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INTERACTION BETWEEN STEEL MELT AND REFRACTORY MATERIALS IN TUNDISH

ODDZIAŁYWANIE KĄPIELI METALOWEJ Z WYŁOŻENIEM OGNIOTRWAŁYM KADZI POŚREDNIEJ URZĄDZENIA COS

In Štore Steel steelworks steel is casted on a three strand continuous casting machine. Lining of tundish is mainly made from a magnesia based material. Tundish cover powder is based on alumina and silica. It also contains aluminum and carbon.

During casting, the composition of cover slag is constantly changing. When steel in casted in sequences the change in cover slag composition depends on the amount of CaO rich ladle slag. The composition of tundish cover slag at the end of the casting sequence lies in the area of gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) in ternary phase diagram $CaO{\cdot}Al_2O_3{\cdot}SiO_2$.

The result of the reaction between melted steel, refractory material and tundish cover slag are enstatite ($MgO{\cdot}SiO_2$) and monticellite ($CaO{\cdot}MgO{\cdot}SiO_2$). Merwinite ($3CaO{\cdot}MgO{\cdot}SiO_2$) is formed in the end of the casting sequence because of high basicity of the gehlenite based tundish cover slag.

Clogging on the inner side of submerged entry nozzles (SEN) are made of calcium aluminates ($CaO{\cdot}2Al_2O_3$) and spinel $(MgO,MnO){\cdot}Al_2O_3$. Only when steel is casted in sequence composition changes in tundish cover slag and clogging occurs.

Keywords: continuous casting, tundish slag, clogging

W stalowni Štore Steel stal odlewana jest na trzyżyłowej maszynie COS. Wyłożenie ogniotrwałe w kadzi pośredniej tej maszyny wykonane jest głównie na bazie materiałów magnezytowych. Żużel w kadzi pośredniej tworzony jest na bazie tlenków glinu i krzemionki i zawiera również glin i węgiel.

Podczas odlewania skład chemiczny żużla w kadzi pośredniej ulega ciągłym zmianom. W przypadku odlewania sekwencyjnego zmiany w składzie zależą od ilości CaO żużla kadziowego. Pod koniec sekwencji odlewania skład żużla zbliża się do obszaru fazowego gelenitu ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) w trójskładnikowym diagramie fazowym $CaO{\cdot}Al_2O_3{\cdot}$ SiO_2.

Produktami reakcji pomiędzy ciekłą stalą, wyłożeniem ogniotrwałym i żużlem kadziowym są enstatyt ($MgO{\cdot}SiO_2$) i monticzellit ($CaO{\cdot}MgO{\cdot}SiO_2$). Merwinit ($3CaO{\cdot}MgO{\cdot}SiO_2$) tworzy się pod koniec sekwencji odlewania z powodu wysokiej zasadowości bazującego na gelenicie żużla w kadzi pośredniej.

Zarastanie wewnętrznej powierzchni wylewów zanurzeniowych spowodowane jest tworzeniem się glinianów wapnia ($CaO{\cdot}2Al_2O_3$) i spinelu $(MgO,MnO){\cdot}Al_2O_3$. Zarastanie wylewów oraz zmiana składu żużla w kadzi pośredniej występują tylko podczas odlewania sekwencyjnego.

1. Introduction

Steel consumers dictate ever more rigorous limitations of nonmetal inclusions size and content, especially when steel is used for mechanically demanding construction parts such as flat springs. Production of steel occurs in various reactors, which are lined with MgO, $CaO{\cdot}MgO$, Al_2O_3 etc., based materials. During production process steel melts, especially slag, which reacts with reactor linings and form new compounds [1, 2, 3, 4, 9].

During continuous casting of steel, melt is poured from ladle to tundish where its flow is divided to each strand. Tundishes role isn't just as a steel melt dispenser, but also as the last major reactor where refining processes are still underway. Main surface where steel melt can be deoxidized is on top, where liquid steel is in contact with the atmosphere. There are many ways which prevent reoxidation such as air tight covers, establishing an argon gas rich atmosphere under the cover, powder covering etc. In practice is normally used a combination of different assets. Some flow modifying devices, such as stoppers are prone to reactions with steel melt either on top surface or at the tip of the stopper. Analysis of the chemical interaction between the steel and tundish has also been made. Focus of this work is on analysis of change in composition of tundish cover slag (TCS) and reactions with other fire resistant materials mainly tundish lining.

Tundish cover powders main purpose is reducing heat loss through radiation and forming a barrier between atmosphere and melt. Recent developments have been done to improve capabilities of TCS to incorporate inclusions that arrive to the phase boundary between steel and TCS. Composition of tundish cover powder must be just right, so that it forms a liq-

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uid slag layer on the contact, and is still solid above. The liquid phase protects steel from reoxidation and solid phase acts as a thermal insulator. Traditionally TCS is made from rice hull which contains up to 90 mas. % SiO_2 and provides excellent protection from heat loss. Rice hull forms high viscosity liquid slag which is unable to successfully absorb inclusions and high silica content is a source of reoxidation. That's why modern steel plants use custom made cover powders that form complex phases according to users wishes. Figure 1 shows cut through a typical layer of tundish cover powder and slag [1, 2, 3, 5].

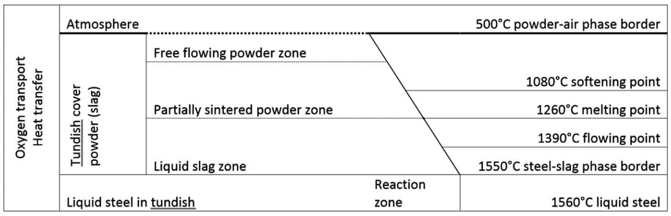

Fig. 1. Cut-through of tundish cover layer [6]

2. Experimental work

Experiments were held at Štore Steel plant. Production path there consists of 60 MVA electric arc furnace and 12.5 MVA ladle furnace. The 3-stranded continuous casting machine has a radius of 6 m, mold size is 180×180 mm and billet lengths are between 2 and 6 m. Main spring steels, forging steels and engineering steels steel grades are produced. Capacity of tundish is 9 t. Melt is transferred to mold via submerged entry nozzle (SEN) and flow control is provided by stopper rod guided with Cs-137.

During pouring from ladle to tundish steel is protected by shroud and Ar ring, while tundish is covered with cover powder, which composition is shown in Table 1. On Figure 2 X-ray diffraction (XRD) diagram of "raw" cover powder is shown.

TABLE 1

Chemical composition of tundish cover powder

Compound	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Na_2O	C	Al met.	TiO_2
mas. %	11.76	0.55	52.17	3.7	0.63	1.2	22	3	1.89

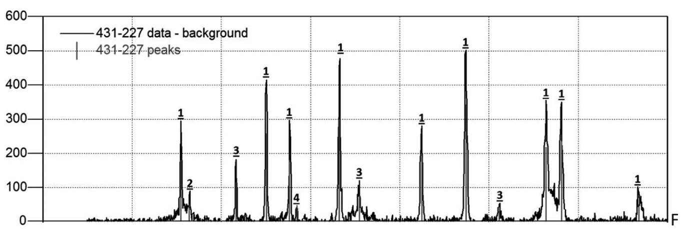

Fig. 2. XRD diagram of cover powder, phases marked with: 1- Al_2O_3, 2- SiO_2, 3-C, 4-Al

Samples of cover slag and other materials were taken at casting of steel grade 52CrMoV4, which is used for high strength spring steel. Slag sample is shown in Figure 3.

To examine interaction between refractory materials of flow modifying devices and cover slag, a sample of thermocouple protective shroud was taken. Its chemical composition is exactly the same as of stopper rod (Figure 4).

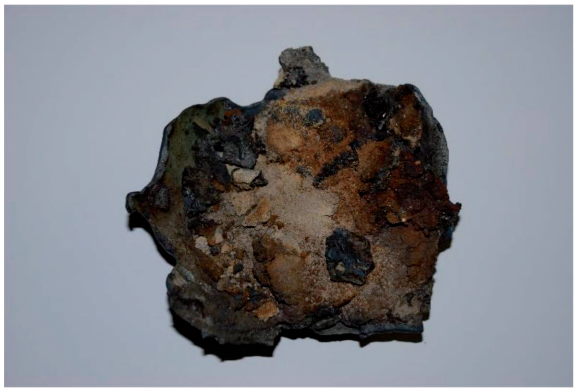
Fig. 3. Cover slag sample


Fig. 4. Solidified cover slag on the thermocouple protective shroud

A sample from tundish refractory material after casting which was in contact with steel melt is shown in Figure 5. The dark layer on top of the sample was in contact with steel during casting.


Fig. 5. Refractory material based on MgO

We sampled submerged entry nozzles for any signs of deposits or some other anomalies. Figure 6 shows there weren't much deposits on SEN walls.

Fig. 6. Deposits in the bottom part of SEN (glassy phase is an added resin for structural stability)

3. Results

Tundish cover slag

After cover slag is added to steel melt processes like sintering of powder and oxidizing of Al and C start. During the sintering process cover slag starts to melt and forms liquid phase. Figure 7 shows tundish cover slag sample taken after 40 min. of casting. We were still able to find solid well block sand made out of (MgO,MnO)·Al_2O_3·Cr_2O_3 with some free Al_2O_3. Liquid slag, which surrounds the well block sand has a similar composition to spessartite 3MnO·Al_2O_3· 3SiO_2. MnO that reacted with cover powder must have originated from reoxidation of steel melt. Liquid phase rich on MnO occurred in very small quantities. The most important change to tundish cover slag composition comes from ladle slag carryover due to vortex effect.

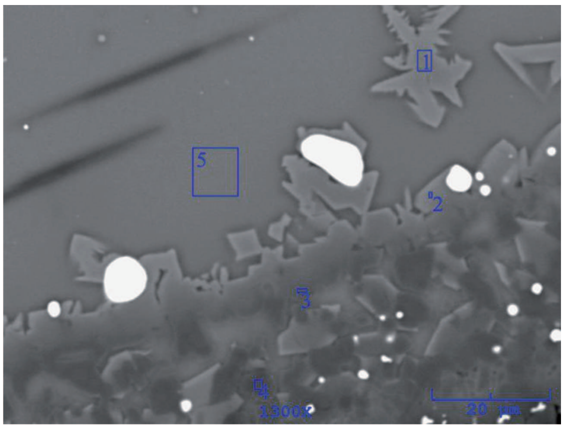

Fig. 7. Tundish cover slag with grains of well blocking sand

Well blocking sand is enriched with MnO and Al_2O_3 which is shown on Figure 8, amount of Cr_2O_3 is reduced.

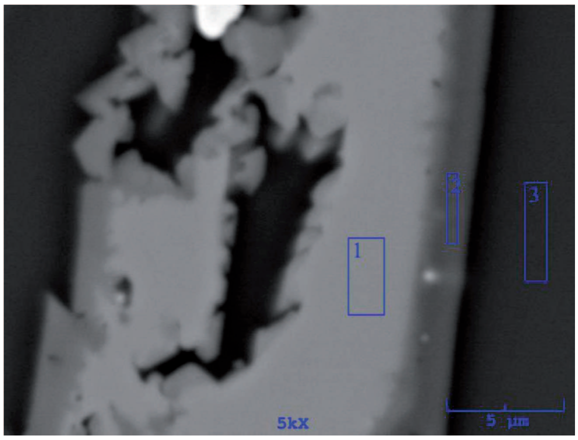

Fig. 8. Chromite grain with MnO enriched border area

Figure 9 shows microstructure of cover slag after 2 heatings casted in a sequence. Sample contains remnants of ladle slag. Figure 10 shows us a detail from Figure 9 and shows different phases found throughout these samples. We found following phases: 1-CaS, 2-TiO_2, 3-CaO·2Al_2O_3, 4-2CaO·Al_2O_3·SiO_2, 5-(MgO,MnO)·Al_2O_3. Figure 10 shows us that cover slag contains matrix made from gehlenite where different other phases are embedded.

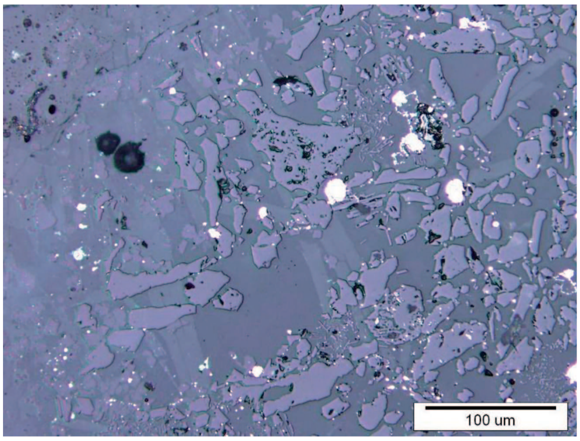

Fig. 9. Microstructure of a melted cover slag

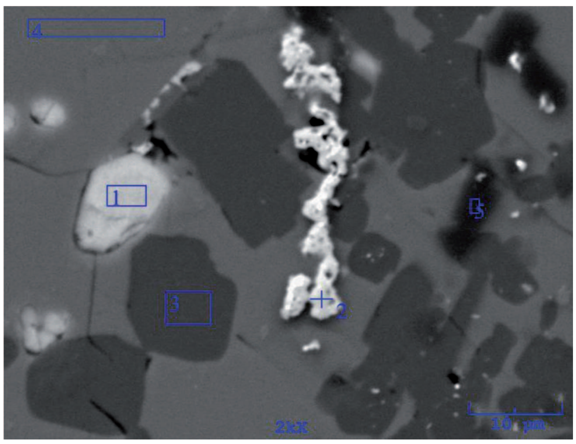

Fig. 10. Scanning electron microscope (SEM) scan with markings of EDS analyzing points

Figure 11 shows a XRD image of this cover slag, phases found by EDS are confirmed.

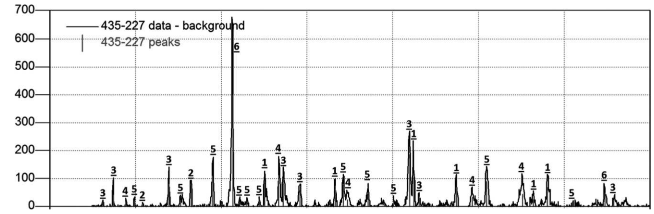

Fig. 11. Cover slag deposits on thermocouple protective shroud. 1: Al_2O_3, 2: SiO_2, 3: $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$, 4: $MgO{\cdot}Al_2O_3$, 5: $CaO{\cdot}2\ Al_2O_3$, 6: CaS

Tundish lining

In the reaction zone between refractory and cover slag we found $MgO{\cdot}SiO_2$ and $CaO{\cdot}MgO{\cdot}SiO_2$. Reaction has occurred because of presence of ladle slag.

Figure 12 shows EDS image of a penetrated work layer of tundish lining after casting. Different oxide phases are marked with following numbers: 1-MgO, 2-$MgO{\cdot}SiO_2$, 3-$3CaO{\cdot}MgO{\cdot}2SiO_2$ and 4-$2CaO{\cdot}Al_2O_3{\cdot}SiO_2$.

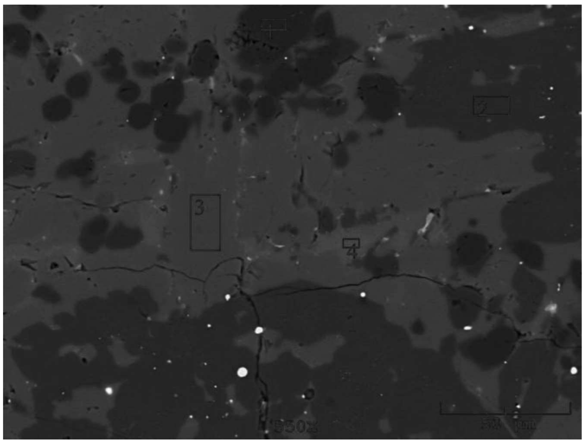

Fig. 12. Microstructure of a penetrated area of tundish lining in the cover slag zone

Submerged entry nozzle deposits

Deposits on SEN wall shown on Figure 13, are mainly composed from $CaO{\cdot}2Al_2O_3$ (1) and $MgO{\cdot}Al_2O_3$ (2).

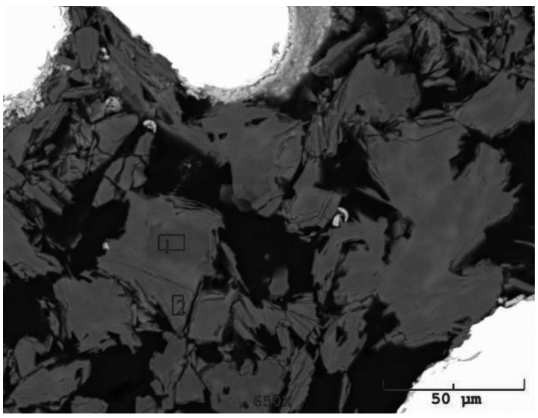

Fig. 13. SEM scan of a SEN deposit

4. Discussion

Liquid steel in tundish comes in contact with cover slag and lining refractory, which are based on Al_2O_3 and SiO_2 or MgO, respectively. Figure 14 shows the shift in chemical composition of TCS during casting from binary system Al_2O_3-SiO_2 based mullite ($3Al_2O_3{\cdot}SiO_2$) over spessartite ($3MnO{\cdot}\ Al_2O_3{\cdot}3SiO_2$) towards gehlenite ($2CaO{\cdot}\ Al_2O_3{\cdot}SiO_2$) and calcium aluminates. Influx of CaO in such great quantities could have come through ladle slag carryover.

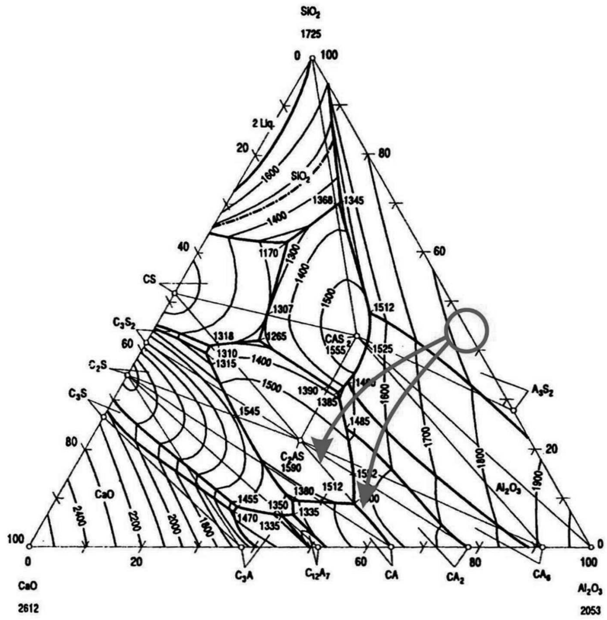

Fig. 14. Ternary phase diagram Al_2O_3-CaO-SiO_2 [7]

In penetrated zone of contact lining with cover slag are phases that have transformed from original periclase (MgO) towards enstatite ($MgO{\cdot}\ SiO_2$), monticellite ($CaO{\cdot}MgO{\cdot}SiO_2$) and merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$).

Spinel ($MgO{\cdot}Al_2O_3$) found in cover slag might have originated from ladle slag or from a reaction between Al_2O_3 in cover slag and MgO from tundish lining.

5. Conclusion

Tundish is a metallurgic reactor where liquid steel comes in contact with the atmosphere, cover slag and tundish refractory materials. Main goals of tundish cover slag are preventing heat loss and reoxidation of steel, but an important feature is entrapment of inclusions from steel. Cover powders composition must be such that it doesn't react with tundish lining.

Cover powder consists mainly of Al_2O_3 and SiO_2 but also of Al and C. After Al and C oxidize main component in cover powder are alumosilicates. During sequence casting composition of cover slag changes dramatically. Main components of cover slag at the end of casting are gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) and calcium aluminate ($CaO{\cdot}2Al_2O_3$).Also spinel ($(MgO,MnO){\cdot}Al_2O_3$) which might have originated from refining process in ladle can be found in it.

In this work we analyzed the composition of different tundish contained materials during continuous casting of steel and their interaction. Formation of CaO containing compounds shows that some ladle slag carryover has occurred. We also found some chromite in cover slag, which must have originated from well blocking sand.

In the boundary zone between tundish lining, steel and cover slag it can come to penetration of the latter. Magnesia based lining transforms to merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$). Depth of penetration is from 2 to 3 mm for 2 heats casted in a sequence.

Deposits from SEN are mainly composed from calcium aluminate ($CaO{\cdot}\ 2Al_2O_3$) and spinel ($(MgO,MnO){\cdot}Al_2O_3$).

With further research we will optimize cover slag composition, so that it would entrap more inclusions while sufficiently protecting the steel from heat loss and reoxidation.

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