Reactions between slag and a dry-hardened tundish lining

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Abstract

The tundishes at SSAB Tunnplåt AB are lined with dry mass and an organic binder, which is hardening at room temperature. The lining resists the conditions during casting. After casting it falls out easily with the remaining scull. A study was made on the interaction between slag metal and the dry-cast lining. Samples of new and used lining were characterised by means of Chemical analysis, X-ray diffraction and Micrographic studies. The results are compared with Thermodynamic calculations and Thermal analysis. A limited penetration was observed, with subsequent chemical reactions and modification of the grain size. However, these reactions seem to produce mainly high melting products, and do not seem to be harmful to the lining stability. This is also confirmed by thee production experience at SSAB Tunnplåt AB.

Introduction

SAAB Tunnplåt AB is fitted with two 105 tonne BOF converters, two CAS-OB stations and two slab casters. A ceramic shroud with Ar atmosphere protects the steel stream from the ladle into the tundish. The strand dimensions are 800 - 1700*220 and 800 - 1600*220 respectively. The tundish volume corresponds to 17.5 tonne of steel. Both ladles and tundishes are mounted on turning towers and can be changed during casting. Sequence casting is used. The length of the sequences depends on logistics, steel grades etc. The casting time is 35 – 70 minutes per heat dependent on steel grades, dimensions etc. Usually the tundish is changed every 5-6 heats. Thus, the lining is in contact with steel 4-7 hours during those heats. After 5-6 heats the tundish is turned upside down to take out scull etc and a new wear lining is inserted.

To protect the steel from air contact it is protected by a ceramic shroud between the ladle and the tundish and a Submerged Entry Nozzle (SEN) between the tundish and the mould. The top surface of the steel in the tundish is protected from air contact and heat loss by a cover slag. To create this cover slag, regular additions of slag powder are made during casting. The top slag in the tundish consists of a molten slag closest to the steel and a highly insulating powder on top of the molten slag.

During the period 1990 - 1997 the relining of the tundish was carried out by means of gunning. The gunning mass was wet and had to be dried before casting. This was accomplished by means of a special electric heater, which gave a well-controlled temperature increase during the drying period. The drying time was considered a bottleneck. To overcome this a new method was developed where the relining is made using a dry self-hardening mass.

The scope of this study is to describe the new method and the metallurgical behaviour of the new lining material. The paper starts with a description of the dry-casting method. Next, laboratory experiments and metallographic studies on samples from the steel plant are carried out. The result is used to investigate the interaction of the lining with the liquid slag and metal in production tundishes.

A new method for tundish relining (Dry-casting)

Design of tundish lining at SSAB Tunnplåt AB

The present design of the lining in the tundishes at SSAB Tunnplåt AB is shown in **Figure 1**. There is a 30 mm wear lining which is dry-cast onto a permanent lining. The permanent lining consists of two parts, a safety lining of chamotte bricks and a cast lining on top of that. The thickness of the chamotte is 32 mm on the wall and 64 mm on the bottom. On the end walls there is also a 6 mm insulation board between the bricks and the steel shell. The cast lining is made from approximately 4 tonnes of a self-floating low-cement mass. This mass contains approximately 80 % Al_2O_3 . The life of the permanent lining is approximately 1100 heats. The wear lining is made to last during one sequence, usually 1-6 heats, sometimes up to 8 heats. The lining is cast using the new dry-cast method.

The dry-casting process

A general flow sheet of the dry-casting process is shown in **Figure 2**. The process involves the following main operations:

- 1. A metal template is inserted and fixed into position in the tundish. Dry hardening mass is added in the space between the template and the tundish wall.
- 2. The mass is allowed to harden. The template is removed. Nozzles etc are inserted.
- 3. The tundish is sent to the slab caster, and the casting of steel begins.
- 4. After finishing the casting sequence, the tundish is turned upside down, so the scull and the remaining wear lining fall out. After cooling, the tundish is sent to the relining bay and the process starts again beginning with operation 1.

The photographs in **Figure 3** show the practical arrangements during the dry-casting step, operation 1 in **Figure 2**. In **Figure 3 a,** a template of steel is lowered into the tundish. In **Figure 3 b** the template has been fastened into a fixed position inside the tundish. A dry-hardening mass is then fed into the space between the permanent lining and the template. This mass is prepared by mixing the ceramic component with organic binder and hardener. This mixing is done in the feeding machine immediately before feeding. Approximately 640 kg mass/tundish is added. The ceramic part of the mass is a mixture of MgO and Olivine. The amount of organic binder is 4-4.5% including hardener. The hardening time of the binder is approximately 20 min.

The finished dried mass is hard and resistant enough to last during casting, but when the tundish is emptied after casting it falls out like sand together with the tundish scull (operation 4 above). Dust emission cannot be avoided during emptying. It is carried out in a special stand, where an exhaust hood covers the tundish.

Production experience

The process in itself is very simple and has caused very few practical problems. Likewise, the life of the permanent lining has increased and the material cost is approximately the same as with the old method. The major benefits of the new method are instead the differences in practical handling. Some of them are listed below.

• **Figure 4** shows the time used by the different operations with the new and old methods. The total time consumed by the operations decreases from 9h 45 min to 5 h 45 min, i.e. approximately 40%. The main reason for the decreased time is that drying is no longer needed. The time decrease can be used to minimise the number of

tundishes needed during a given production level, or alternatively to increase the productivity with a given amount of tundishes.

- Also the amount of lifting operations is decreased. This decreases the transport costs, the amount of overhead cranes needed etc.
- The handling is much easier when there is no water in the system
- Constant inside volume.
- Possibility for automation and reduced working cost.
- It is easier to dispose of sculls during emptying.

Masses with a resin binder have also been tested. These binders tended to stick to the template, which led to an increased effort for cleaning and lubrication. Because of the higher hardening temperature there were big problems with deformation of the template as well. For this reason that type of mass was abandoned.

One practical problem that occurred during the beginning of the project was that the viscosity of the binder was temperature dependent. This influenced the adsorption in the mass during the summer period, when the temperature was higher. A constant storage temperature eliminated the problem.

Investigation of the interaction of dry-cast lining with liquid steel and metal

Expected physical interactions between steel, slag and lining during a normal casting sequence.

A normal sequence for one tundish consists of 5-6 heats. As soon as the tundish is filled during the first heat, a protective slag is created by slag powder that is thrown on top of the steel. Part of the powder melts and creates a molten slag, the rest forms an insulating layer on top of that slag. More powder is added regularly to compensate for the gradual melting of the slag during the sequence. Also the slag composition is gradually modified by adsorption of inclusions, desoxidation products and ladle slag. In the sequence there is a time-interval of several minutes from the end of one heat to the start of the teeming from the next ladle. As the casting is not interrupted the tundish is partially emptied during that time. These emptying and filling sequences cause an interaction between iron, slag lining and air, which is illustrated in **Figure 5**.

When the steel level sinks, a layer of slag and in some cases steel remains on the wall and can be expected to partly oxidise by air contact. When the teeming starts from the next ladle the layer of slag and partly oxidized metal is covered with steel melt and can be expected to react with the lining. E.g., during a sequence of 6 heats this phenomenon is repeated 5 times.

Sampling

The samples were taken for two purposes

- 1. Metallographical studies of the infiltration
- 2. Laboratory simulation of the infiltration process

For the metallographical studies, samples of the infiltrated lining were needed as well as comparison samples of unaffected lining, reacted slags etc. The disintegration of the infiltrated lining during emptying of the tundish causes a sampling problem. The main part of the lining falls into peaces and is accumulated as a heap of gravel in the emptying pit. (C.f. the lower left

picture in **Figure 3**). However it was noticed that some cakes of the lining remained on the tundish scull (Also sketched **Figure 3**). The samples of infiltrated lining were taken from lining cakes remaining on the tundish scull. Totally five different samples of slag and lining material were studied:

- 1. Residue of top slag
- 2. New lining,
- 3. Infiltrated lining A
- 4. Infiltrated lining B
- 5. Used lining

The slag residue sample (sample 1) was collected from a cold tundish after a casting sequence. New lining (sample 2) was collected after the lining material was hardened in a tundish. Three different samples (sample 3, 4 and 5) were collected from used infiltrated lining material. Sample 3 and 4 were taken from a position close to the inner surface of the lining, which has been in contact with liquid steel and slag. Sample 5 was taken from a position close to the permanent lining. This used lining material had not been in contact with the melt.

For the experimental simulation of the infiltration, samples were needed of the original materials that took part in the process, tundish slag and the ceramic components of the dry mass. The slag sample was taken with a cup sampler in the middle of the tundish after 20 min of casting. The other materials were taken directly from the storage bags.

Metallographic studies

The following experimental methods were used in the characterisation work.

Chemical analysis

The chemical analysis was made at SSAB Tunnplåt Luleå. The sample was ground and heated at 925°C during ≥ 4 hours, to determine ignition loss. Then the sample was dissolved in a glass melt and analysed by X-Ray Fluorescence.

Scanning electron microscopy

Scanning electron microscopy (SEM) analysis was conducted on a Philips XL 30 instrument. Six thin, transparent samples were samples were prepared.

X-Ray diffraction analysis

X-ray diffraction analysis was made on a Siemens D5000 powder diffractometer. The samples were finely ground before analysis. Raw data was evaluated using a computer database.

Thermodynamic calculations

Computer based thermodynamic calculations are a powerful tool to simulate chemical reactions occurring in a process. The simulation gives the amount of stable products at equilibrium which then can be compared with the experimental results. In this way it is possible to determine from the calculations if the experimental results are close to equilibrium or not. In this work the reaction between tundish slag and tundish lining has been simulated.

The free energy minimisation computer program ChemSage [1] has been used in the calculations. The system components in the calculations have been selected as O, Si, Al, Ca, Fe, Mg, Mn, C and N. The gas phase is treated as ideal and consists of the following gas

species: O₂, CO, CO₂, N₂, Al, Ca, Fe, Mg, Mn and Si. Thermodynamic data has been extracted from Barin et al [2]. The model for the slag phase is based on a statistical thermodynamic model for liquid multicomponent silicates. The model has been developed by Gaye et al [3] and shows good agreement with experimental data for systems with the components SiO₂, Al₂O₃, CaO, FeO, MgO and MnO. The following condensed invariant phases were considered in the calculations: CaSiO₃, Ca₃Si₂O₇, Ca₂SiO₄, Ca₃SiO₅, Fe₂SiO₄, FeO, Fe₃O₄, Fe₂O₃, MgSiO₃, Mg₂SiO₄, MnSiO₃, Mn₂SiO₄, Ca₃Al₂O₆, CaAl₂O₄, CaAl₄O₇, CaAl₁₂O₁₉, FeAl₂O₄, MgAl₂O₄, MnAl₂O₄, Si₂Al₆O₁₃, Ca₂Al₂SiO₇, CaSi₂Al₂O₈, CaMgSi₂O₆, CaMgSiO₄, Ca₂MgSi₂O₇, Ca₃MgSi₂O₈, Al₂O₃, MnO, SiO₂, CaO, MgO, Fe and Mn. Thermodynamic data for the condensed invariant phases were taken from Barin et al. [2] and Gaye et al. [3]. The calculations were carried out for the following three materials:

- 1. Tundish lining
- 2. Tundish slag
- 3. A mixture of tundish slag and tundish lining with a mass ratio of 1:10

The temperature was varied from 1600 to 100°C. Amounts of the reactants for calculations 1 and 2 are given in table 1. In calculation 3 the amounts in calculations 1 and 2 were added.

Thermal analysis

The aim of the thermal analysis study was to investigate the thermogravimetric (TG) and differential thermal (DTA) behaviour during interaction between tundish slag and tundish lining. The materials used were grinded tundish lining and tundish slag. The chemical composition of the materials used is given in table 2. The tundish slag was collected in the tundish after 20 heats. The TG/DTA unit used in this study was a Netzsch STA 409 thermal analyser, using a TG/DTA sample holder with A_2O_3 crucibles. Three sets of experiments were performed in this unit. In the first two sets pure tundish lining and pure tundish slag were investigated separately. In the third set a 50:50 mixture of both materials was investigated. During a typical run about 100 mg of the sample mixture was heated at a heating rate of 20° C/min from 20° C to 1500° C. The sample compartment was flushed with Ar at a constant rate of 100 ml/min. Both temperature and TG/DTA signals were recorded as functions of time.

Hot table microscope

The melting point of the tundish slag was investigated with a hot table microscope according to the DIN 51730 standard. The slag sample was ground and mixed with ethanol. A cylinder of approx. 2*2*2 mm was made. The sample was observed through an optical microscope during heating. The heating rate was 10° C/min. The sample compartment was flushed with N_2 .

Results

Chemical analysis

The results from the chemical analysis are given in table 2 and 3. The values are given in weight %. Sample 1, residue of top slag, consists mainly of FeO, CaO, SiO₂, MnO, Al₂O₃ and MgO. Other oxides occur in minor amounts. Sample 2, new lining material, consists mainly of SiO₂, MgO and smaller amounts of FeO and Al₂O₃. Samples 3-4, infiltrated lining close to the slag residue, consists mainly of SiO₂ and MgO, as the hardened lining material, but also some slag components such as FeO, CaO, MnO and Al₂O₃. Sample 5, used lining close to the permanent lining, consists mainly of SiO₂ and MgO.

Scanning electron microscopy

Each sample was analysed at different distances from the melt in order to examine differences in sample structure and composition. Two of these SEM images are presented in pictures 1 and 2. In these pictures both analogue and mapping images for some selected elements are given. In the SEM images of new lining, pictures 1, corresponding to sample 2, it can be seen that the particles consist either of the elements Mg and O only or also include Si. This indicates that the phases MgO and Mg₂SiO₄ are present in the lining material. The elements Si and O were also found in the grain boundaries between the MgO particles. Also some small amounts of Al were found in the Mg₂SiO₄ particles, and Fe in both MgO and Mg₂SiO₄ particles. In the SEM image of infiltrated lining (picture 2), corresponding to sample 4, almost pure iron particles were found in this sample together with MgO and Mg₂SiO₄ particles. The sample also contains some slag components, where Al coexists with Mg and O, and Ca with Mg, Si and O. In table 4 the results from the SEM investigation are summarised.

Sample 1, residue of top slag

The particles consist of Mg-Al-Fe-O, Al-Ca-Mn-Si-O and Fe-Mn-Mg-Ca-O compounds. These particles can be found everywhere in the sample. The shape of the particles differs at different positions. This phenomenon probably occurs due to different rate of the solidification of the slag.

Sample 2, new lining

The material consists of solid particles made up of Mg-O and Mg-Si-O compounds. Two different Mg-Si-O regions were found, as relatively large Mg₂SiO₄ particles, and in the narrow grain boundaries between the MgO particles.

Sample 3, infiltrated lining

The material close to the melt seems to have been partially melted. The solid material consists of Mg-O, Mg-Si-O and Ca-Al-Si-O compounds, indicating slag penetration.

Sample 4, infiltrated lining

In the lining material close to the melt, iron droplets were found, indicating a penetration of liquid steel. Also particles with Mg-O, Mg-Si-O, Mg-Al-O, Ca-Si-O compounds were found. The particle size was relatively large. In the middle part of this sample, less iron particles were found. On the other hand an increasing amount of Ca-containing particles was found, indicating that a penetration of slag into the lining material has occurred.

Sample 5, used lining

Close to the region of sample 3 and 4, Mg-O and Mg-Si-O particles were found. A small number of particles with high Ca-concentration were found together with Mg-Si-O in the grain boundaries between the MgO particles. These particles probably originate from penetrated slag and from the small CaO content in the pure lining material. In the middle part of this sample the amount of CaO particles decreased.

X-Ray diffraction analysis

Results from the XRD analysis are given in tables 5 and 6. An estimation of the relative amounts was made from the peak height. Large amounts are indicated by ****; almost detectable amounts with an *.

The new lining material consists mainly of MgO (Periclase), Mg₂SiO₄ (Forsterite) and almost in detectable amounts of Mg₃Fe₂(SiO₄)₃. In the infiltrated samples, which have been in contact with slag, the amount of MgO decreases and the amount of Mg₂SiO₄ increases indicating that SiO₂ in the slag reacts with MgO forming Mg₂SiO₄. Relatively small amounts of phases related to slag penetration were found in samples 3 and 4. In sample 3 the phases CaMgSiO₄, MgAl₂O₄ and Ca(Mg,Fe,Al)(Si,Al)₂O₆ could be found, and in sample 4 the phases CaMgSiO₄, MgAl₂O₄. The presence of these phases can be explained by reactions between lining material and infiltrated slag. Other reaction products are amorphous, or do not form large enough amounts detectable with this method. It was not possible to confirm the presence of metallic iron in the samples.

Thermodynamic calculations

The results from the thermodynamic calculations are presented in tables 7-8. The tables show the gradual formation of solid compounds during cooling from 1600 to 100°C. The solids are given in the order of decreasing amounts.

Tundish lining

In the temperature range 1600 to 100°C the solid phases MgO and Mg₂SiO₄ are dominating. At 1600°C the liquid slag consists of the components FeO, CaO, Al₂O₃. At this temperature SiO₂ and MgO are partially melted. With decreasing temperature, the liquid components start to solidify in different solid phases. Below 1100°C the liquid slag becomes solid. The first solid phase, MgAl₂O₄, is formed at T<1600°C. At lower temperature the solids are formed in the following order: FeO, CaMgSiO₄, MgAl₂O₄, FeAl₂O₄, MnO, MnAl₂O₄ and Ca₃MgSi₂O₈. Below 900°C FeO forms Fe and Fe₃O₄. Below 300°C, Fe and Fe₃O₄ react with MgAl₂O₄ to FeAl₂O₄ and MgO. Below 700°C CaMgSiO₄ decomposes to Ca₃MgSi₂O₈ and Mg₂SiO₄. At 900°C MnO reacts with MgAl₂O₄ forming MnAl₂O₄ and MgO. Between 1200 and 1600°C about 12 % of MgO and 6 % of Mg₂SiO₄ has melted.

Tundish slag

At 1600° C the liquid slag consists of the components FeO, CaO, Al₂O₃, SiO₂ and MgO. The liquid slag has completely solidified at temperatures below 1100° C. The first solid phase, Si₂Al₆O₁₃, is formed at T< 1300° C. At lower temperature the solids are formed in the following order: SiO₂, FeAl₂O₄, CaSi₂Al₂O₈, MgSiO₃, CaSiO₃, Si₂Al₆O₁₃, MnAl₂O₄ and Al₂O₃.

Tundish slag mixed with tundish lining

The gradual formation of solid compounds during cooling from 1600 to 100°C is similar to the solidification of pure lining material. The main difference is that the amount of the phases Fe, Fe_3O_4 and FeO is lower compared to the results with pure lining material.

Thermal analysis

TG curves

In figure 6 the TG curves for tundish lining, tundish slag and for a 50:50 mixture of both is shown. The total weight loss, in the temperature range studied, is 3.2 % for the tundish lining and 1.9 % for the tundish slag. The weight loss curve for the 50:50 mixture is close to the average of the two other curves.

DTA curves

For all three samples, the DTA measurements show an exothermal effect at temperatures below 1000°C. For the tundish lining the exothermal effect has its maximum at 700°C. The tundish slag has two exothermal peaks at 500 and 900°C. The strongest exothermal effect is observed for the 50:50 mixture at 550°C. At higher temperatures endothermal effects can be observed for the tundish slag and for the 50:50 mixture.

Hot table microscope

During heating, a softening of the sample could be observed at 1217°C. At higher temperatures the sample began to melt. At 1335°C the melting was complete.

Discussion

Reaction mechanisms

Figure 9 shows the ternary diagram MgO - FeO - SiO_2 . The chemical compositions of new and infiltrated lining as well as of tundish slag and tundish cover are included in the same diagram. These samples also contain CaO and Al_2O_3 . For this reason the contents of MgO + CaO are plotted on the MgO-axis and the contents of Al_2O_3 + SiO_2 are plotted on the SiO_2 -axis. The tundish slag has a composition comparatively close to the one of the Tundish cover. The infiltration has moved the composition of the lining in a direction that corresponds to a reaction with slag and/or tundish cover. The Fe- content is lower than the one corresponding to a direct mixing. The reason could be reaction of the iron oxide with the deoxidised steel.

The sample used for analysis of the infiltrated lining was a piece of the lining cake that was taken out as close to the surface of the steel scull in the tundish. It was avoidable that this contained both material from the surface and some of the layers below. Thus the value for infiltrated slag actually represents a mean of layers with different degree of infiltration close to the surface, not a point analysis.

The measurements by SEM and X-ray diffraction indicate that the new lining material consists of the solid phases MgO and Mg_2SiO_4 with small amounts of dissolved iron oxide. In the used lining material, slag components such as CaO, MnO, Al_2O_3 , and SiO_2 were observed. These components react with the lining material. The amount of Mg_2SiO_4 has increased and the following new reaction products have been detected: $CaMgSiO_4$ and $MgAl_2O_4$. Thus, the following reactions can be proposed:

$$2MgO + SiO2 \rightarrow Mg2SiO4$$
(1)

$$CaO + SiO2 + 2Mg2SiO4 \rightarrow 2CaMgSiO4$$
(2)

$$MgO + Al2O3 \rightarrow MgAl2O4$$
(2)

Metallic iron was also found in the used lining material. The slag seems to penetrate deeper into the lining material than the steel.

Thermal analysis

The ignition weight change from the chemical analysis has been included in the TG curves of Figure 6. The values are plotted at the temperature used during the determination of ignition weight change (925°C). The weight change for the lining material corresponds fairly well to the weight loss during the thermal analysis at the same temperature. For the slag a slight weight increase (+1.3%) was obtained during the ignition test, but a weight decrease during the thermal analysis. One explanation could be that the ignition weight change is determined by heating in oxidising atmosphere (air), and that the thermal analysis was carried out under Argon atmosphere.

For the 50/50 mixture the weight change behaves as a mean value of the curves for the components. The material behaves as a mixture and there seems to be no reactions between the components that affect the weight change. This behaviour is completely different for the DTA diagram in Figure 7. For the temperature range up to around 600°C the mixture shows a much higher exothermal effect than its components. This shows that there is an exothermal reaction between the components.

Expected influence of infiltration on lining behaviour

All the studies carried out in this work indicate that there is a chemical interaction between the lining and the infiltrated slag. The main end products are oxides with very high melting point (Mg₂SiO₄, MgAl₂O₄). Some mechanisms involve Ca attack giving e.g. CaMgSiO₄ with a moderate melting point (around 1400°C). Quantitatively, these attacks seem to be of limited magnitude. Generally, the lining material can be expected to have a comparatively good stability also after the infiltration.

Conclusions

- A technique to use dry mass for relining of continuous casting tundishes has been developed. The technique is simple and has caused few practical problems.
- The main benefit is a dramatic improvement in handling effort, e.g. a 40% reduction in time consumption.
- The interaction between the dry-cast lining, slag and metal has been investigated by means of metallographical studies and laboratory experiments, including sampling of used and old lining, chemical analysis, SEM and TG/DTA, Hot table microscope and. simulations with Thermodynamic calculations
- There is a penetration of slag close to the melt. Also some traces of metallic iron were detected, but this penetration is less deep than that of the slag.
- There is a reaction between lining and infiltrated slag. However, these reactions seem to produce mainly high melting products, and do not seem to be harmful to the lining stability.

• The production experience at SSAB Tunnplåt AB confirms the good stability of the material.

Acknowledgement

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Pictures

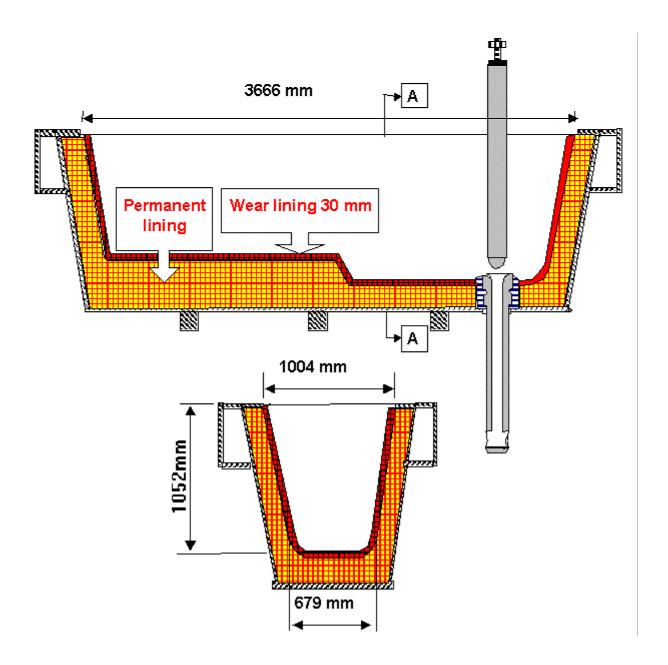


Figure 1: Tundish layout at SSAB Tunnplåt AB in Luleå

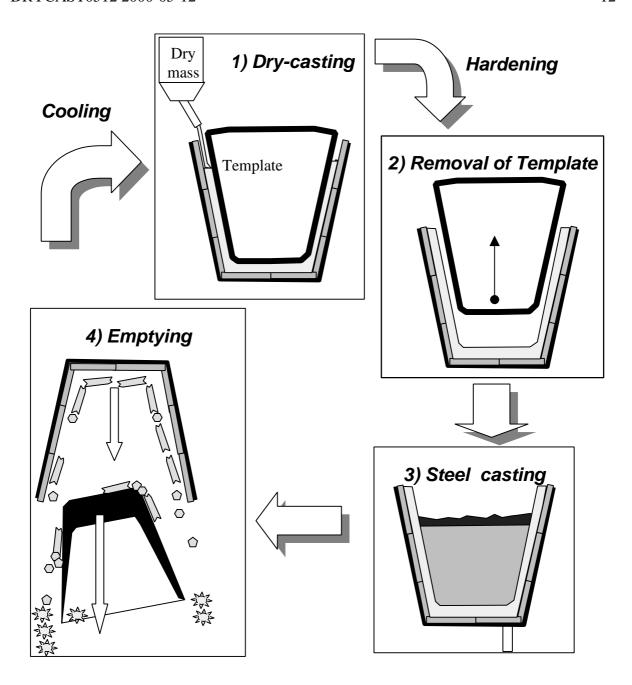
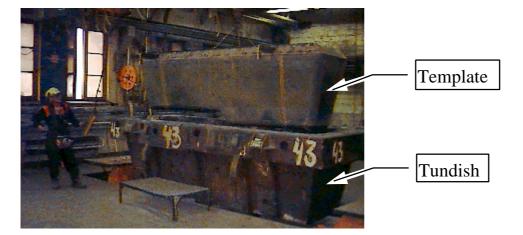


Figure 2: Schematic flow-sheet of the dry-casting process



a) Insertion of Template into the Tundish



a) Feeding of dry mass into the space between the template and the permanent lining

Figure 3: Dry casting of tundishes: In the upper picture the template is lifted into position and inserted into the tundish. In the lower picture the feeding machine (Svenska Silikaverken) is ready to fill dry mass into the space between the safety lining and the template

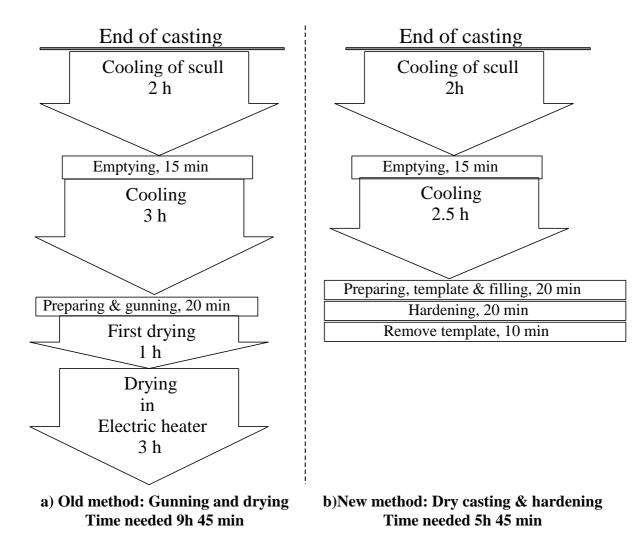


Figure 4: Lining of tundish. Comparison of operations carried out with new and old method

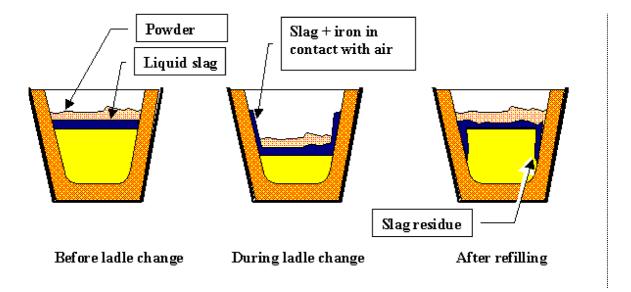


Figure 5: Interaction of slag, air and lining during ladle change.

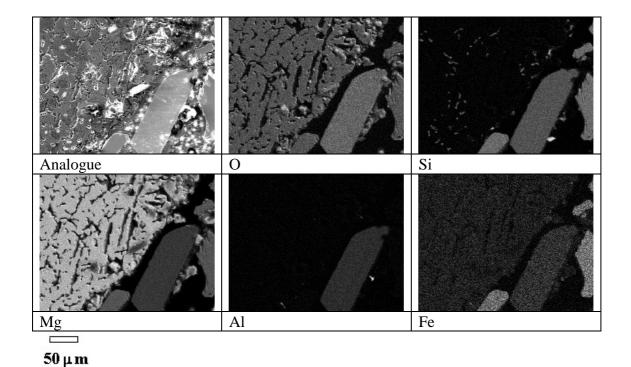


Figure 6: SEM analogue and mapping images of new lining, corresponding to sample 2

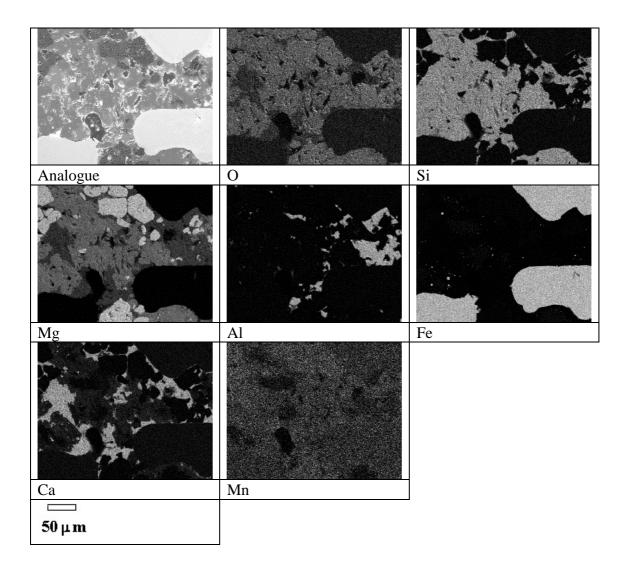


Figure 7: SEM analogue and mapping images of infiltrated lining, corresponding to sample 4.

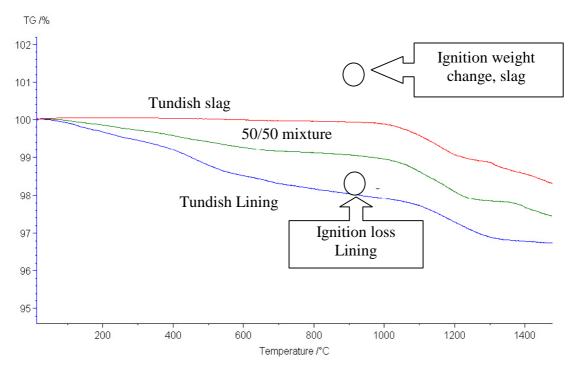


Figure 8: TG-curves obtained for tundish slag, tundish lining, and for a 50:50 mixture. The ignition weight changes from the chemical analysis of the same materials are included for comparison

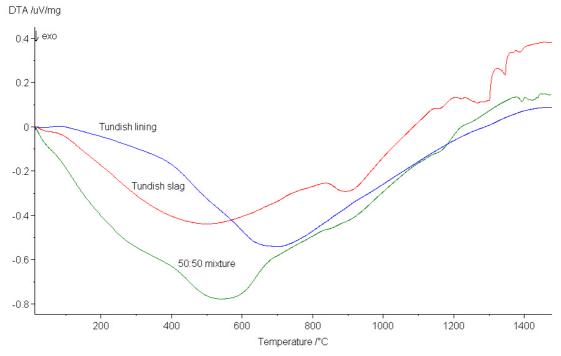


Figure 9: DTA-curves obtained for tundish slag, tundish lining, and for a 50:50 mixture.

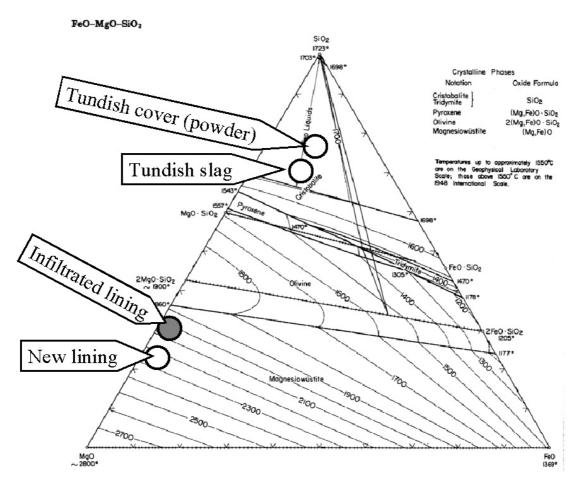


Figure 10: Phase diagram for the ternary system FeO-MgO-SiO2 from ref. 4. The chemical composition of lining, infiltrated lining, tundish slag and tundish cover are included for comparison. For these materials the value on the MgO axis corresponds to CaO + MgO and the value on the SiO2 axis corresponds to CaO + MgO and the value on the SiO2 axis corresponds to CaO + MgO axis corresponds to CaO + MgO and the value on the SiO2 axis corresponds to CaO + MgO axis CaO +

Tables

Reactants	Tundish lining/g	Tundish slag/g
FeO	0.977	6.14
CaO	0.798	1.12
SiO_2	4.35	21.3
MnO	0.195	0.180
Al_2O_3	2.69	1.36
MgO	0.357	66.8
Na ₂ O	0.197	0.110
K ₂ O	0.314	0.330

Table 1. The reactants and amounts used in the thermodynamic calculations.

Sample	Fe	CaO	SiO ₂	MnO	P_2O_5	Al_2O_3	MgO	Na ₂ O	K_2O	V_2O_5	TiO_2	Cr_2O_3
Slag	7.58	7.98	43.46	1.95	0.19	26.86	3.57	1.97	3.14	0.07	0.76	0.43
Lining	4.64	1.26	19.95	0.13	0.06	0.41	69.24	0.00	0.09	0.07	0.06	0.35

Sample	IWC	C	S
Slag	1.3	0.68	0.15
Lining	-1.6	1.06	0.02

Table 2: Chemical composition of the samples used for thermodynamic calculations and TG/DTA analysis, in weight %. (IWC = Ignition Weight Change)

Sample	Fe	CaO	SiO_2	MnO	P_2O_5	Al_2O_3	MgO	Na ₂ O	K_2O	V_2O_5	TiO_2	Cr_2O_3
1	2.39	18.8	37.13	11.53	0.02	24.51	4.16	0.08	0.33	0.23	0.32	0.31
2	4.78	1.12	21.3	0.18	0.03	1.36	66.82	0.01	0.11	0.01	0.05	0.3
3,4	2.94	7.19	25.42	1.07	0.04	3.39	58.37	0.01	0.11	0.01	0.13	0.2
5	3.32	1.03	22.2	0.11	0.04	0.48	70.56	0.11	0.33	0.01	0.04	0.26

Table 3: Chemical composition of the samples collected from a cold tundish, in weight %.

Sample	Point	Lining phases	Slag phases	Steel phases
1	1,2,3	-	Mg-Al-Fe-O, Al-Ca-Mn-Si-O,	
			Fe-Mn-Mg-Ca-O	
2	1,2	Mg-O, Mg-Si-O		
3	1,2	Mg-O, Mg-Si-O	Ca-Al-Si-O	
4	1,2	Mg-O, Mg-Si-O	Ca-Si-O, Mg-Al-O	Fe
4	3,4	Mg-O, Mg-Si-O	Ca-Mg-Si-O, Mg-Al-O	
4	5,6	Mg-O, Mg-Si-O	Ca-Si-O, Mg-Al-O	
5	1,2,3,4	Mg-O, Mg-Si-O		

Table 4: A summary of phases identified in the SEM investigation.

Sample	CaAl ₂ Si ₂ O ₈	CaAl ₂ O ₄	Mn_2AlO_4	MgO	CaAl ₂ SiO ₆
1	****	*	*	*	*

Table 5: Phases identified with XRD in the slag residue sample.

Sample	MgO	Mg ₂ SiO ₄	Mg ₃ Fe ₂ (SiO4) ₃	CaMgSiO ₄	MgAl ₂ O ₄	Ca(Mg,Fe,Al)(Si,Al) ₂ O ₆
2	****	**	*			
3:1	**	***				
3:2	**	***			*	
3:3	**	***		**		*
4:1	***	**		**	**	
4:2	****	*		**	*	
5:1	****	*				
5:2	****	**				
5:3	****	**				

Table 6: Phases identified with XRD in the hardened lining (no. 2), lining in contact with slag (no. 3-4) and lining close to the permanent lining (no. 5)

Temperature	Solid phases
1600°C	MgO, Mg ₂ SiO ₄
1400°C	MgO, Mg ₂ SiO ₄ , MgAl ₂ O ₄
1300°C	MgO, Mg ₂ SiO ₄ , MgAl ₂ O ₄ , FeO, CaMgSiO ₄
1100°C	MgO, Mg ₂ SiO ₄ , FeO, CaMgSiO ₄ , MgAl ₂ O ₄ , MnO
900°C	MgO, Mg ₂ SiO ₄ , FeO, CaMgSiO ₄ , MgAl ₂ O ₄ MnO
800°C	MgO, Mg ₂ SiO ₄ , Fe, Fe ₃ O ₄ , CaMgSiO ₄ , MgAl ₂ O ₄ , MnAl ₂ O ₄
600°C	MgO, Mg ₂ SiO ₄ , Fe, Fe ₃ O ₄ , MgAl ₂ O ₄ , Ca ₃ MgSi ₂ O ₈ , MnAl ₂ O ₄
200°C	MgO, Mg ₂ SiO ₄ , Fe, Fe ₃ O ₄ , FeAl ₂ O ₄ , Ca ₃ MgSi ₂ O ₈ , MnAl ₂ O ₄

Table 7: Calculated temperature stability ranges of the solid phases during cooling of lining material from $1600 \text{ to } 100^{\circ}\text{C}$.

Temperature	Solid phases
1600°C	
1300°C	$Si_2Al_6O_{13}$
1200°C	Si ₂ Al ₆ O ₁₃ , SiO ₂ , FeAl ₂ O ₄
1100°C	SiO ₂ , CaSi ₂ Al ₂ O ₈ , FeAl ₂ O ₄ , MgSiO ₃
1000°C	SiO ₂ , CaSiO ₃ , FeAl ₂ O ₄ , MgSiO ₃ Si ₂ Al ₆ O ₁₃ , MnAl ₂ O ₄
300°C	SiO2, CaSiO ₃ , FeAl ₂ O ₄ , Al ₂ O ₃ , MgSiO ₃ , MnAl ₂ O ₄

Table 8: Calculated formation temperatures of solid phases during cooling of tundish slag from 1600 to 100° C.

Temperature	Solid phases
1600°C	MgO, Mg ₂ SiO ₄
1400°C	MgO, Mg ₂ SiO ₄ , MgAl ₂ O ₄
1200°C	MgO, Mg ₂ SiO ₄ , FeO, MgAl ₂ O ₄ , CaMgSiO ₄
1000°C	MgO, Mg ₂ SiO ₄ , FeO, MgAl ₂ O ₄ , CaMgSiO ₄ , MnO
800°C	MgO, Mg ₂ SiO ₄ , MgAl ₂ O ₄ , CaMgSiO ₄ , Fe, Fe ₃ O ₄ , MnAl ₂ O ₄
600°C	MgO, Mg ₂ SiO ₄ , MgAl ₂ O ₄ , CaMgSiO ₄ , Fe, Fe ₃ O ₄ , Ca ₃ MgSi ₂ O ₈ , MnAl ₂ O ₄
200°C	MgO, Mg ₂ SiO ₄ , MgAl ₂ O ₄ , Fe, Fe ₃ O ₄ , MnAl ₂ O ₄ , Ca ₃ MgSi ₂ O ₈
200°C	MgO, Mg ₂ SiO ₄ , FeAl ₂ O ₄ , Fe, Fe ₃ O ₄ , Ca ₃ MgSi ₂ O ₈ , MnAl ₂ O ₄

Table 9: Calculated formation temperatures of solid phases during cooling of a mixture of tundish slag and lining (1:10) from 1600 to 100°C.