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A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S

Volume 57 2012 Issue 1

DOI: 10.2478/v10172-012-0029-0

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INFLUENCE OF INCLUSIONS MODIFICATION ON NOZZLE CLOGGING

WPŁYW MODYFIKACJI WTRĄCEŃ NIEMETALICZNYCH NA ZARASTANIE WYLEWÓW ZANURZENIOWYCH

During the secondary refining of high strength steel in a ladle furnace aluminum is used for the melt deoxidation. Aluminates inclusions are modified with a calcium silicon injection in a melt. On the basis of the binary diagram CaO-Al_20_3 solid and liquid calcium aluminates with different composition and shape are formed after calcium treatment. During the calcium silicon injection manganese sulphide is also modified and CaS or (Ca,Mn)S is formed and wrapped around calcium aluminates.

Because of rising of calcium bubbles during the calcium silicon injection a powerful melt stirring occurs. This enables inclusion coagulation and a reaction with a slag. Additionally, the MgO·Al_20_3 spinels are formed.

Clogging of a tundish nozzle may occur during continuous casting of steel billets. Scull which forms on the nozzle's inner wall consists of spinel, calcium aluminates with various composition and calcium manganese sulphide.

Keywords: clogging, inclusion modification, spinel, calcium aluminates, calcium manganese sulphides

W czasie rafinacji pozapiecowej stali o podwyższonej wytrzymałści, jako odtleniacz stosowane jest w piecu kadziowym aluminium. Wtrącenia w postaci tlenków glinu modyfikowane są w tym procesie poprzez wprowadzanie do kąpieli CaSi. Na podstawie analizy układu fazowego CaO-Al_2O_3 można przewidzieć tworzenie się zróżnicowanych kształtem wtrąceń o składzie stałych lub ciekłych glinianów wapnia. W czasie modyfikacji przemianom podlegają również siarczki manganu tworząc wtrącenia typu CaS oraz (Ca,Mn)S otaczające gliniany wapnia.

Z uwagi na wzrost objętości tworzących się w czasie wprowadzania CaSi pęcherzy gazowego wapnia, w procesie zachodzi intensywne mieszanie kąpieli metalowej. Zjawisko to umożliwia koagulację wtrąceń niemetalicznych oraz ich rekcję z żużlem. Dodatkowo zachodzi również tworzenie spinelu typu MgO·Al_2O_3

W procesie ciągłego odlewania kęsów może zachodzić proces zarastania wylewów zanurzeniowych kadzi pośredniej. Narosty, które tworzą się na wewnętrznej ściance wylewu zanurzeniowego zawierają w składzie chemicznym spinel MgO·Al_2O_3, gliniany wapnia oraz (Ca,Mn)S .

1. Introduction

In the production of liquid steel composition, shape and size of non-metallic inclusions have changed considerably. Non-metallic inclusions, which are formed in liquid steel, are in most cases products of the melt deoxidation. By using various deoxidizers different gaseous, liquid or solid deoxidation products might be formed. Smaller liquid inclusions coagulate in a melt into larger inclusions which can float up into the slag.

Inclusions in a melt also influence casting properties. Due to scull formation the possibility of nozzle and sheath tube clogging exist [1, 2]. The influence of thermal field and melt flow during continuous casting could not be neglected [3].

2. Modification

In the present work the modification of non-metallic inclusions in a ladle furnace in the case of production of steels with good machinability will be presented. It is done by injecting a calcium silicon wire into an aluminum deoxidized melt.

Ladle treatment starts with tapping from a 50 ton EAF. During tapping time, alloying and deoxidation elements can be added (ferromanganese, silicon, carbon, aluminum). As a result, manganese sulphides and manganese silicates are presented in a melt after the tapping. In Fig. 1 manganese sulphide found in a melt after the tapping is shown.

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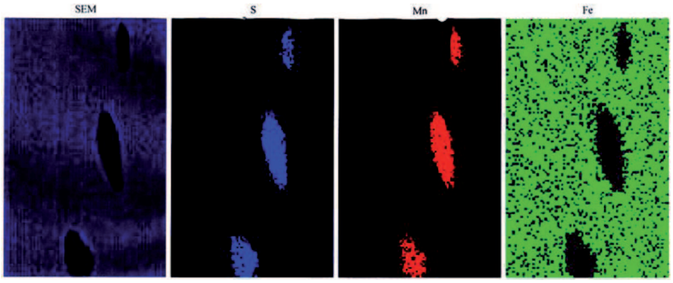

Fig. 1. Manganese sulphide found in a melt after the tapping

Modification of alumina inclusions is achieved with calcium which is added in form of calcium silicon [4]. With the modification of alumina inclusions nozzle clogging should be prevented.

Deoxidation, desulfurization and modification of non-metallic inclusions is made with calcium silicon alloy with calcium content between 28 and 33 mass. %. This alloy is produced with reduction of calcium oxide (CaO) or calcium carbonate ($CaCO_3$) and quartz (SiO_2) in electric furnace.

Alloying of calcium silicon is normally made with injecting of wire into a melt. In the of cored wire is crashed calcium silicon with granulation between 0.5 and 1.5 mm. Size of grains in the cored wire is presented in Fig. 2.

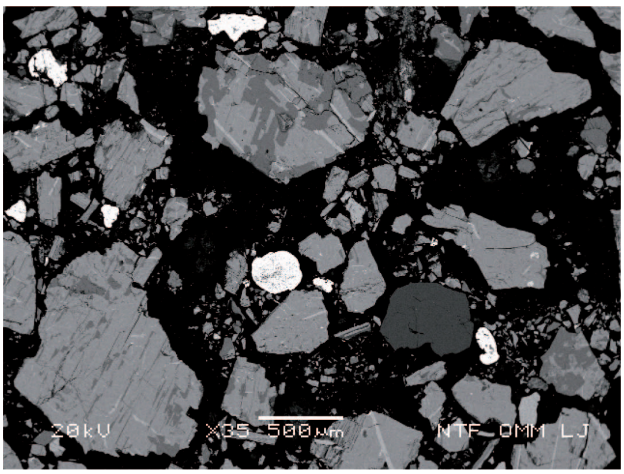

Fig. 2. Calcium silicon grain size used for injecting

Figure 2 shows that grains have different sizes and also that their composition is heterogeneous (Figure 3).

Figure 3 presents detail from Fig. 2, grain with diameter of 1×0.75 mm which consists of three phases. Silicon is marked with number 1, calcium silicon with number 2 (consisting in 44 mass percent of calcium, 54 mass percent of silicon and 1 mass percent of iron) and ferrosilicon with number 3 (with around 51 mass percent of silicon and 48% mass percent of iron). Melting points for all three components are similar. In some cases there can be found phases which contain also titanium, beside silicon and iron [5].

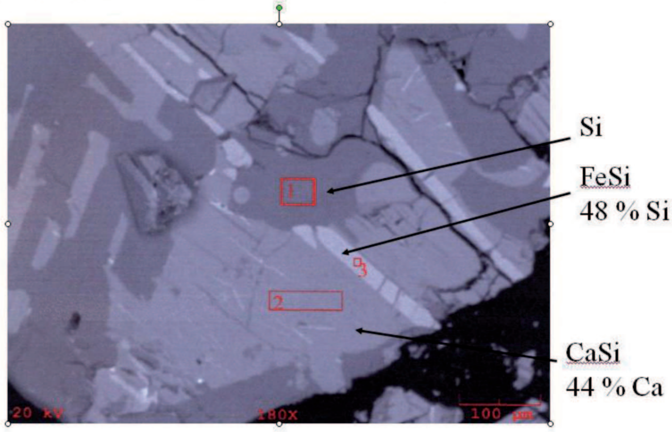

Fig. 3. Phases in a CaSi grain from the cored wire

The aim of modification of aluminates inclusions into the calcium aluminates is to get inclusions, which are liquid during the production and casting of steel. Liquid calcium aluminates in steelmaking are formed only in a narrow area in the system CaO-Al_2O_3, when CaO/ Al_2O_3 ratio is about 1.

Calcium vapor is generated during the injection of calcium to the bottom of a ladle. Due to increases in volume strong mixing of a melt arises. Calcium vapor bubbles rising to the surface of a melt and react with alumina inclusions on the way. During the reduction of aluminates inclusions various oxides, which are characteristic for the system CaO- Al_2O_3, can form (Fig. 4). These are, beside the two pure oxides (CaO and Al_2O_3): CaO·6Al_2O_3 (CA_6), CaO·2Al_2O_3 (CA_2), 12CaO·7Al_2O_3 ($C_{12}A_6$), CaO·Al_2O_3 (CA) and 3CaO·Al_2O_3 (C_3A) [6].

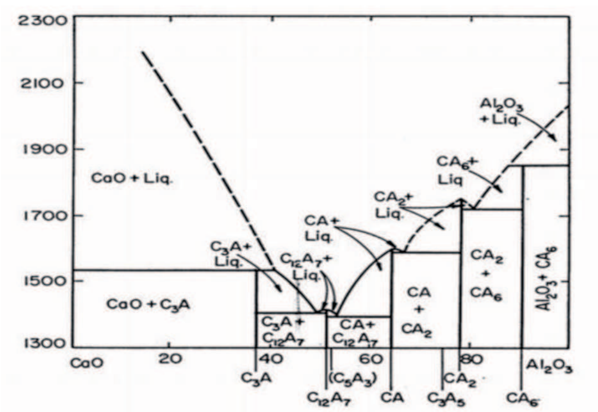

Fig. 4. Binary diagram CaO- Al_2O_3 [6]

Calcium, apart from being a strong deoxidizer; has also a high affinity for sulfur and forms calcium sulphides. In the production of steel sulfur is bounded to manganese sulphide; calcium manganese sulphides (Ca,Mn)S are formed during the melt treatment with calcium, too.

When calcium is added to a molten Al-killed steel, at the beginning alumina inclusions are modified to calcium aluminates. These inclusions have a high sulphide affinity. At lower temperatures the solubility of sulphur decreases thus during cooling CaS precipitates formed [7], resulting in a duplex inclusion of CaS and calcium aluminates. Sphere-shaped inclusion of calcium aluminates with calcium sulphide is presented in Fig. 5.

Inclusions presented in the Fig. 6 are formed in the case when calcium aluminates of type $CaO \cdot 2Al_2O_3$ with melting point being higher than $12CaO \cdot 7Al_2O_3$ are the main ones created during modification. Those non-metallic inclusions are calcium aluminates and calcium sulphide; however, calcium sulphide does not encircle calcium aluminates.

During the modification the reduction of aluminates inclusions takes place, but only to the degree at which $CaO \cdot 2Al_2O_3$ has formed. The conversion of manganese sulphide to the (Ca,Mn)S occurs parallel.

3. Clogging

During continuous casting of steel process a melt flows through sheath tubes made of refractory material from a ladle into tundish and from tundish into a mould. They are used to protect the metal stream from reoxidation and from gas absorption.

There are various reasons for clogging. Deoxidation products (ie. aluminumoxide) [1, 8, 9] with size from 1 to 20 μm can sinter together and form scull [2]. Clogging can also arise because of solid steel accumulation on nozzle wall when

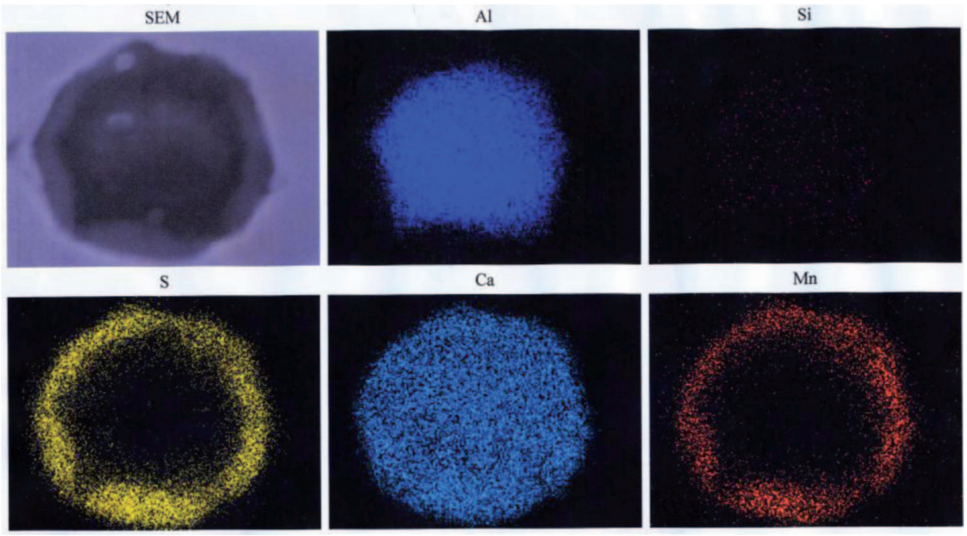

Fig. 5. Spherical inclusions of calcium aluminates and calcium and manganese sulphide

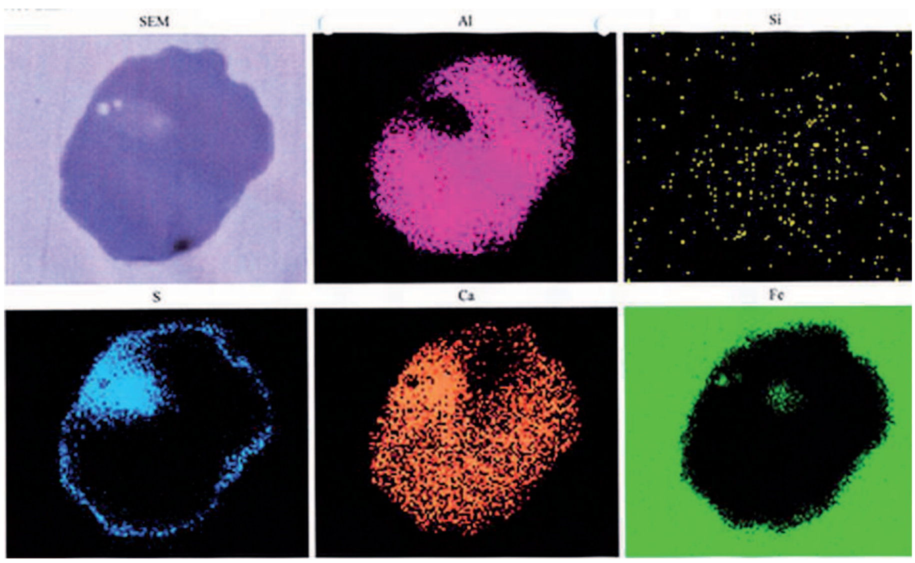

Fig. 6. Inclusions of calcium aluminate and calcium sulphide [4]

melt's temperature is too low. Third reason is sticking of complex oxides on the walls. Scull in this case consists of combination of deoxidation products and mold flux [10].

Mechanism of clogging is also not unique. Clogs from solidified steel and reaction products are formed at a nozzle wall and thus also grow from that origin. Other mechanism that leads to the formation of scull on a nozzle consists of two steps. First step is the transportation of deoxidation products to a nozzle wall. In case of turbulent zones fluctuations toward the wall can cause deposition of inclusions. Probability of interception of deoxidation products is obviously higher in the case of rougher nozzle wall. Second step in scull building is the process of attaching deoxidation products to a nozzle wall. First particles are attached to the wall by surface tension which is strengthened by sintered bond if given enough time [11].

Due to strong mixing and swirling of a melt in the transition area from a tundish to a mould coagulation of inclusions takes place. The first place where it occures is when mono-block regulates speed of melt flow into a sheath tube. Another place is an outlet of sheath tube where a melt flows into a mould.

In Fig. 7 the macroscopic image of sheath tube section, which connects the tundish with the mould is presented. The scull, which is firmly glued to the tube wall, was built on the part of the sheath tube, which is on the outside of the tundish lower part. While waiting for the tundish to get filled and the start of casting this part of the sheath tube cooled rapidly.

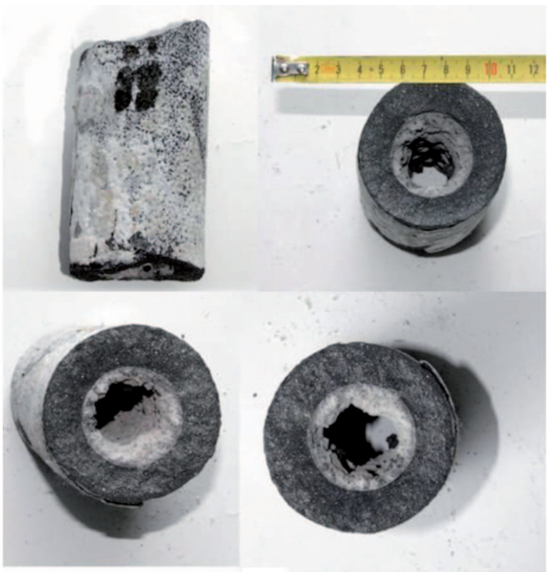

Fig. 7. Scull in the sheath tube

Figure 8 shows the microstructure of this scull. Scull consists of three phases that have formed in the melt, from calcium aluminates ($xCaO \cdot yAl_2O_3$), spinel ($MgO \cdot Al_2O_3$) or ($MgO\ MnO) \cdot Al_2O_3$) and calcium sulphide (CaS), which occurred after complete modification of manganese sulphide.

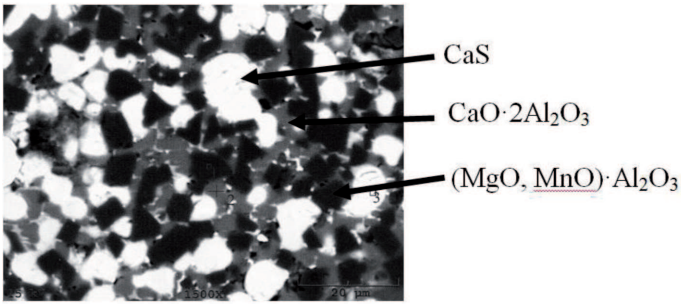

Fig. 8. The microstructure of the scull from the sheath tube with CaS, $CaO \cdot 2Al_2O_3$ and $(MgO, MnO) \cdot Al_2O_3$)

Although there is no added magnesium, the addition of calcium also caused the formation of phases such as $MgO \cdot Al_2O_3$, which is found in scull. It can hinder or even stop the steel casting process.

Figure 9 shows the microstructure of the scull with CaO ·Al2O3, $CaO \cdot 2\ Al_2O_3$ and $MgO \cdot Al_2O_3$.

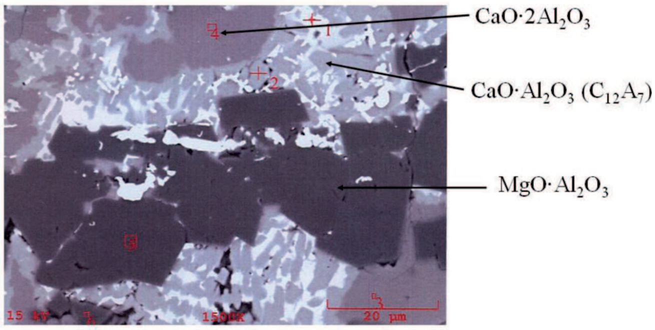

Fig. 9. The microstructure of the scull from the sheath tube

Figure 10 shows microstructure of the clog composed of Al_2O_3, $CaO \cdot 6Al_2O_3$ and $CaO \cdot 2Al_2O_3$.

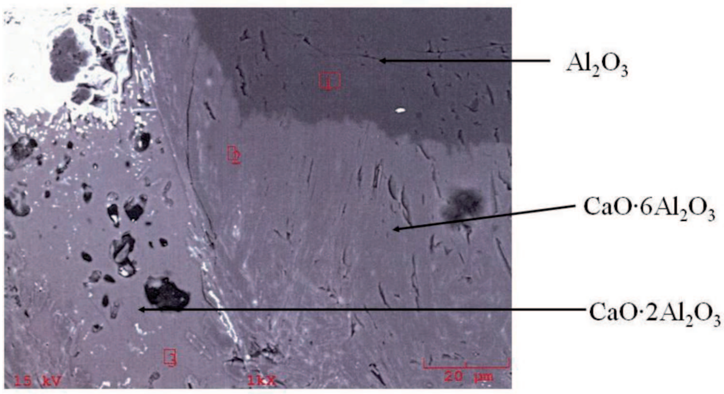

Fig. 10. The microstructure of the scull from the sheath tube

In the Figures 11 and 12 there are XRD diagrams of two different samples of clogs from sheath tube with different types of calcium aluminates, spinel, Al_2O_3) and quartz.

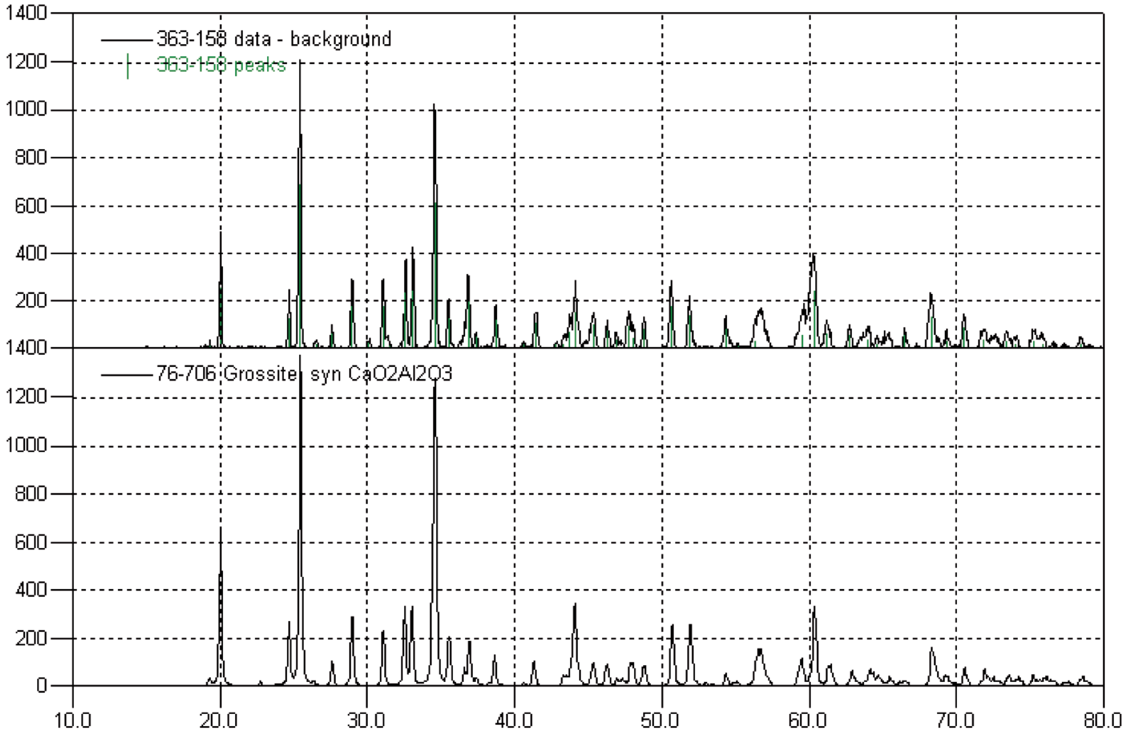

Fig. 11. The XRD diagram of the scull from the sheath tube which contains CaO $\cdot 2Al_2O_3$

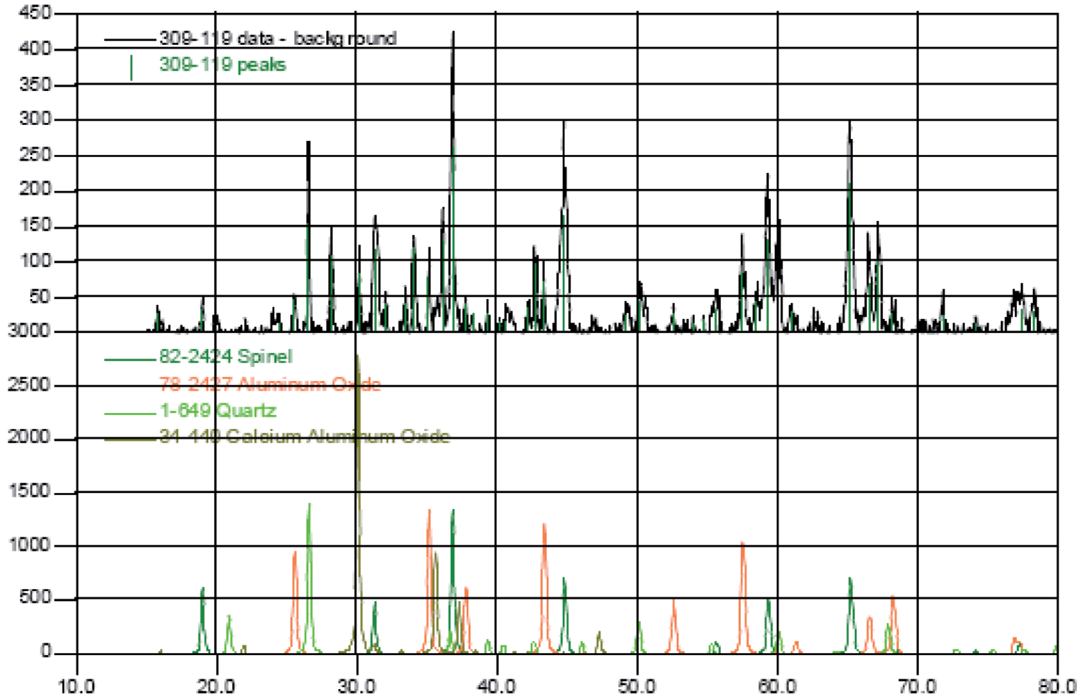

Fig. 12. The XRD diagram of the scull from the sheath tube which contains spinel, Al_2O_3, CaO $\cdot Al_2O_3$ and quartz

Formation and composition of oxide inclusions in a melt can be represented in the four component system Ca-Al-Mg-O (Fig. 13).

The cross section CaO- Al_2O_3-MgO (shown in Fig. 14) is important for understanding of the non-metallic inclusions formation and of the scull formation. Important phases for the formation of non-metallic inclusions in steel and scull in steels deoxidized with aluminum and treated with calcium are calcium aluminates CA_6, CA_2 and CA) , which are in equilibrium with MgO $\cdot Al_2O_3$ and calcium aluminates C_3A, $C_{12}A_7CA$ which are in equilibrium with MgO.

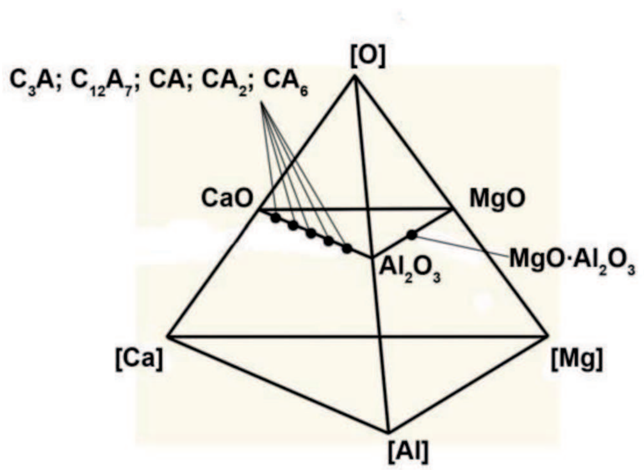

Fig. 13. Schematic presentation of the four component system Ca-Al-Mg-O

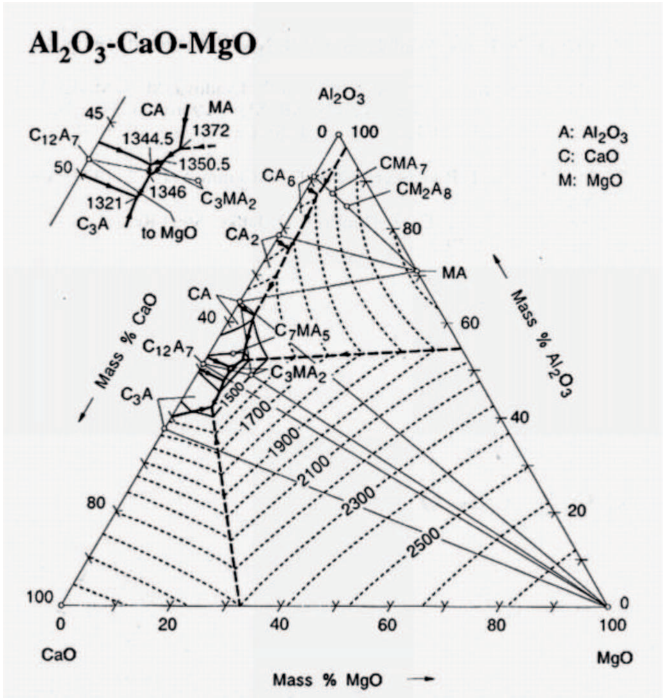

Fig. 14. The ternary system CaO- Al_2O_3-MgO [Slag Atlas]

4. Conclusions

The injection of calcium silicon wire can be used for modification of aluminates inclusions in an aluminum deoxidized melt. Calcium vapor strongly mix a melt and because of local chemical composition's inhomogeneity calcium aluminates with different compositions may be formed.

Clogging is a result of inclusions stacked on a nozzle wall. They form during the modification of calcium aluminates and during the formation of calcium sulphide. These inclusions move to tube wall, because of melt flow and stick to it.

Spinel (MgO,MnO)$\cdot Al_2O_3$ forms at temperatures typical for production and casting of steel. It is a product of metallurgical reactions between magnesium, which is formed during the MgO reduction with calcium, and aluminates. Because of spinel the time for formation of scull decreased.

In the region between melt, slag and refractory material inclusions with composition similar to gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) can be formed.

From the modelling we assume that clogs with a high melting point are a result of swirl which is formed between a mono block and a nozzle. Non-metallic inclusions with a high melting point are pushed toward the surface of melt stream and then agglomerate on the wall.

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Received: 10 September 2011.