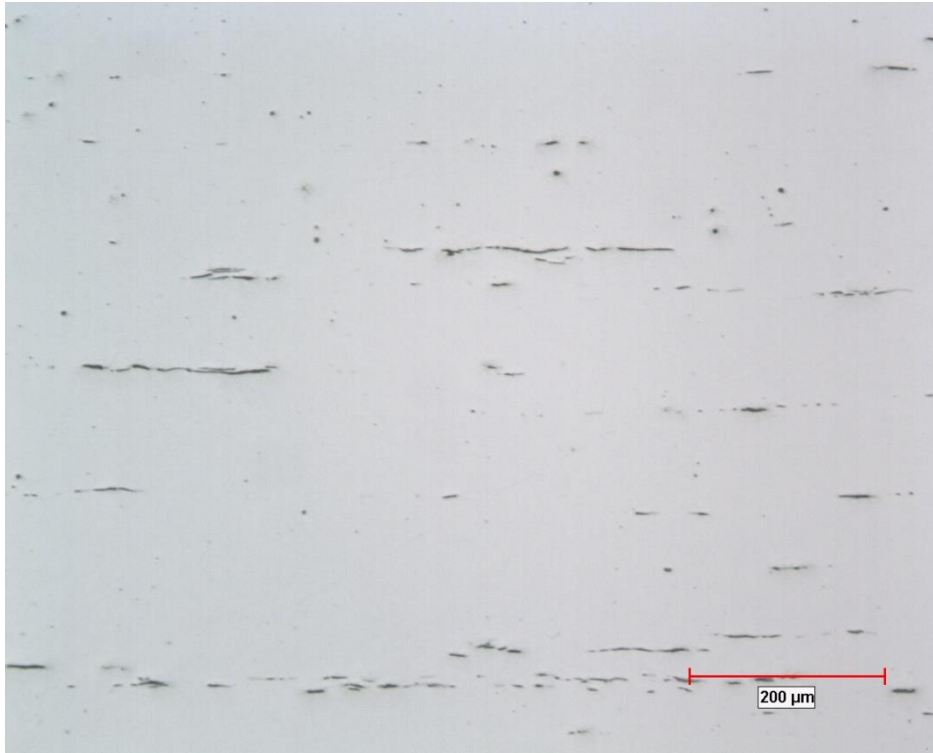**Table 3.5:** 160693 heat number non-metallic inclusion index reports

160693 42CrMoS4		NON-METALLIC INCLUSION INDEX (According to DIN 50602)										
Specimen No	Area of polished section evaluated, in mm^2	Types of inclusion as in diagram plate No.1	Number of inclusions classified by rating number								Multiplication and first subtotal	
			0	1	2	3	4	5	6	7	8		
			Factor f_g										
			0,05	0,1	0,2	0,5	1	2	5	10	20	S *)	O *)
1	179,85	SS				0	0	0	0	0	0	0,0	
		OA				0	0	0	0	0	0		18,5
		OS				0	0	0	0	0	0		
		OG				37	0	0	0	0	0		
2	203,83	SS				0	0	0	0	0	0	0,0	
		OA				0	0	0	0	0	0		3,5
		OS				0	0	0	0	0	0		
		OG				7	0	0	0	0	0		
3	183,38	SS				0	0	0	0	0	0	0,0	
		OA				0	0	0	0	0	0		4,5
		OS				0	0	0	0	0	0		
		OG				9	0	0	0	0	0		
4	158,69	SS				5	0	0	0	0	0	2,5	
		OA				1	0	0	0	0	0		27,5
		OS				0	0	0	0	0	0		
		OG				54	0	0	0	0	0		
5	158,69	SS				0	0	0	0	0	0	0,0	
		OA				0	0	0	0	0	0		2,0
		OS				0	0	0	0	0	0		
		OG				4	0	0	0	0	0		
Total	**884**					Second subtotal						S : 2,5	O : 56,0
						Total index K 3 **)						S : 2,8	O : 63,3
						Overall total index K 3						**66,1**	
						Specification						*****	

SS : Sulfides, elongated form
OA : Oxides, fragmented form (aluminium oxides)
OS : Oxides, elongated form (silicates)
OG : Oxides, globular form

*) S : Sulfides
*) O : Oxides
**) Converted to a polished section area of 1000 mm^2 and rounded to the nearest whole numbers.

Sample was taken before vacuum de-gassing process for this reason S peaks were not observed in SEM micrograph (Fig. 3.23a-b). This heat was killed by aluminum so Al_2O_3 was main phase in inclusion structure. MnO formation was observed at outer shell of aluminum inclusions. This formation gone weak Mn's peak. In addition Mg peak was observed. It was believed that Mg come from refractory materials used in ladle lining. These refractory oxides disappeared after vacuum de-gassing. This indicates that the molten steel was effectively mixed with argon gas and large inclusions passed through the slag. It is easier to float as the diameter of the inclusions increases due to the Stokes law.
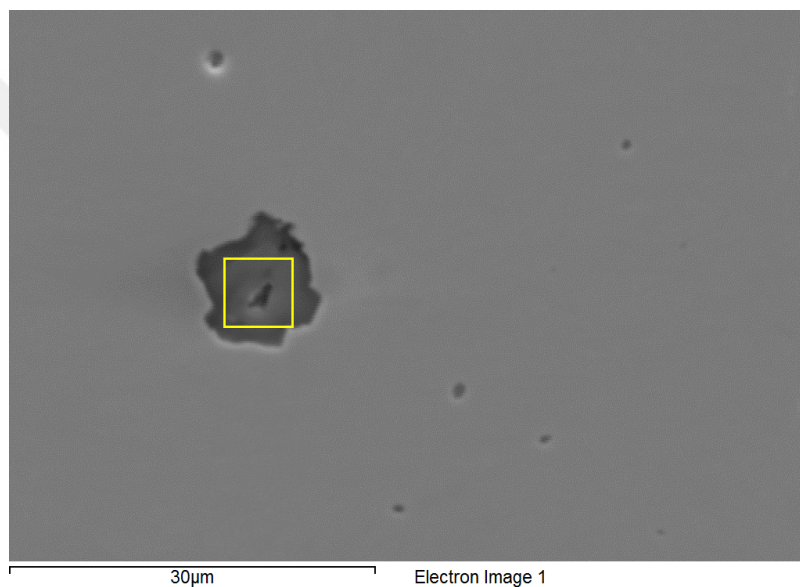

Figure 3.23a: 160693BV SEM
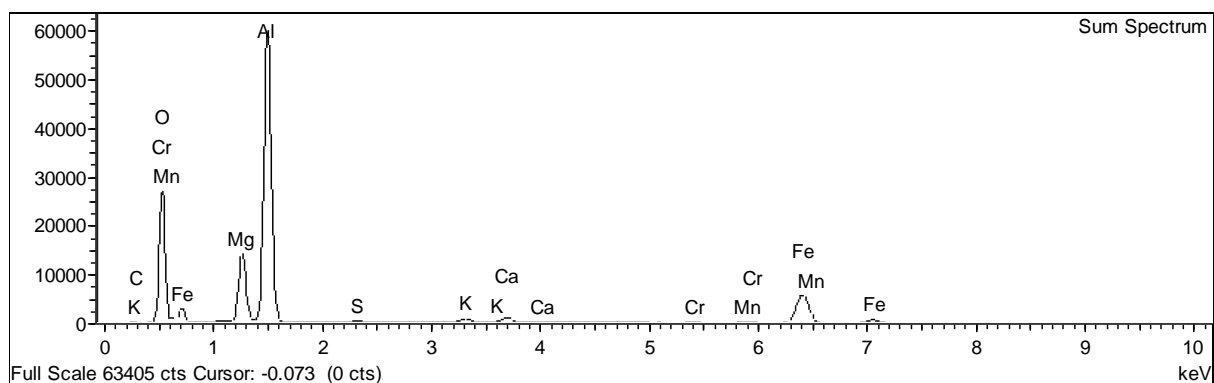
Figure 3.23b: 160693BV SEM migrograph

Sample was taken after vacuum de-gassing process and Ca treatment (Fig. 3.24a-c). Inclusions were globular and small. This indicates that Ca treatment and secondary

metallurgy process were done properly. Bigger size inclusions were not seen in the sample. Therefore flotation of inclusions was done by stirring can be said. Ca content of steel was seems at optimum level. There was no evidence of excess Ca content. In case of excess Ca content in the steel, Ca peak should be expected higher. In addition castability of the heat was very good, no clogging was observed during casting.
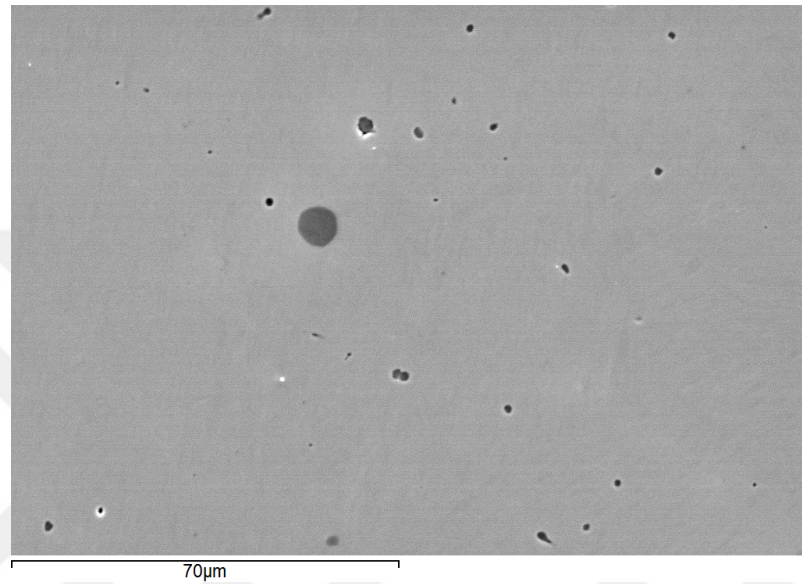
Figure 3.24a: 160693AV SEM
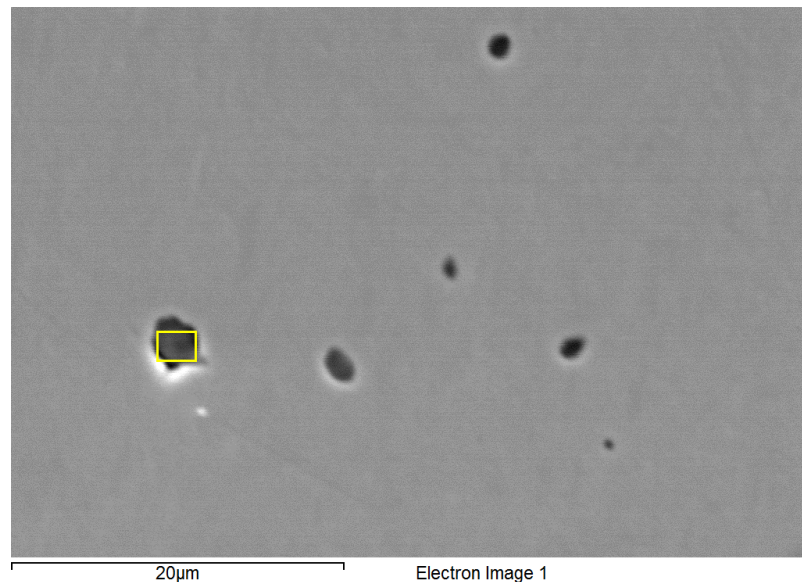
Figure 3.24b: 160693AV SEM
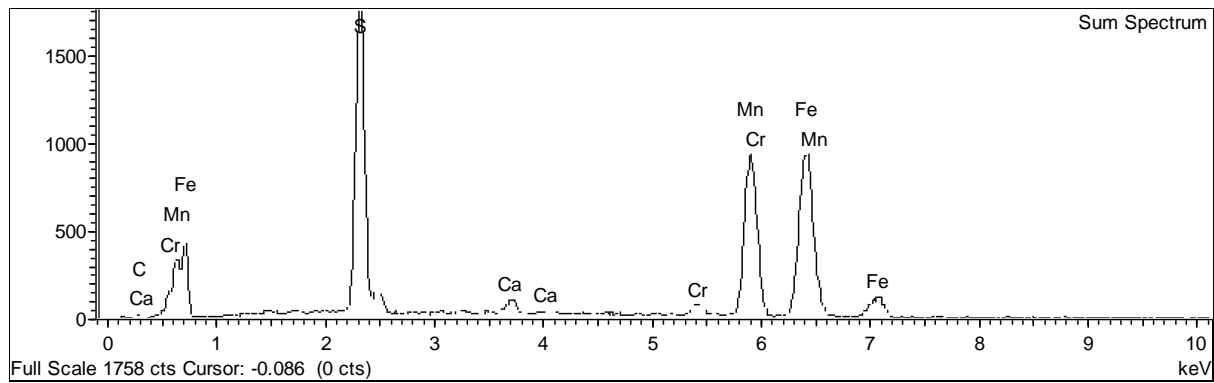
Figure 3.24c: 160693AV SEM migrograph

Globular inclusion was observed on the sample (Fig. 3.25a-b). Optical dark area can be seen rear the inclusion. Formation of optical dark area indicates that the crack propagates in tension mode. CaS formation was limited due to Ca content of steel. MnS and aluminate type inclusions were main phases in inclusion structure.

Figure 3.25a: 160693PP SEM

Figure 3.25b: 160693PP SEM migrograph

4. CONCLUSION

The variation and modification of the nonmetallic inclusions in the steel production during the production process was investigated. For the research, two heats was selected, which were deoxidized with aluminum and then calcium was added. One of the heats selected is 16MnCr5 grade and is a member of the BS EN 10084 standard case hardening steel group. The other one is 42CrMoS4 grade and is BS EN 10083-3 standard steels for quenching and tempering.
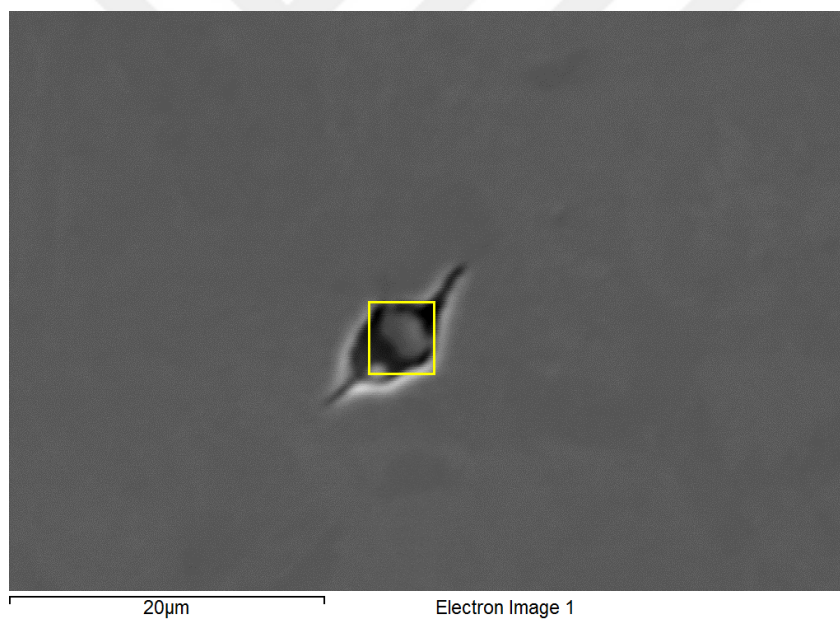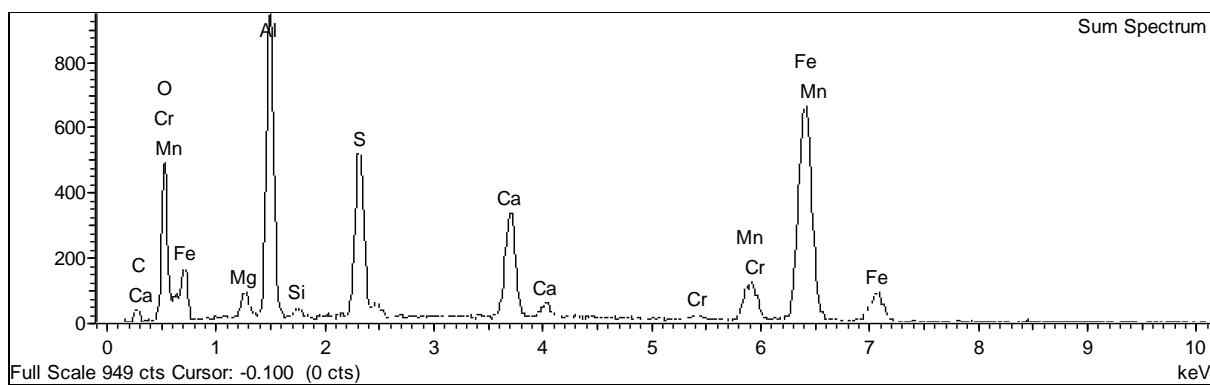
In the optical microscope image of 16MnCr5 steel grade, small globular non-metallic inclusion before vacuum de-gassing was seen. In the image of the sample after the vacuum de-gassing it was seen that the small non-metallic inclusions turned into bigger. In the image of the sample taken after the vacuum de-gassing it was seen that the small non-metallic inclusions turned into bigger ones.

After the vacuum process, the non-metallic inclusions became globular and their diameters have grown.

But the sample taken from product, both optical microscope and SEM image big globular inclusions were seen. The micrograph showing the chemical composition of the sample was examined and it was seen that the calcium application was successful. As a result, the modification of the residues was successful but it was understood that they were trapped in the liquid steel without passing through the slag.

The non-metallic inclusion report, which belongs to the number 160693 42CrMoS4 steel grade, has been observed to be densely extended sulphite inclusion at K3 level (Table 3.4). It was expected that these types of inclusion would be seen on the samples. Because in the production of 42CrMoS4 steel grade, ferro-sulfur was added to molten steel to obtain the desired chemical analysis.

Before vacuum de-gassing proses Al_2O_3 inclusions were seen in both optical microscope and SEM images (Fig. 3.20, Fig. 3.23a). This was an expected situation.

After vacuum process, the amount of sulfur in the liquid steel was drastically reduced, and then firstly calcium was added after then sulfur was added to heat.

Sulfur peaks were observed on the SEM micrograph of the sample taken after the above mentioned procedures. As well as elongated sulfide inclusions was seen in optical microscope images of sample which was taken from product. Also CaS peaks were observed in the SEM micrograph of the sample of the product (Fig. 3.25). But CaS formation was limited due to Ca content of steel. MnS and aluminate type inclusions were main phases in inclusion structure. This showed that the desired inclusion morphology was obtained.

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CURRICULUM VITAE

IBRAHIM BAKAR

QUALITY CONTROL SPECIALIST

Mustafa Kemal Mah. Korfezkoy Sitesi 72/18 Karsıyaka/IZMIR

GSM: (532) 6314586

bakaribrahim@yahoo.com

WORK EXPERIENCE

Ozkan Steel A.Ş. / Izmir   06/2010 -Working

Quality Control Specialist

Management of 27 person Quality Control department. Coordination of the relations with Ozkan Rolling mills and Ozkan Meltshop. Follow up of daily quality report, production schedule. Directing the daily quality department operations. Follow up of the chemistry laboratory analysis report follow the calibration times of the devices and equipment in the quality control department.

Cer Steel A.Ş. / Izmir   04/2007 - 06/2010

Chemist

Follow up of the chemistry laboratory analysis report follow the calibration times of the devices and equipments in the quality control department.

EDUCATION

| **University** | Aegean University/Chemistry | 09/1999 - 06/2004 |
| **High School** | Ataturk Super High School | 09/1993 - 06/1997 |

ADDITIONAL EDUCATION & CERTIFICATES

IATF 16949:2016   AGC Education Center
2018

ISO 9001:2015   AGC Education Center
2018

COMPUTER SKILLS

Netsis, MS Office, ARL Oxas Program

LANGUAGE SKILLS

English   Reading: Advanced, Writing: Intermediate, Speaking: Good

REFERENCES

Çetin Basaranhincal	President Çorum Chamber of Commerce	05322624466
Kenan Malatyali	Former President of TSE	05322745288
Osman Elbirlik	Ozkan Steel Meltshop/Production Manager	05352787512

PERSONAL INFORMATION

Date of Birth	: 15/04/1979
Nationality	: Turkish
Marital Status	: Married
Sex	: Male
Driving License	: B (1998)